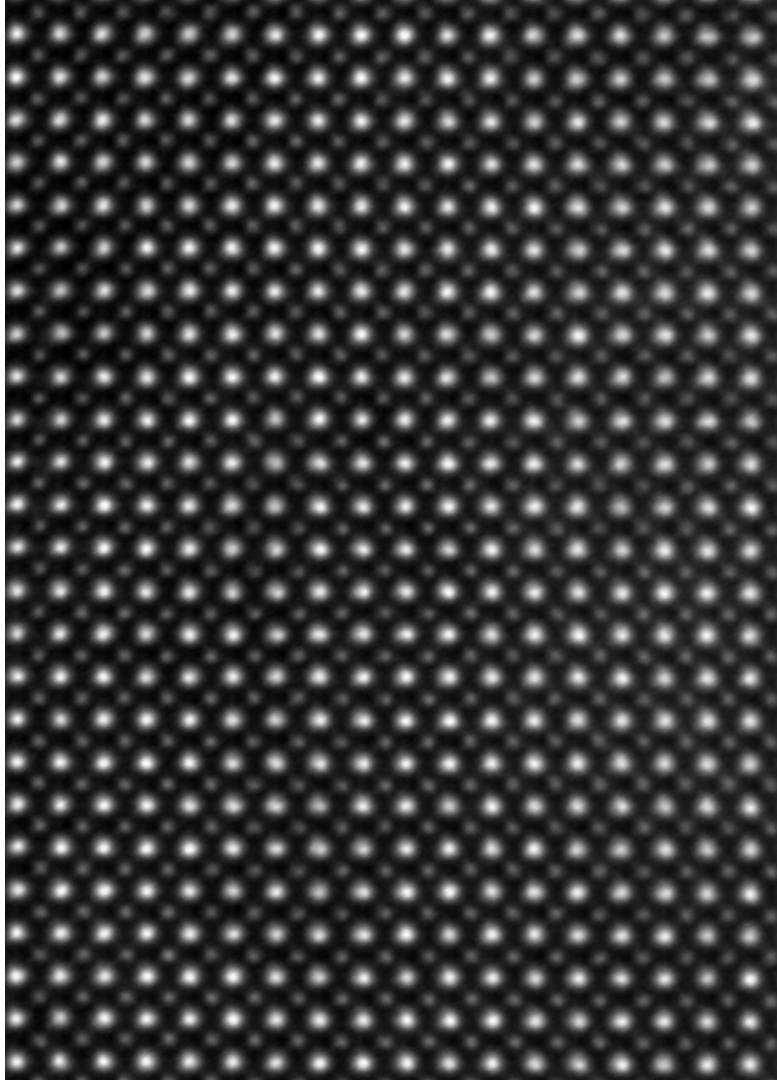




Scanning and Analytical Transmission Electron Microscopy

Introduction to STEM

MSE-735

Summer 2023

Principles of STEM

STEM components

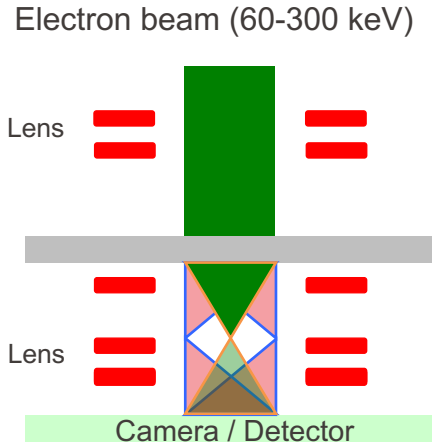
Imaging modes

Spectrum imaging

Summary

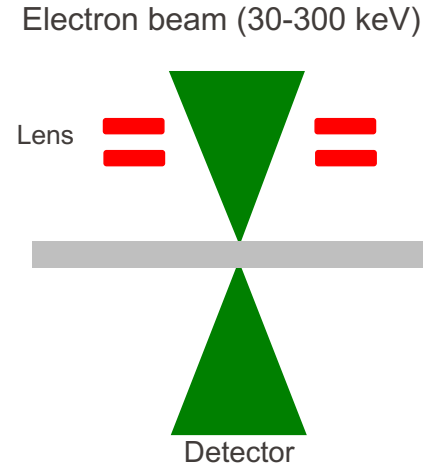
Types of transmission electron microscopes

Conventional mode (CTEM)

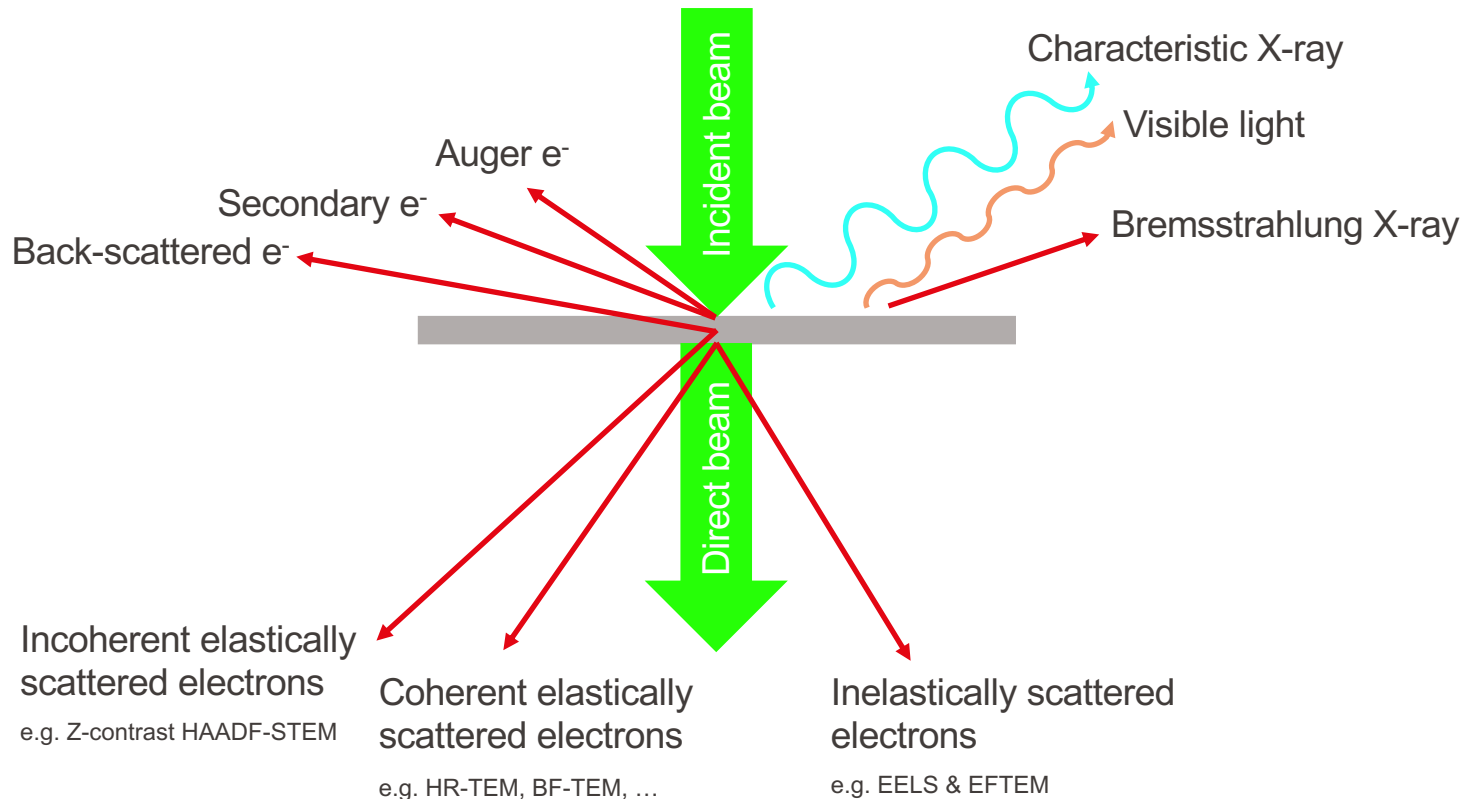


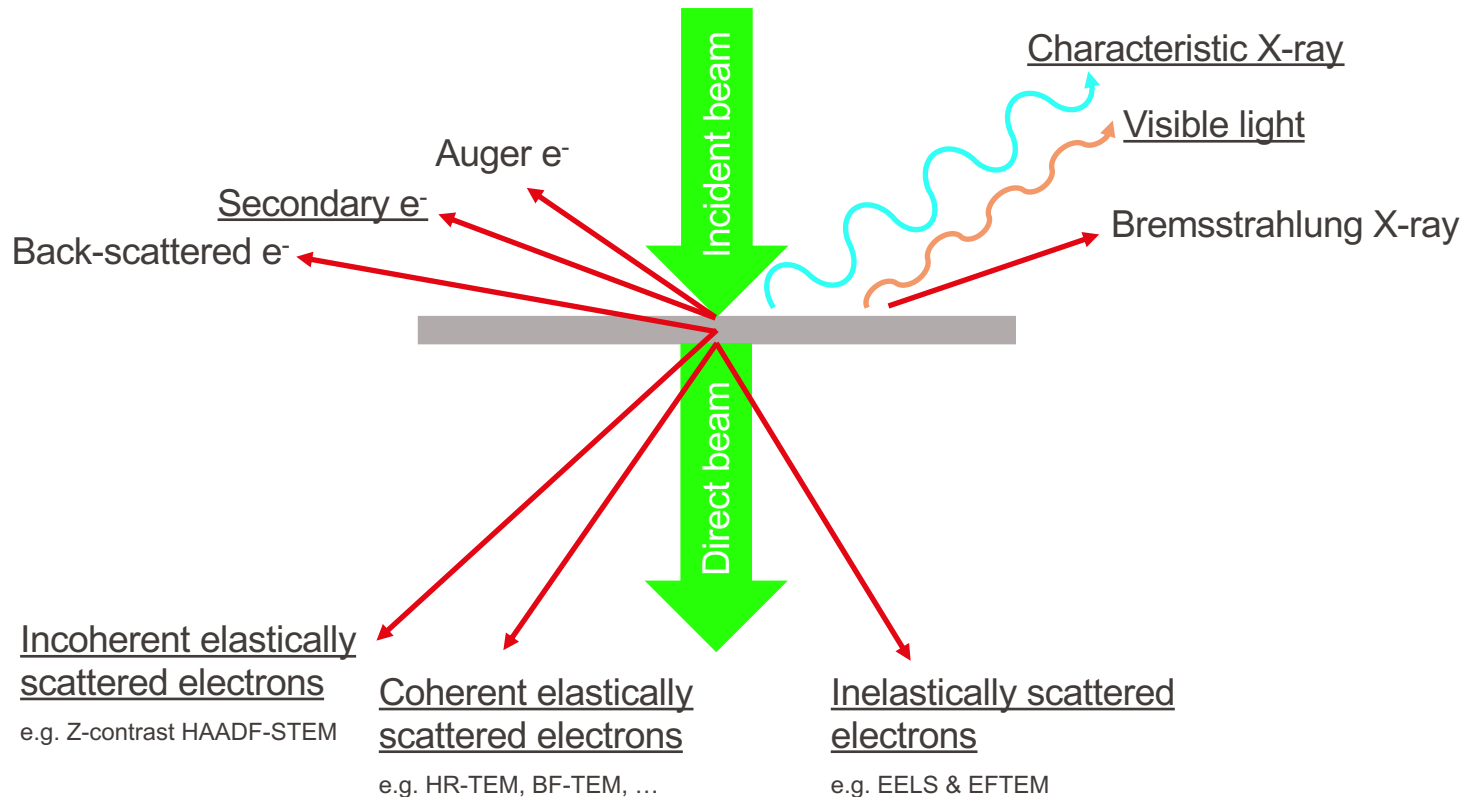
The most important lens:
Objective lens

Scanning mode (STEM)



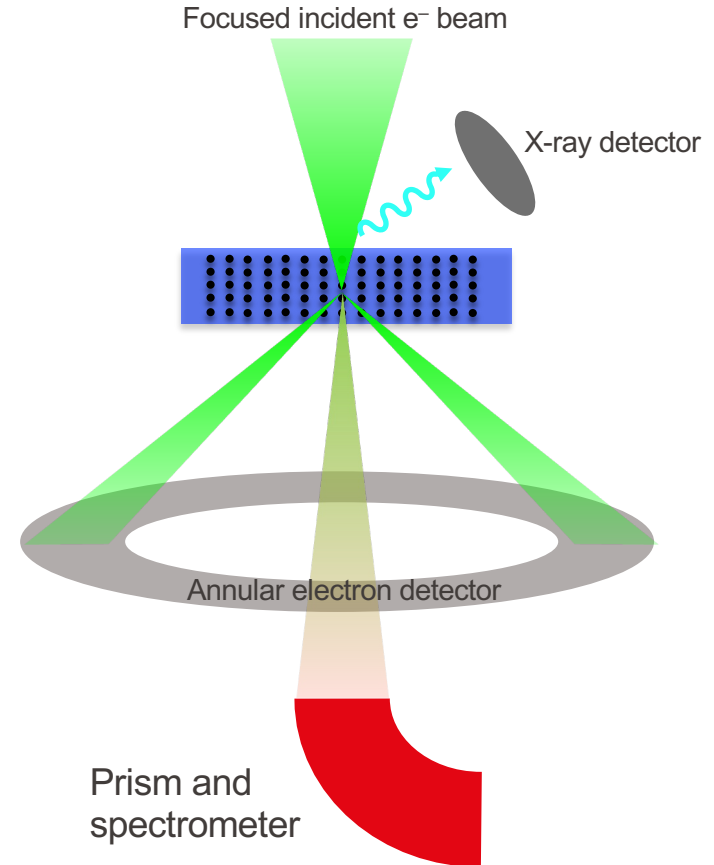
The most important lens:
Condenser lens





In STEM the electron beam is focused to a fine spot which is then scanned over the sample in a raster. This is similar to how scanning electron microscopy works.

By rastering the beam across the sample, STEM is suitable for analytical spectrum imaging techniques such as EDX and EELS.

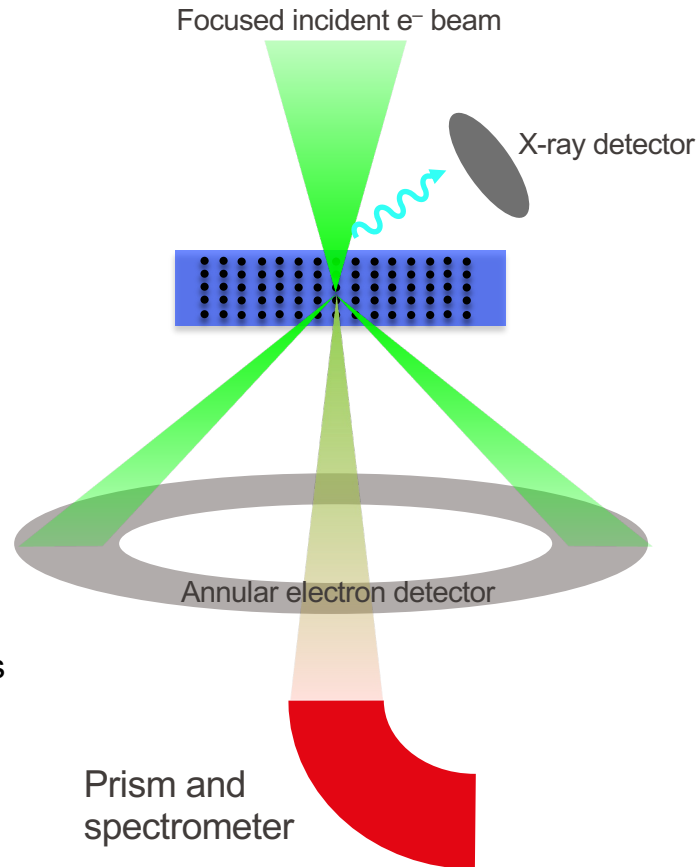


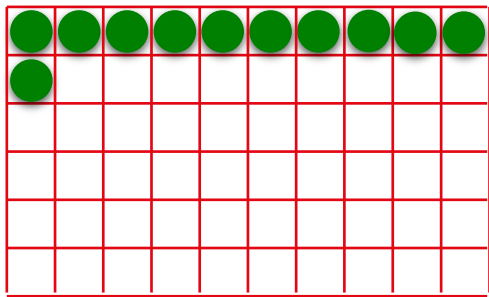
Electromagnetic lens focuses electrons from FEG on to the sample (Condenser systems)

Beam deflectors scan beam across the sample

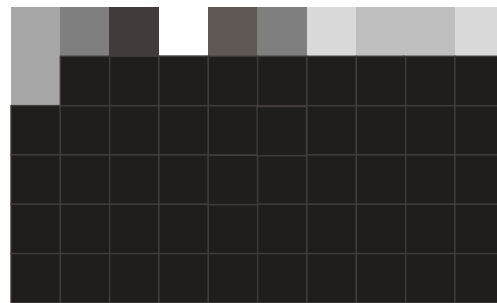
For each probe position (x,y) record on:

- Detector: Signal intensity $I_{(x,y)} \rightarrow$ Image
- Spectrometer: Integrated signal from hyperspectral datasets $\rightarrow$ 3D data-cube (e.g. EELS and EDX spectrum image)





Beam locations on the specimen



Area scanned on the screen

Information transfer $f(x,y,S)$

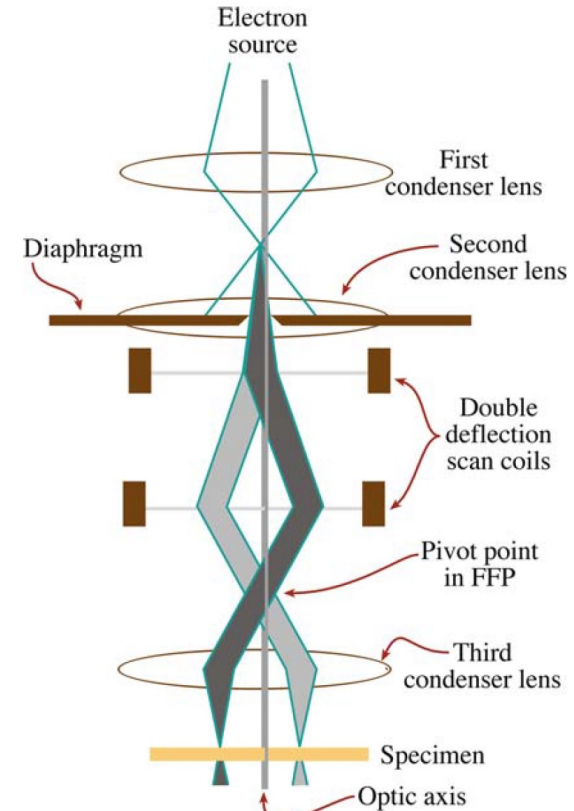
- Image formed by recording the time sequence of intensities for any particular small portion of diffraction pattern as the incident beam is scanned over the sample (using pair of deflector or scan coils)
- Monitor and scanning coils are synchronized
- Intensity of each pixel is proportional to signal collected by the detector
- When changing the magnification, we just change the raster size (no change in optics)

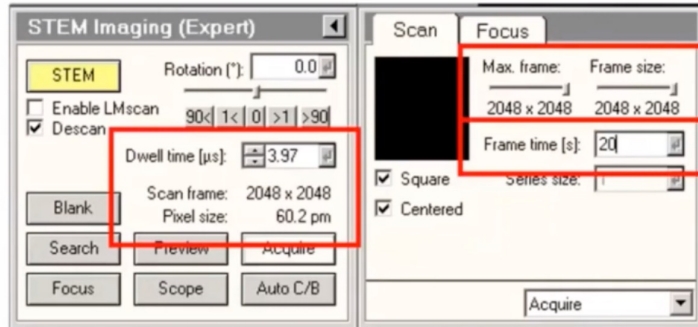
Magnification = Image size (e.g. display) / Raster size on the specimen

All the STEM images appear on the computer screen at a magnification that is controlled by the **scan dimensions** on the specimen, not the lenses of the microscope.

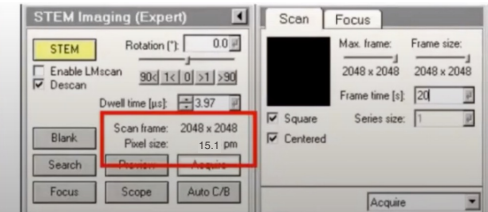
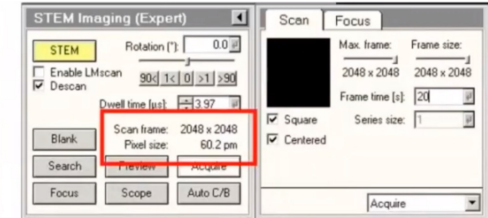
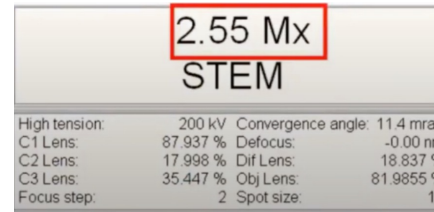
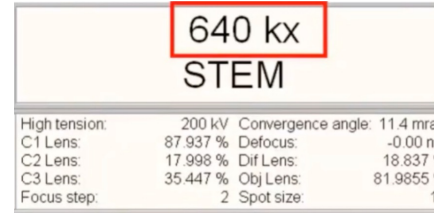
This is a fundamental difference between scanning and static image formation.

Magnification = Size of the screen / Raster size on the sample





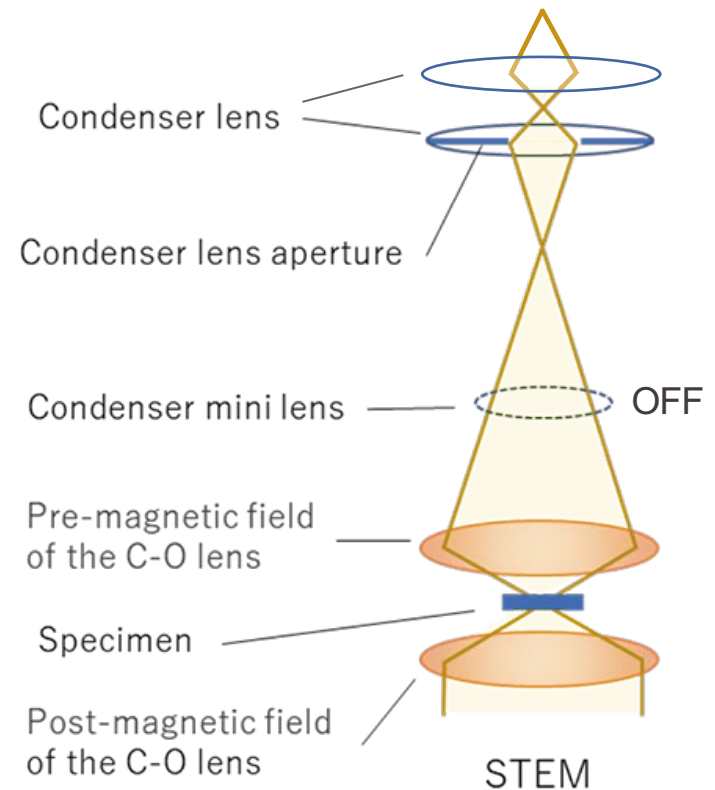
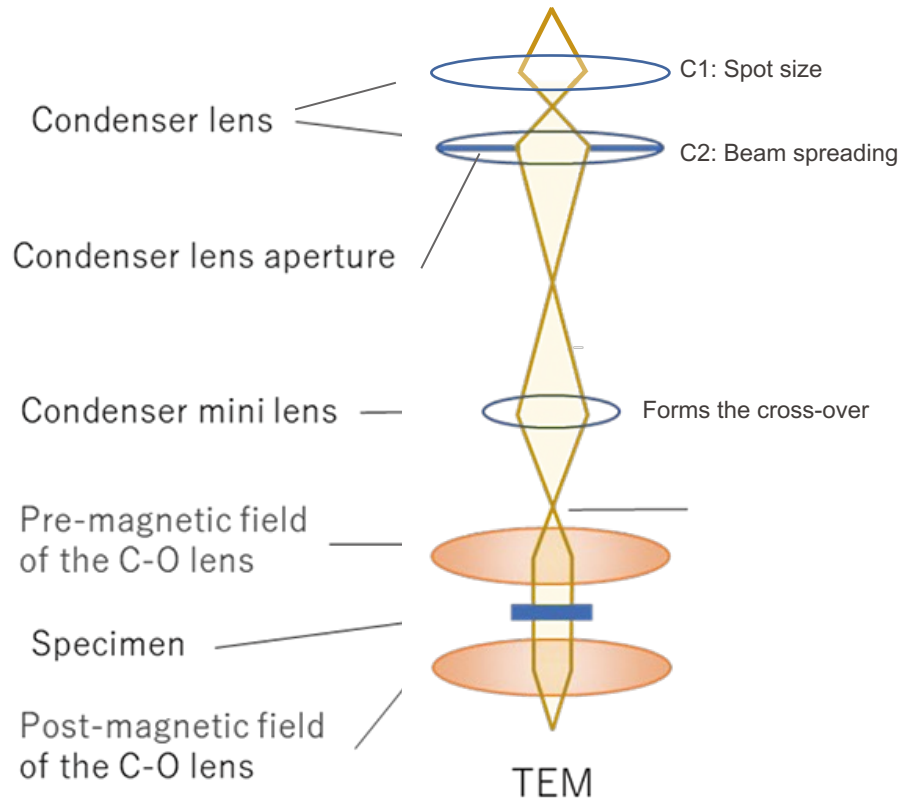
Scan frame x Dwell time = Frame time
 e.g. $2048 \times 2048 \times 3.97 \text{ usec} = 20 \text{ Sec}$



If for Mag. = 640 kx, the Pixel size is 60.2 pm, for Mag. = 2.55 Mx calculate:

- The pixel size,
- Scan area, and
- Size of the screen

Probe forming | 2-condensor lens system



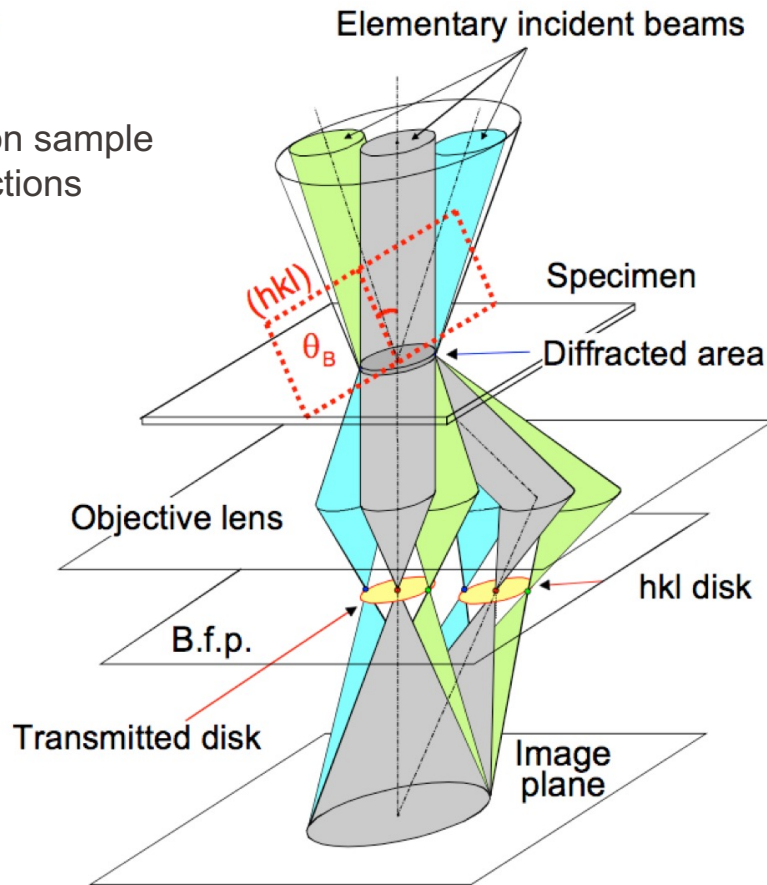
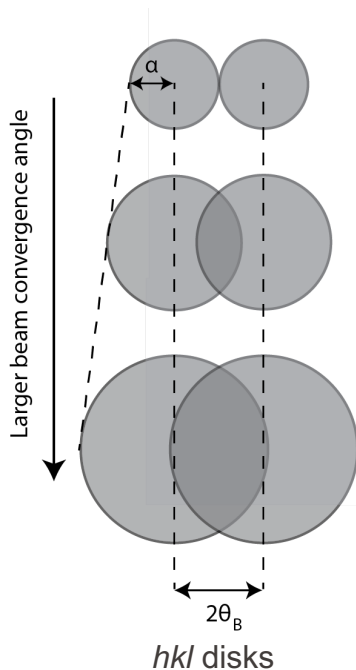
C-O lens: condenser-objective lens

Probe forming

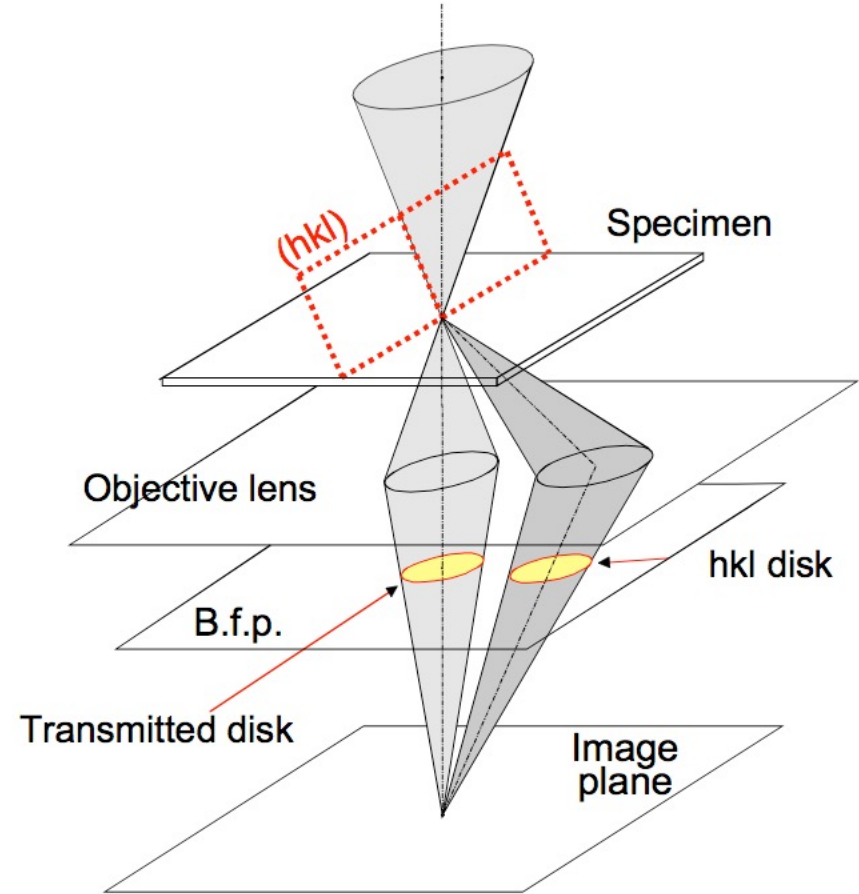
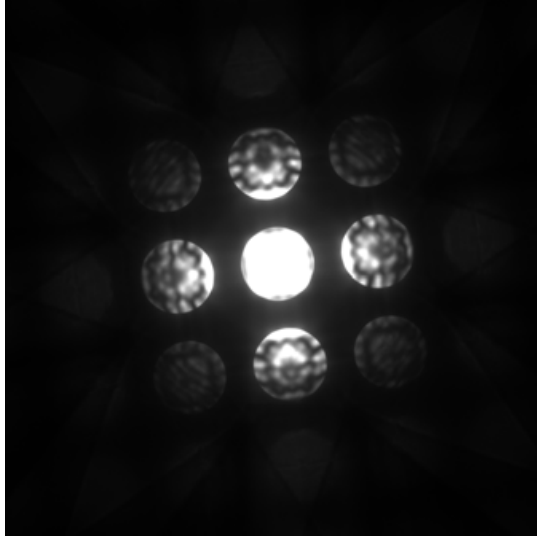
Consider exact 2-beam condition:

Imagine a convergent beam, not fully focused on sample

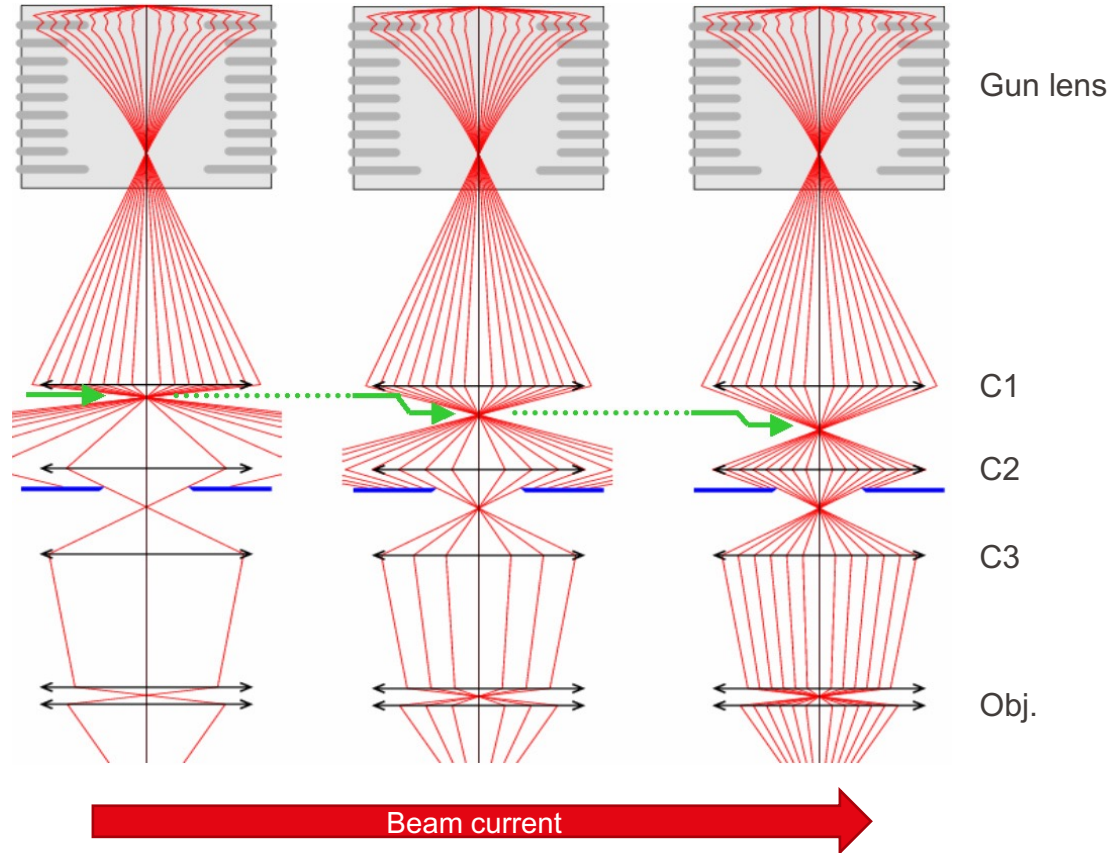
→ Decompose as parallel rays of different directions



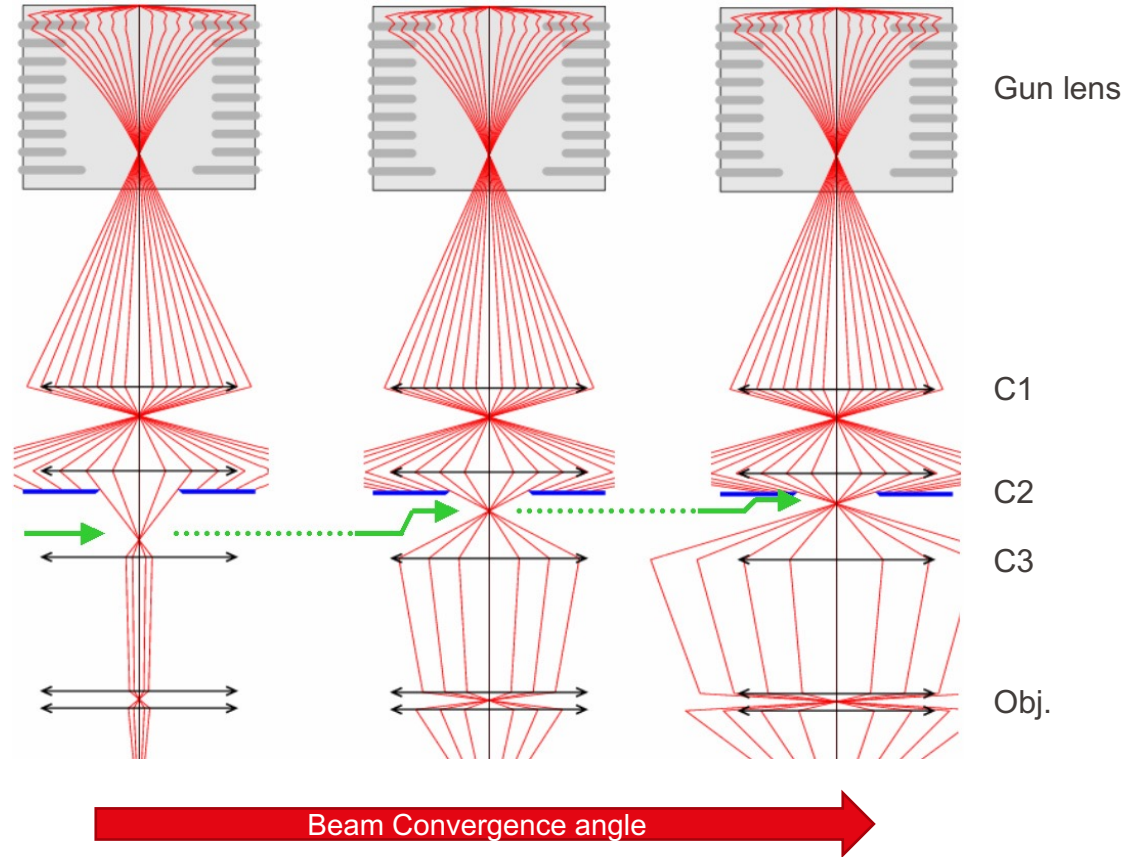
Probe forming



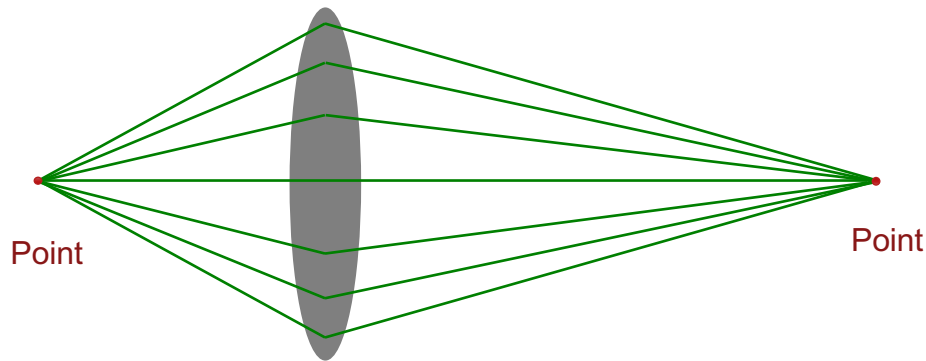
Probe forming | 3-condensor lens system



Probe forming | 3-condensor lens system

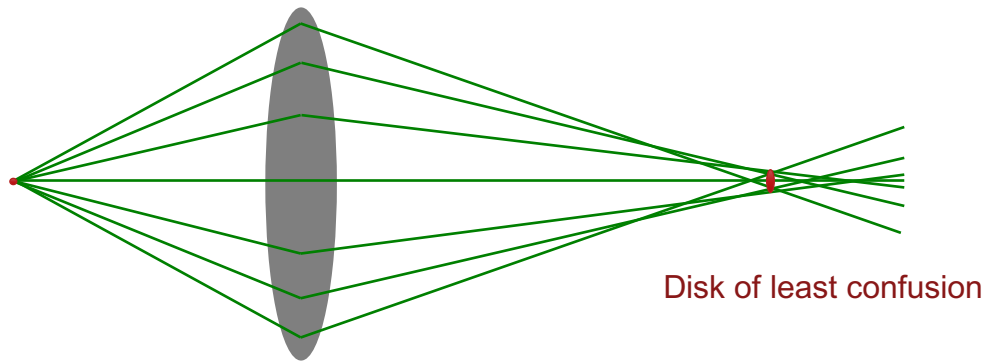


Ideal lens



A point source is focused to a point

Real lens



A point source is focused to a disk

Lens aberrations limits resolution!

■ Lens aberrations

- Chromatic aberration
- Spherical aberration
- Astigmatism

Diffraction effect (aperture limit)

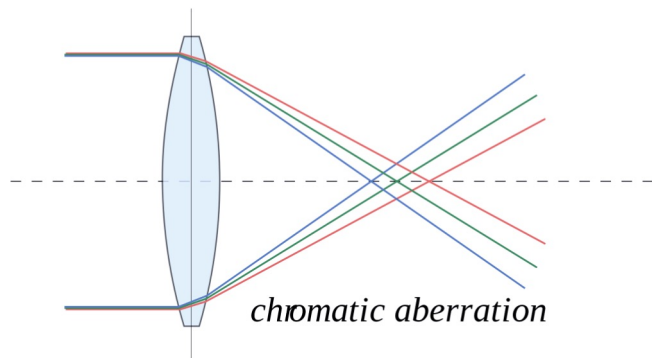


STEM resolution is determined by the size of the probe and stability of the instrument

Resolution in HR-S/TEM limited by aberrations, especially C_s

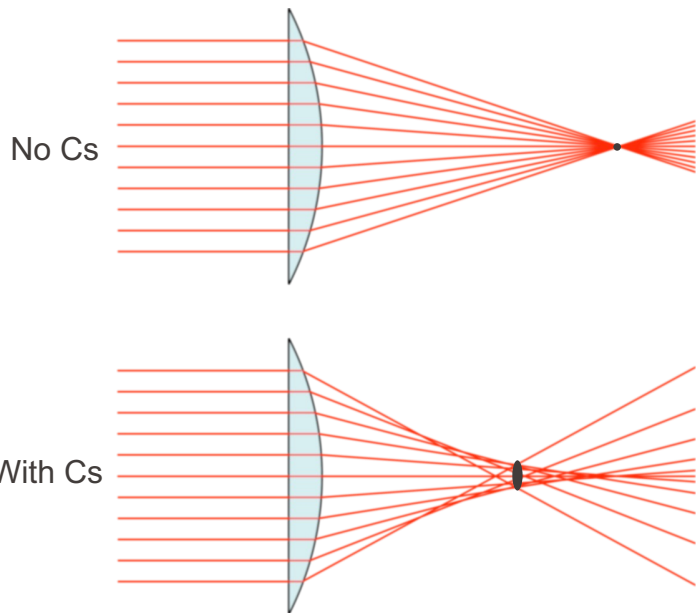


- Chromatic aberration (C_c)

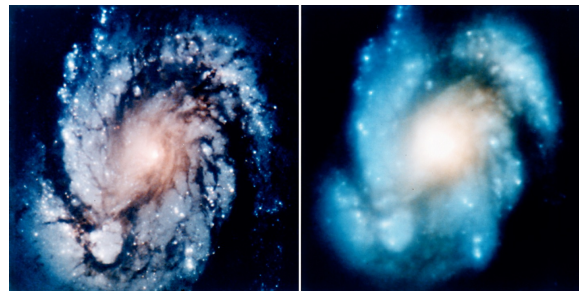


- Lens cannot focus all energies to the same convergence point.
- Electrons of lower energy will be bent more strongly.
- Correcting the aberration is necessary, otherwise the resulting image would be blurry and delocalized, a form of aberration where periodic structures appear to extend beyond their physical boundaries.
- C_c increases with source energy spread.

- Spherical aberration (Cs)

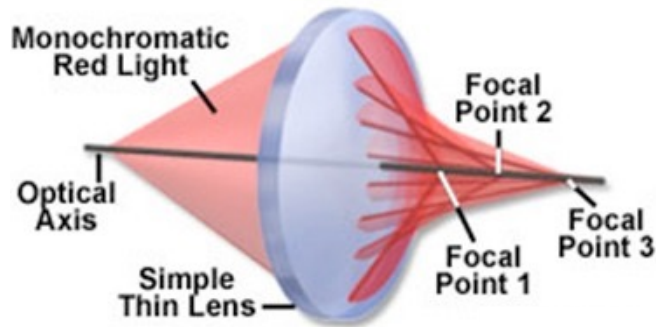


- Parallel rays that pass through the central region of the lens focus farther away than the rays that pass through the edges of the lens.
- Results in multiple focal points and thus a blurred image.
- Larger probe and lower resolution.



Core of the galaxy M100 ©NASA

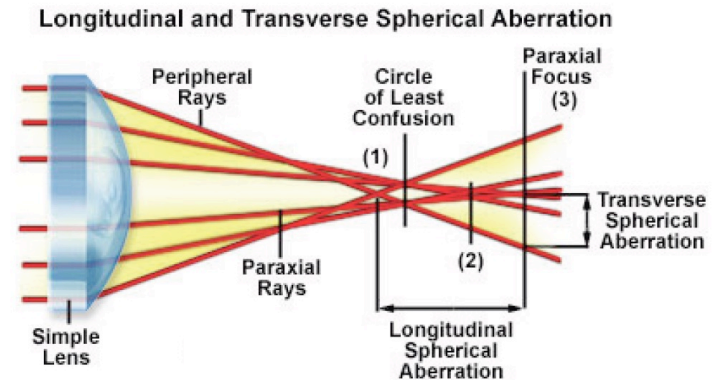
- Spherical aberration (C_s)

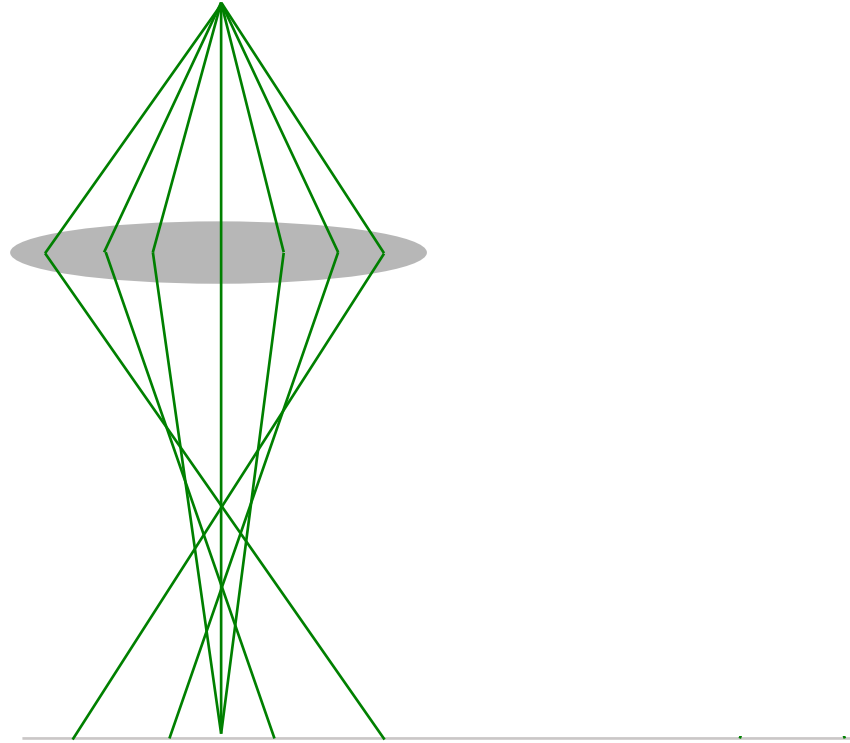


$$\alpha_{opt} = \left(\frac{4\lambda}{C_s} \right)^{\frac{1}{4}}$$

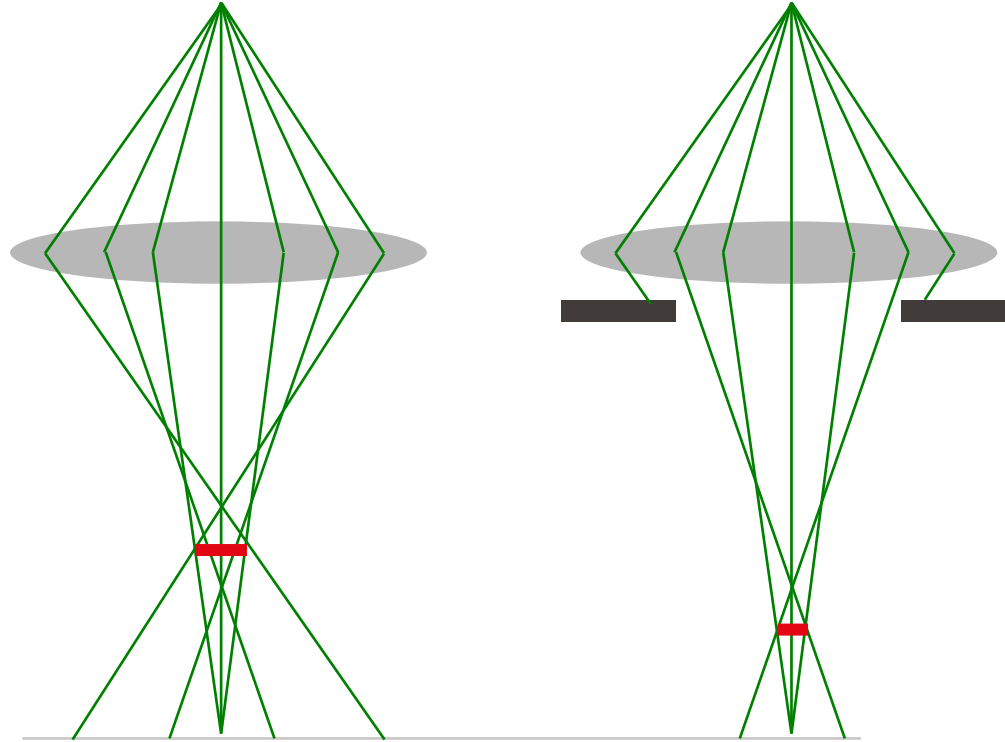
$$d_{opt} = 0.61 \frac{\lambda}{\alpha_{opt}} = 0.43 \lambda^{\frac{3}{4}} C_s^{\frac{1}{4}}$$

- Focal length depends on the distance from optical axis
- Image of the object is dispersed along the optical axis





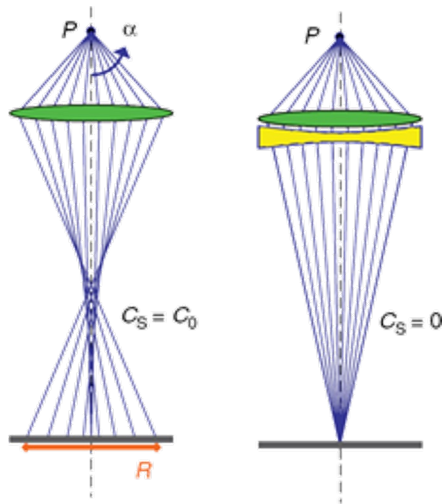
How to lower the effect of spherical aberration?



Inserting an aperture can lessen the effect of spherical aberration
But it comes with a cost → Lower current and more diffraction effect

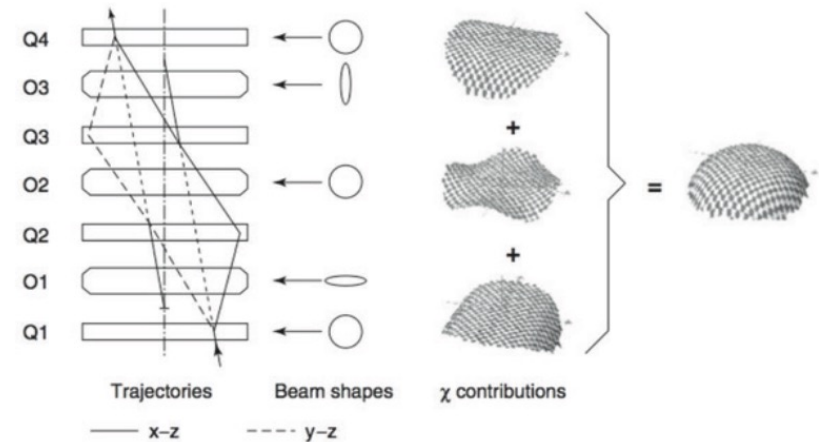
■ Cs correction in light optics

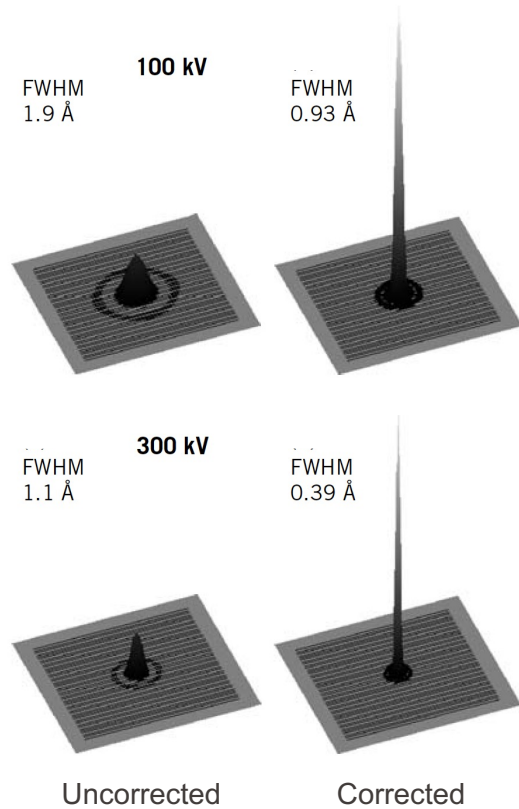
- Correction with combination of convex and concave lenses



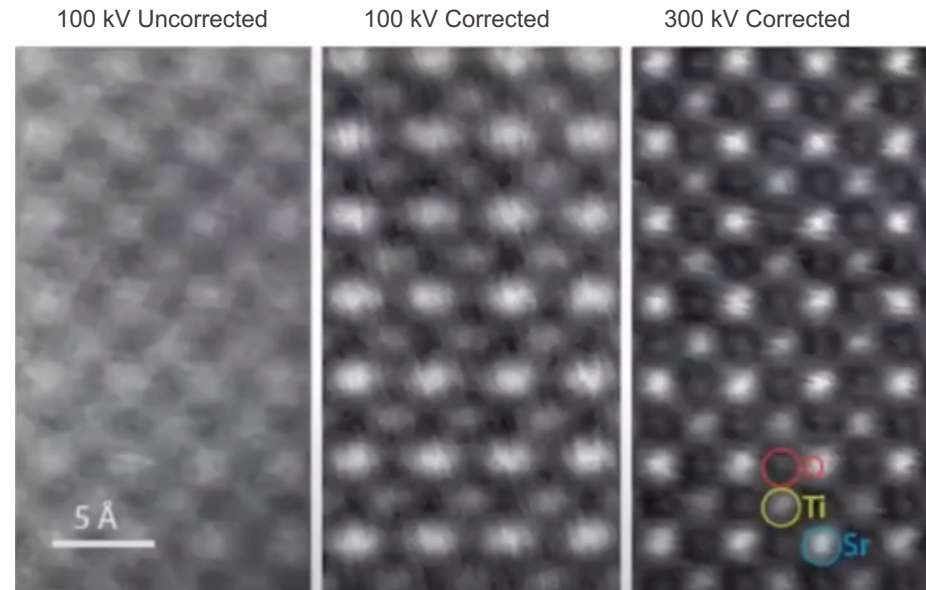
■ Cs correction in electron optics

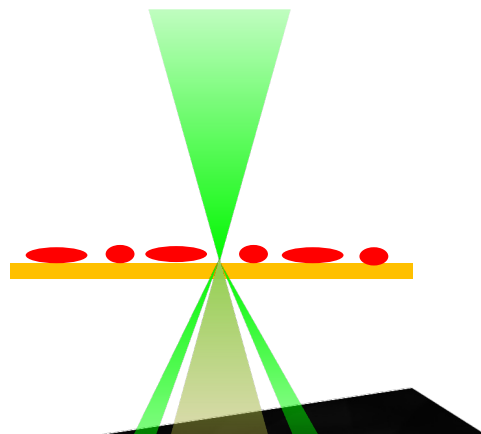
- Combination of standard radially-symmetric convergent lenses with multipole divergent lenses (e.g. tetrapoles, hexapoles) to tune C_s .
- Compensate C_s and other distortions with equivalent but opposite components to add together with aim of giving ideal spherical wavefront



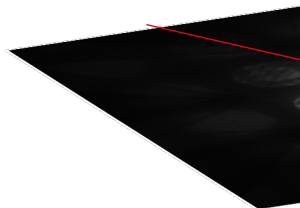


Z-contrast images

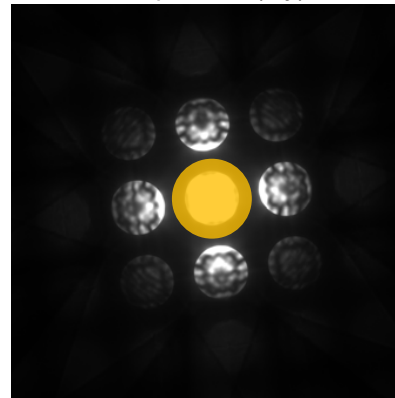




Disk-shape
electron detector



Scan position (x,y)



Defects, crystal tilts relative to incident or changes in thickness,
→ Change in diffraction condition and intensities

→ Change in integrated signal on detector → Signal change on the image

Zone axis CB

- Instead of spot pattern, obtain disc pattern
- Larger convergence semi-angle $\alpha \Rightarrow$ large

$\alpha = 3.9 \text{ mrad}$

$\alpha = 8.6 \text{ mrad}$

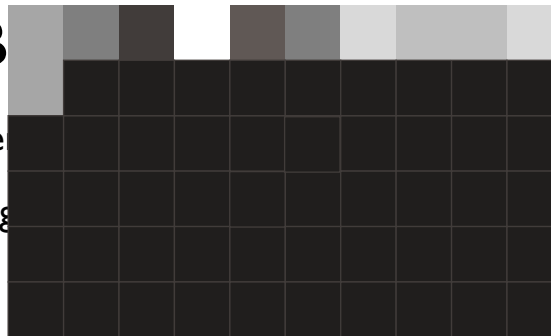
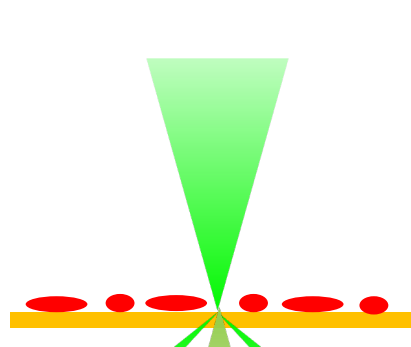


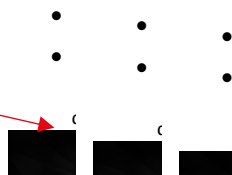
Image formation



Disk-shape
electron detector

■ MSE-735 | Introduction to STEM

Ar



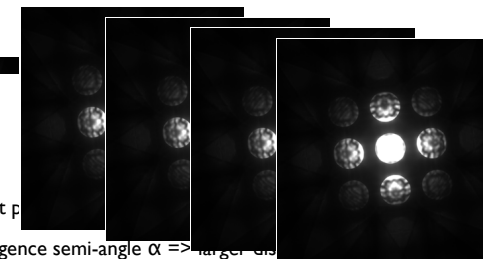
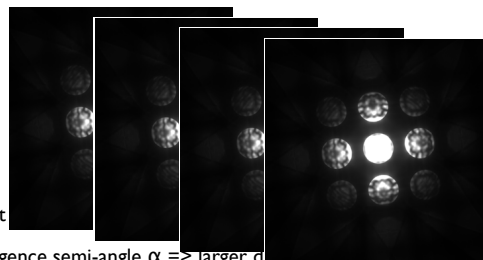
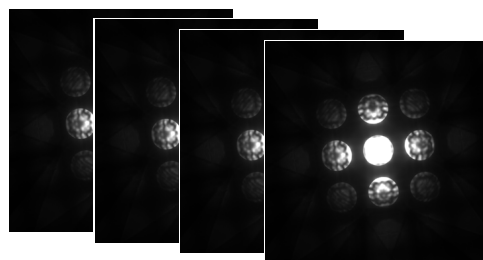
- Instead of spot
- Larger convergence semi-angle $\alpha \Rightarrow$ larger disk

$\alpha = 3.9$ mrad



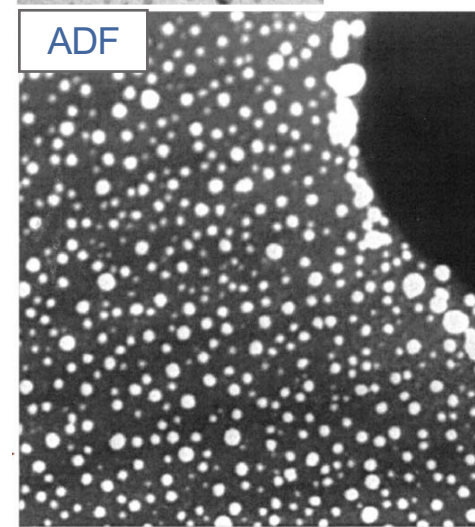
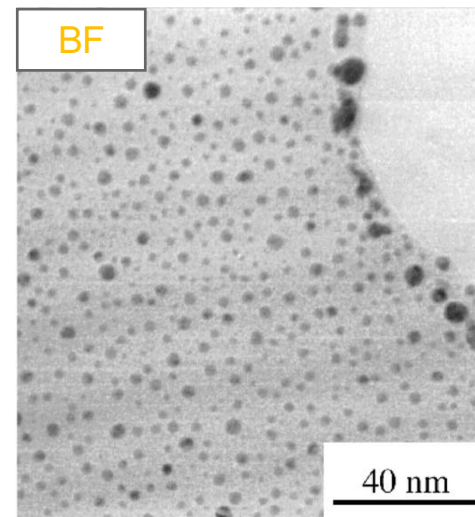
- Instead of spot p
- Larger convergence semi-angle $\alpha \Rightarrow$ larger disk

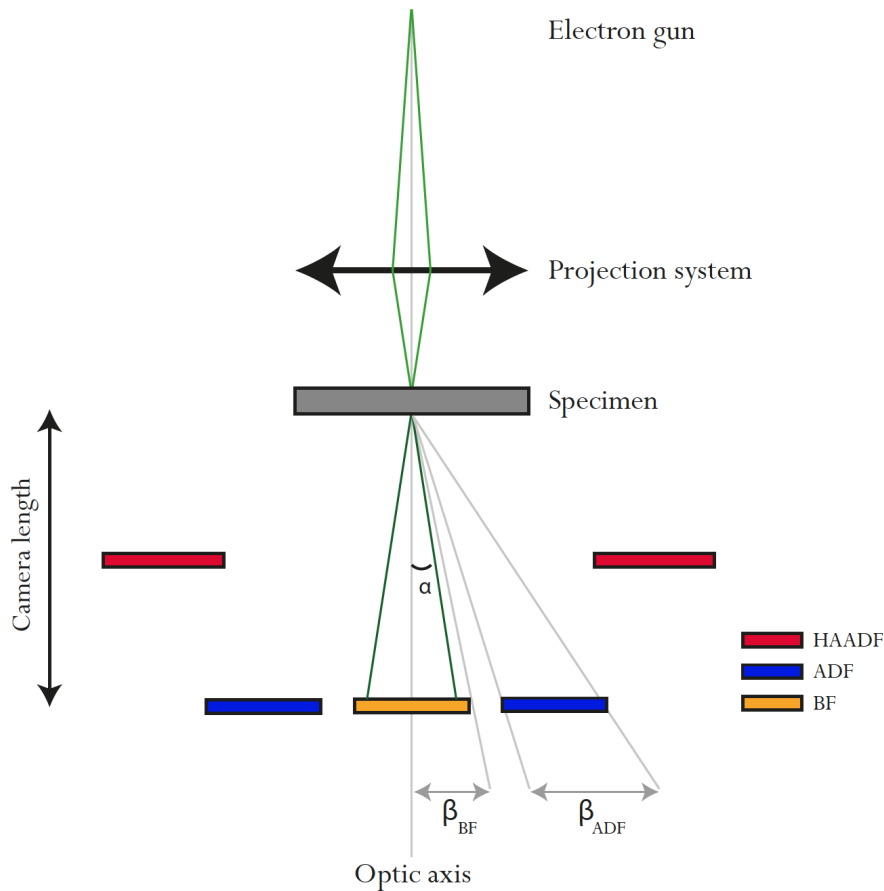
$\alpha = 3.9$ mrad



$\alpha = 8.6$ mrad

$\alpha = 19.3$ mrad





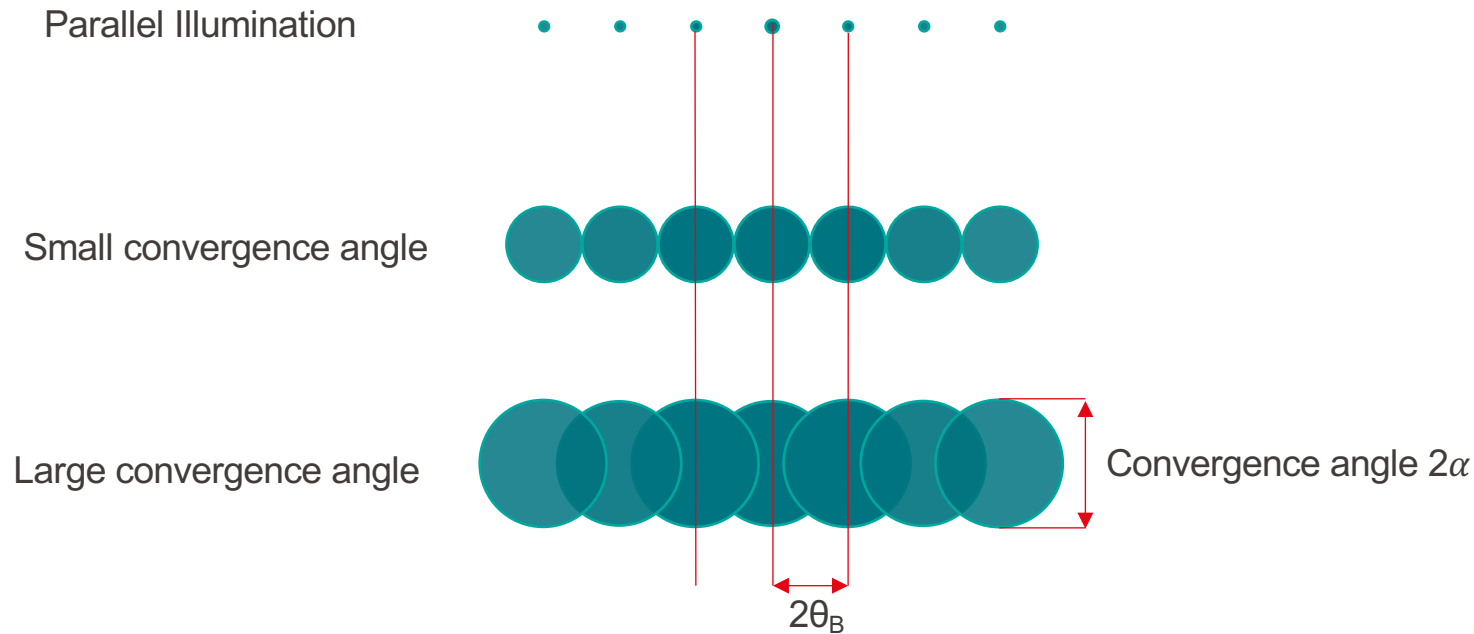
The focused probe is a convergent electron beam.

The BF and DF detectors are radially symmetric. Therefore all of them are characterised by angles – angle of convergence for the beam; collection of scattering angles for the detectors

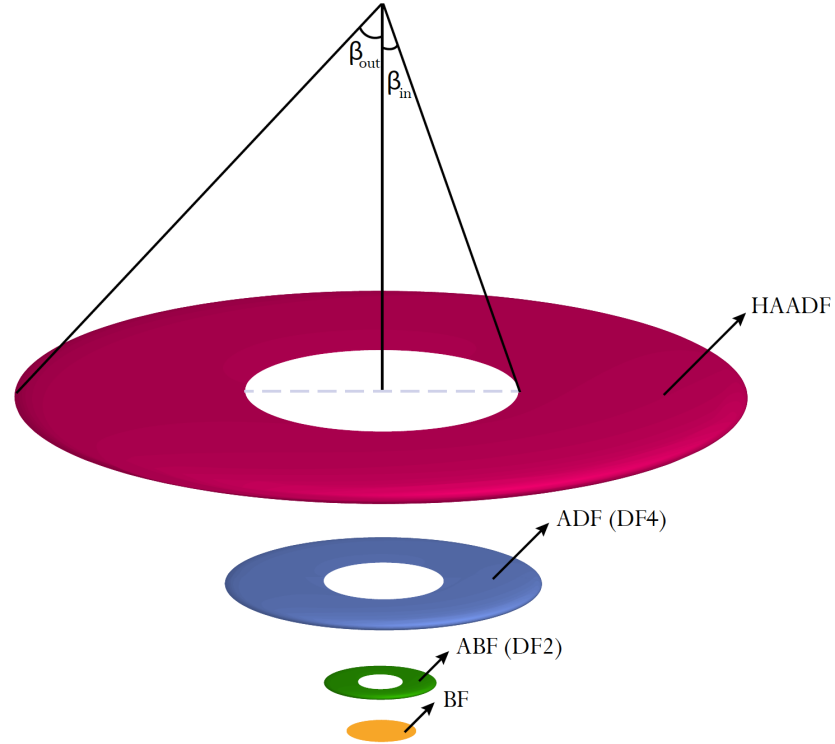
The convergence semi-angle of the probe is called α

A collection semi-angle for a detector is called β

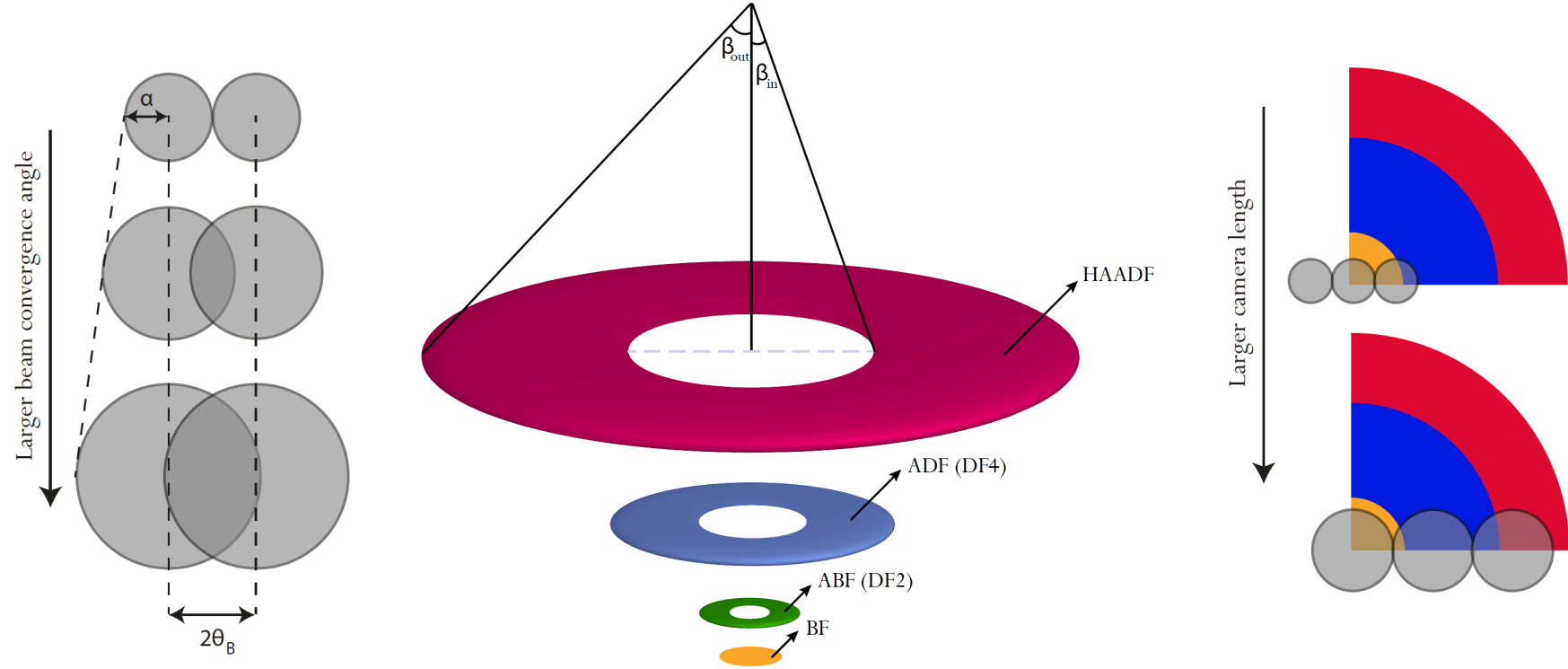
Knowledge of these angles is important for STEM imaging

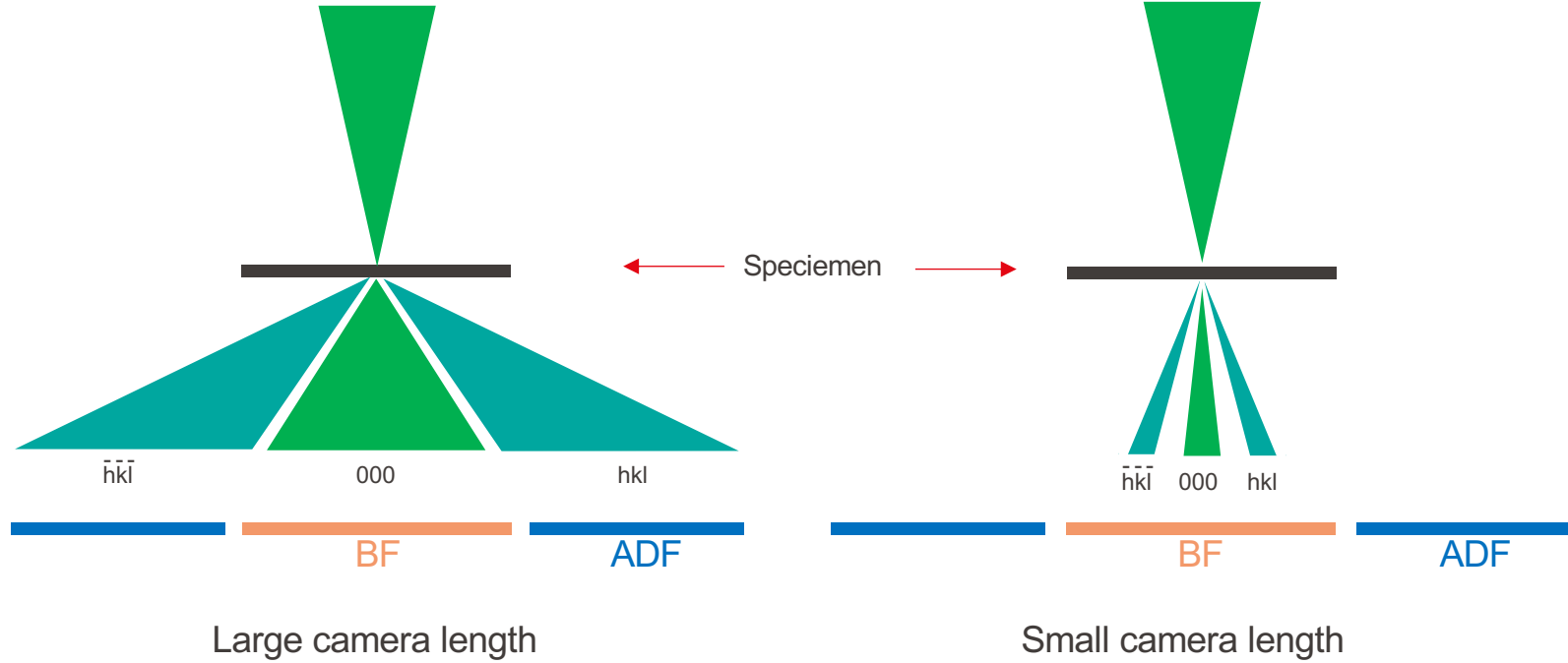


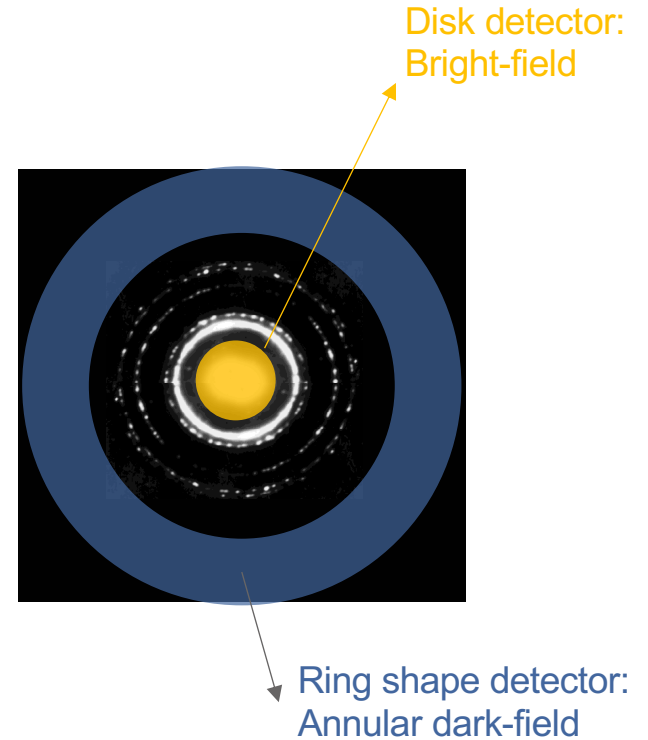
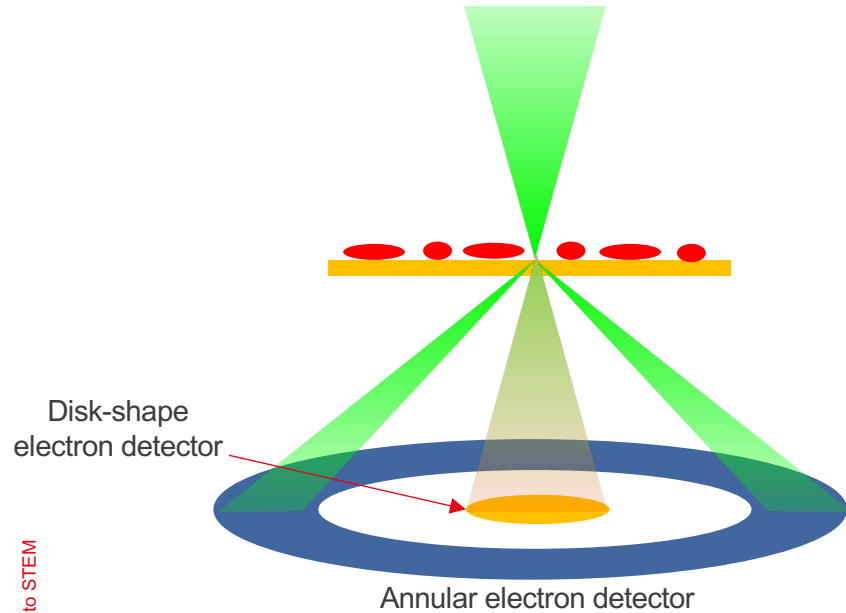
Disks overlap if $\theta_B < \alpha$

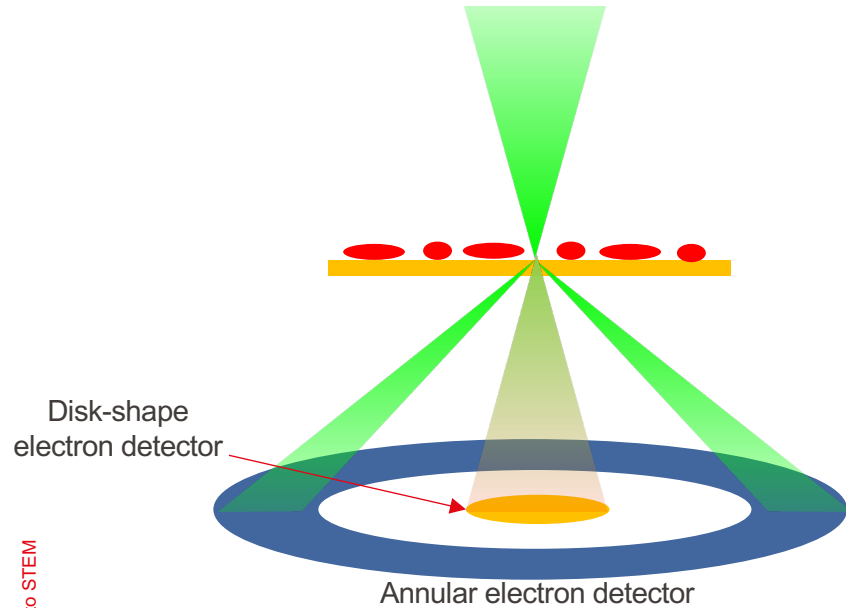


Schematic showing the configuration of the STEM detectors in the Tecnai-Osiris and Titan-Themis installed at CIME.

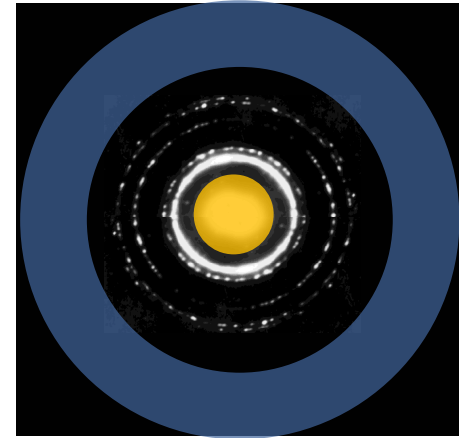




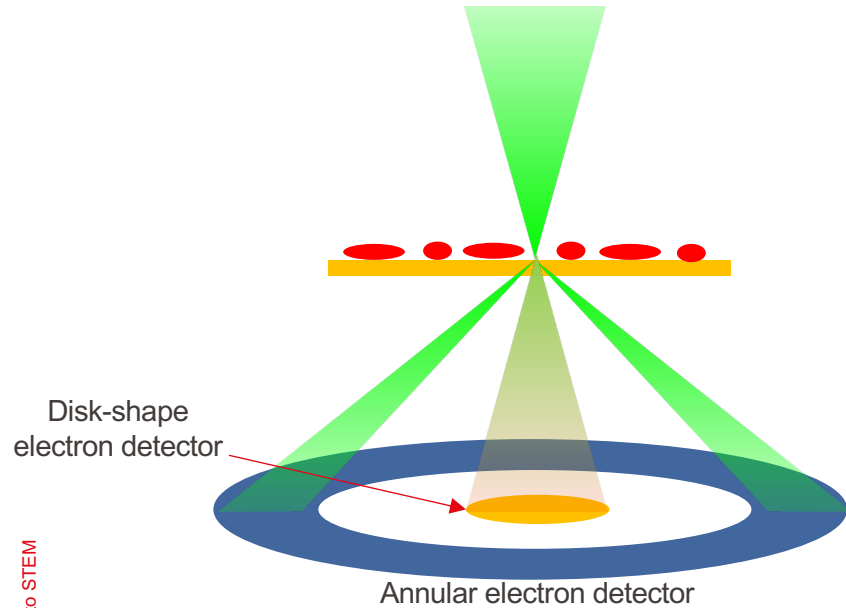




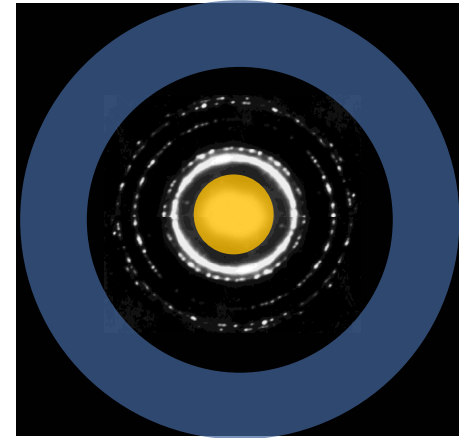
BF detector is a solid disc that picks up the direct beam which varies in intensity depending on the specific point on the specimen illuminated by the probe at that specific time.



Bright-field: On axis | Electrons pass through the sample without being scattered → Coherent imaging



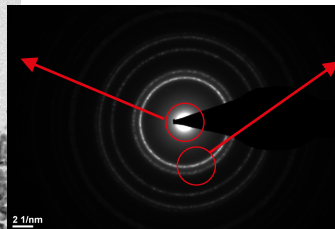
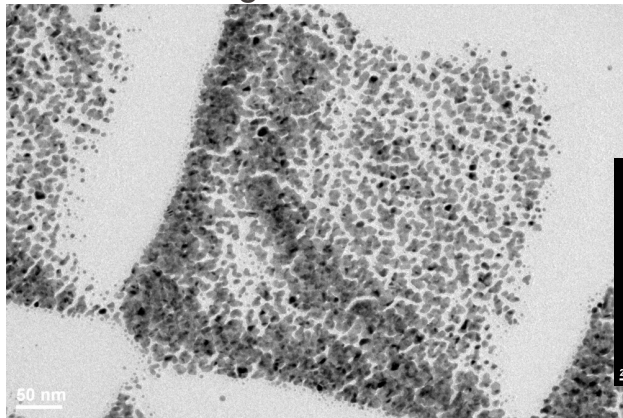
For dark-field imaging, we use an annular detector, with certain inner and outer collection semi-angles, which surrounds the BF detector, and then all the scattered electrons fall onto that detector.



- Proposed by Crewe and co-workers during the initial development of the modern STEM.
- Detector consists of an annular sensitive region that detects electrons scattered over an angular range. The radii can both vary over a large range, but typically the inner radius would be in the range of 30–100 mrad and the outer radius 100–200 mrad.
- High scattering angles ($> \sim 100$ mrad) would enhance the compositional contrast and that the coherent effects of elastic scattering could be neglected because the scattering was almost entirely thermally diffuse $\rightarrow$ Incoherent imaging

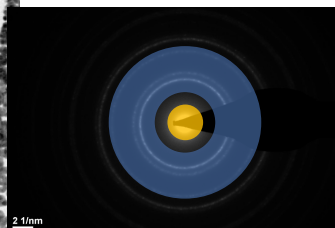
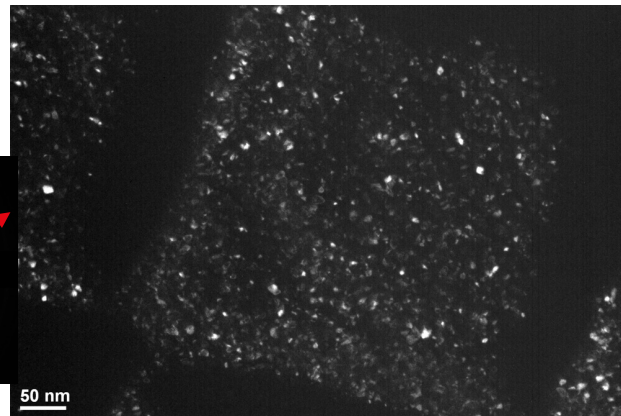
Imaging modes

Bright-field TEM



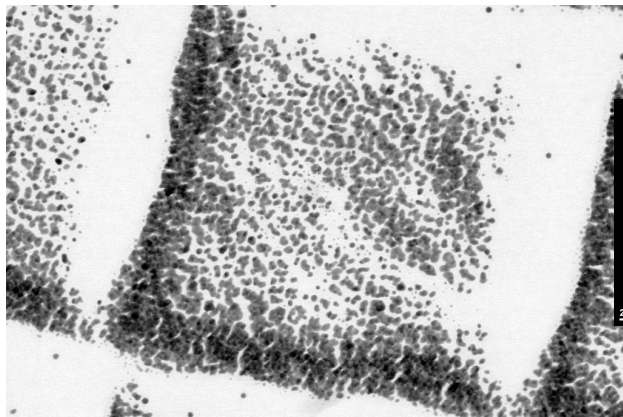
Aperture

Dark-field TEM

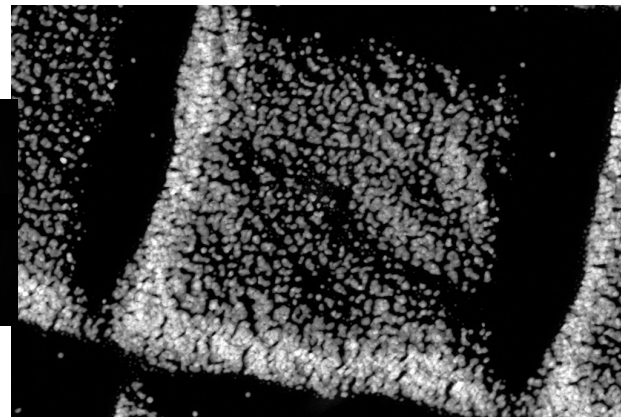


Detector

Bright-field STEM

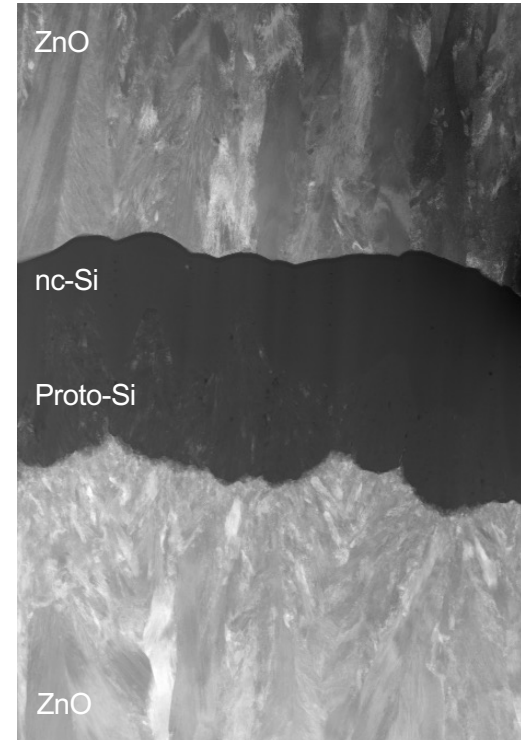
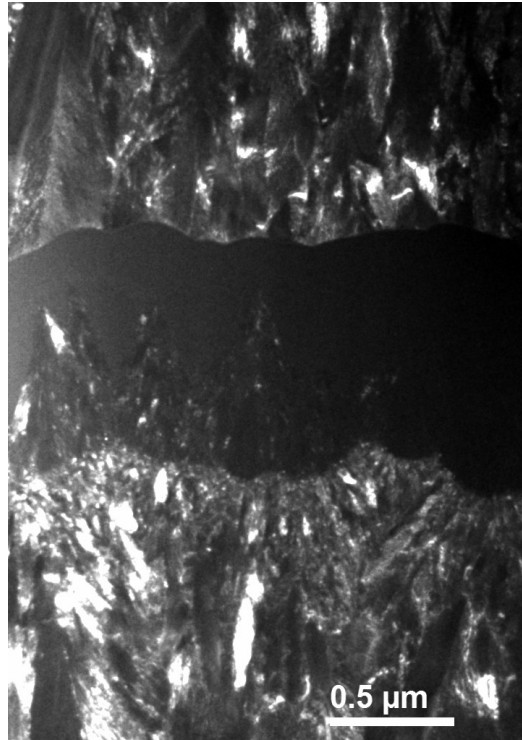


Annular dark-field STEM



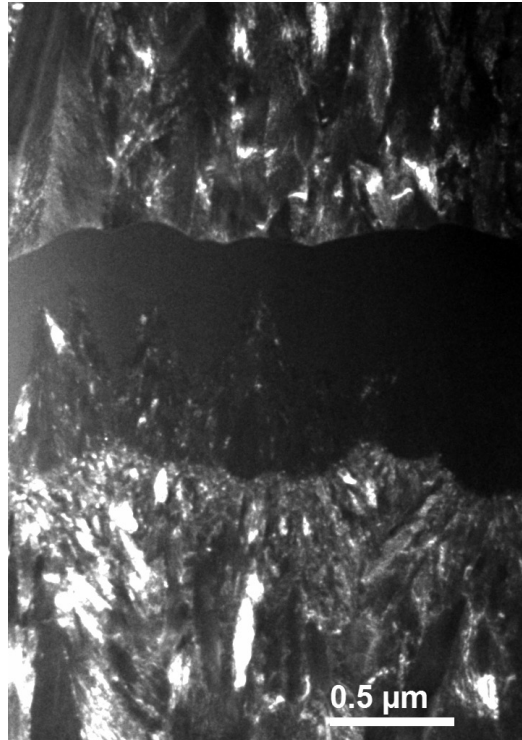
Imaging modes

ADF-STEM and DF-TEM images of a photovoltaic stack
Visible: Protocrystalline/crystalline Si interface, B-doped layer in proto-Si, voids

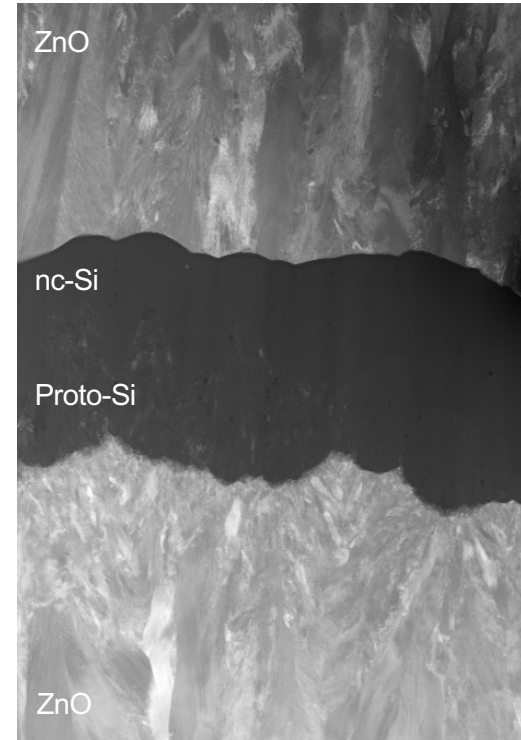


Which one is the annular dark-field STEM image?

ADF-STEM and DF-TEM images of a photovoltaic stack
Visible: Protocrystalline/crystalline Si interface, B-doped layer in proto-Si, voids

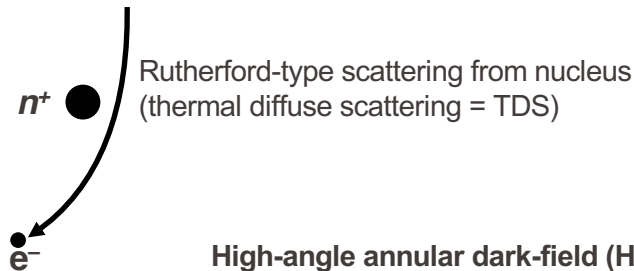
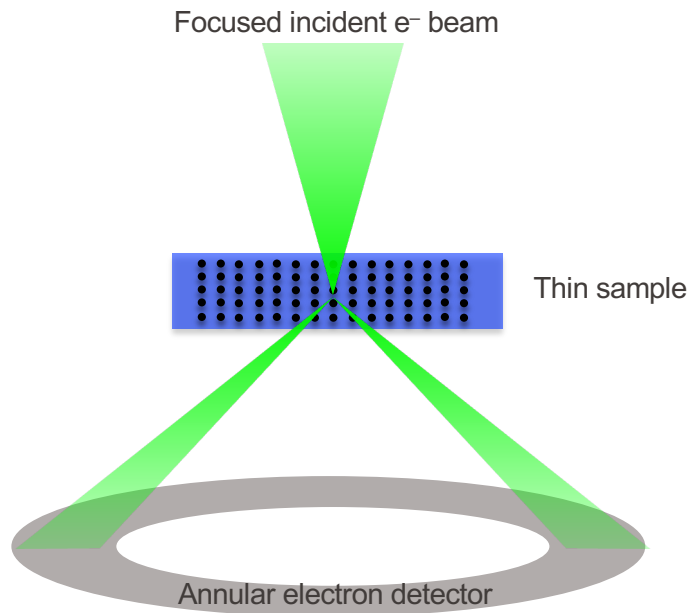


Few grains have intensity
strong contrast

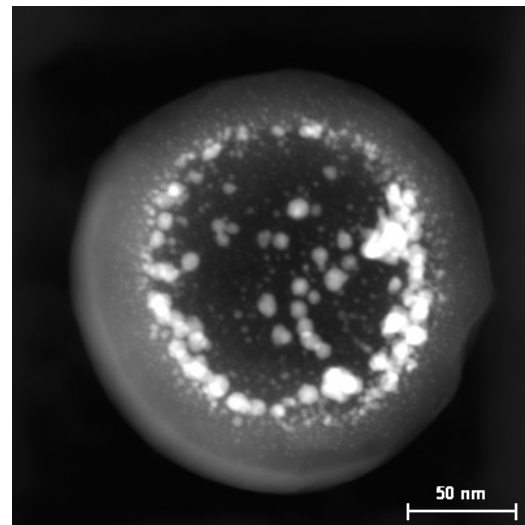


More grains have intensity
More grain visibility & less contrast

Imaging modes | High-angle annular dark-field



High-angle annular dark-field (HAADF) image

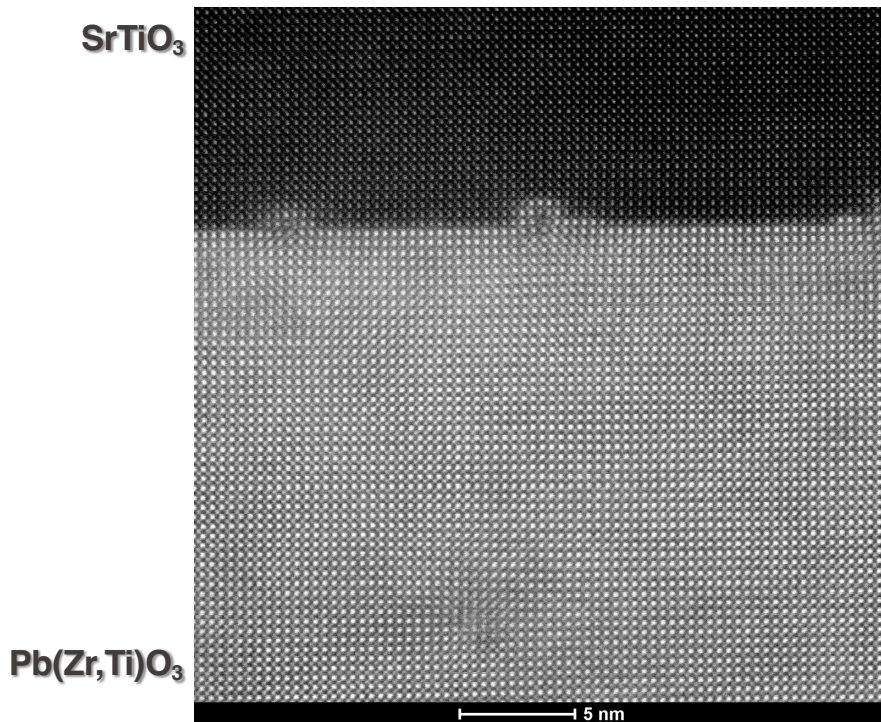


Ni-Rh catalytic nanoparticles in carbon shell

Mass/thickness contrast image

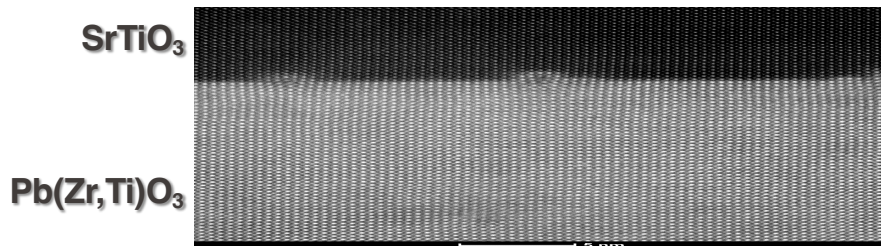
- Incoherent Rutherford-type scattering deflects transmitted e^- to high angle of scattering;
- larger nucleus / thicker the specimen $\rightarrow$ more scattering
- Map image intensity as function of probe position (x, y)
- Image intensity: $I(x, y) \propto t * Z^{1.6-2}$

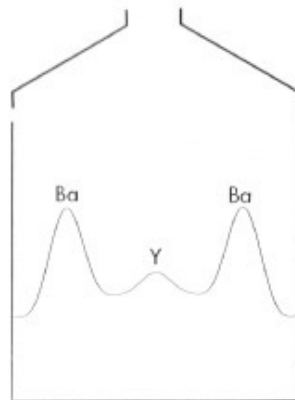
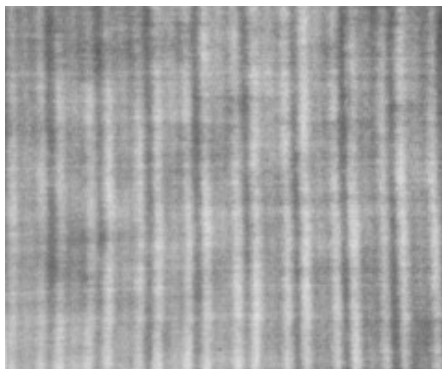
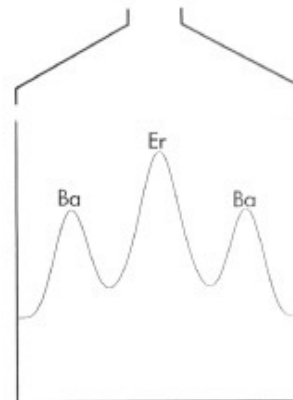
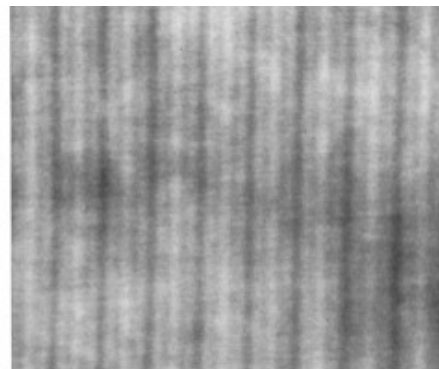
Cs-corrected atomic resolution HAADF-STEM of perovskite interface (300 kV)



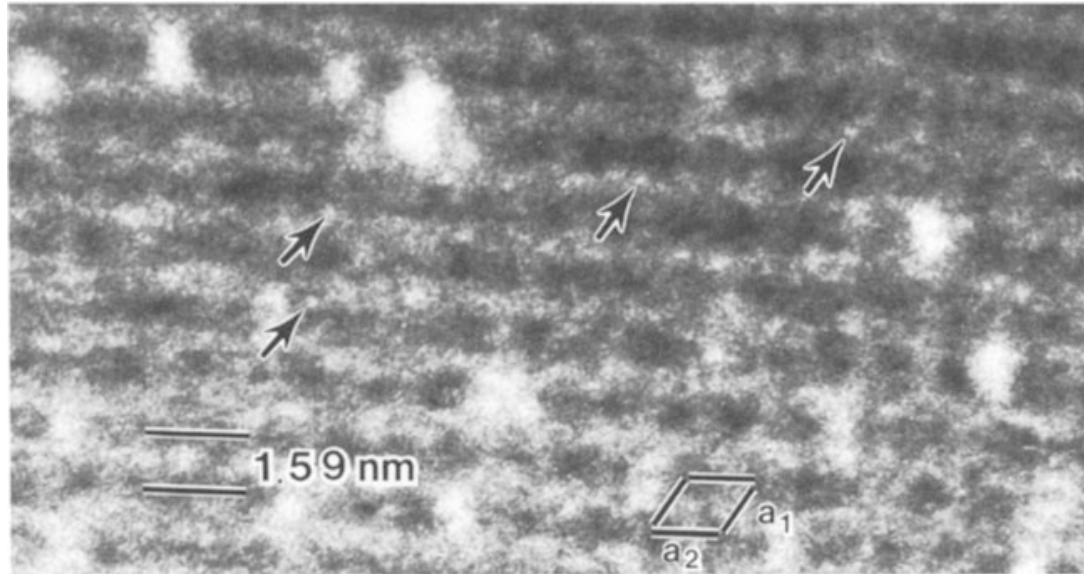
Imaging modes | High-angle annular dark-field

Cs-corrected atomic resolution HAADF-STEM of perovskite interface (300 kV)

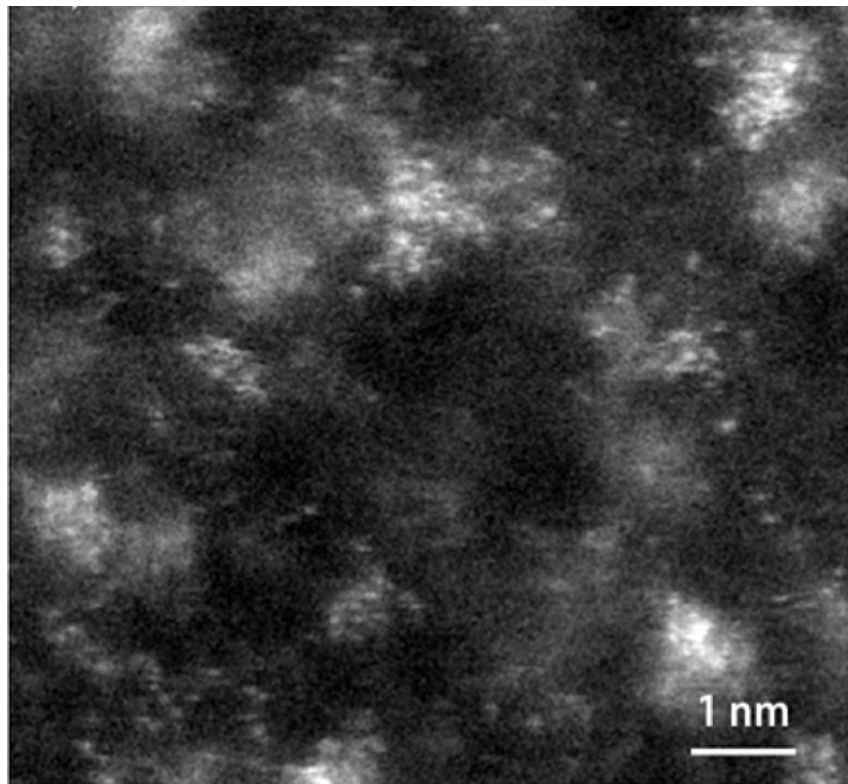


$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 

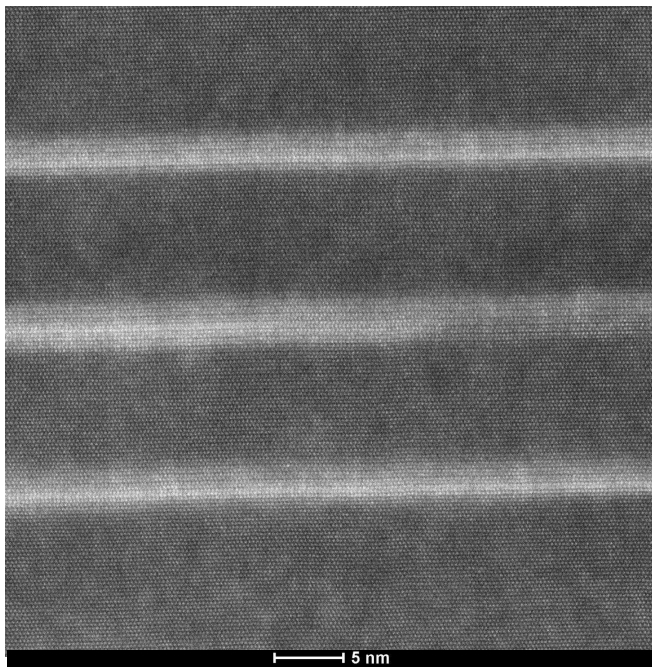
HAADF image showing individual Pt atoms in a zeolite framework



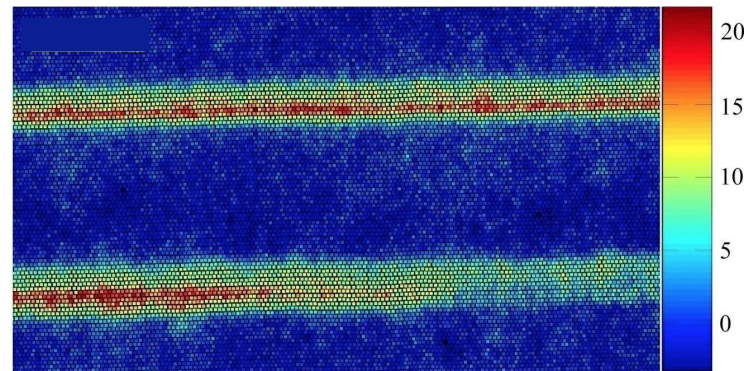
Pt clusters inside a metallosupramolecular polymer



In / Ga multilayer



Evaluated map of the In concentration

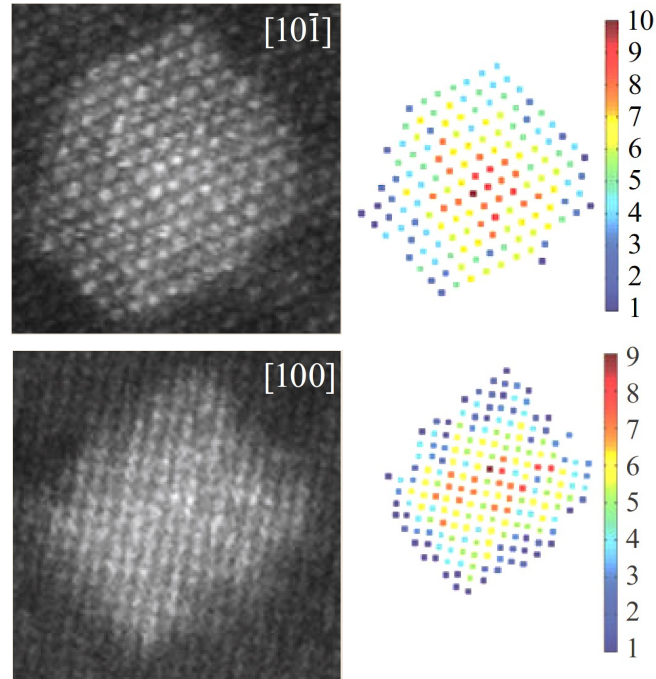


Quantitative STEM allows measurement of composition

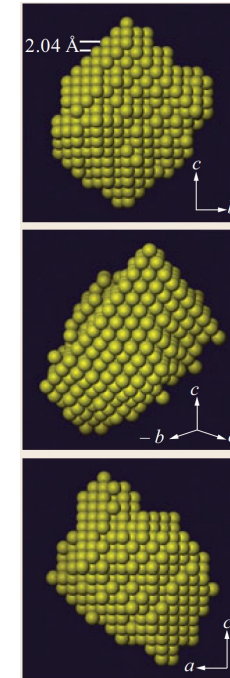
Requires detector calibration

Imaging modes | High-angle annular dark-field

Ag cluster embedded in an Al matrix together with the number of Ag atoms per column

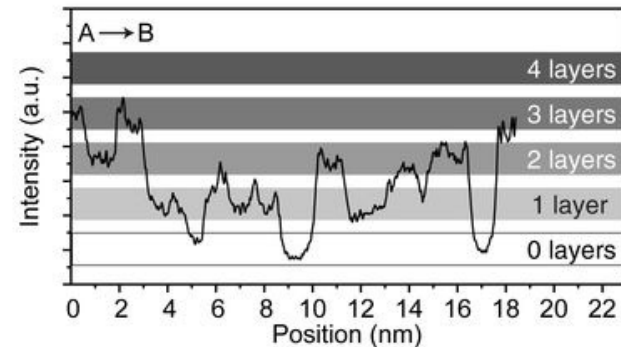
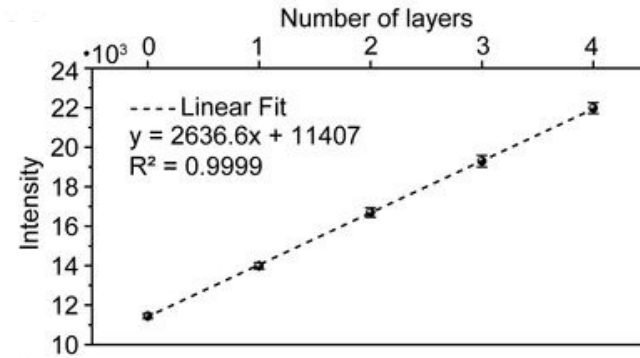
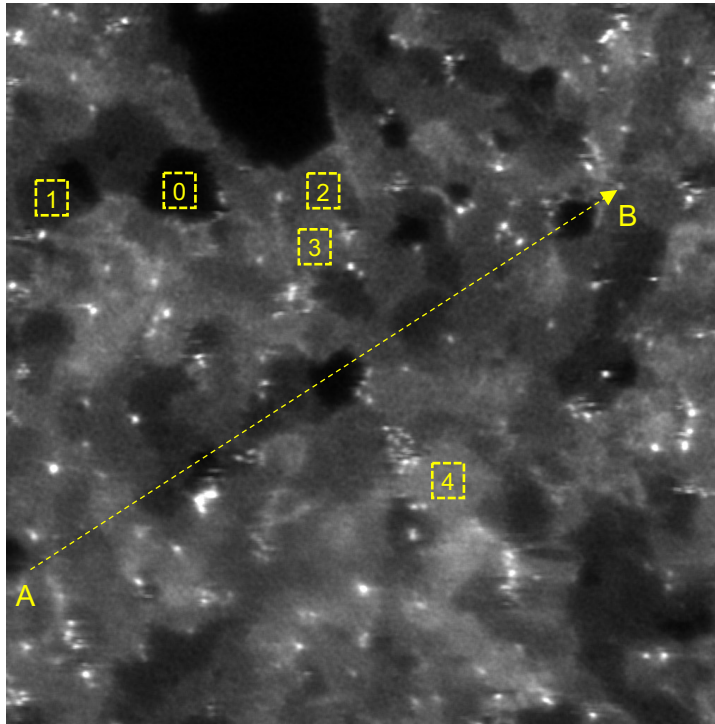


Computed 3-D reconstruction of the cluster viewed along three different directions



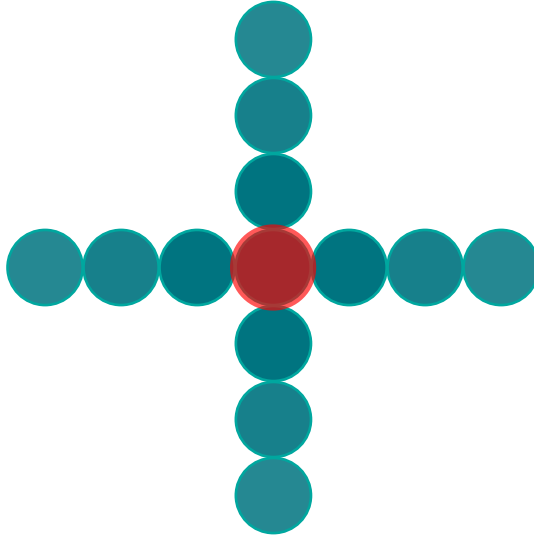
Atom counting implies precise detector calibration and assumptions about the sample

Example : Variation of the intensity according to the number of graphene layers



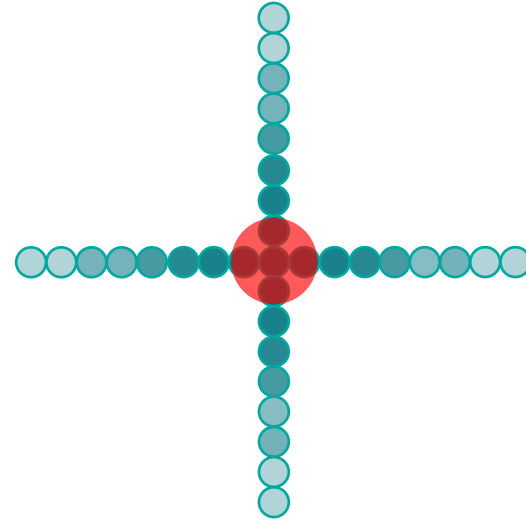
Imaging modes | Effect of camera length

High camera length



Directly transmitted disk on the solid disk detector
→ BF-STEM image

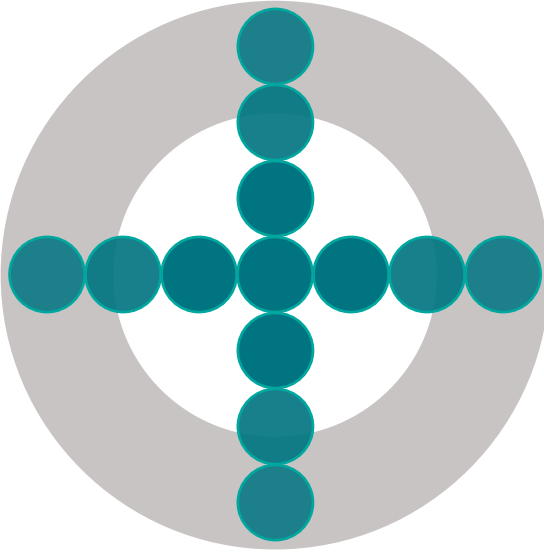
Low camera length



Both direct and diffracted disks
on the solid disk detector

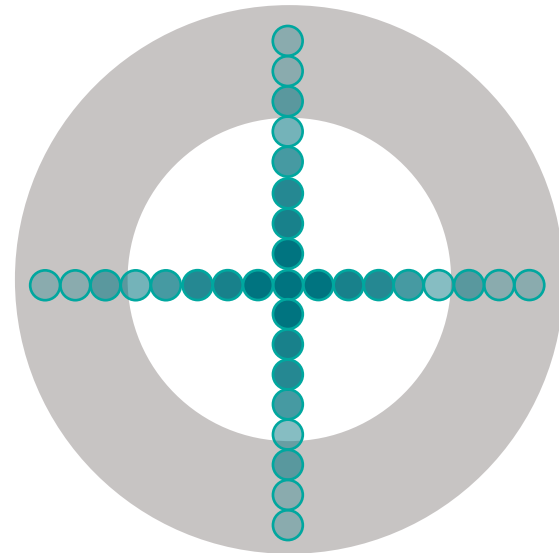
Imaging modes | Effect of camera length

High camera length



Dominant diffraction contrast

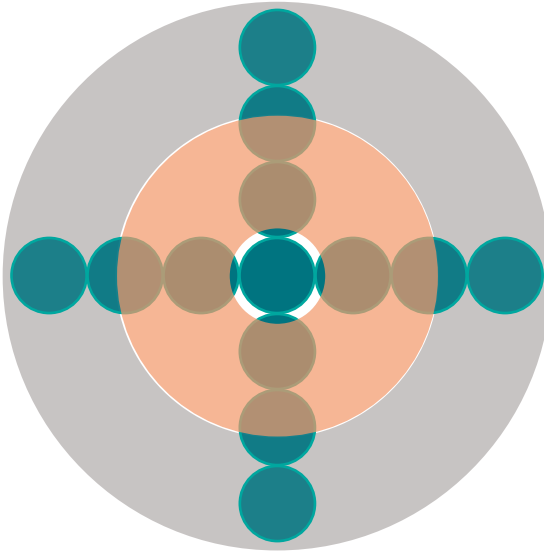
Low camera length



Dominant Z-contrast (TDS)

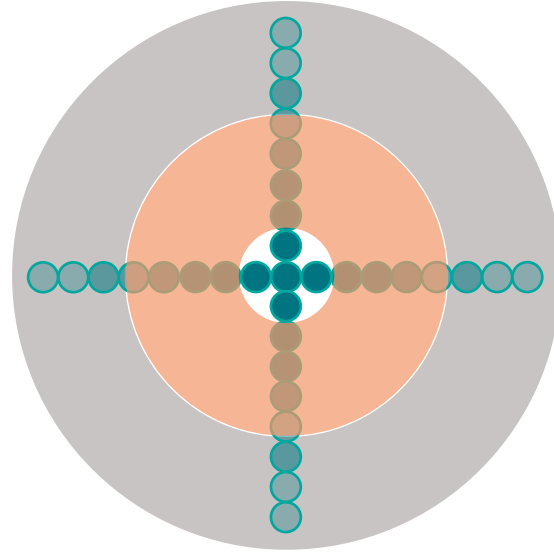
Imaging modes | Effect of camera length

High camera length



Mixed diffraction and Z-contrast → MAADF
Pure diffraction contrast → LAADF

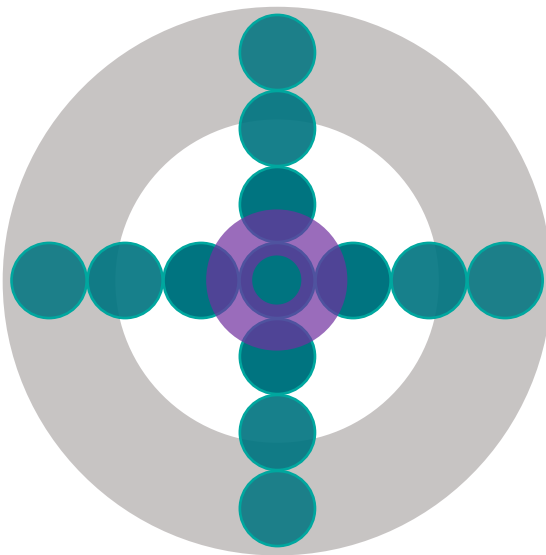
Low camera length



Z-contrast image → HAADF
Mixed diffraction and Z-contrast → MAADF

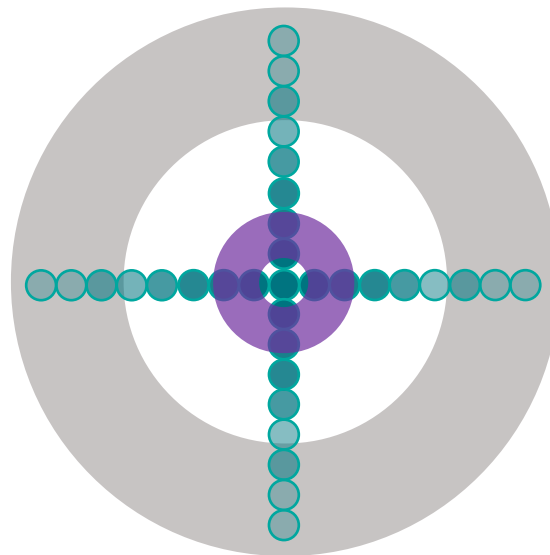
Imaging modes | Effect of camera length

High camera length



Mixed diffraction and Z-contrast $\rightarrow$ MAADF
Annular bright-field (ABF) image

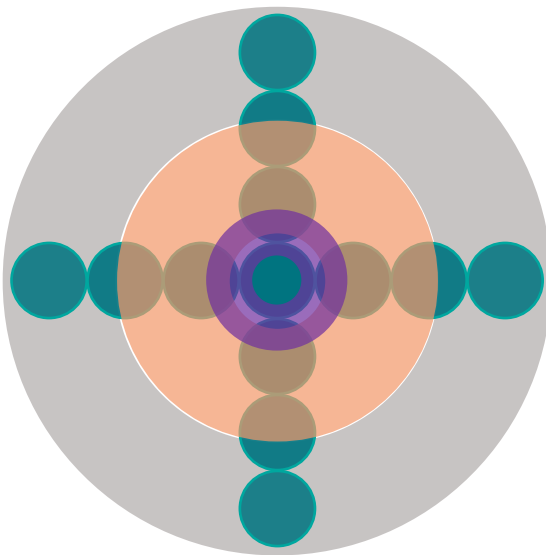
Low camera length



Z-contrast image $\rightarrow$ HAADF
Pure diffraction contrast $\rightarrow$ LAADF

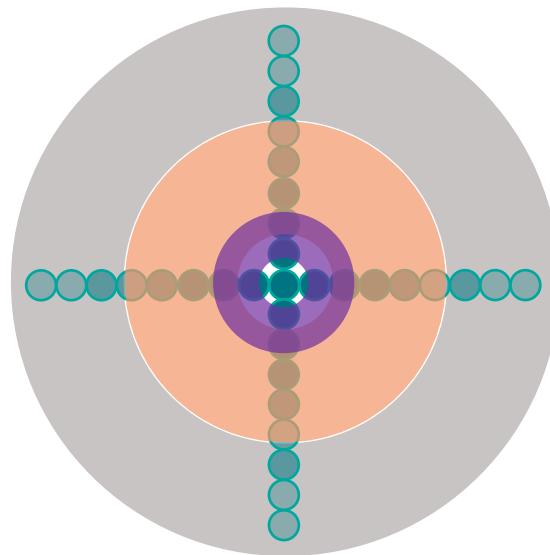
Imaging modes | Effect of camera length

High camera length



Mixed diffraction and Z-contrast → MAADF
Pure diffraction contrast → LAADF
Annular bright-field (ABF) image

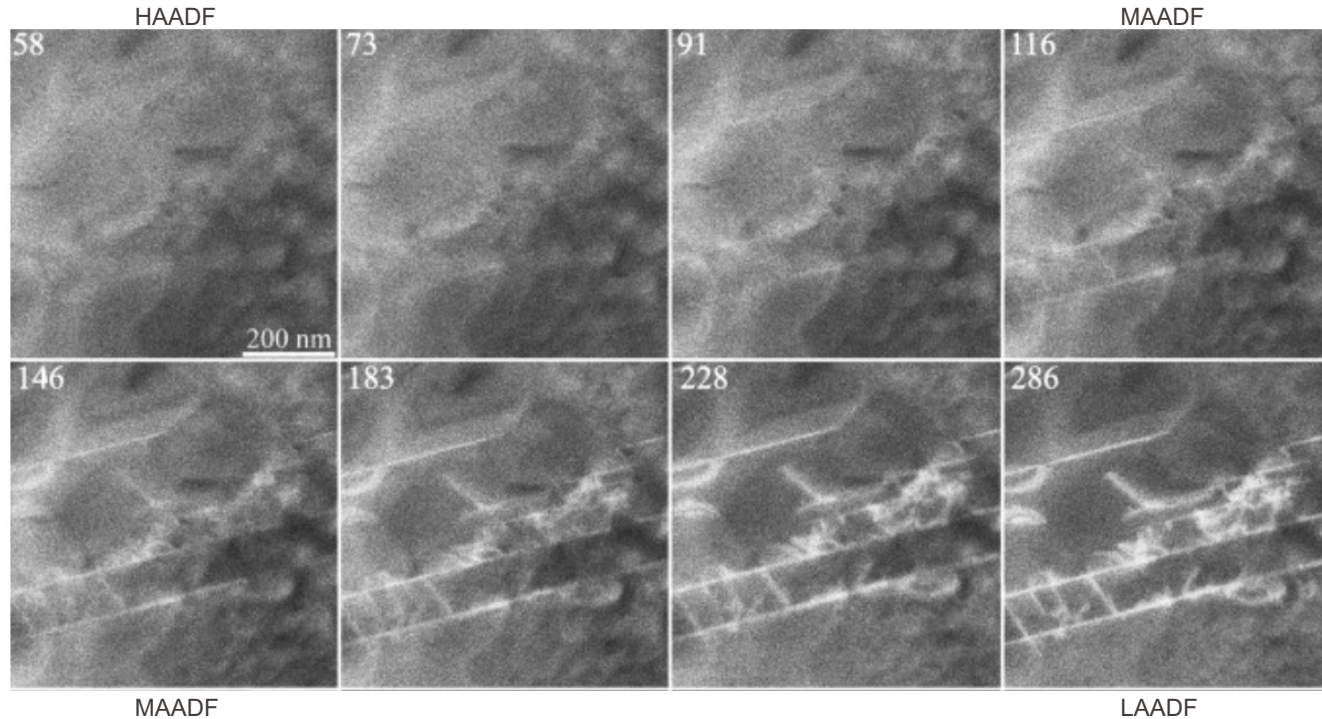
Low camera length



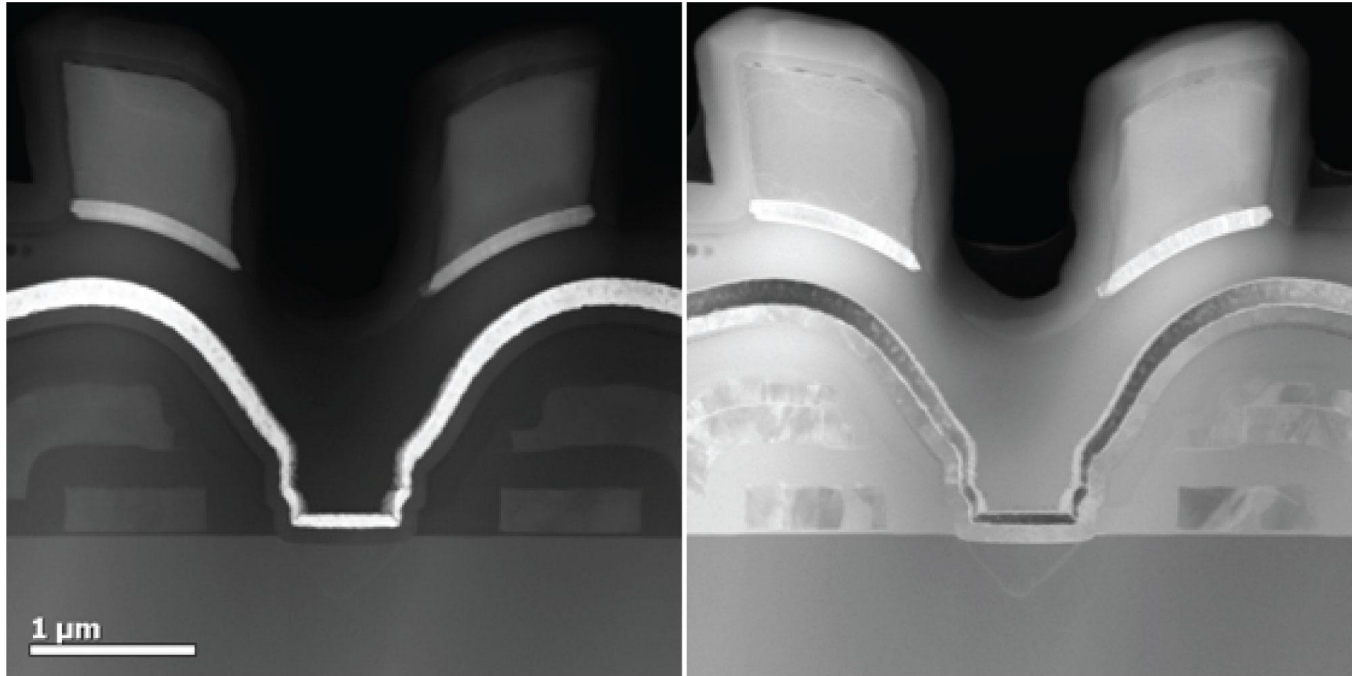
Z-contrast image → HAADF
Mixed diffraction and Z-contrast → MAADF
Pure diffraction contrast → LAADF

Imaging modes | Low-angle annular dark-field

Example: Variation of defect contrast with camera length in γ / γ' region of Ni-superalloy



Imaging modes | Medium-angle annular dark-field

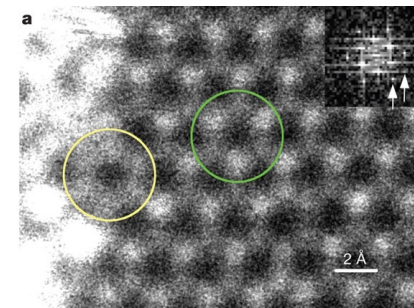
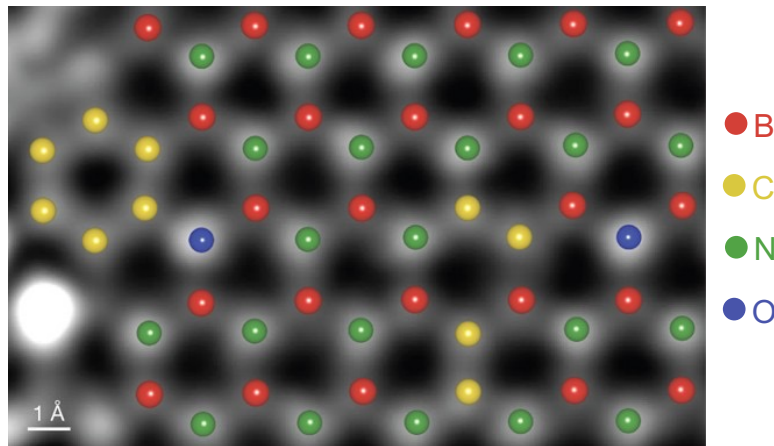


Jointly acquired HAADF and MAADF signals

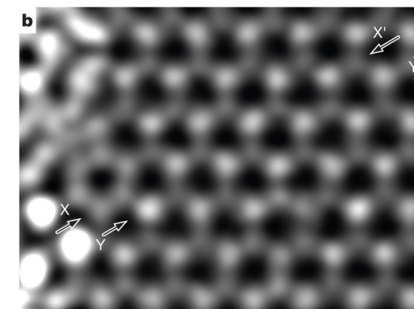
The HAADF signal (left) contrast is easily interpreted in terms of mass thickness of the material while the diffraction contrast MAADF signal (right) reveals highly detailed structural changes in the material. The optimized geometry makes this possible.

Imaging modes | Medium-angle annular dark-field

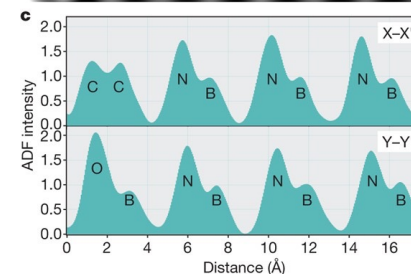
Example: Doped graphene, BN monolayer – C_s STEM



As recorded.



Corrected for distortion, smoothed, and deconvolved to remove probe tail contributions to nearest neighbours.



Line profiles showing the image intensity (normalized to equal one for a single boron atom) as a function of position in image **b** along X-X' and Y-Y'.

Low kV essential to prevent knock-on damage; here 60 kV used

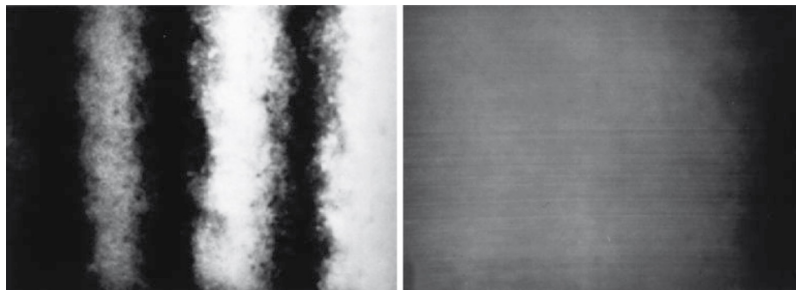
As λ increases aberration correction even more important for obtaining atomic resolution

Medium-angle ADF gives intensity $I \propto Z^{1.7}$ but with increased signal intensity compared to true HAADF image. This intensity is needed for imaging single atom by single atom (here $\beta = 58\text{--}200$ mrad)

Definition of incoherent imaging: the image gives a representation of the object, which is blurred by the size of the probe.

i.e. “The sharper the probe, the clearer the atoms appear. Different atoms will have spikes with different heights, dependent on their cross-sections, which are roughly proportional to Z^2 . As the probe is focused and defocused the atoms come into clear view and blur out again
→ Camera-like characteristic.

Example: Si <110>



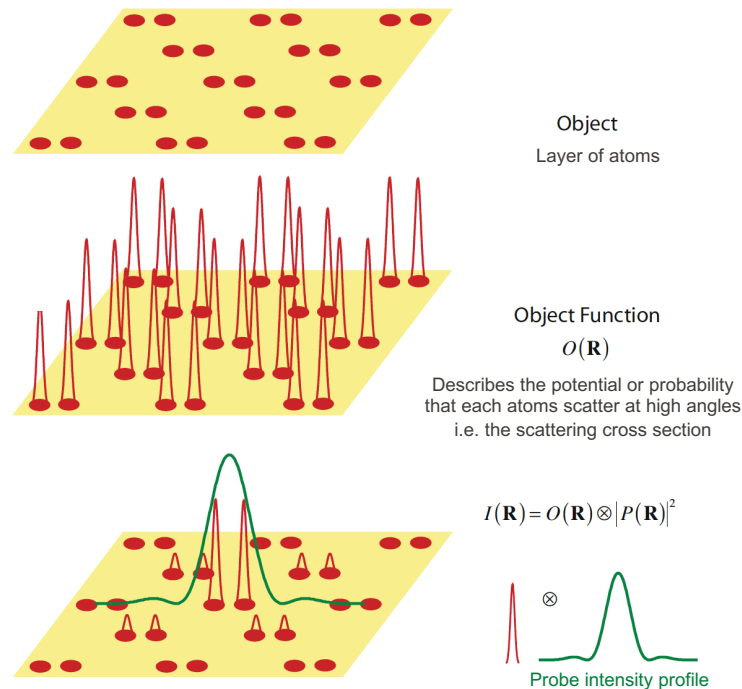
BF-STEM: Thickness fringes visible
→ Coherent

Z-contrast image
→ Incoherent

Ultramicroscopy, 37 (1991), pp. 14-38

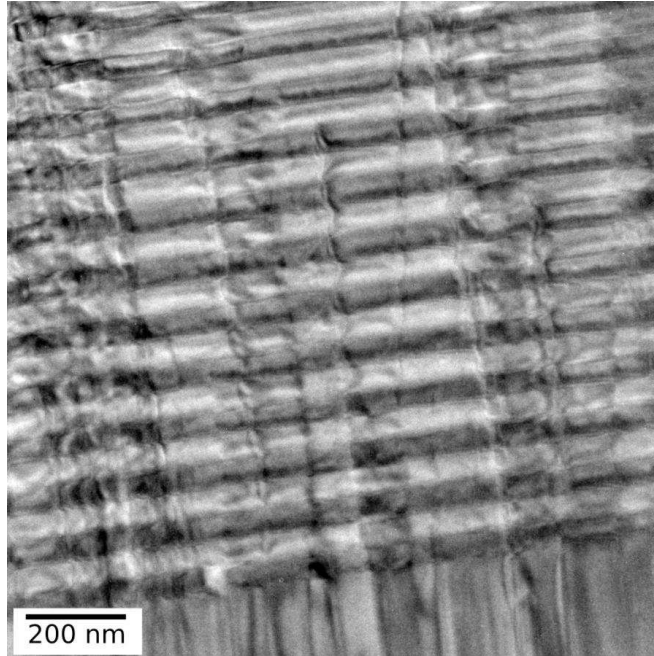
Incoherent:

All phase relationships between electrons ‘emitted’ (in reality scattered) between one atom and the next are random, and each atom can be considered an incoherent source of diffuse scattering.



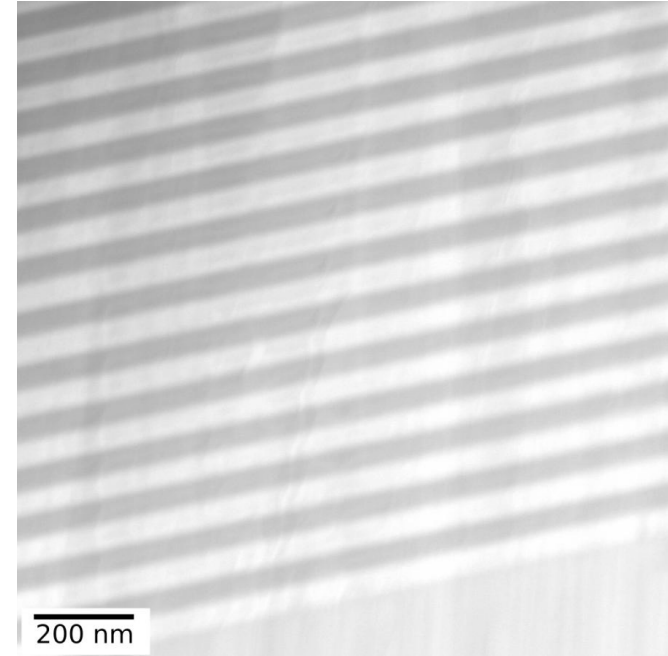
Imaging modes | Coherent vs incoherent image

BF-TEM



Contrast due to strain and diffraction effects

HAADF-STEM



Contrast determined by atomic number

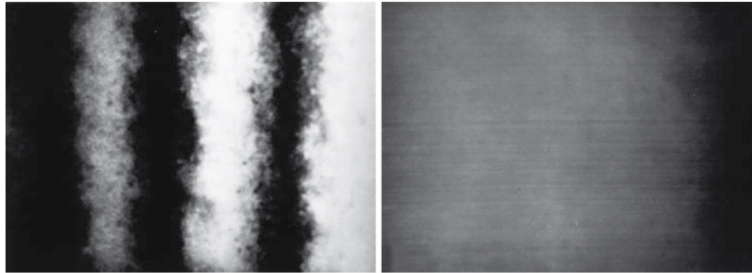
$\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$

GaN

$\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$

Imaging modes | Coherent vs incoherent image

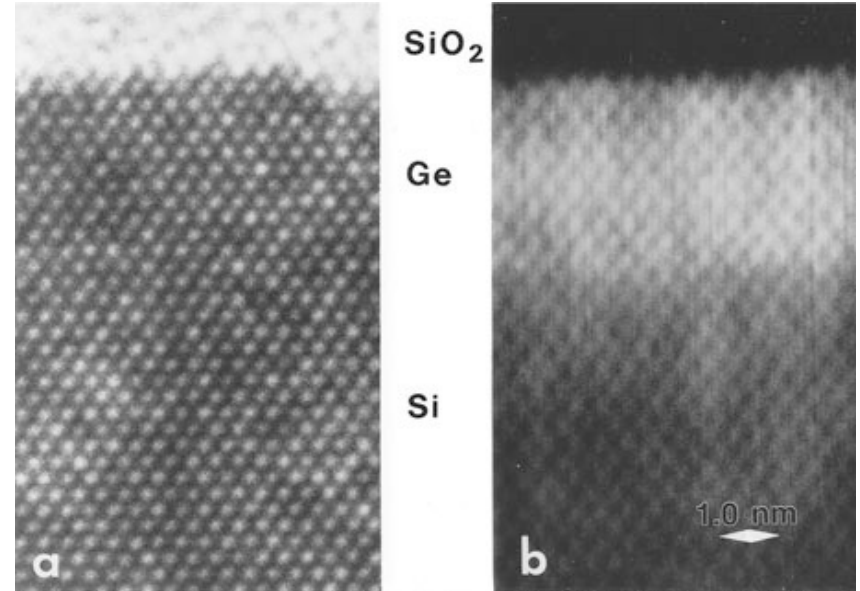
Example: Si <110>



BF-STEM: Thickness fringes visible
→ Coherent

Z-contrast image
→ Incoherent

Example: Images of a Ge film grown epitaxially on Si

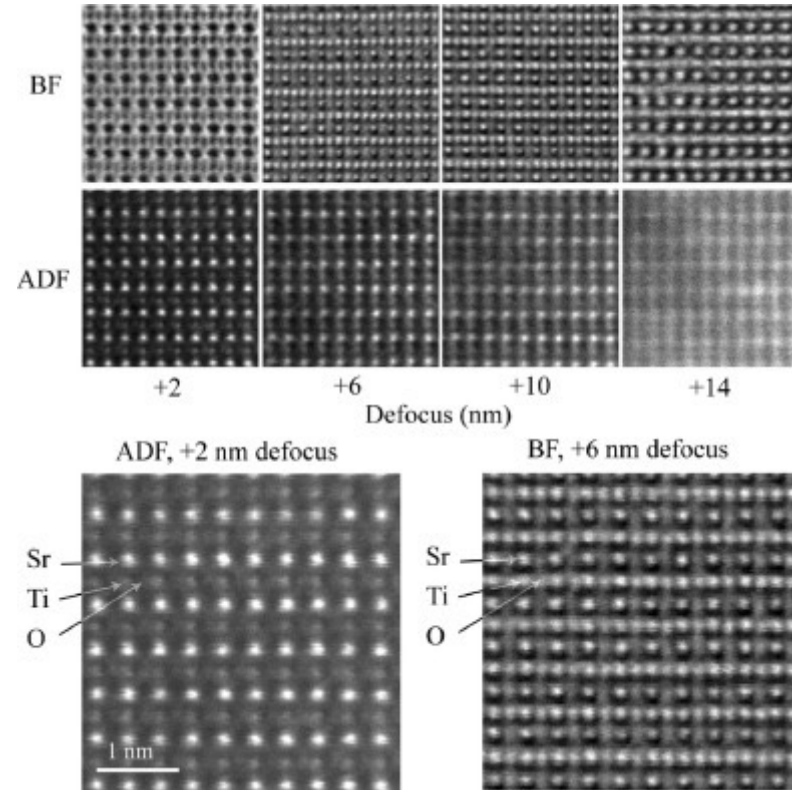
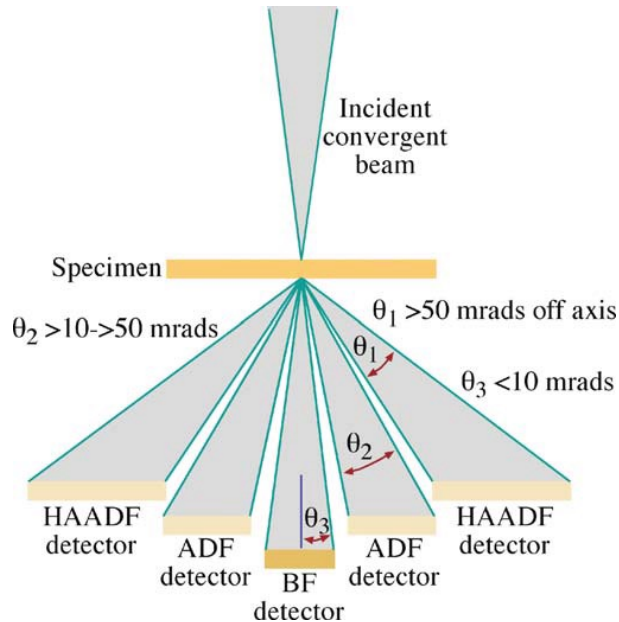


Conventional TEM image

Z-contrast image clearly
delineating the Ge layer

Scattering at high angle is dependent on atomic number
No contrast reversal with focus
Images are directly interpretable: Camera characteristic

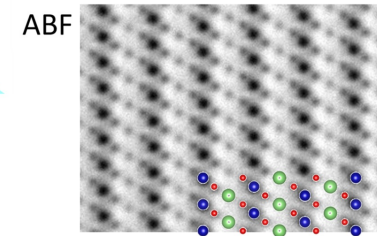
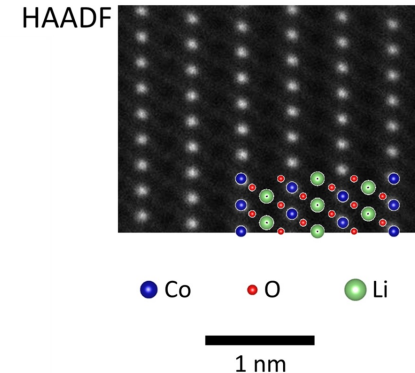
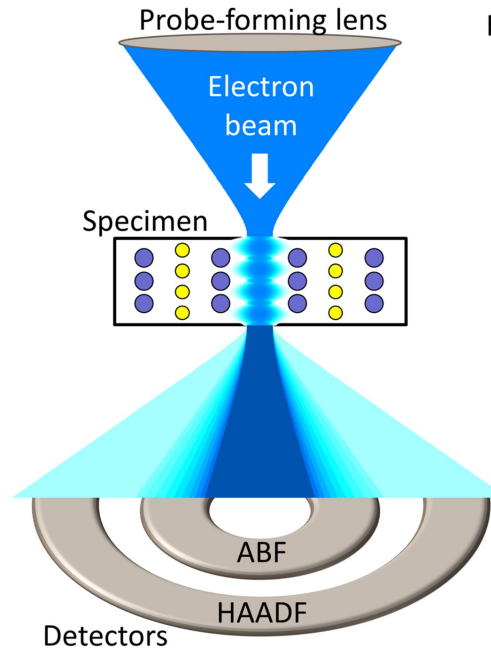
Imaging modes | Coherent vs incoherent image



BF | On-axis $\rightarrow$ Coherent : Contrast reversal with focus/thickness

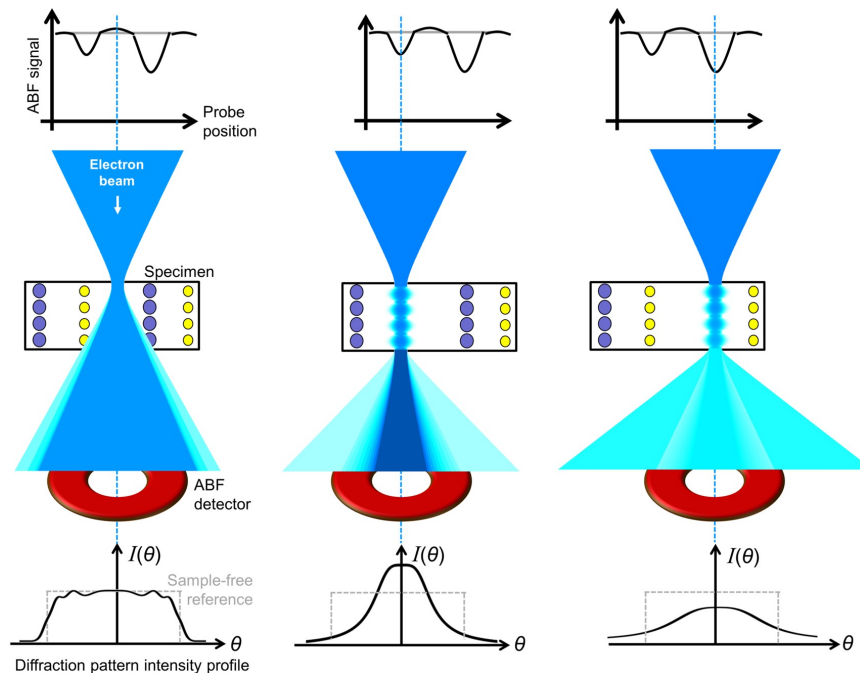
ADF | Off-axis $\rightarrow$ Incoherent (no phase relation with the incident beam) : No Contrast reversal with focus/thickness

- HAADF not useful for imaging light atoms in a sample with heavy atoms because contrast so strongly dependent on atomic number.
- BF imaging has same disadvantages for imaging light atom columns similar to phase-contrast HR-TEM imaging.
- Harald Rose's annular bright-field (ABF) imaging (with aberration correction), where central part of BF detector is obscured, solves these problems.
- It is a phase-contrast image, however, because it is a sum over many point detectors, each with a different CTF; **the contrast is quite incoherent in nature over a large range of thickness and defocus.**
- Typically, the collection angle would run from half the probe angle to the full probe angle. For instance, for $\alpha = 22$ mrad, use $\beta = 11$ – 22 mrad

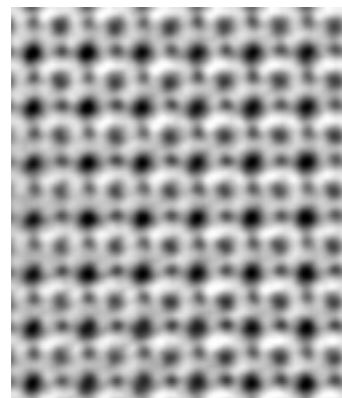


Since the ABF image is formed from low-angle scattering, it is not strongly dependent on Z , and low- Z and high- Z atoms can be seen clearly in the same image.

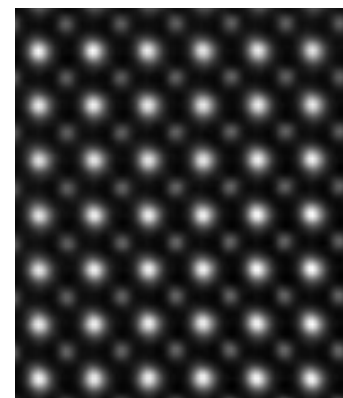
Simple theory: Channelled electrons scattered mostly into centre of BF detector by light columns giving some dark ABF contrast.



Example: $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$



ABF

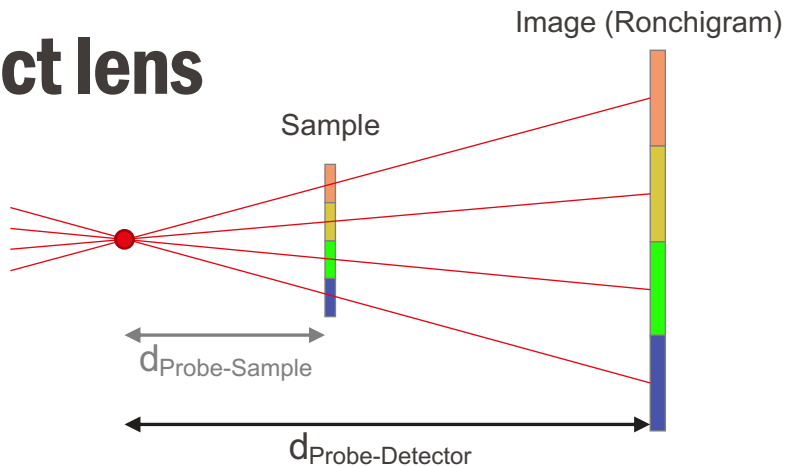


HAADF

Scattered more strongly to diffracted beams by heavy columns giving darker ABF contrast. Off column little scattering, so brighter ABF contrast.

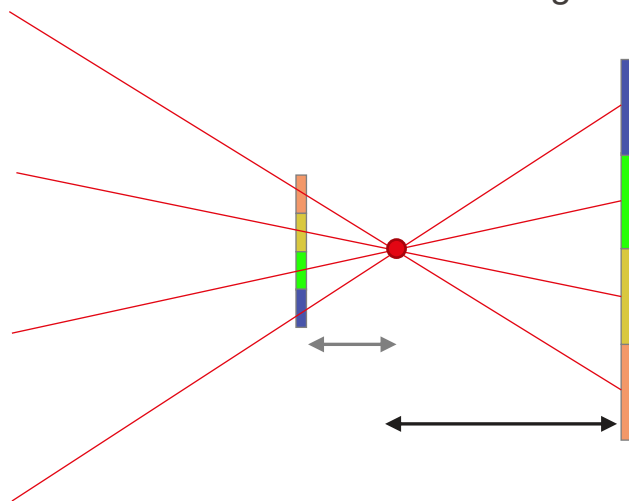
Shadow image | Perfect lens

Assuming perfect optics, overfocus condition

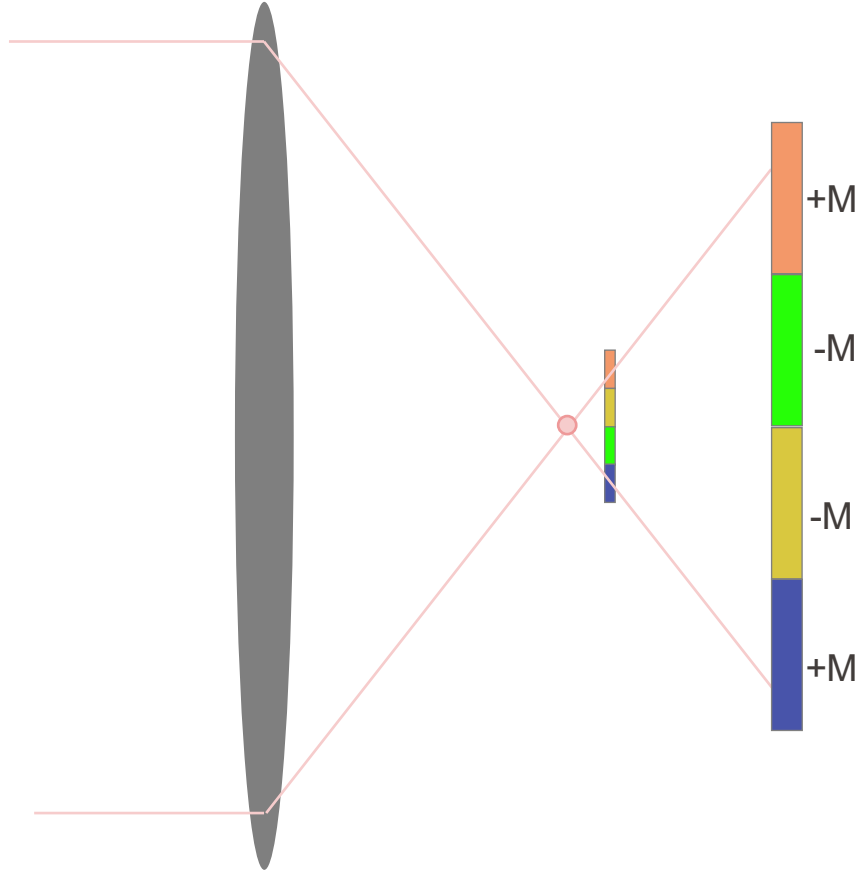


$$\text{Magnification} = \frac{d_{\text{Probe-Detector}}}{d_{\text{Probe-Sample}}}$$

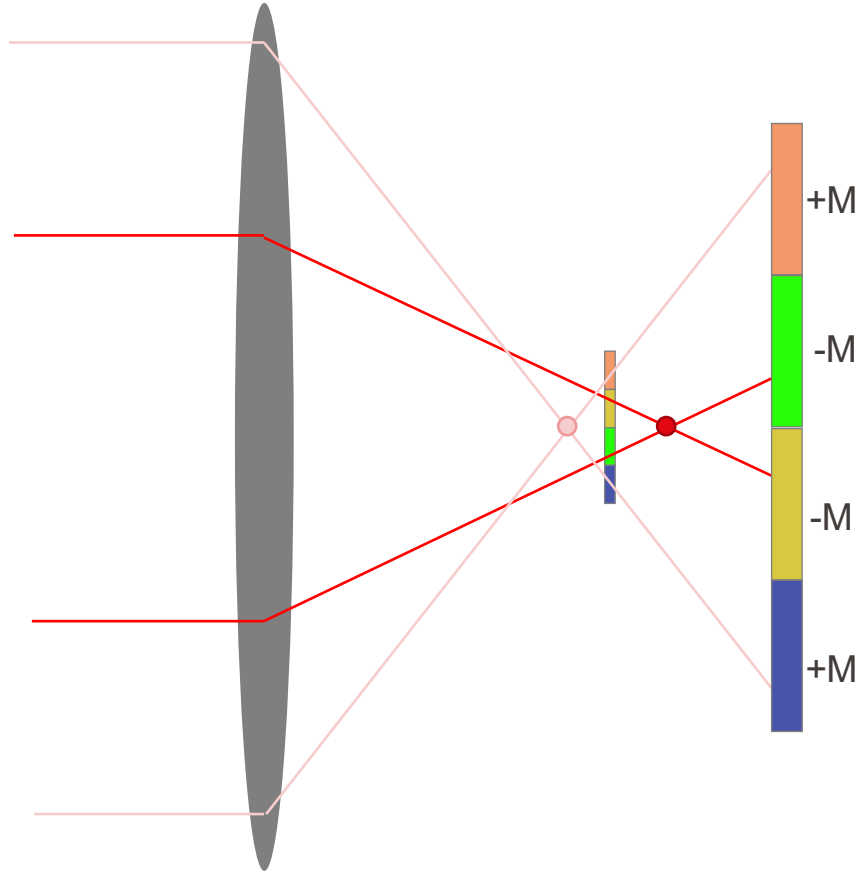
At underfocus the image will magnify, but also inverted



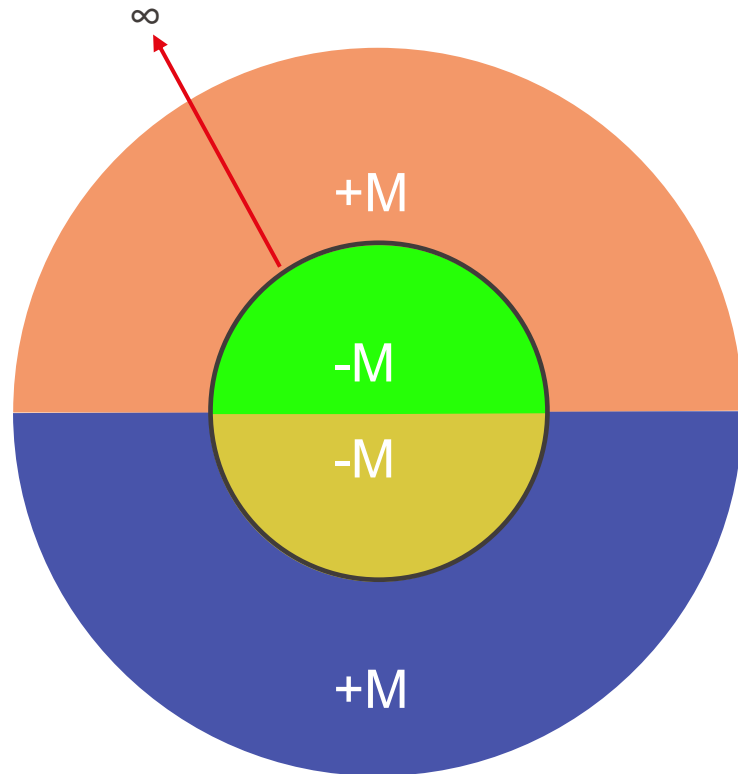
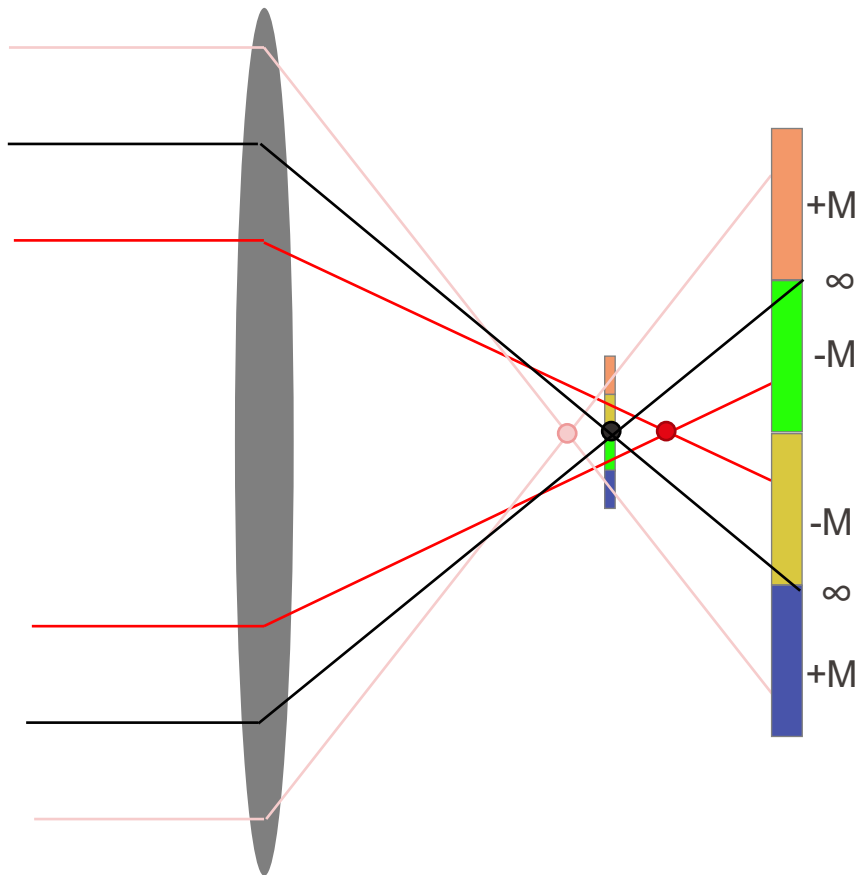
Shadow image | Real lens



Shadow image | Real lens



Shadow image | Real lens



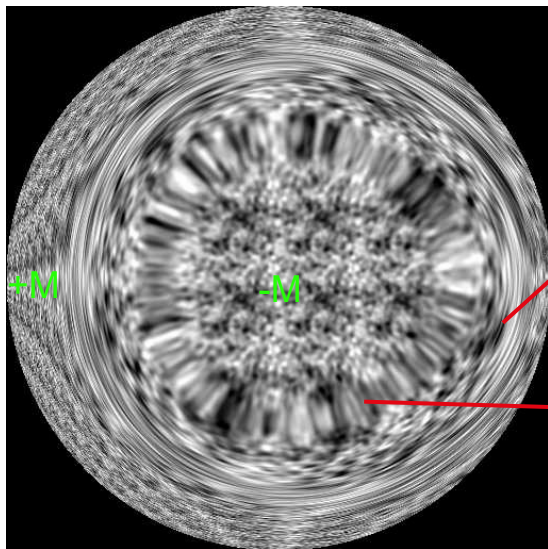
Shadow image | Real lens

In the presence of spherical aberration, for defocus Δ and wavevektor $\mathbf{k}$, magnification M' is:

$$M' = \frac{M}{1 + C_s \lambda^2 |k|^2 / \Delta}$$

In 1-D infinite magnification occurs at defocus $\Delta = -\lambda^2 C_s |k|^2$ or $|k|^2 = \frac{-\Delta}{\lambda^2 C_s}$

In 2-D there are two critical angles for which radial and circumferential magnifications are equal to zero:



Azimuths

Radii

$$|k|^2 = \frac{-\Delta}{\lambda^2 C_s}$$

Circumferential

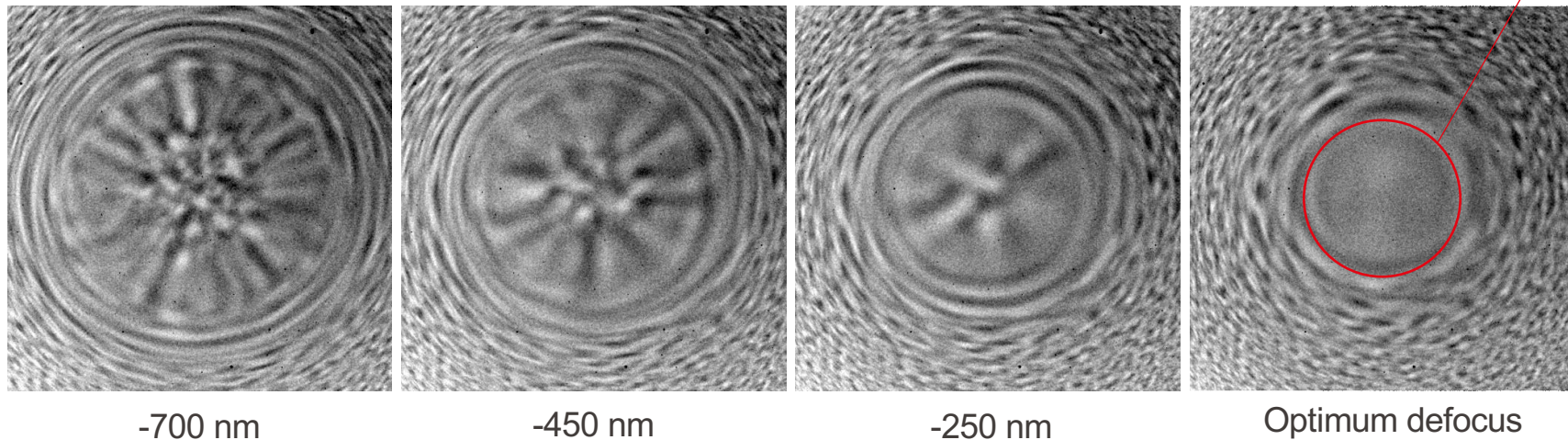
$$|k|^2 = \frac{-\Delta}{3\lambda^2 C_s}$$

Radial

Different Δ if there is astigmatism

The more defocus, the bigger the region in the centre which is inverted

The more defocus, the bigger the region in the centre which is inverted



In practice:

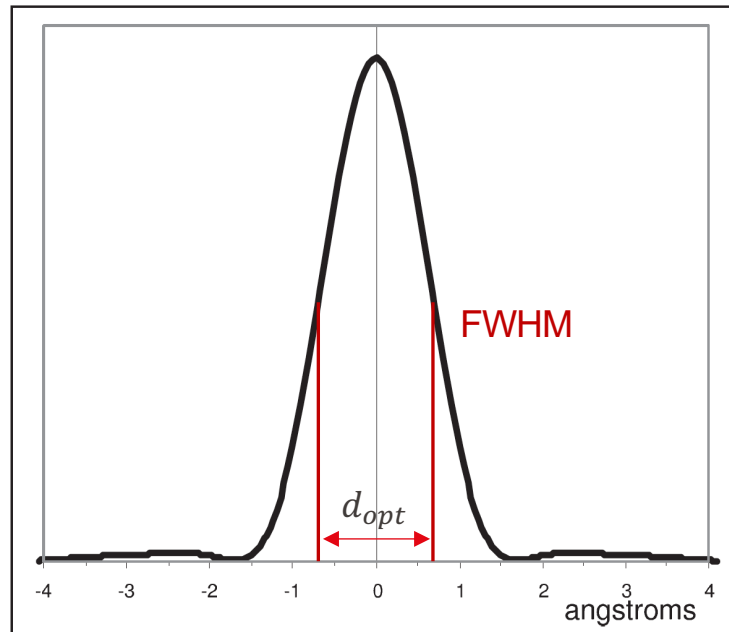
- Reduce under-focus until infinite-magnification rings are of minimum diameter
→ optimum defocus (c.f. Scherzer defocus in HR-TEM) ›
- Fit probe-forming aperture to the “sweet spot” region of constant phase within this

STEM resolution is determined by the size of the probe and stability of the instrument

$$\alpha_{opt} = \left(\frac{4\lambda}{C_s} \right)^{\frac{1}{4}}$$

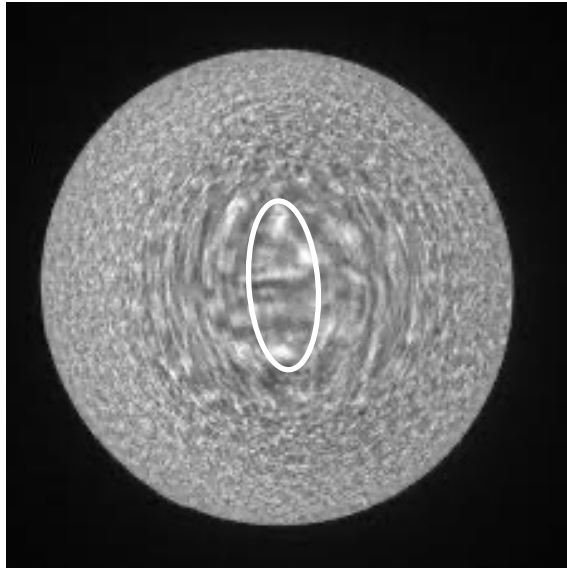
At optimum defocus and with the correct aperture size, the probe FWHM is given by:

$$d_{opt} = 0.61 \frac{\lambda}{\alpha_{opt}} = 0.43 \lambda^{\frac{3}{4}} C_s^{\frac{1}{4}}$$

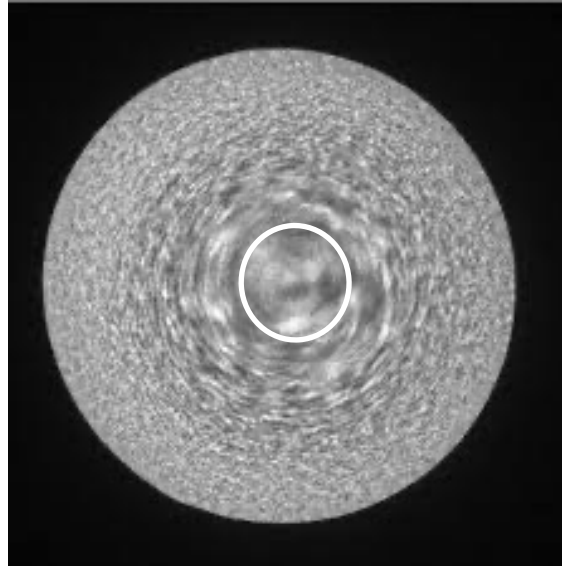


The intensity of a diffraction-limited STEM probe for the illumination conditions: Cs 1mm, and defocus $z = 35.5$ nm, 200kV. An objective aperture of radius 9.3 mrad has been used

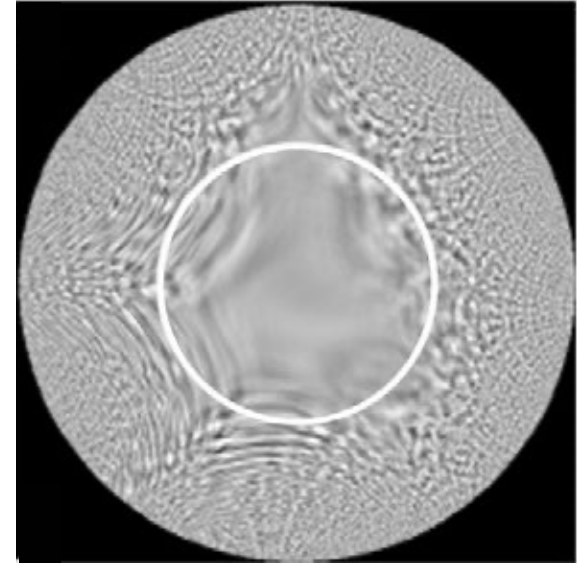
Different Δ if there is astigmatism $\rightarrow$ Elliptical Roncigram instead of round



With astigmatims



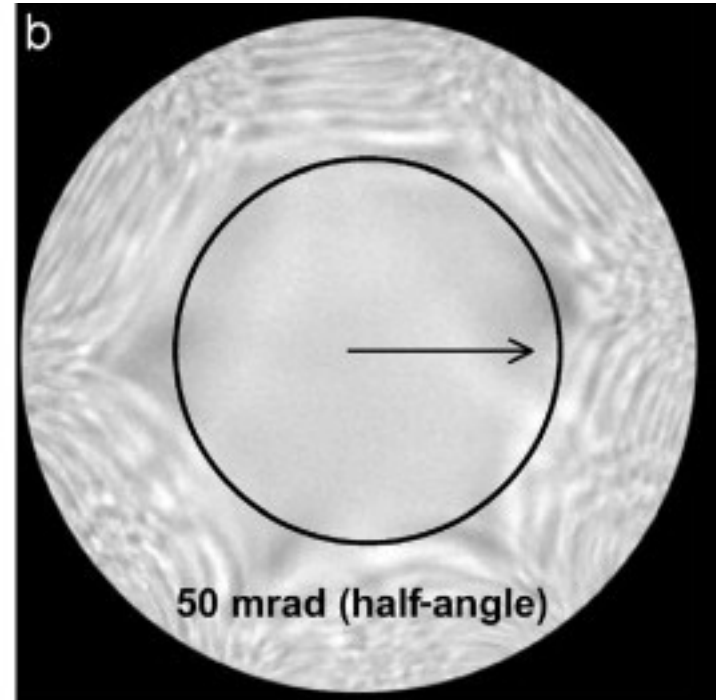
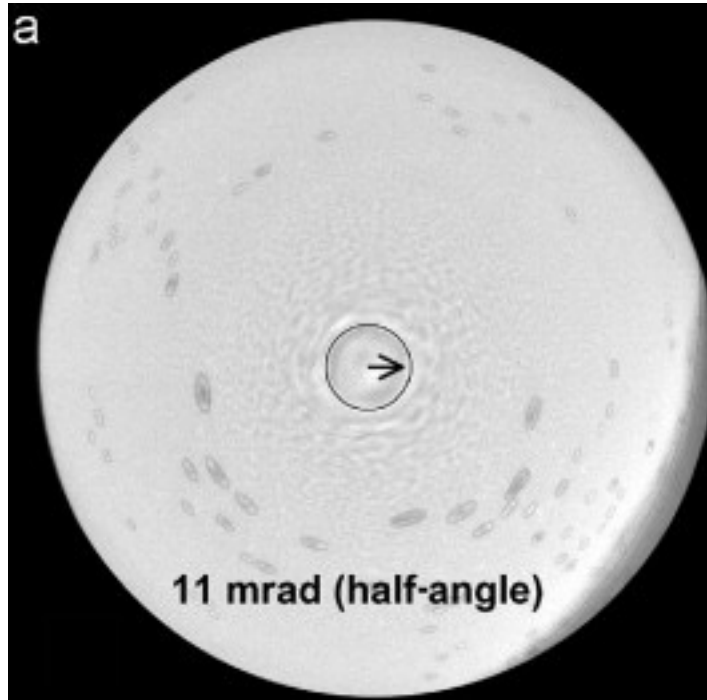
Astigmatims corrected



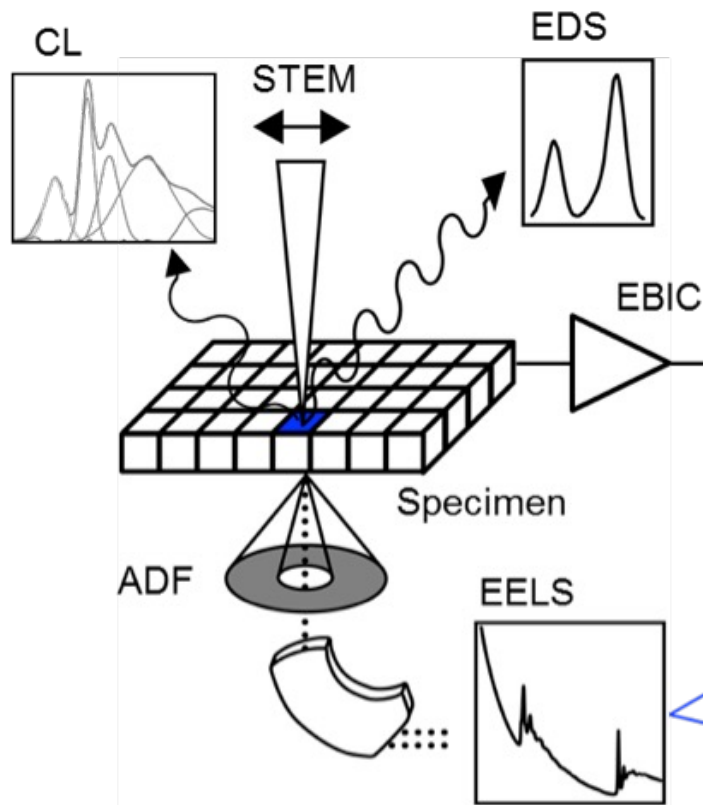
Cs corrected

Shadow image | Cs-Corrected

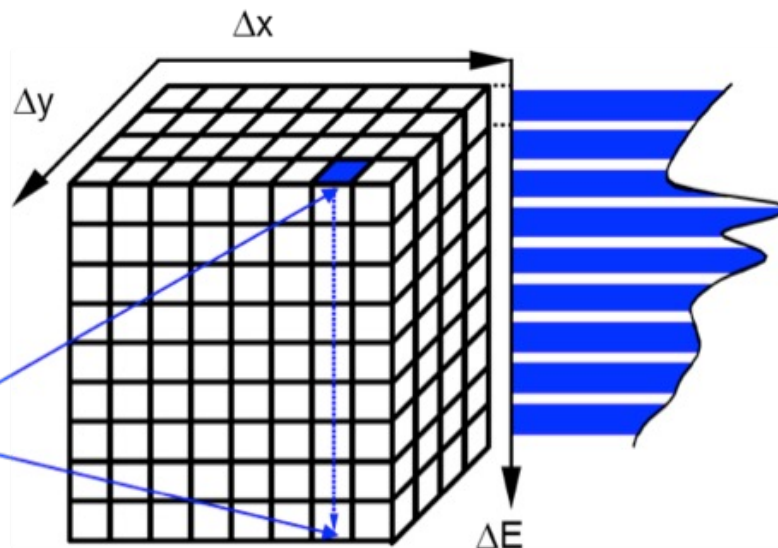
Cs correction increases the size of the sweet spot



Spectrum imaging

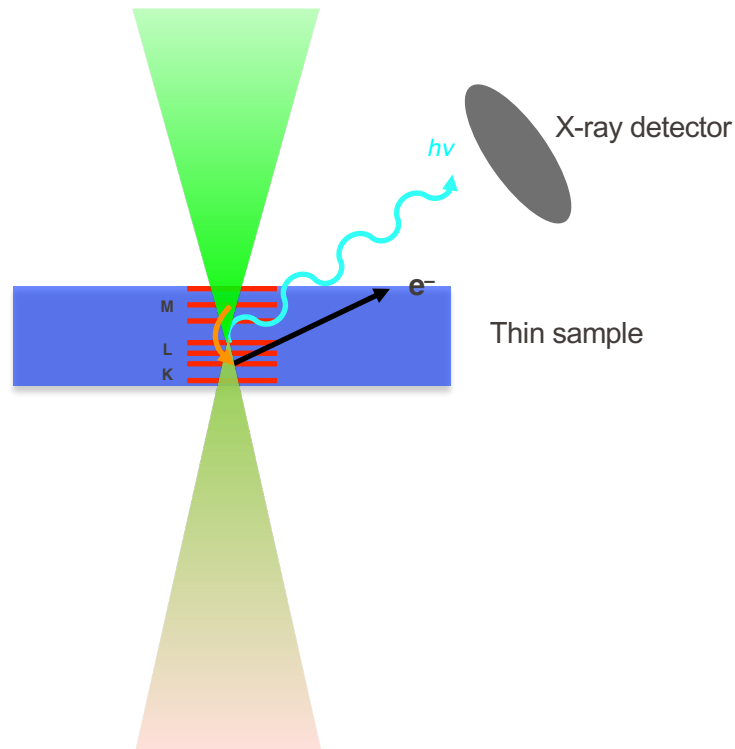


Record spectrum as function of probe position (x, y)



- High energy incident electrons (ballistic)
- → Ejection of inner shell e^-
- Upper shell e^- descends
- Transition energy emitted as X-ray;
characteristic of element | $E_{X\text{-ray}} = E_{\text{Upper shell}} - E_{\text{Inner shell}}$

Focused incident e^- beam: high energy!



Thin sample

Map X-ray intensity as function of probe position (x, y)

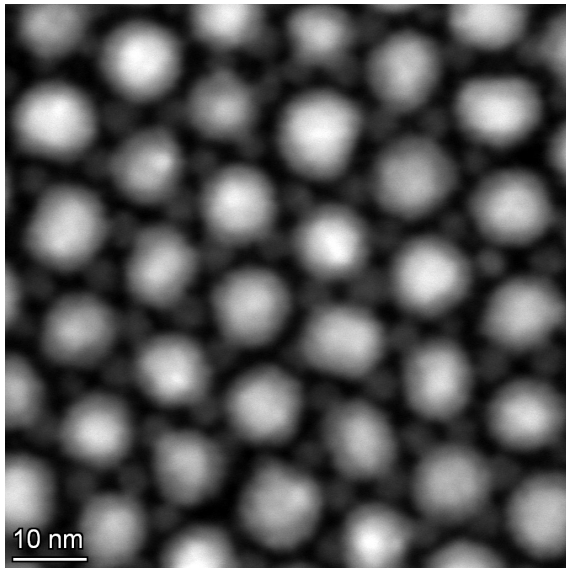
Transmitted beam suffers energy loss → Used in EELS

Energy-dispersive X-ray (EDX) STEM mapping

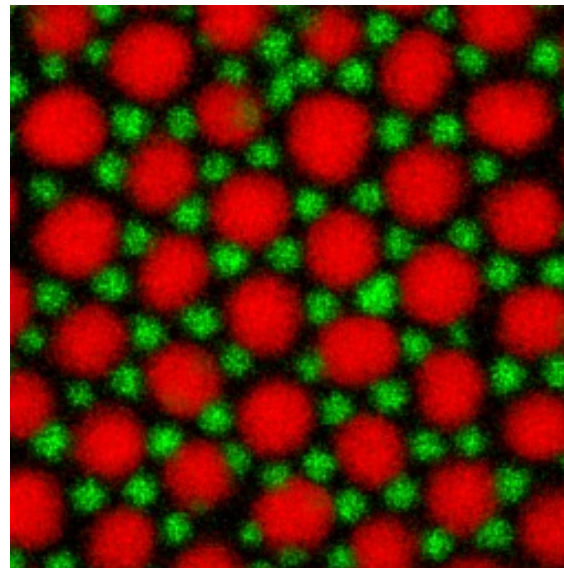
With fast mapping STEM-EDX has become a regular feedback tool for materials synthesis.

Sample characterized in a couple of minutes.

Example : Assembly of Fe_3O_4 and Cu particles



HAADF image



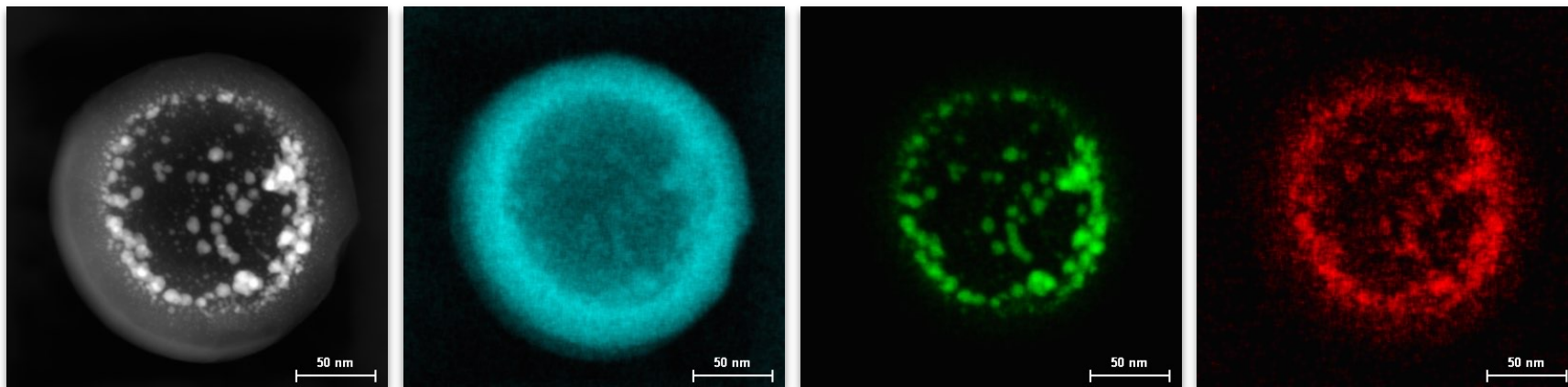
Map of Cu and Fe

Energy-dispersive X-ray (EDX) STEM mapping

With fast mapping STEM-EDX has become a regular feedback tool for materials synthesis.

Sample characterized in a couple of minutes.

Example : Ni-Rh catalytic nanoparticles in carbon shell



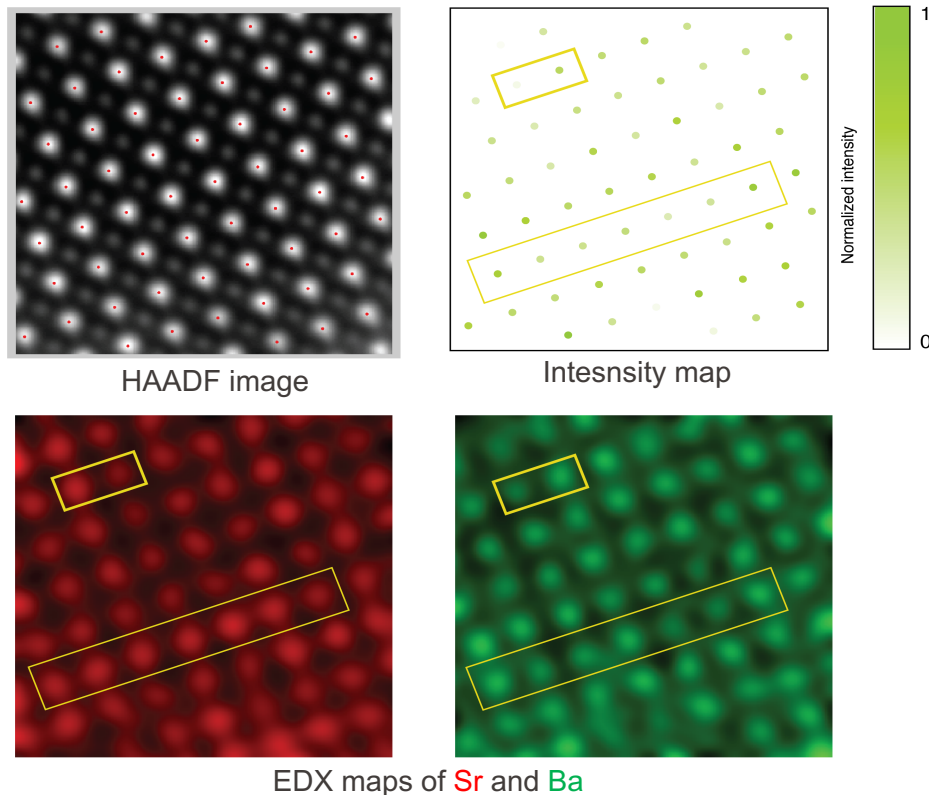
HAADF image

EDX maps of C, Rh and Ni

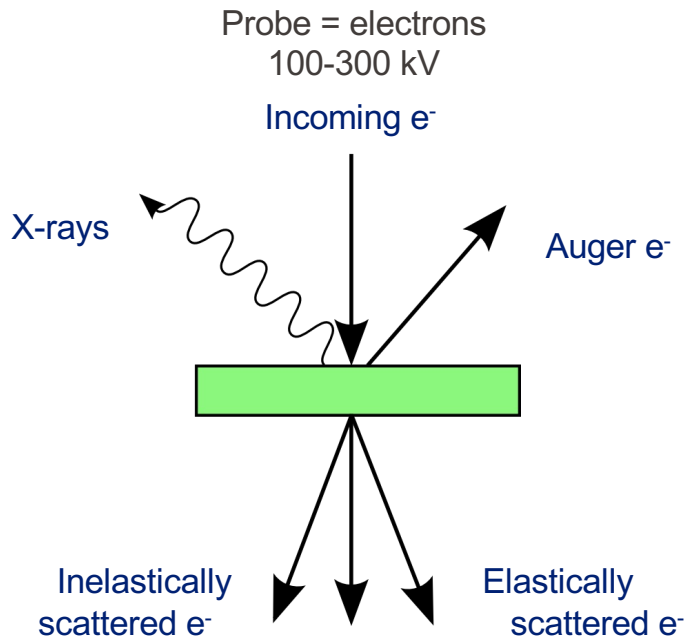
Energy-dispersive X-ray (EDX) STEM mapping

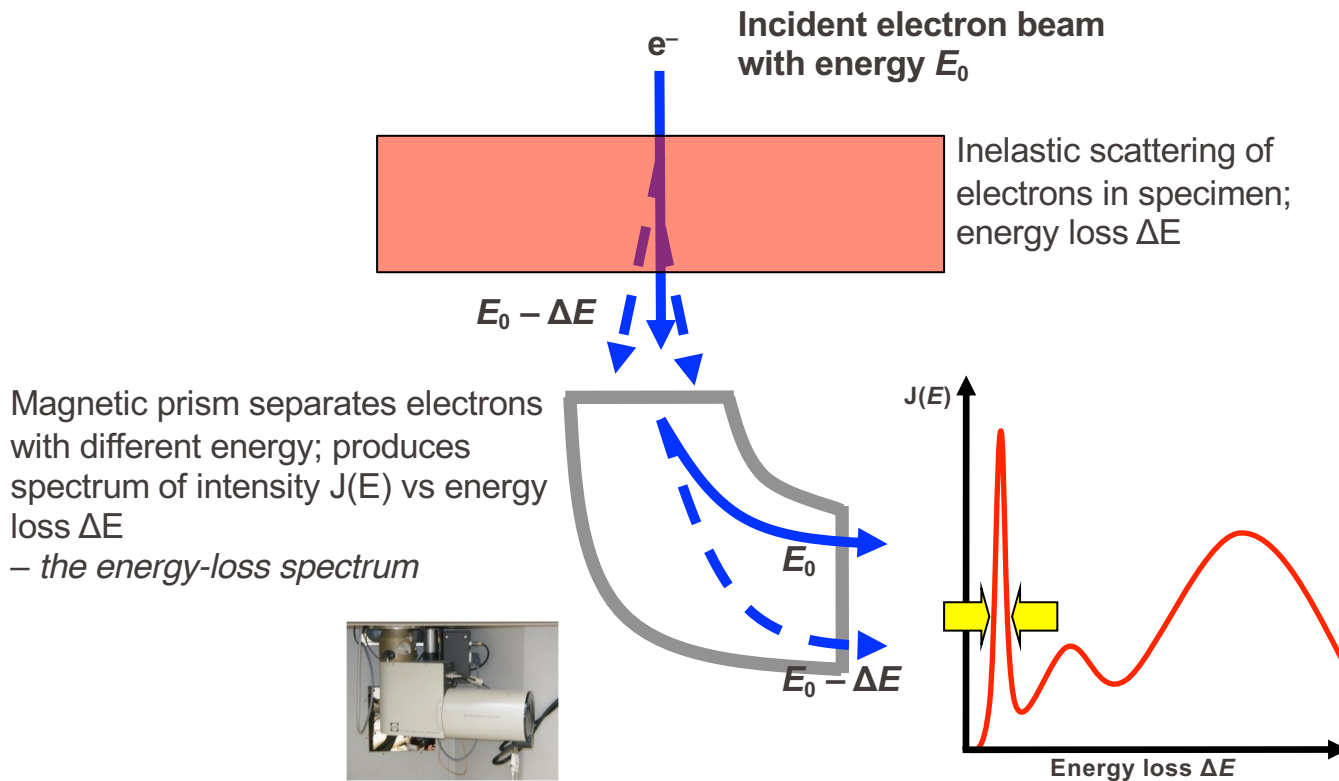
With aberration-corrected STEM, atomic resolution EDX became possible

Example: $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$

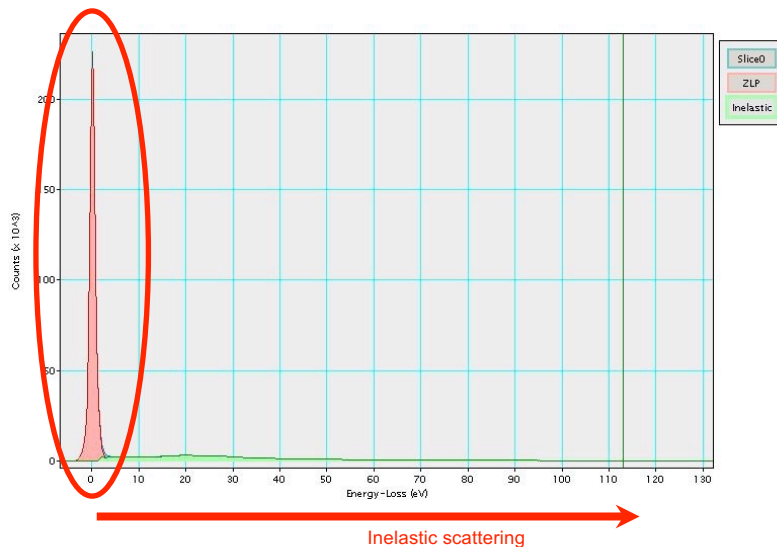


The TEM specific microanalysis technique!





e.g. Gatan Enfina

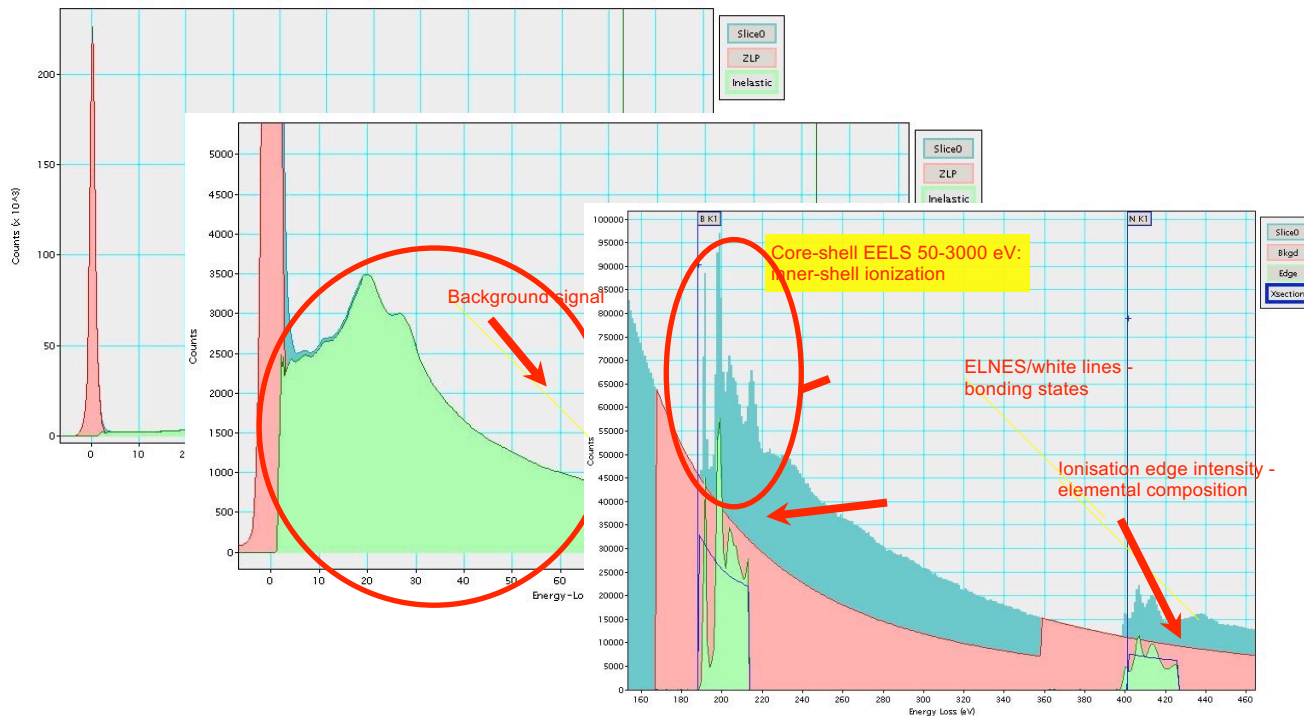


Zero-loss: Elastically-scattered e^-
Information about specimen thickness



Interaction with outer electrons (conduction/valence)

Low-loss spectrum 0-50 eV: valence excitations -
plasmons (bulk & surface),
band gaps, optical properties



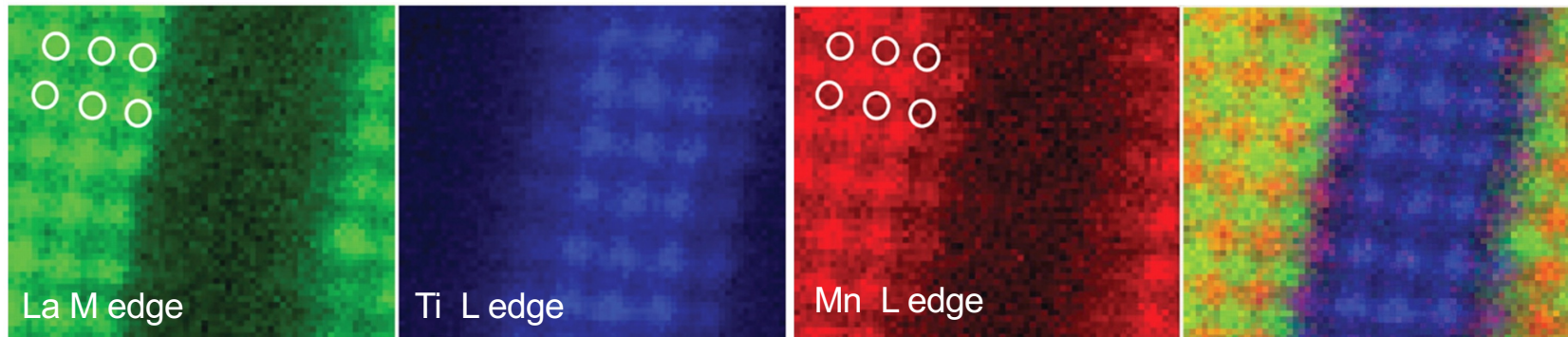
Interaction with core electrons

Core-loss spectrum 50-3000 eV: inner shell ionization

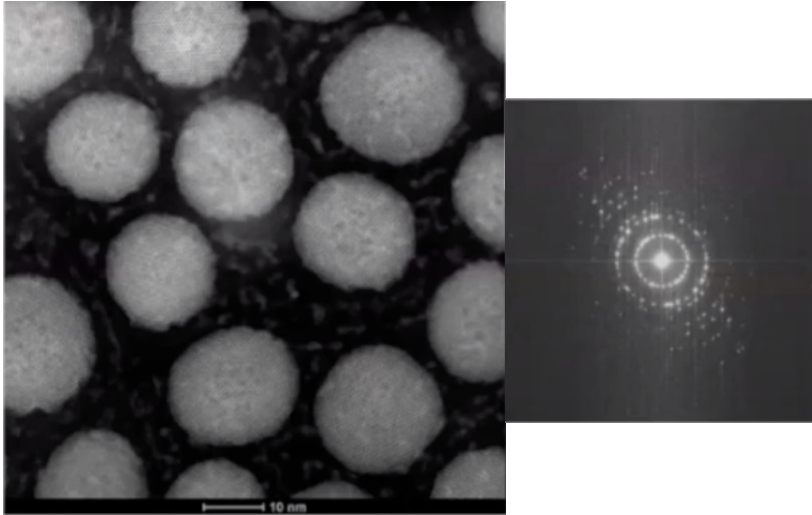
ELNES/white lines: Bonding state

Ionisation edge intensity: elemental composition

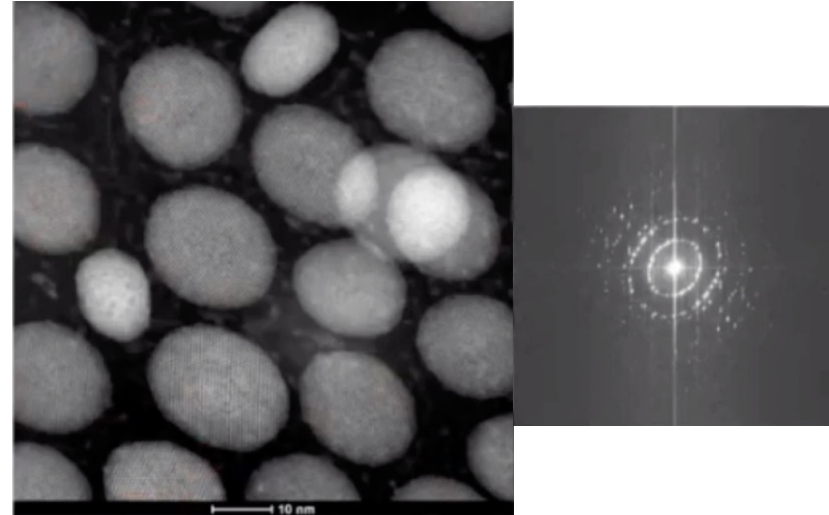
Example: Atomic resolution spectroscopic imaging of a $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 / \text{SrTiO}_3$ multilayer, showing the different chemical sublattices in a 64×64 pixel spectrum image extracted from 650 eV-wide electron energy-loss spectra recorded at each pixel.



Sample quality and imaging concerns

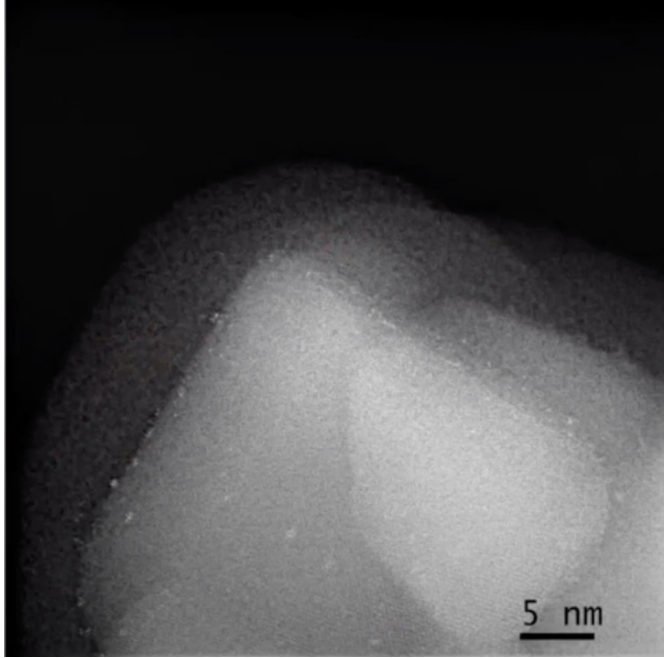


Without sample drift

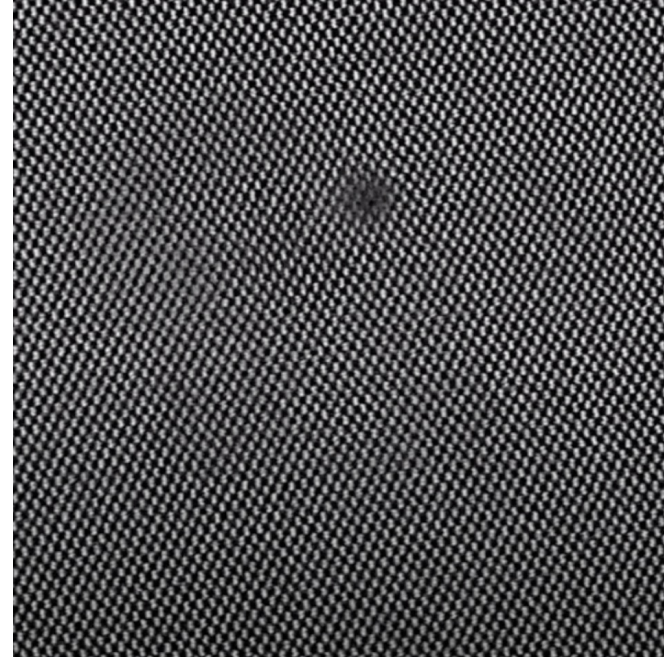


With sample drift

Sample quality and imaging concerns



Beam induced contamination



Beam induced damage (hole)

Sample quality and imaging concerns

Representative of sample

Thin

Stable under vacuum and probe current

Free of contamination

Uniform thickness

Conductive

Aberration-correction and improved instrument stability give sub-Å resolution in STEM.

With lower beam voltages lighter elements can be analyzed without beam damage.

Faster, more sensitive spectrometers give unprecedented access to composition, chemistry and physics of materials.

Computer interfaces and software allow acquisition and processing of large datasets.

STEM is now not one technique that can be easily summarized, but is split into many specialisms.

Many other possible uses (e.g. imaging of magnetic domains, optical plasmon mapping, *in situ* studies) exist. The new equipment at CIME cover the majority of these possibilities, creating a state-of-the-art facility at EPFL.

With the latest instrumentation, the sample and specimen preparation are often the limiting factor!

Scanning Transmission Electron Microscopy by S.J. Pennycook and P.D. Nellist (eds) (Springer)

Aberration-corrected imaging in transmission electron microscopy: an introduction by R. Erni

Transmission Electron Microscopy by D.B. Williams and C.B. Carter (Springer)

Large Angle Convergent Beam Electron Diffraction by J.-P. Morniroli

Transmission Electron Microscopy and Diffractometry of Materials, Fultz and Howe

Science of Microscopy by C.W. Hawkes and J.C.H. Spence (eds) (Springer)