Electron Microscopy School, Belgrade, April 2011

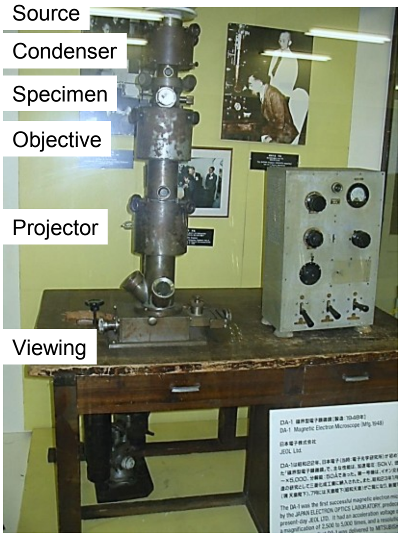
High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM)

Sašo Šturm
Jožef Stefan Institute, Slovenia

Lecture key points:

- Why are we doing HAADF-STEM?
- The reciprocity theorem of elastic electron scattering
- The origin of thermal diffuse scattering
- The electron probe
- The ronchigram
- Quantitative HAADF-STEM imaging
  - Image simulations
  - Quantitative interpretation of atomically-resolved HAADF-STEM images

TEM microscope in the begining…



TEM/STEM microscopes

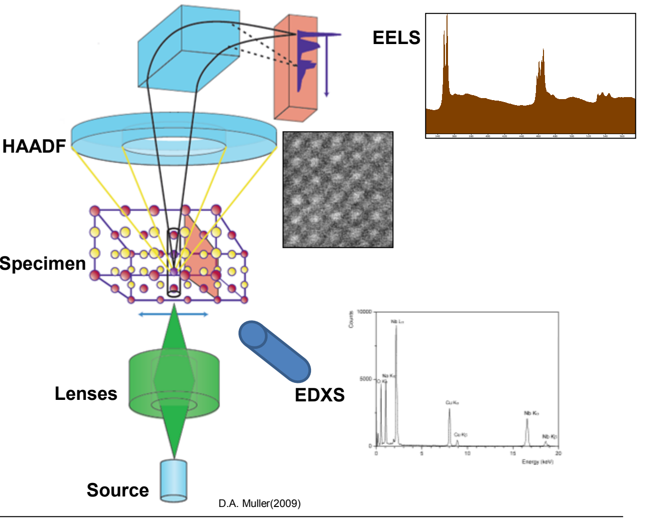
TEM/STEM microscopes

Dedicated STEM microscopes

Two basic operation modes in transmission electron microscopy (TEM):

- using stationary electron beam (conventional TEM mode)
- using scanning electron probe (STEM mode)

Dedicated STEM microscope

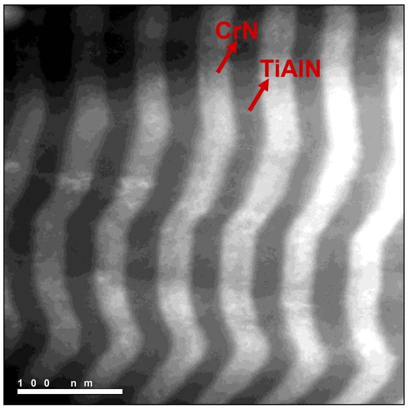


D.A. Muller(2009)

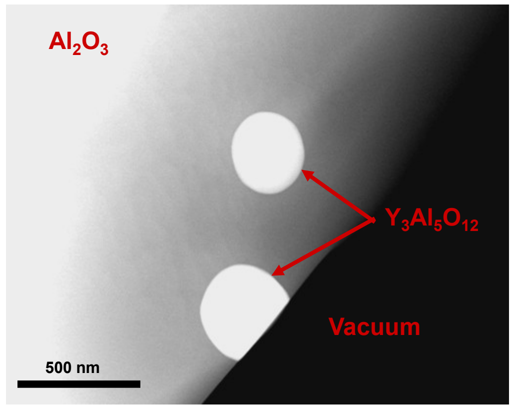
Combined atomically-resolved structural, compositional and chemical information:

- STEM: Scanning Transmission Electron Microscope
- HAADF: High-Angle Annular Dark-Field detektor

Why are we doing HAADF-STEM?



M. Panjan (2007)

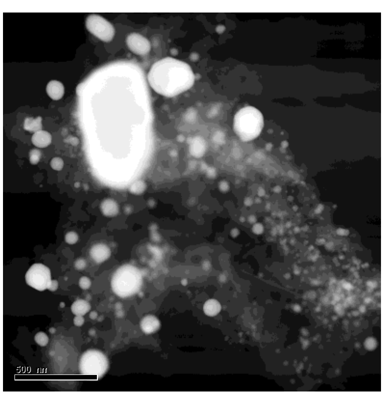


S. Šturm (2010)

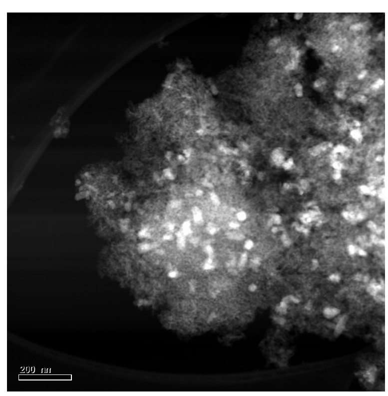
HAADF-STEM of functional materials:

- strong compositional sensitivity

Why are we doing HAADF-STEM?



E. Tchernychova (2011)

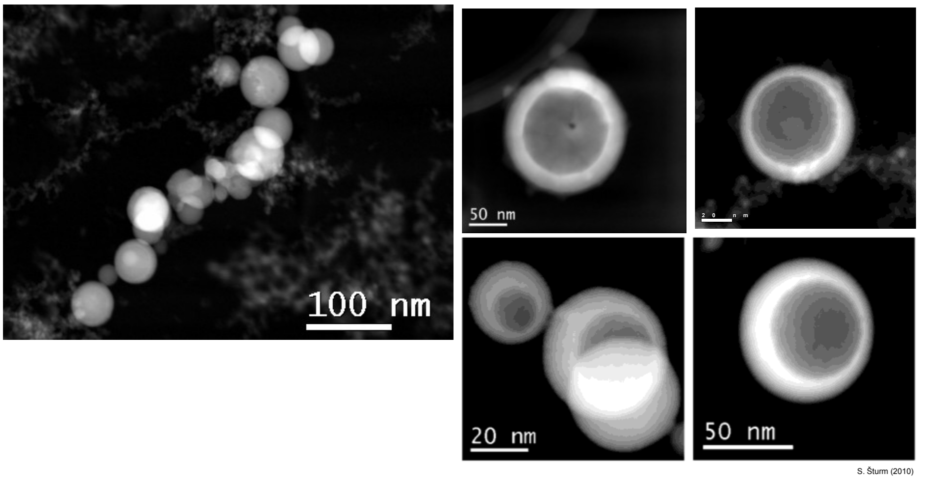


V. Radmilović (2011)

HAADF-STEM of nanoparticles:

- Cu-Ni-Pt nanoparticle in carbon-based matrix
- Ru-O nanoparticles in TiO_2 based matrix

Why are we doing HAADF-STEM?

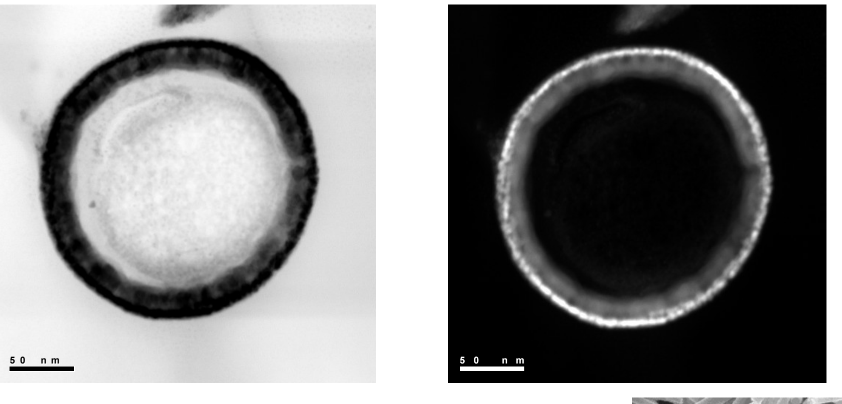


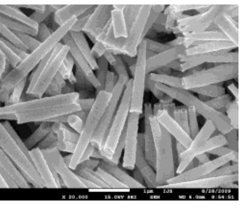
S. Šturm (2010)

HAADF-STEM of hollow structures:

- Hollow nanospheres

Why are we doing HAADF-STEM?



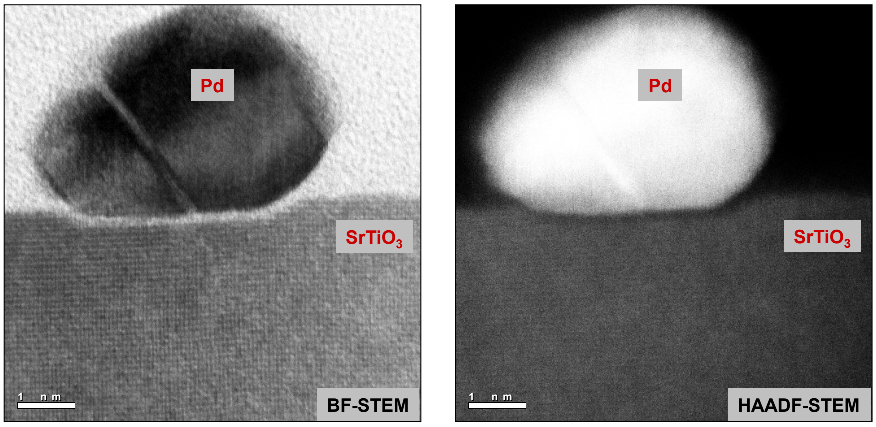


Combining Bright-Field (BF) and HAADF-STEM imaging:

- compositionally complex nanotube

Why are we doing HAADF-STEM?

Pd islands on $SrTiO_3$ substrate



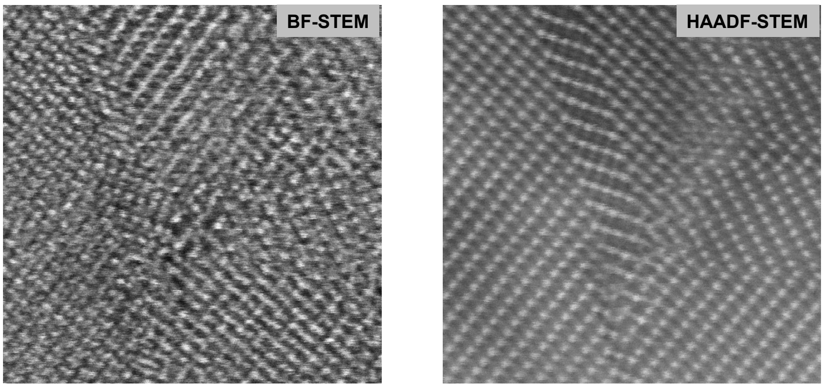
E. Tchernychova (2004)

Combining Bright-Field (BF) and HAADF-STEM imaging:

- Pd on perovskite substrate

Why are we doing HAADF-STEM?

Small region of polycrystalline $BaTiO_3$ tubes



K. Žagar (2010)

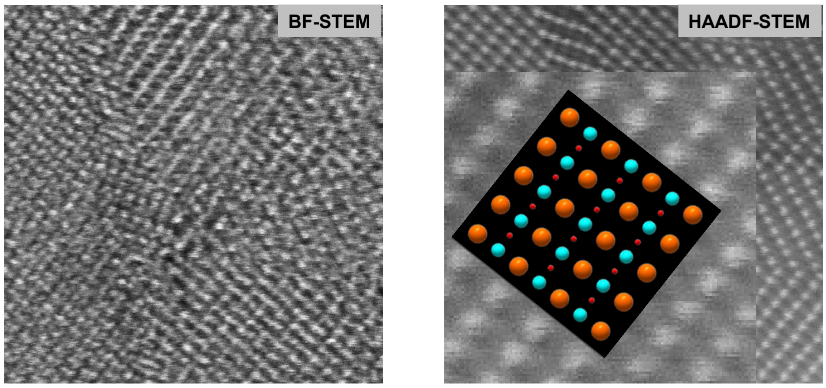
Images were taken at SuperSTEM (Daresbury)

Combining Bright-Field (BF) and HAADF-STEM imaging:

- Atomic-scale sensitivity
- Strong chemical and structural sensitivity

Why are we doing HAADF-STEM?

Small region of polycrystalline $BaTiO_3$ tubes



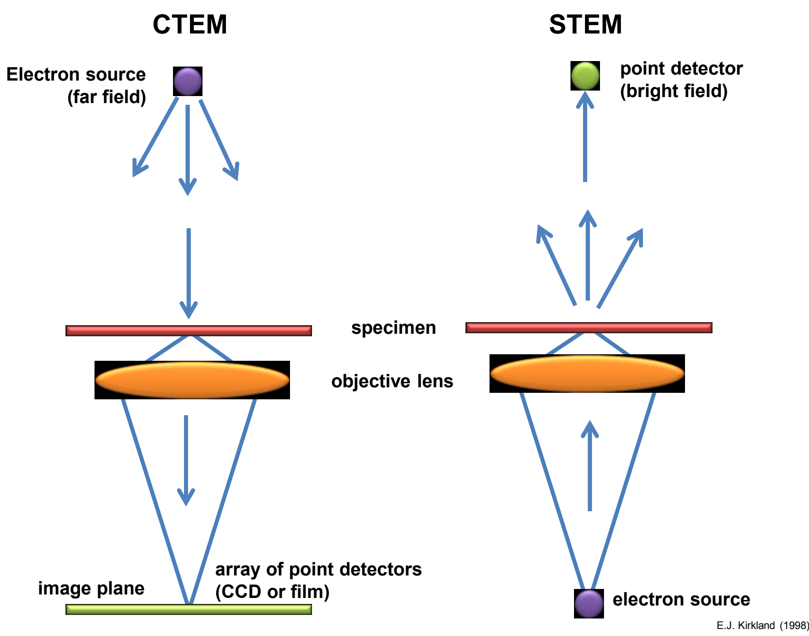
K. Žagar (2010)

Images were taken at SuperSTEM (Daresbury)

Combining Bright-Field (BF) and HAADF-STEM imaging:

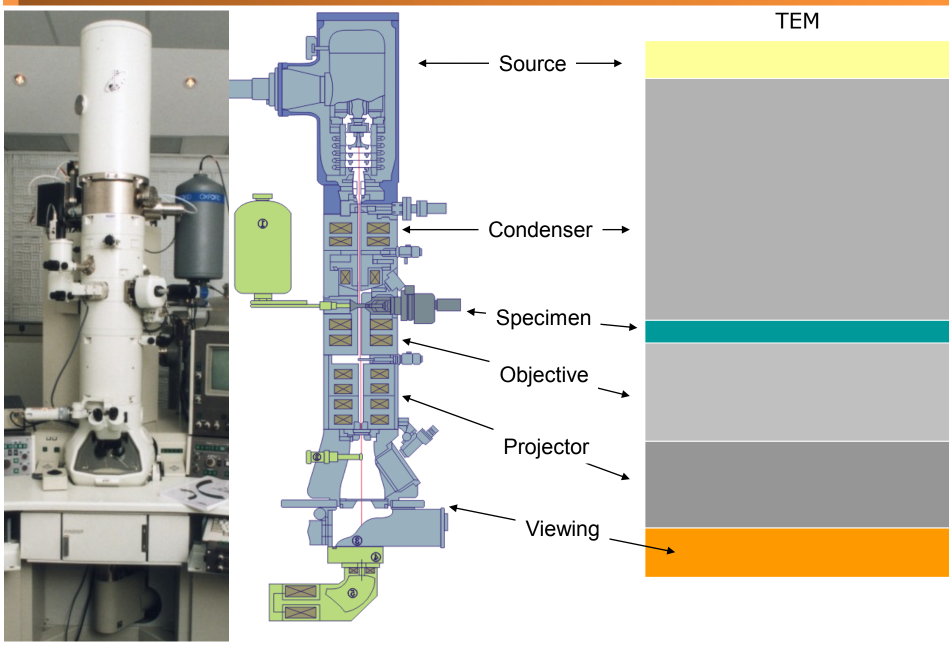
- The interpretation of HAADF-STEM images is more straight forward than BF-STEM

The reciprocity theorem of elastic electron scattering

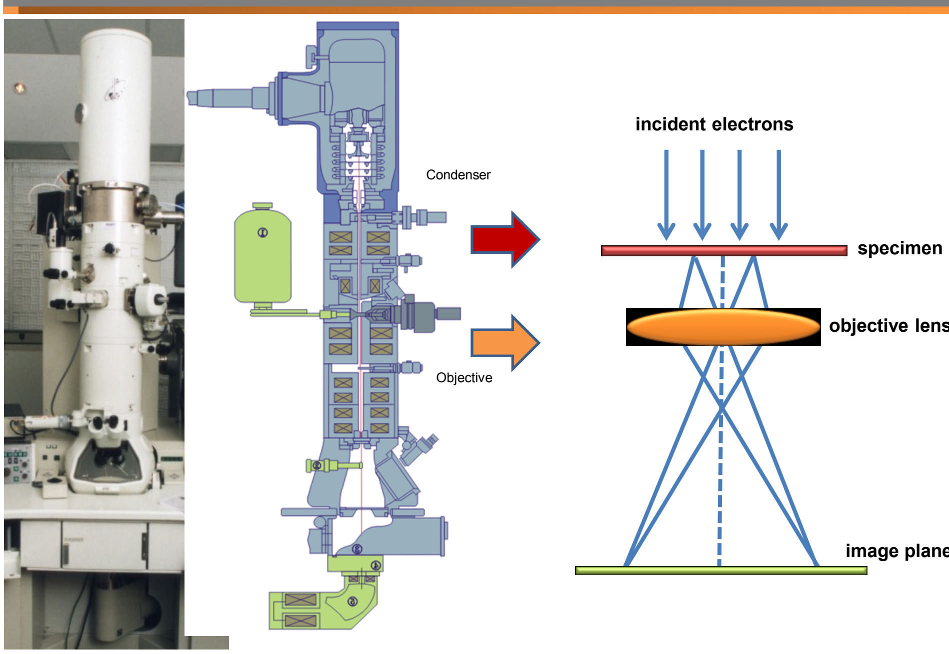


E.J. Kirkland (1998)

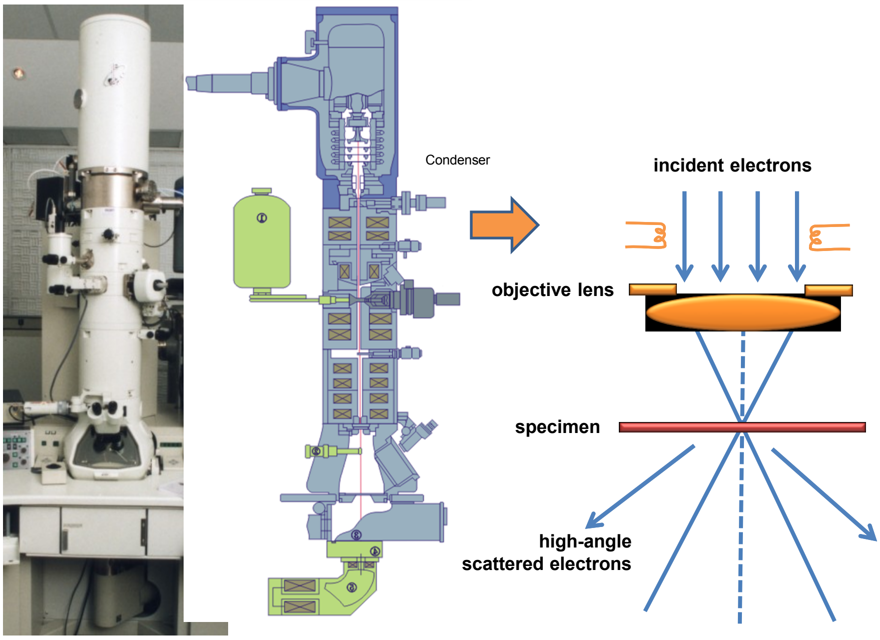
The reciprocity theorem of elastic electron scattering: CTEM



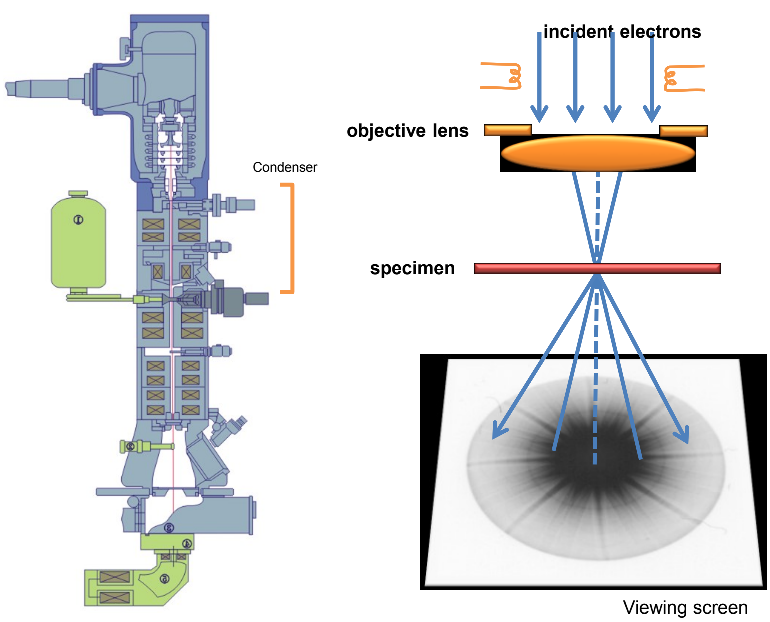
The reciprocity theorem of elastic electron scattering: CTEM



The reciprocity theorem of elastic electron scattering: STEM

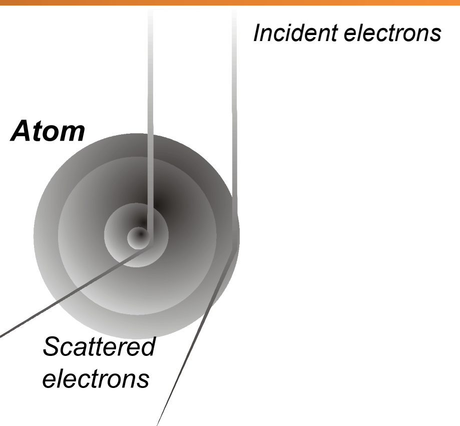


The origin of thermal diffuse scattering



The origin of thermal diffuse scattering

Z : atomic number
E_0 : electron beam energy
θ : scattering angle



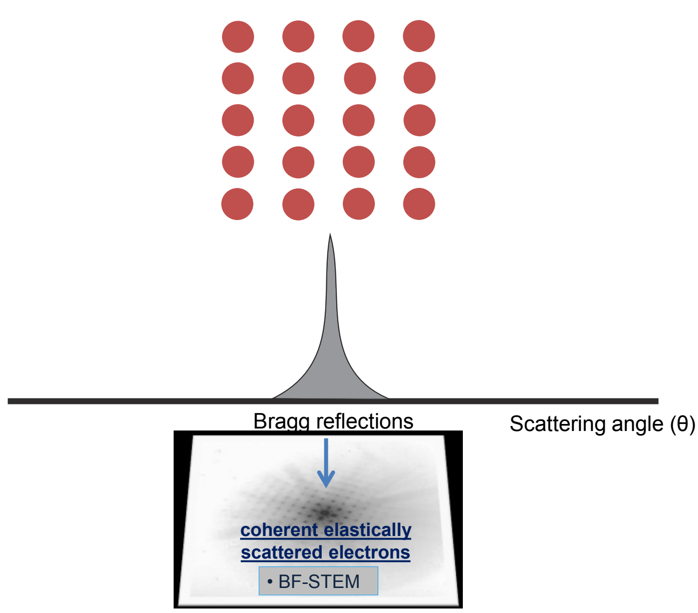
High angle scattered electrons:
- α>>10 mrad
- Scattering occur on tightly bound s-type states
- Reflects chemical information

Bragg scattered electrons:
- α<10 mrad
- Scattering localized on the outer shell structures
- Reflects structure

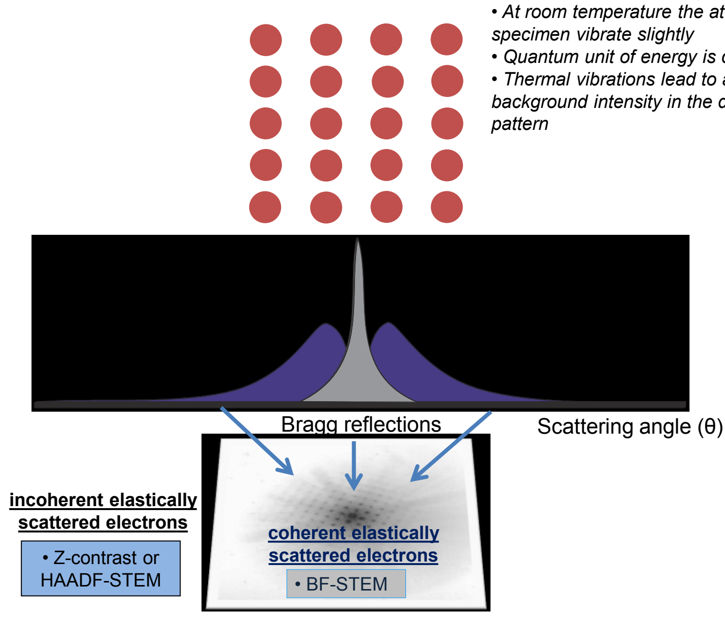
Rutherford cross section:

$$\sigma_{nucleus} = .62\times\ 0^{-4}\left(\frac{Z}{E_o}\right)^{2}\cot^2\frac{\theta}{2}$$

The origin of thermal diffuse scattering



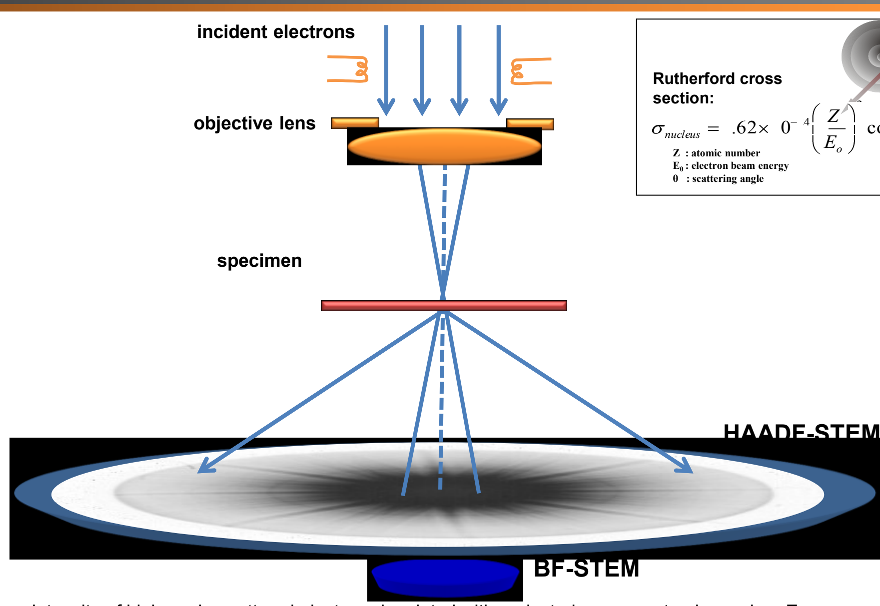
The origin of thermal diffuse scattering



Thermal diffuse scattering (TDS):

- *At room temperature the atoms in the specimen vibrate slightly*
- *Quantum unit of energy is called phonon*
- *Thermal vibrations lead to a diffuse background intensity in the diffraction pattern*

The origin of thermal diffuse scattering



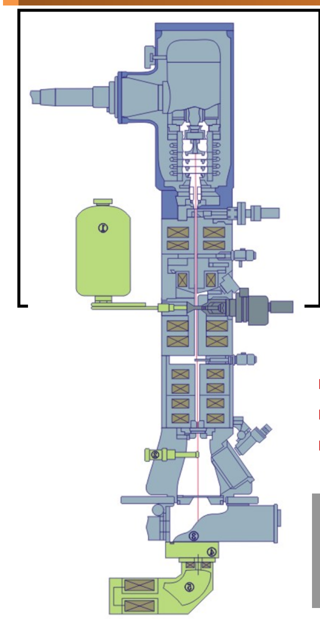
Rutherford cross section:

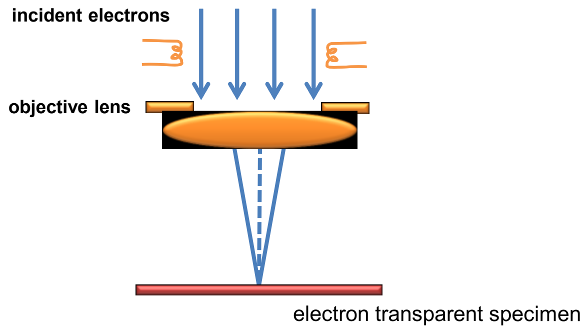
$$\sigma_{nucleus} = .62\times 0^{-4}\left(\frac{Z}{E_o}\right) \cot^2\frac{\theta}{2}$$

Z : atomic number
E_0 : electron beam energy
θ : scattering angle

- Intensity of high-angle scattered electrons is related with projected average atomic number, **Z**
- Proper setting of the detector will collect only high-angle scattered electrons, thus increase the **Z-contrast**

The electron probe



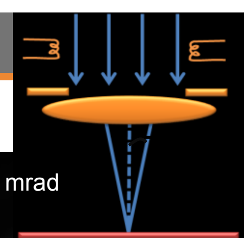


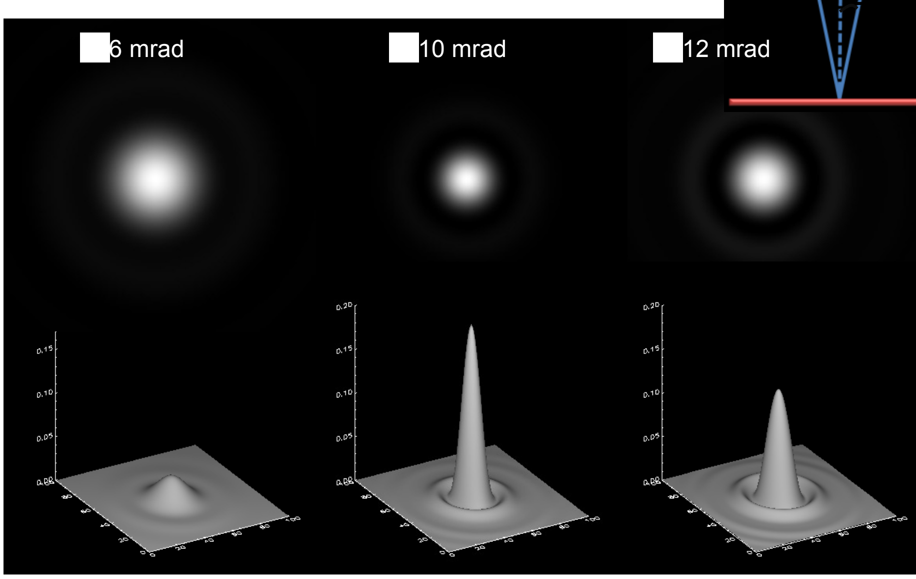
- The probe is scanning across the specimen
- The probe shape is defined by condenser (objective) lenses
- The signal is generated at a scanning point of the specimen

STEM images are not magnified by lenses, but by scanning area (pixel size).

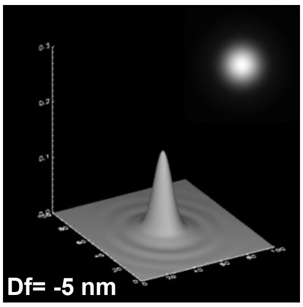
- Pixel size is affected by aberrations of the probe

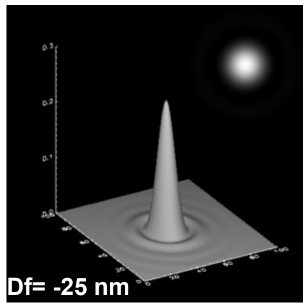
The probe functions at optimum defocus value

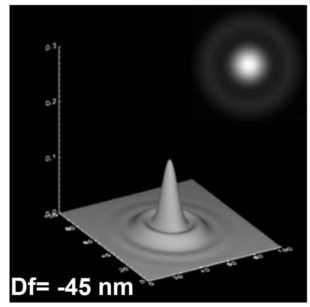




The probe functions at optimum convergence angle



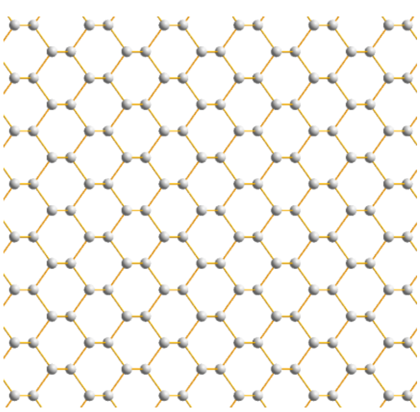




How to define best probe for imaging?

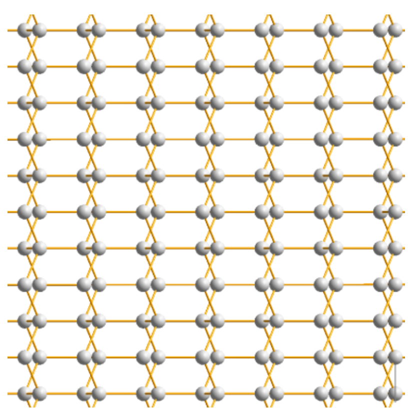
Probe has to be smaller than interatomic distances

Silicon <011>



~ 140 pm

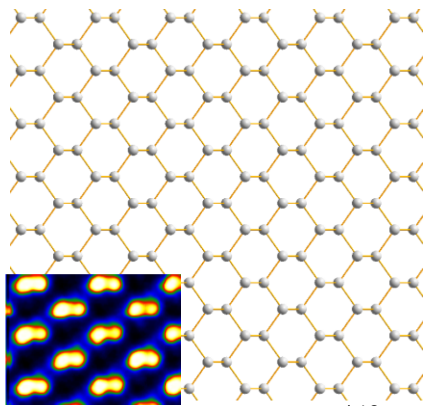
Silicon <112>



~ 80 pm

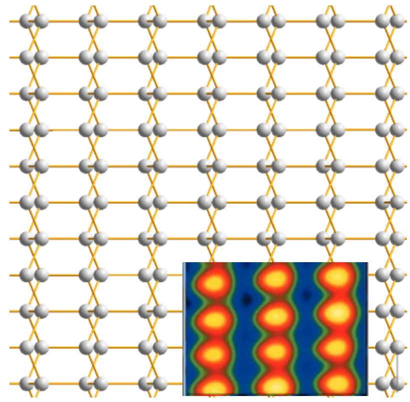
Probe has to be smaller than interatomic distances

Silicon <011>



~ 140 pm

Silicon <112>



~ 80 pm

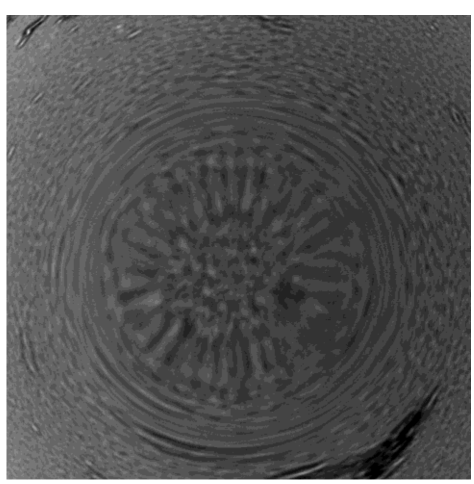
- Atomic columns resolved

- Atomic columns not resolved
- Atomic columns resolved

Oak ridge nationa lab

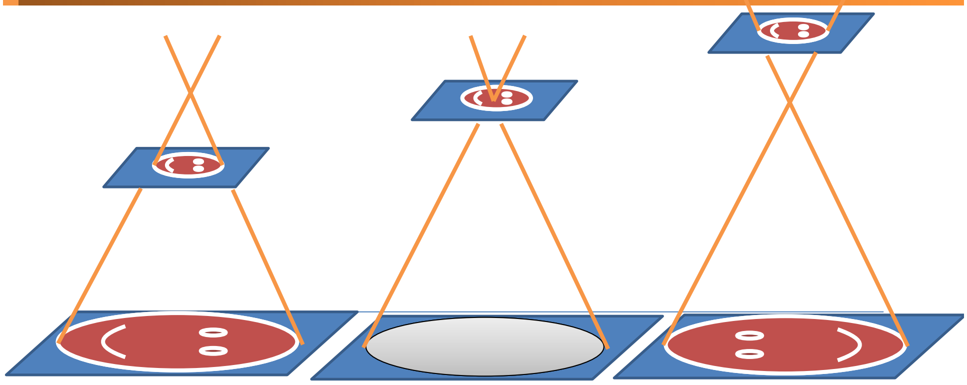
The ronchigram

How to define best probe for imaging?
Make use of a ronchigram

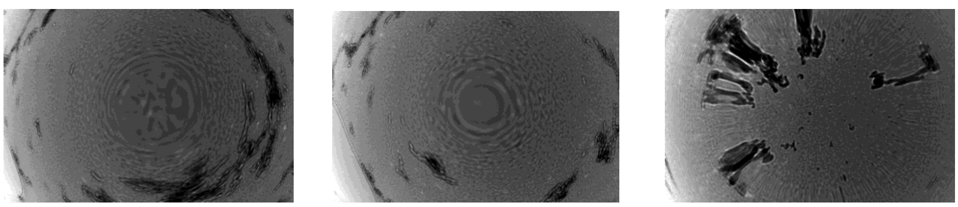


Experimental image taken on JEM-2010F (15.4.2010)

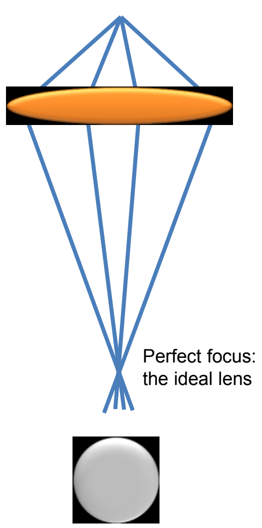
The ronchigram



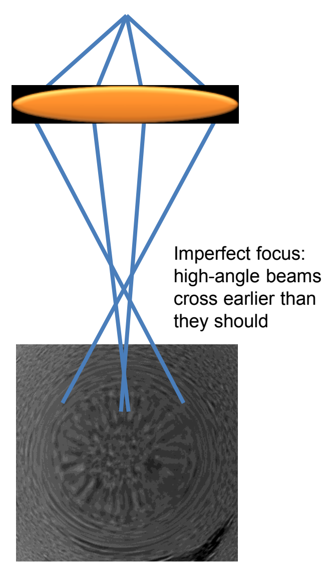
- under focus
- near focus
- “shadow” image
- over focus



The ronchigram



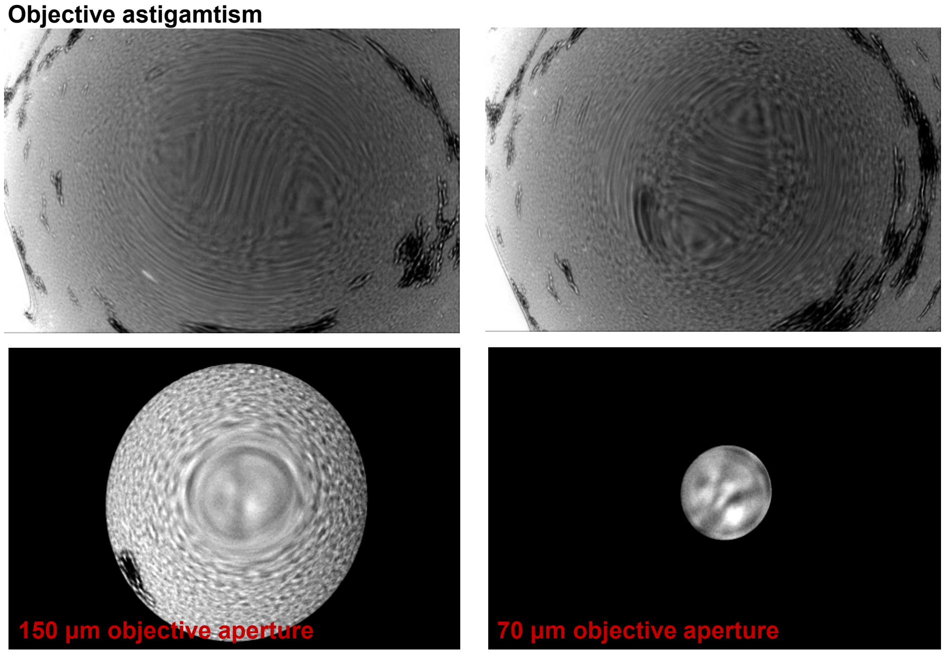
Shadow image



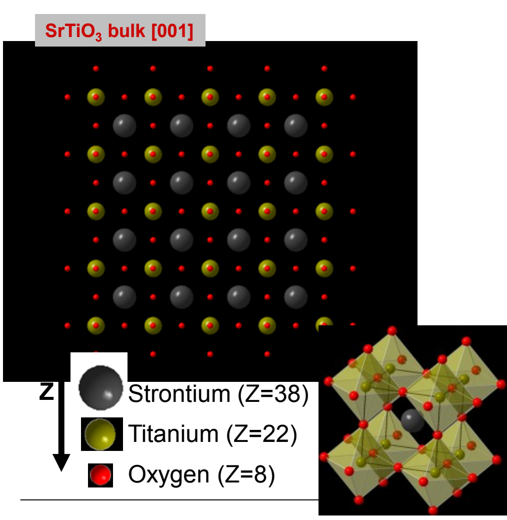
Ronchigram

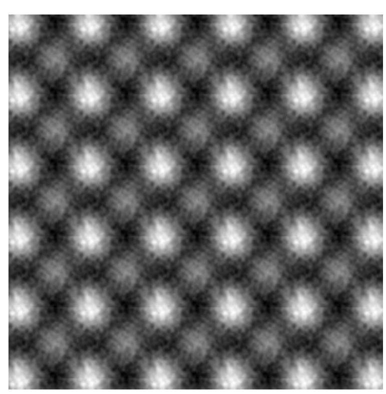
The use of ronchigram

Objective astigamtism



Atomicaly resolved HAADF-STEM imaging





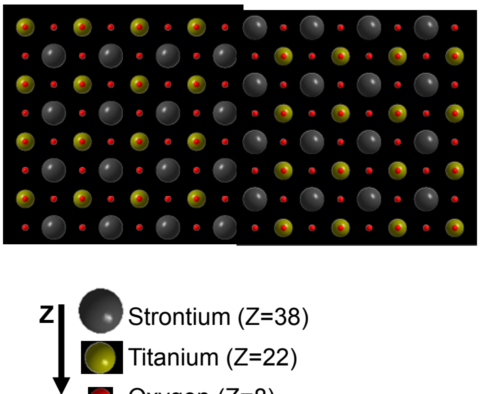
S. Šturm (2009)

HAADF-STEM imaging at high spatial resolution:

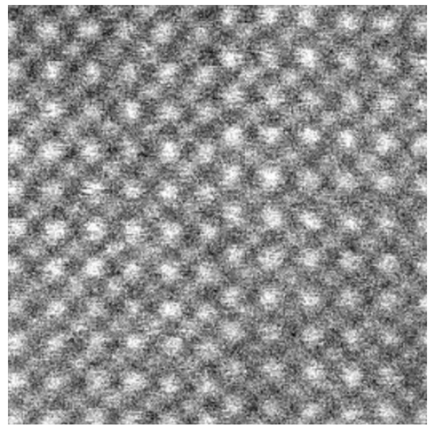
- Z-contrast
- Atomic-scale combined compositional and structural sensitivity

Atomicaly resolved HAADF-STEM imaging

$SrTiO_3$ Ruddlesden-Popper planar fault [001]



SrO-doped $SrTiO_3$



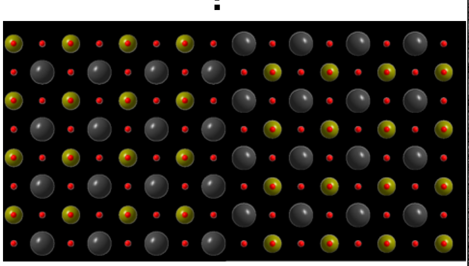
HAADF-STEM imaging at high spatial resolution:

- Z-contrast
- Atomic-scale combined compositional and structural sensitivity

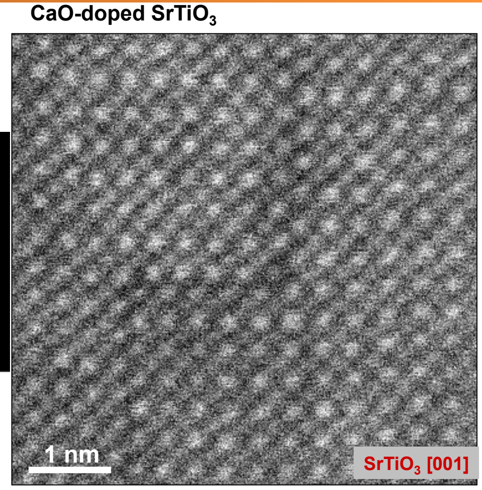
Atomicaly resolved HAADF-STEM imaging

$SrTiO_3$ [001]

?



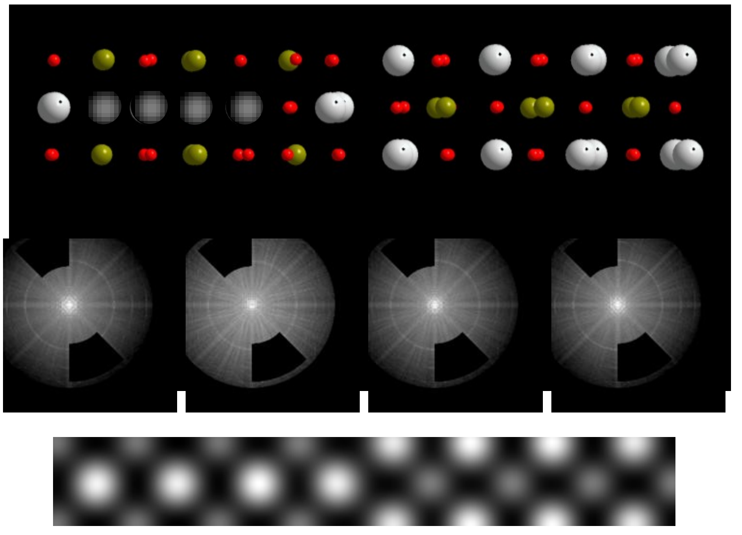
CaO-doped $SrTiO_3$



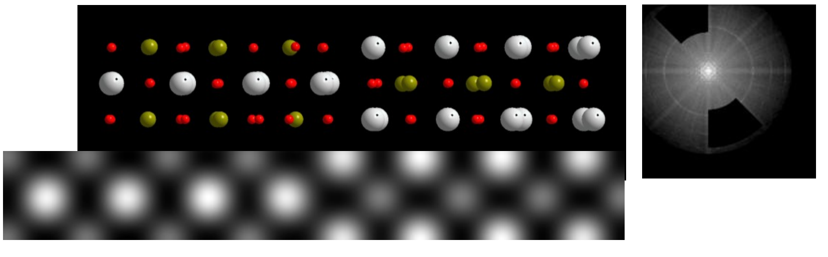
Need for qunatitative interpretation of atomicaly resolved HAADF-STEM images

- HAADF-STEM image simulatons

HAADF-STEM image simulations



HAADF-STEM image simulations



Incomplete list of HAADF-STEM image simulations softwares:

- C. Koch: QSTEM (http://www.christophtkoch.com/stem/index.html)
- E.J. Kirkland: Advanced Computing in Electron Microscopy
- P. Galindo: HAADF-STEM image simulations on large scale nanostructures
- V. Grillo: STEM_CELL (http://tem.s3.infm.it/software)
- http://www.hremresearch.com/ (commercial software)

Quantitative HAADF-STEM image analysis

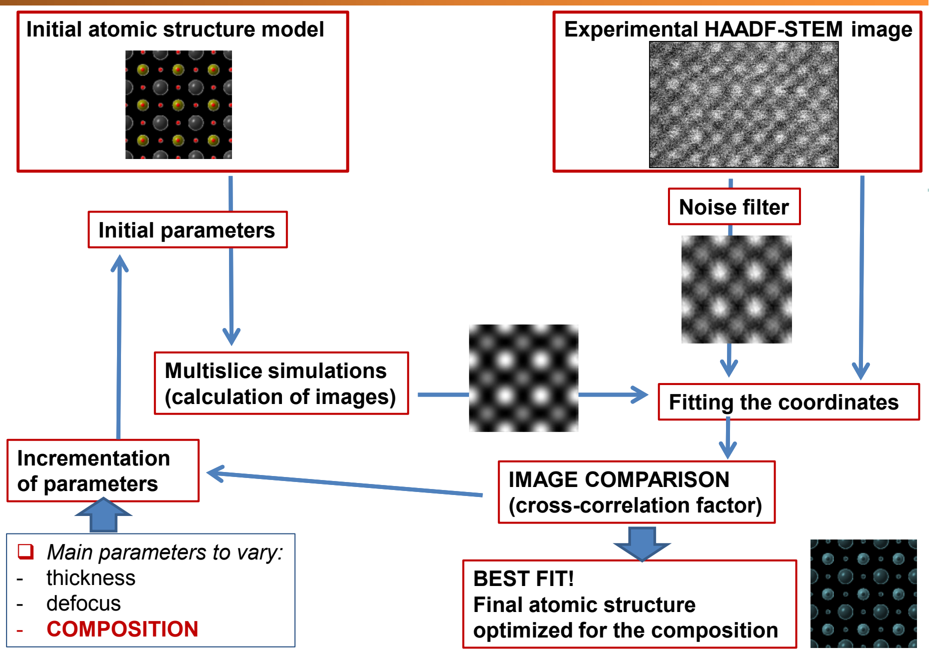
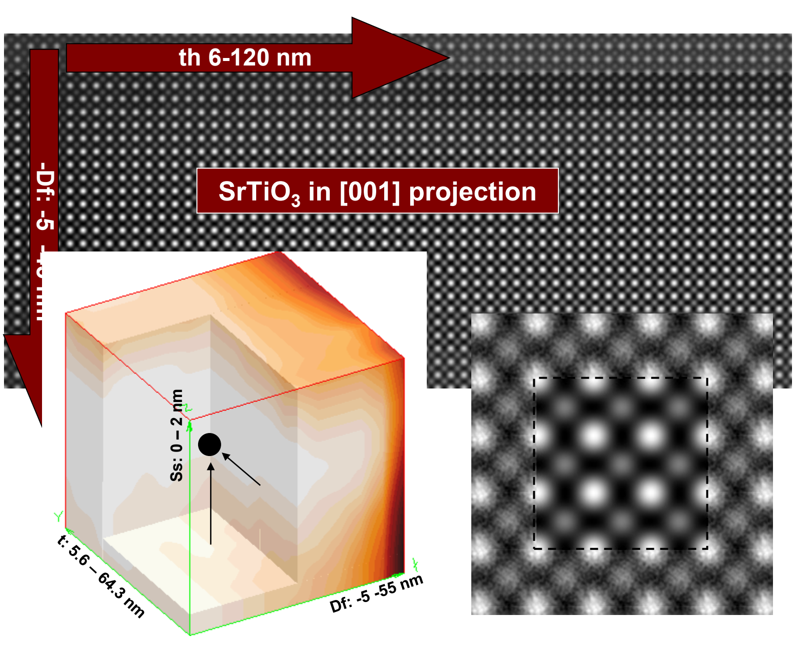
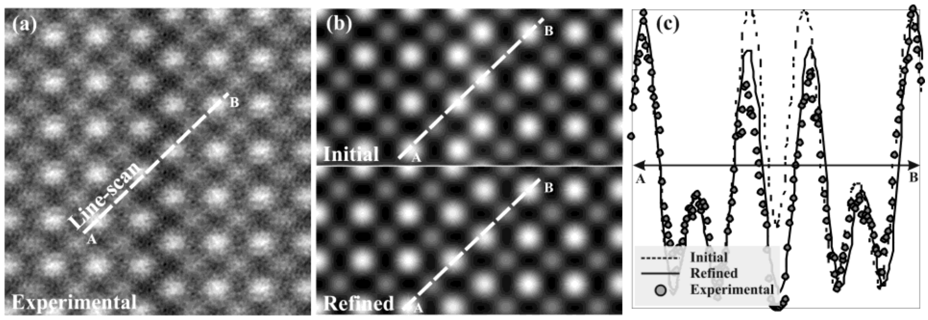


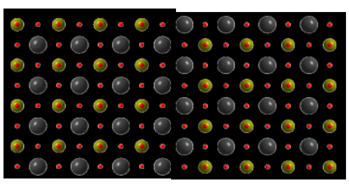
Image matching alghoritm: Cross-correlation data cube



Quantitative HAADF-STEM

$SrTiO_3$ + 10 mol.%SrO





Quantitative HAADF-STEM