Master sciences et technologies
Mention Physique et Applications

Transmission Electron Microscopy

Part #2
High Resolution Imaging
XEDS – EELS spectroscopies
Aberration corrected TEM

Nicolas Menguy

Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie

Part 2 : Advanced TEM

- High resolution imaging
  - TEM lens aberrations
  - influence of TEM aberrations
  - HREM simulations

- STEM- HAADF imaging

- X-ray Energy Dispersive Spectroscopy (XEDS)

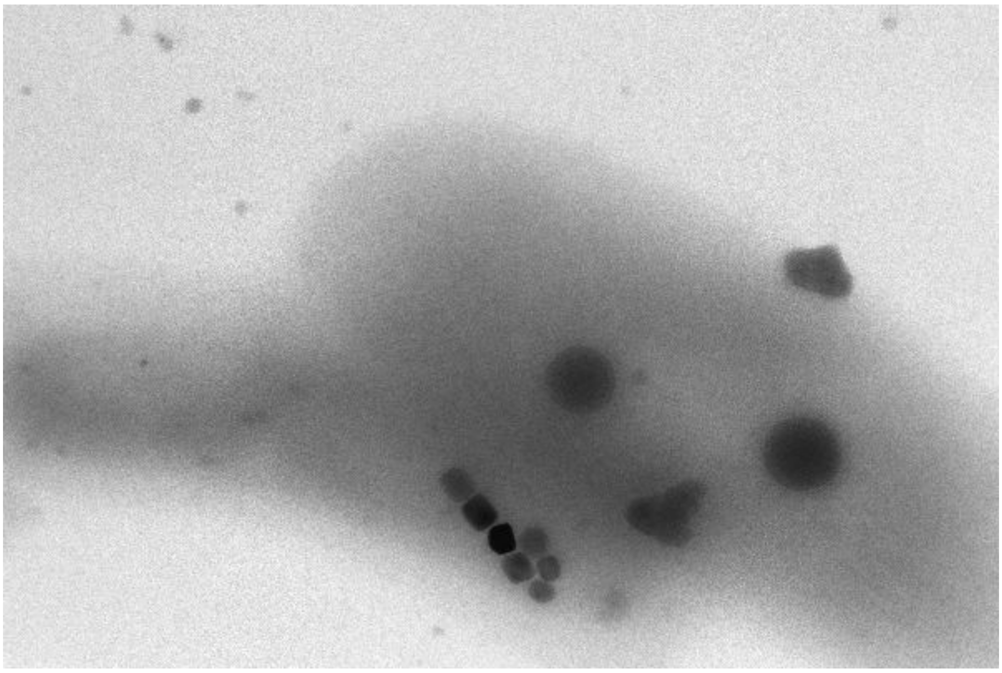
- Electron Energy Loss Spectroscopy (EELS)
  - spectrocopy
  - Energy Filtered Imaging

- Aberration corrected TEM
  - HREM imaging
  - STEM-HAADF imaging
  - EELS / XEDS mapping

Part 2 : Advanced TEM

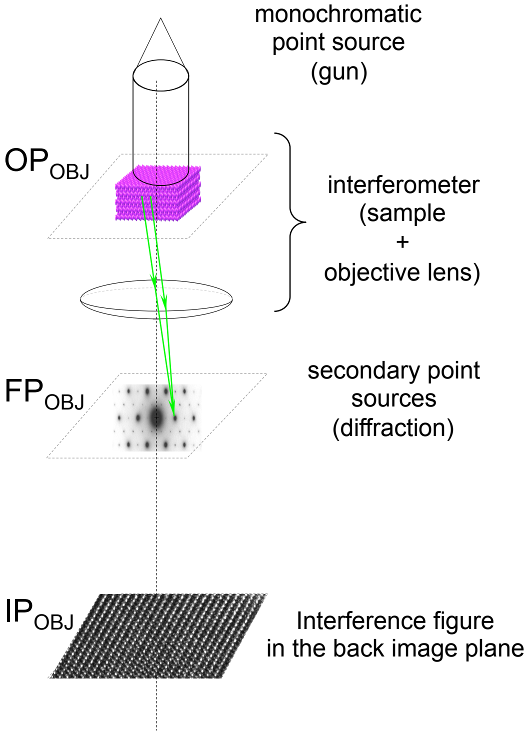
- High resolution imaging
  - TEM lens aberrations
  - influence of TEM aberrations
  - HREM simulations
- STEM- HAADF imaging
- X-ray Energy Dispersive Spectroscopy (XEDS)
- Electron Energy Loss Spectroscopy (EELS)
  - spectrocopy
  - Energy Filtered Imaging
- Aberration corrected TEM
  - HREM imaging
  - STEM-HAADF imaging
  - EELS / XEDS mapping

High Resolution Electron Microscopy HREM



⇒ the crystalline structure is "visible"

High Resolution Electron Microscopy HREM
basic optic approach



- Theroretically, the resolution should be closed to the electron associated wavelength

  → 2.51 pm @ 200 kV

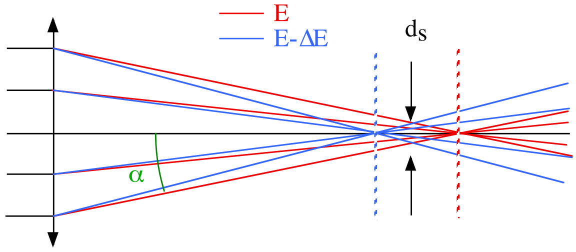
- Typical standard TEM resolution :

  → 190 pm @ 200 kV

The resolution is limited mainly due to lens aberrations

Aberration of electromagnetic lenses
Chromatic aberration – diffraction limit

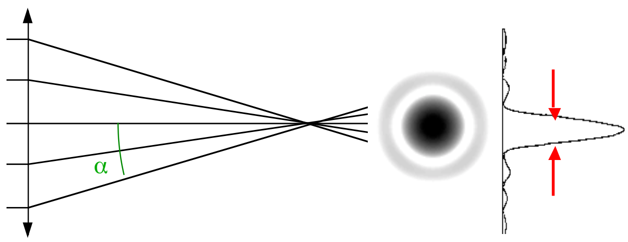
Chromatic aberration



$$d_s = c_c \frac{\Delta E}{E} \alpha$$

Diffraction

May appear, due to the contrast aperture

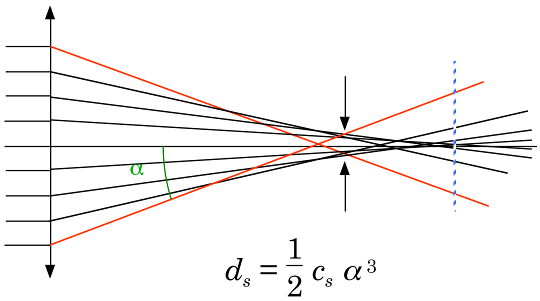


$$d_d = 1.22 \frac{\lambda}{\alpha}$$

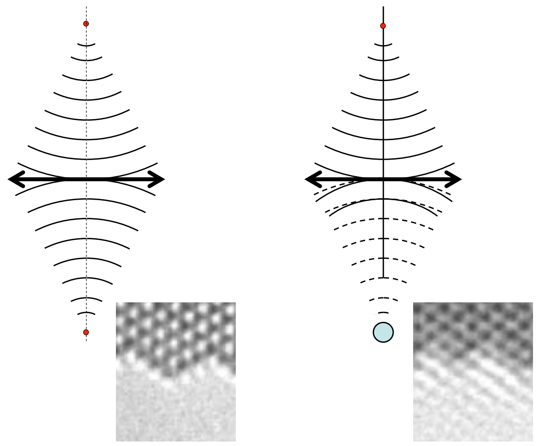
High Resolution Electron Microscopy HREM

Spherical aberration

Spherical aberration



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



• the image of a point is not a point

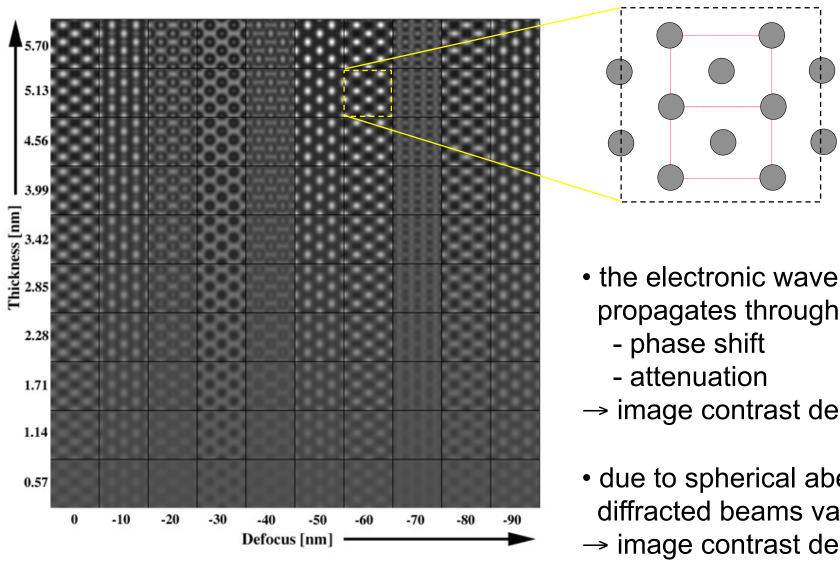
• a phase shift appears between diffracted beams

⇒ lowering the resolution (→ 1.5 Å)

⇒ images may be difficult to interpret

High Resolution Electron Microscopy HREM

Thickness and defocus influence



• the electronic wave is modified when it propagates through the sample thickness
 - phase shift
 - attenuation

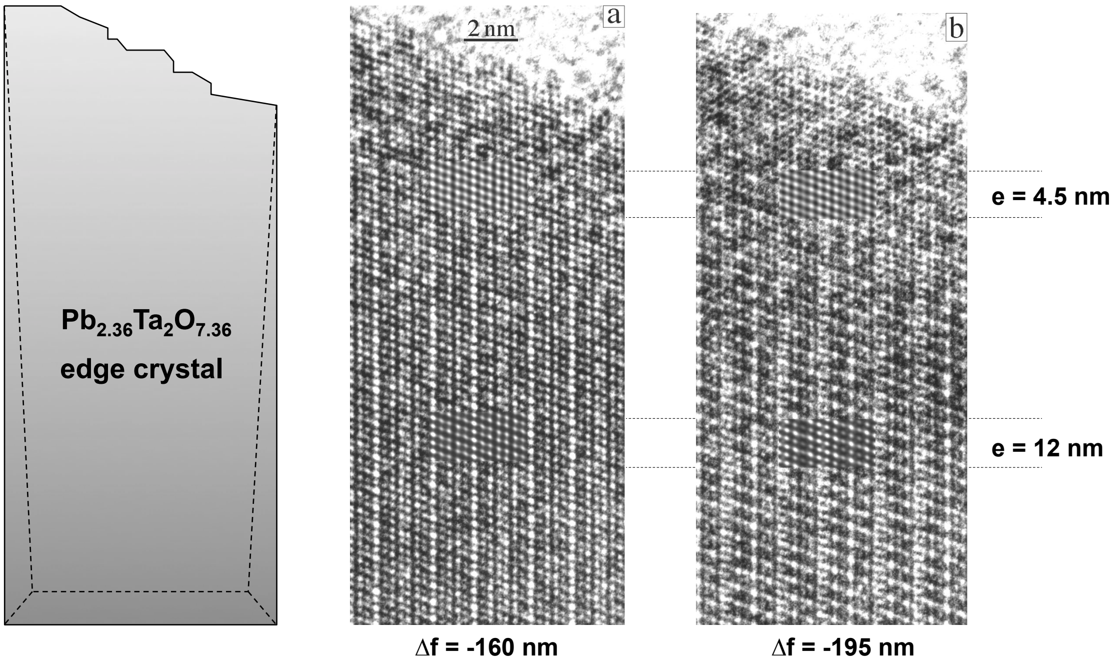
→ image contrast depends on sample thickness

• due to spherical aberration, phase shifts between diffracted beams vary with focus.

→ image contrast depends on defocus

⇒ HREM images may be difficult to interpret

High Resolution Electron Microscopy HREM
influence of sample thickness and focus



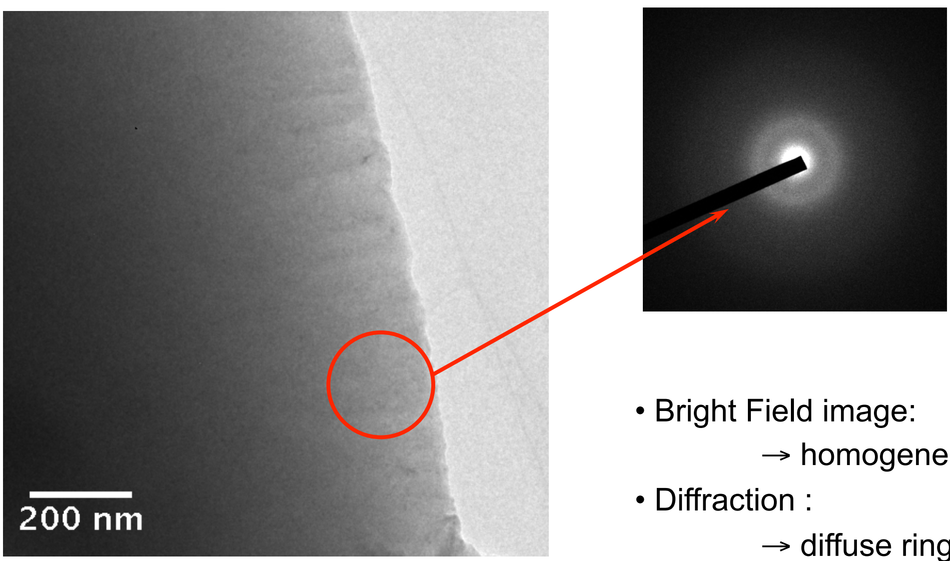
HREM images cannot be directly interpretated

⇒ Images simulations are mandatory

J. Solid State Chemistry **126,** 253–260 (1996)

High Resolution Electron Microscopy HREM
example #1

Crystallization in MgO - Al_2O_3 - SiO_2 glass

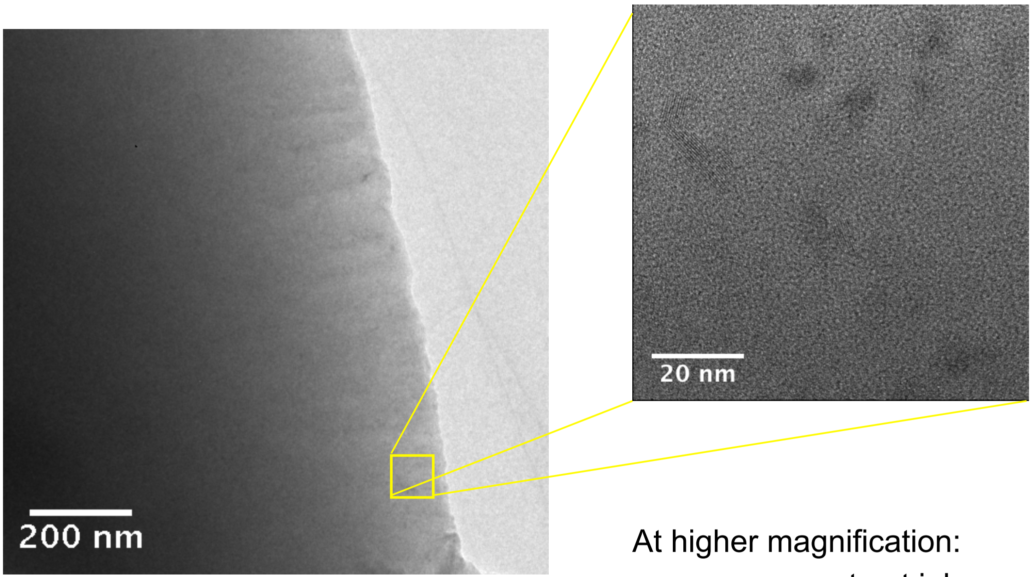


- Bright Field image:
  → homogeneous contrast
- Diffraction :
  → diffuse rings

⇒ The sample seems to be amorphous
⇒ No crystallization …

High Resolution Electron Microscopy HREM
example #1

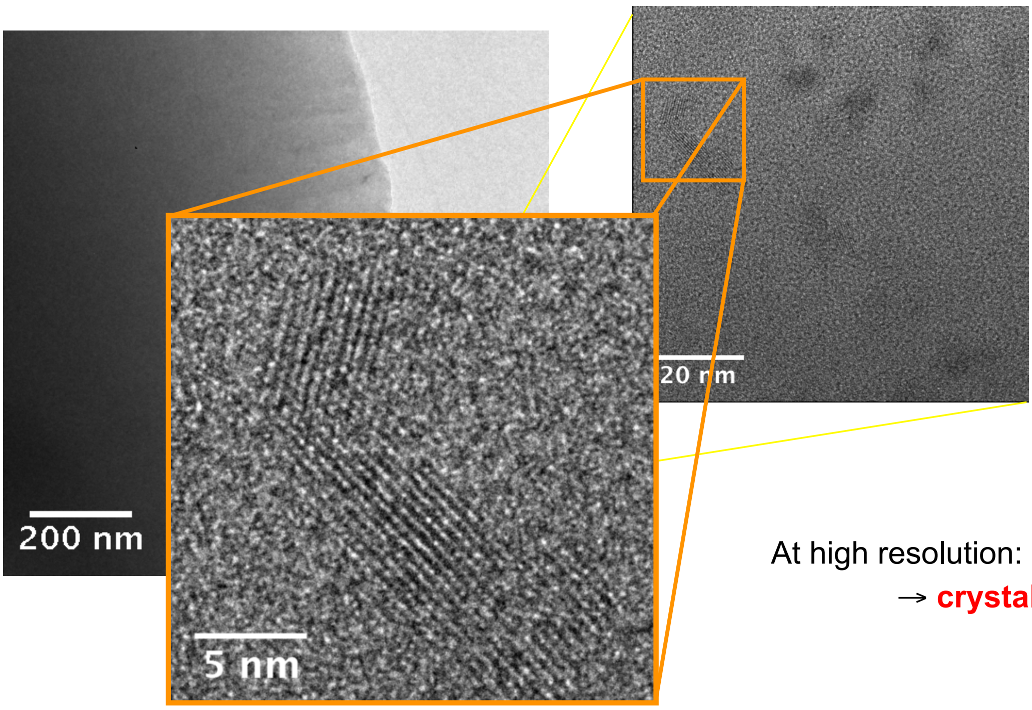
Crystallization in MgO - Al_2O_3 - SiO_2 glass



At higher magnification:
→ contrast inhomogeneities

High Resolution Electron Microscopy HREM
example #1

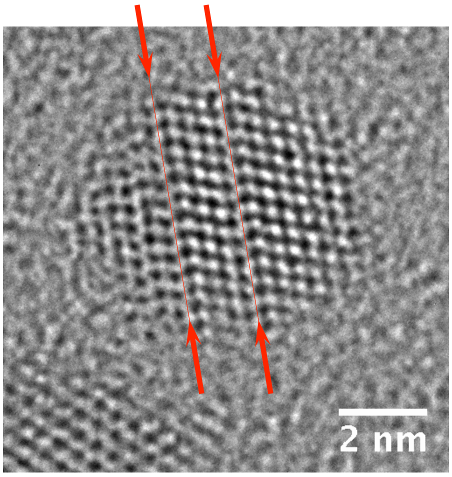
Crystallization in MgO - Al_2O_3 - SiO_2 glass



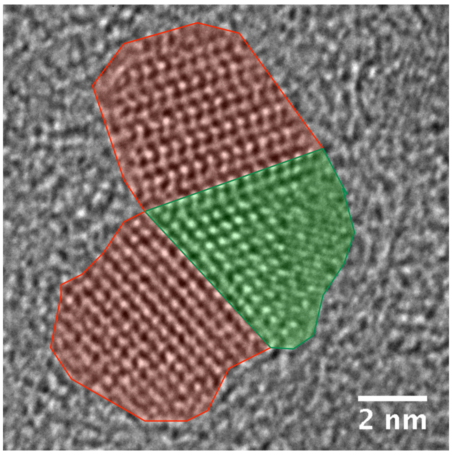
At high resolution:
→ **crystals**

High Resolution Electron Microscopy HREM
example #1

CdSe quantum dots structures



Stacking faults
A B C A B **A** B C



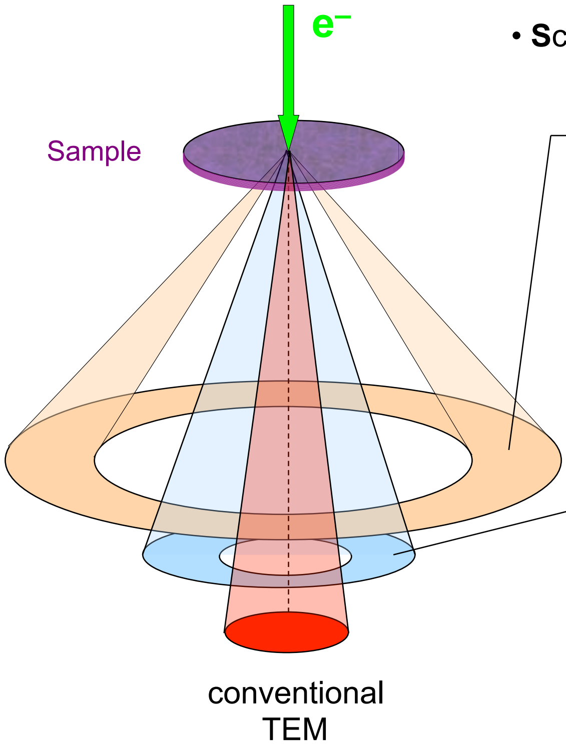
Assemblage **wurtzite** – **sphalerite**
..ABCABC… **..ABABA…**
(cubic) (hexagonal)

Part 2 : Advanced TEM

- High resolution imaging
  - TEM lens aberrations
  - influence of TEM aberrations
  - HREM simulations
- STEM- HAADF imaging
- X-ray Energy Dispersive Spectroscopy (XEDS)
- Electron Energy Loss Spectroscopy (EELS)
  - spectrocopy
  - Energy Filtered Imaging
- Aberration corrected TEM
  - HREM imaging
  - STEM-HAADF imaging
  - EELS / XEDS mapping

High Angle Annular Dark Field in Scanning mode

STEM - HAADF



• **S**canning **T**ransmission **E**lectron **M**icroscopy

High **A**ngle **A**nnular **D**ark **F**ield (HAADF)

• Intensity proportional to $\rho \cdot t \cdot Z^{3/2}$

ρ : density

t : sample thickness

Z : mean atomic number

Annular **D**ark **F**ield (ADF)

⇒ Z - contrast

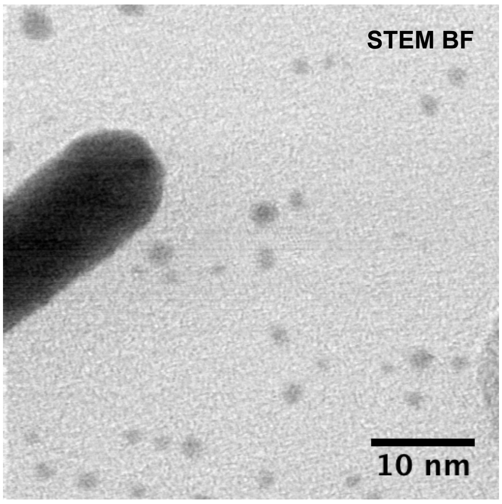
High Angle Annular Dark Field in Scanning mode

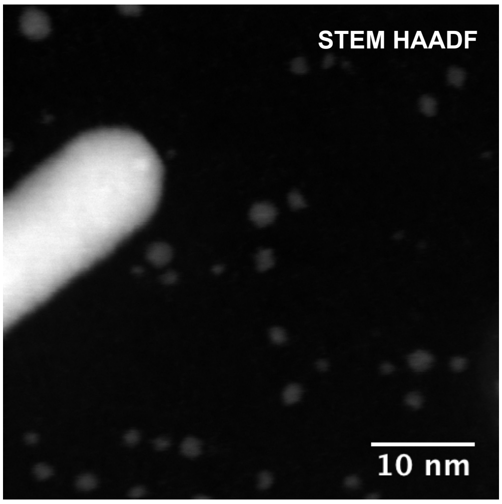
STEM - HAADF

• Image formation: same as for a SEM but in transmission mode

(a) from electrons that have not been scattered or are only under small angles (**BF**)

(b) from electrons that have undergone large-angle scattering events (**HAADF**)

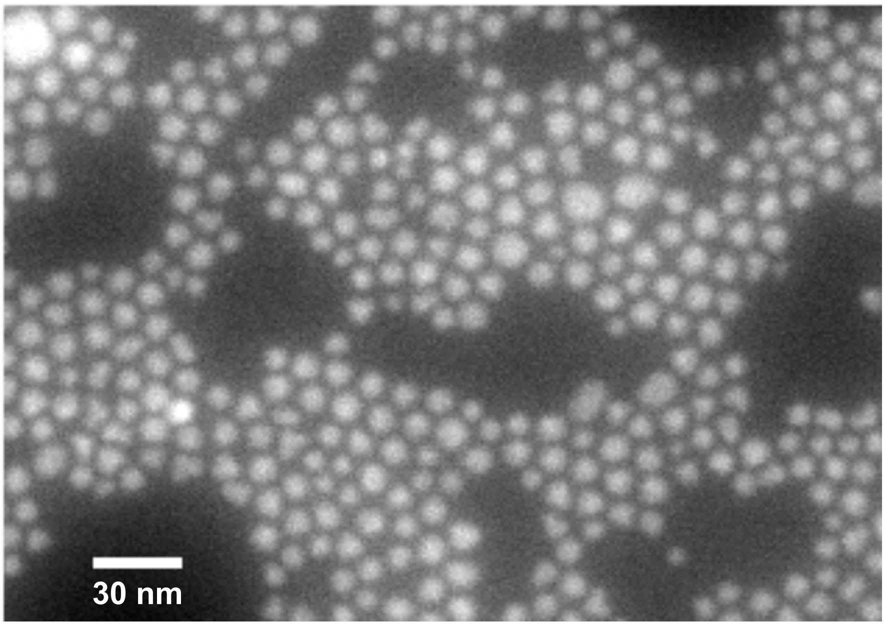




High Angle Annular Dark Field in Scanning mode

STEM - HAADF

CdS quantum dots



© B. Mahler ESPCI

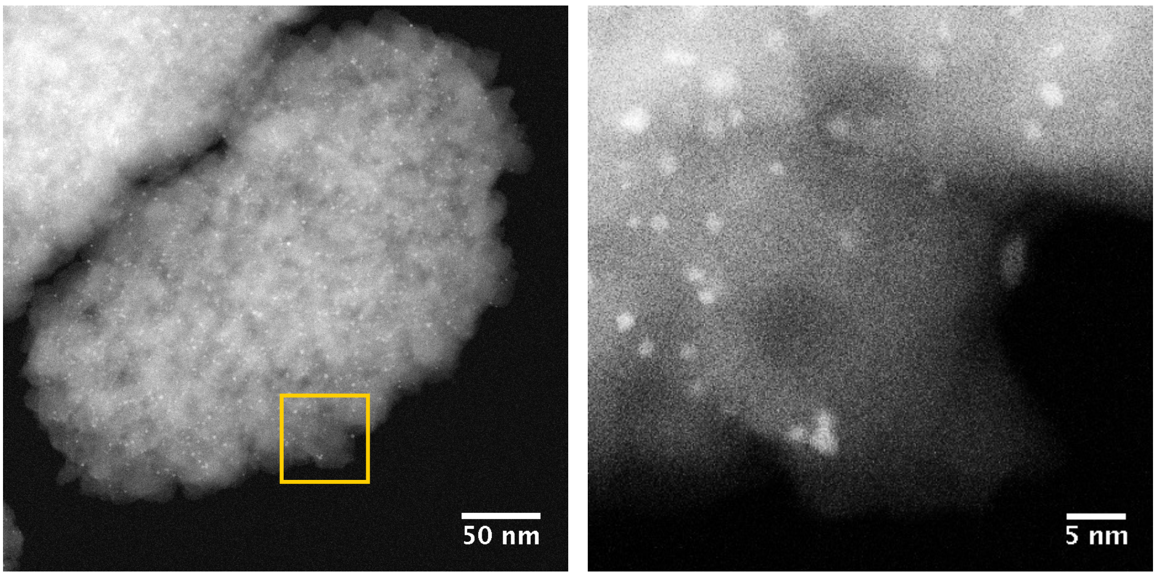
→ Size histogram

High Angle Annular Dark Field in Scanning mode

STEM - HAADF

Interest of Z-contrast

Pt-particles in zeolite



N. Menguy / D. Brouri, S. Casale LRS - UPMC

Part 2 : Advanced TEM

• High resolution imaging
- TEM lens aberrations
- influence of TEM aberrations
- HREM simulations

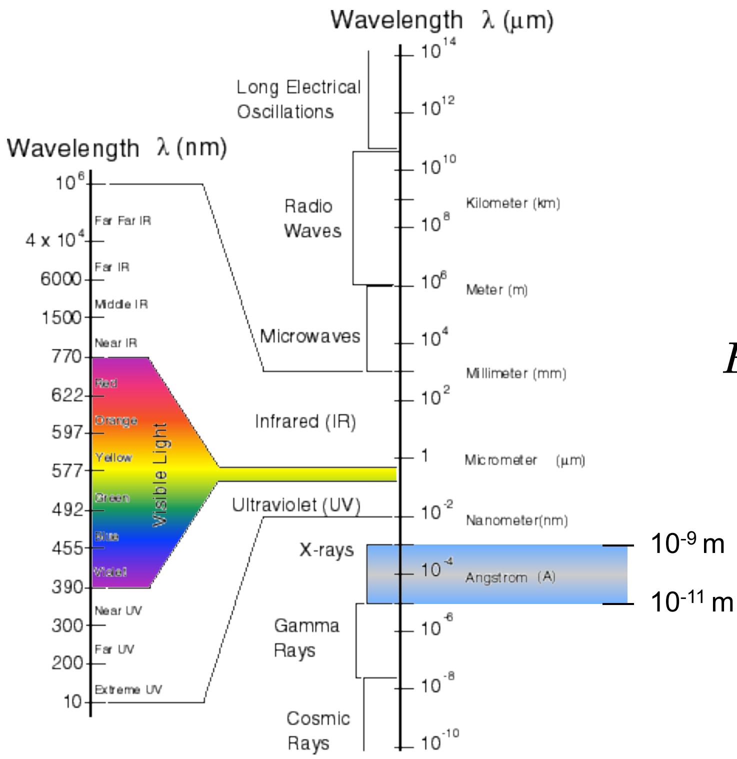
• STEM- HAADF imaging

• X-ray Energy Dispersive Spectroscopy (XEDS)

• Electron Energy Loss Spectroscopy (EELS)
- spectrocopy
- Energy Filtered Imaging

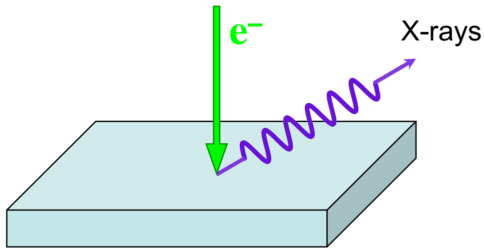
• Aberration corrected TEM
- HREM imaging
- STEM-HAADF imaging
- EELS / XEDS mapping

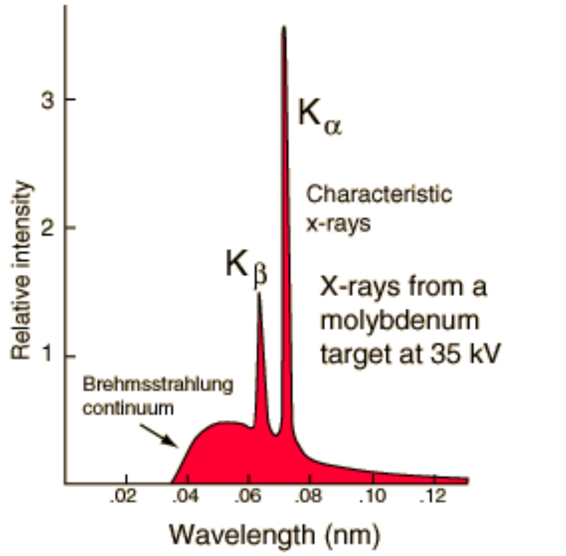
X-rays in the electromagnetic spectrum

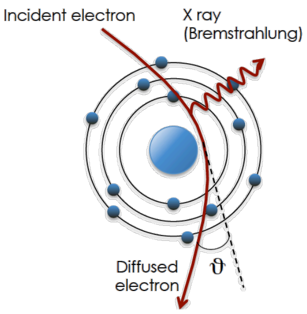


$$E\ (\text{eV}) = 12398.5\ /\ \lambda\ (\text{Å})$$

X-ray emission
main features







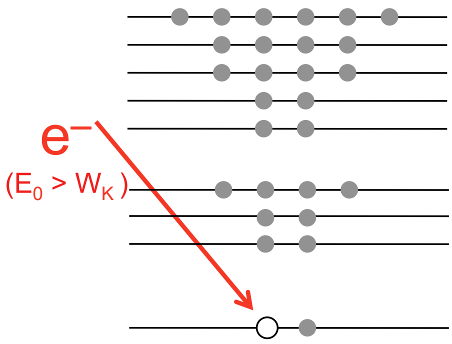
X-ray spectrum:

- continuous background (Brehmsstrahlung)
- characteristic lines

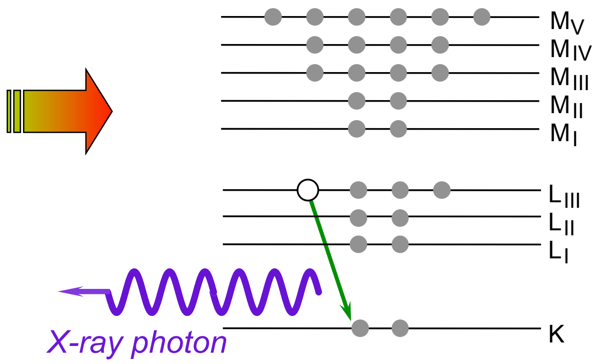
X-ray emission
origin of the characteristic lines

2 step phenomenon

1. Ionisation



2. Radiative transition



FLUORESCENCE

Energies of emitted photons are specific/characteristic to the chemical elements

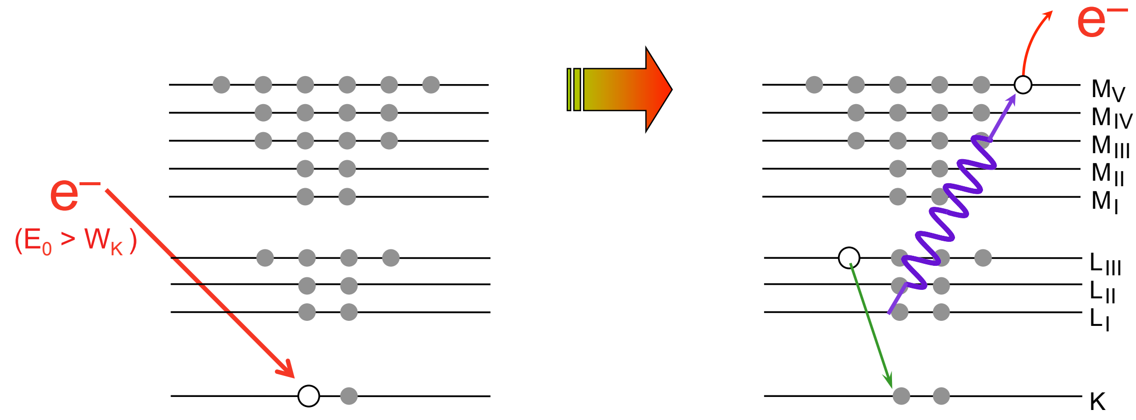
- $K\alpha_1 : h\nu = W_K - W_{L3}$
- $K\alpha_2 : h\nu = W_K - W_{L2}$

X-ray emission
Auger electron emission

The transition may occur through the emission of an Auger electron

1. Ionisation

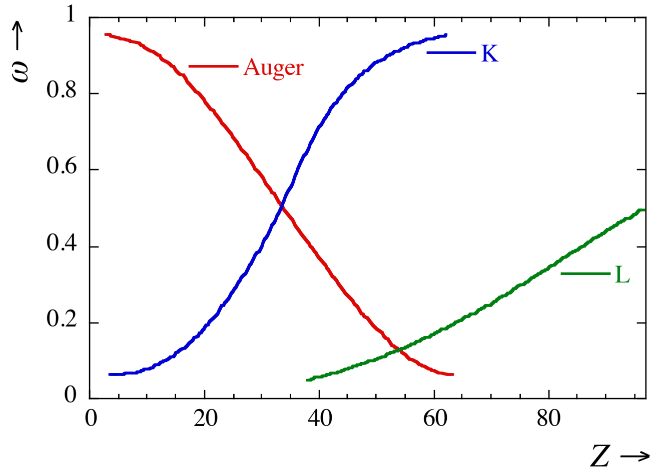
2. Auger transition



Auger Electron Spectroscopy (AES) is used for surface analyses

X-ray emission
X-ray emission vs Auger electron emission

Probability transition depends on atomic number of elements

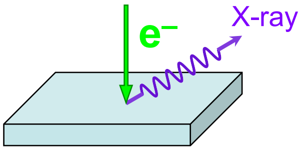


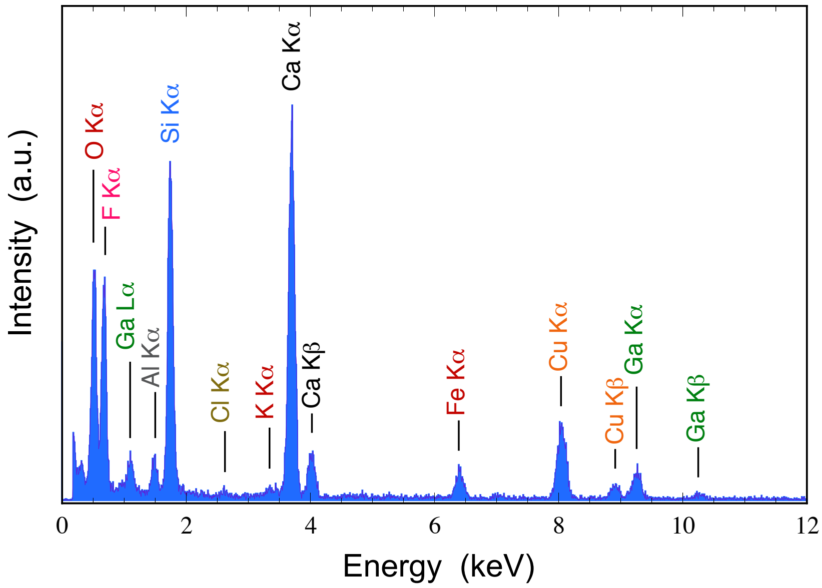
For light elements, Auger transition is more likely

⇒ X-ray fluorescence has a low sensitivity for light elements

X-ray emission

X-ray emission spectrum



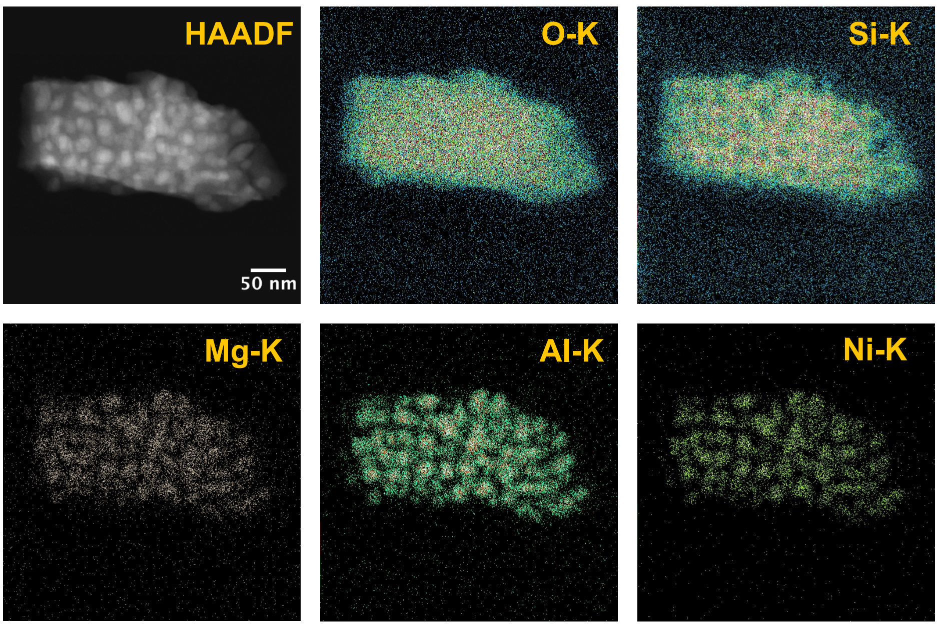


Peak assignation leads to element identification

⇒ quantitification is possible (≈ at%)

STEM + XEDS : X-ray elemental mapping

Chemical composition of the crystalline phases in MAS-NiO 4% glass



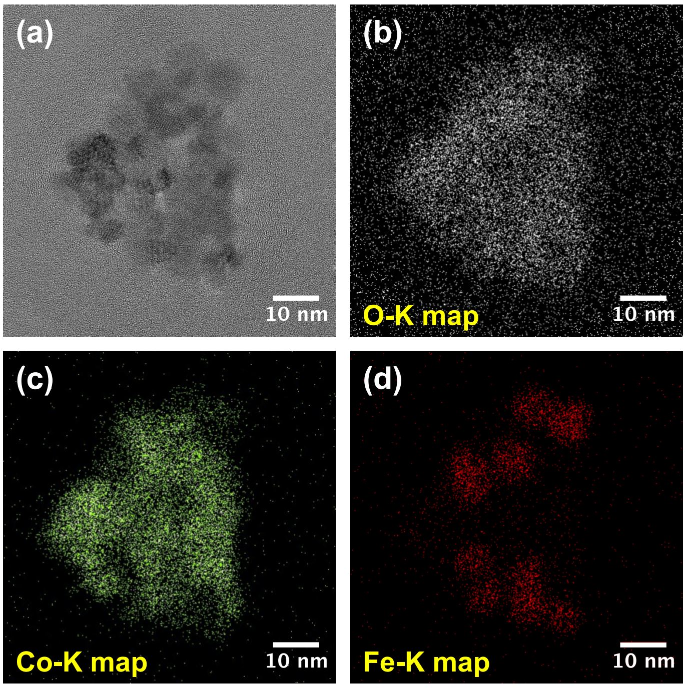
IMPMC
Jeol 2100F

→ composition of crystallized spinelle phase : $Mg_{1-x}Ni_xAl_2O_4$

X-ray elemental mapping

nanoparticles

Fe_3O_4 – CoO composite system

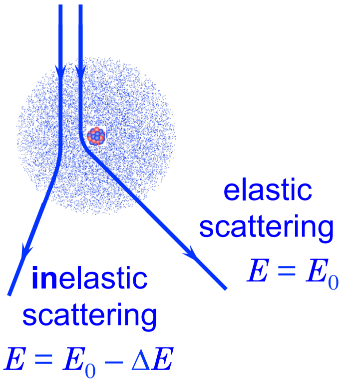


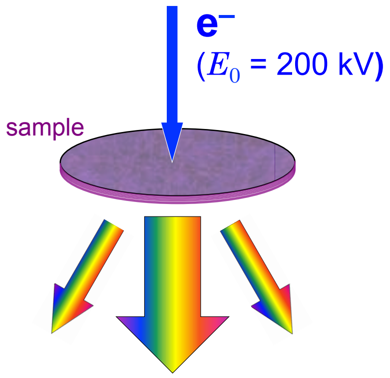
IMPMC
Jeol 2100F

Part 2 : Advanced TEM

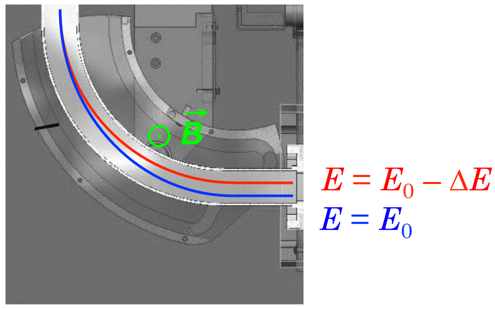
- High resolution imaging
  - TEM lens aberrations
  - influence of TEM aberrations
  - HREM simulations
- STEM- HAADF imaging
- X-ray Energy Dispersive Spectroscopy (XEDS)
- Electron Energy Loss Spectroscopy (EELS)
  - spectrocopy
  - Energy Filtered Imaging
- Aberration corrected TEM
  - HREM imaging
  - STEM-HAADF imaging
  - EELS / XEDS mapping

Electron Energy Loss Spectroscopy (EELS)

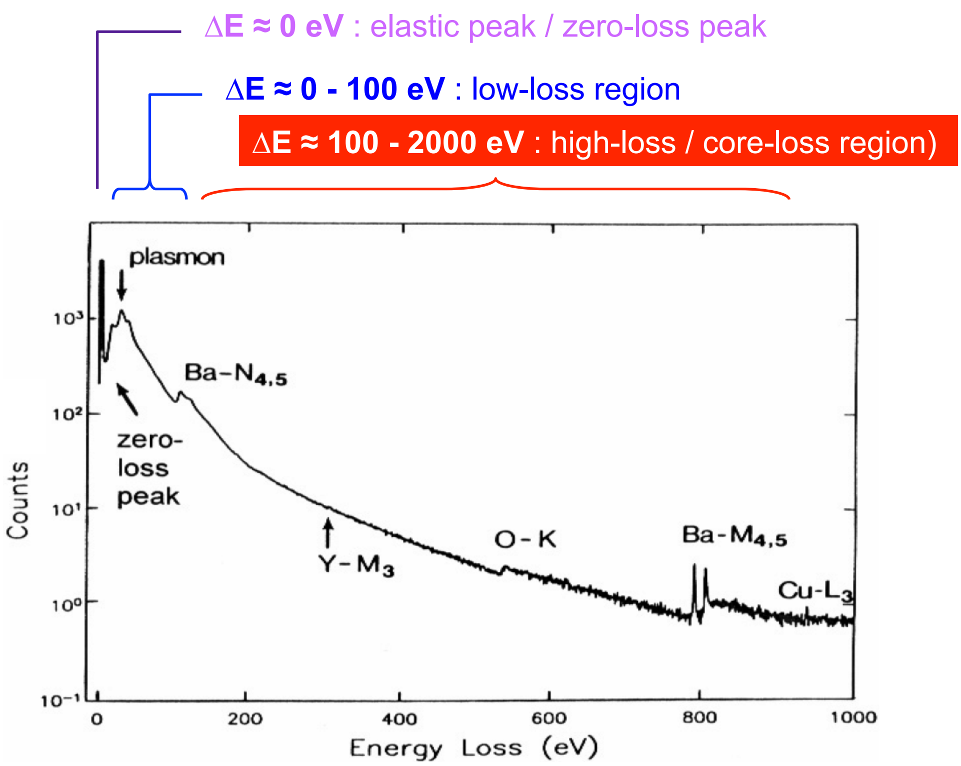




EELS spectrometer

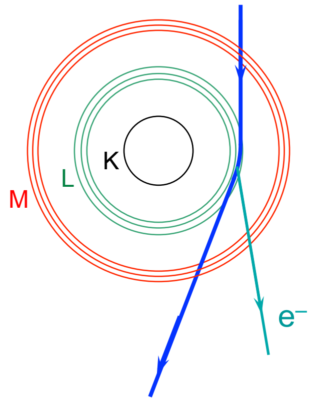


EELS spectrum



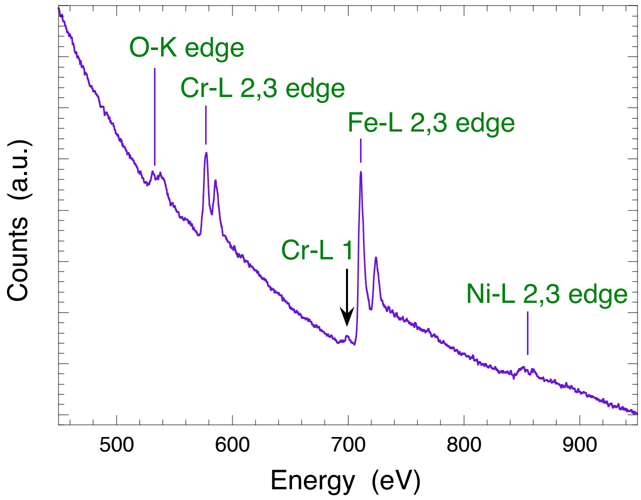
Electron – Matter interactions

Core-loss – ionisations – Chemical analysis



$E = E_0 - W_{L3} \rightarrow$ L3 edge

Energy loss is a signature of the ionized element



Chemical Analysis

Comparison between EELS and XEDS

- For most x-ray detectors : light elements (Z ≤ 5) cannot be detected
  → for B, Li, He and H : EELS is mandatory

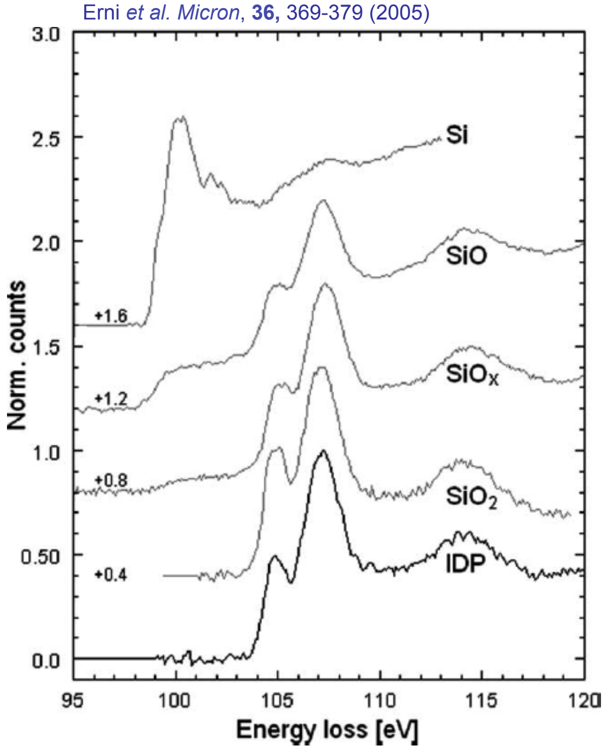
- A complete x-ray spectrum may be acquired in few second
  → chemical analysis using XEDS is very fast

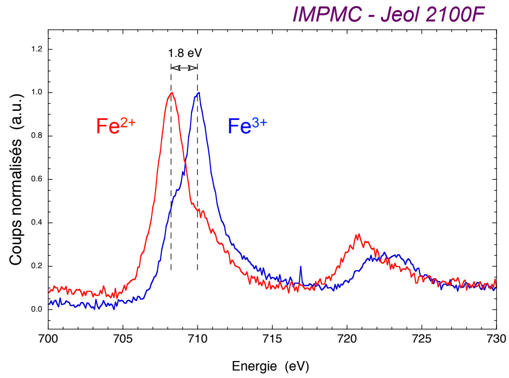
- X-ray detector resolution is low (≈ 125 eV), X-ray spectrum may be difficult to interpret (overlapping peak)
  → a complementary EELS analysis may be very useful

→ EELS may provide other interesting / essential information …

EELS analysis
valence and speciation of elements

Erni *et al.* *Micron*, **36,** 369-379 (2005)

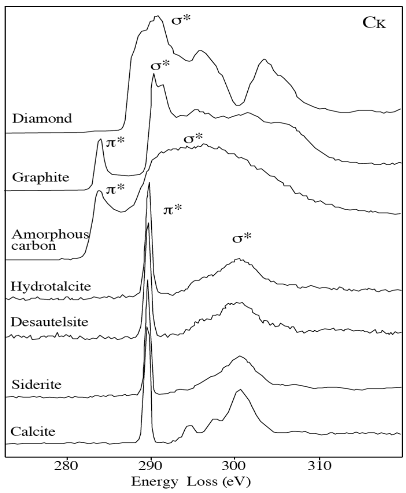


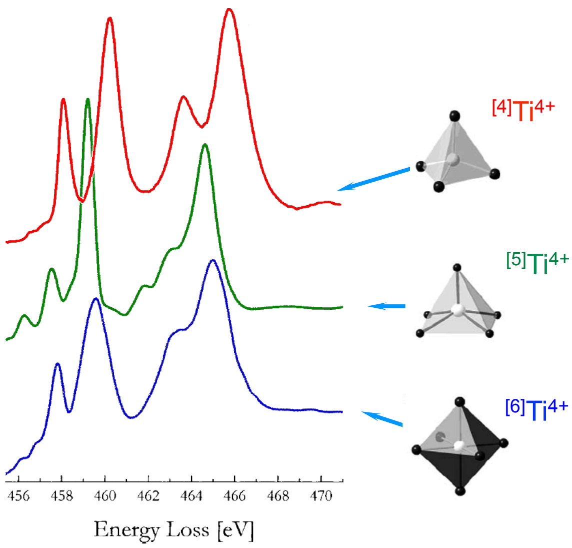


EELS analysis
valence and speciation of elements

EELS spectrum of a compound is specific of :

- the chemical elements of the compound
- the valence of the element(s)
- the local environment of each element

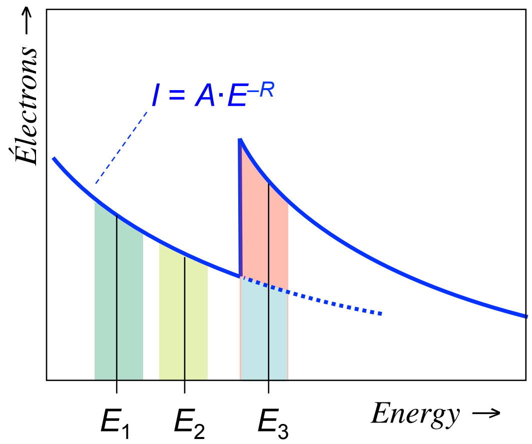


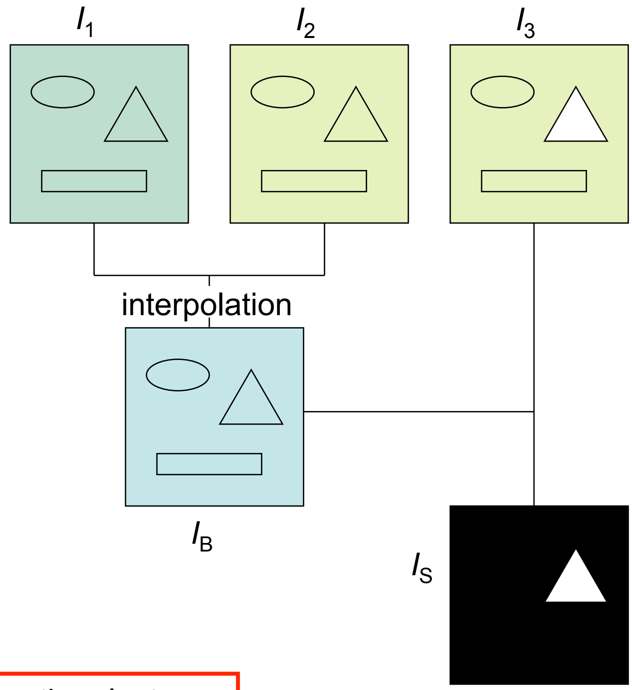


Hoche *et al.* *Phys. Rev. B* **72** (2005)

Energy Filtered Transmission Electron Microscopy
EFTEM

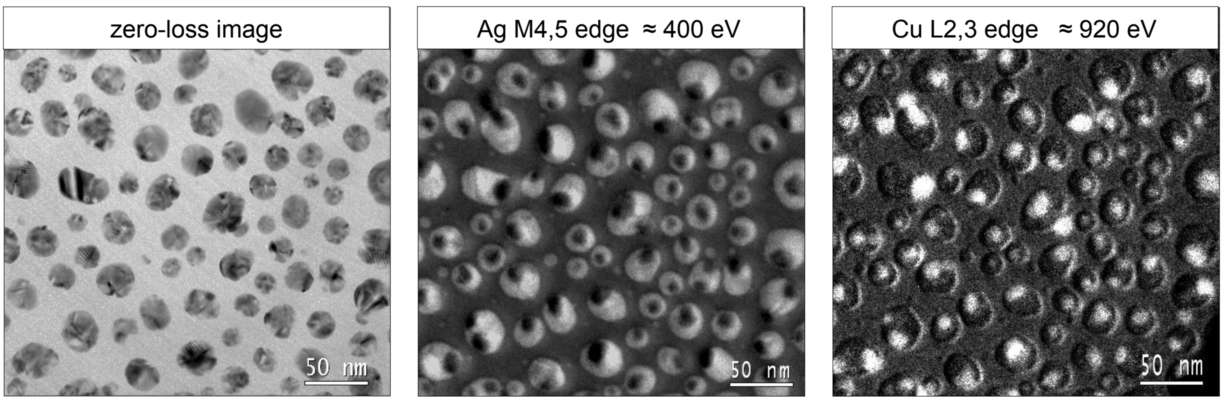
EFTEM basics

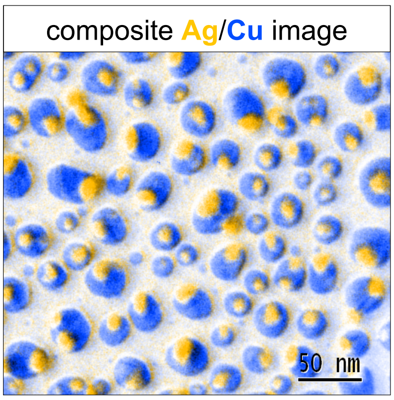




The image is created by selecting the electrons in a specific (interesting) energy range

Energy Filtered Transmission Electron Microscopy
EFTEM



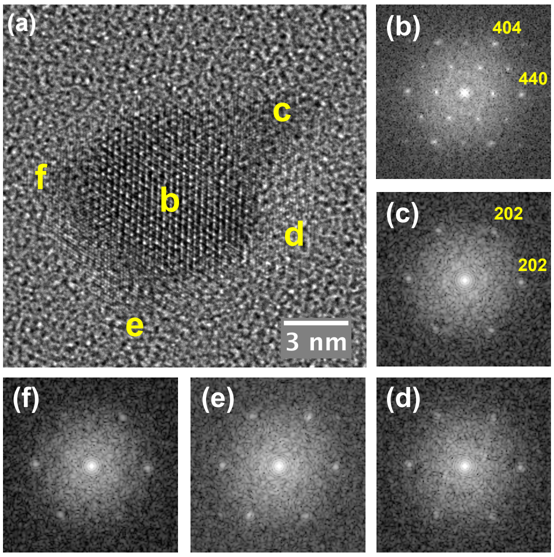


Ch. Ricolleau
Jeol 2100F - IMPMC

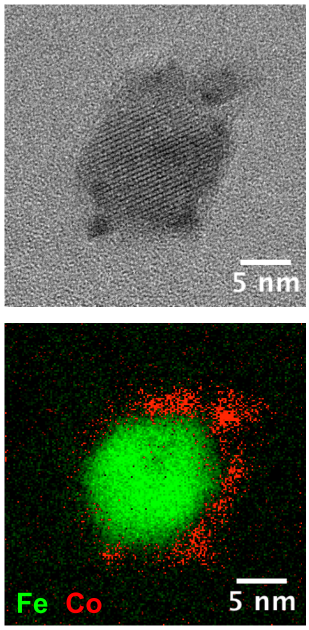
⇒ Elemental mapping with a resolution ≈ 1 nm

Energy Filtered Transmission Electron Microscopy
EFTEM

Core-shell Fe_3O_4 @ CoO



HREM crystallographic analysis



EFTEM observations

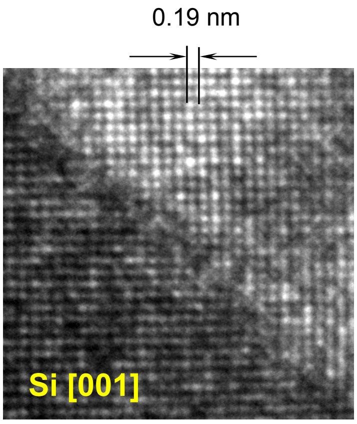
Gaudisson *et al. J. Nanopart. Res.* (2014)

Part 2 : Advanced TEM

- High resolution imaging
  - TEM lens aberrations
  - influence of TEM aberrations
  - HREM simulations
- STEM- HAADF imaging
- X-ray Energy Dispersive Spectroscopy (XEDS)
- Electron Energy Loss Spectroscopy (EELS)
  - spectrocopy
  - Energy Filtered Imaging
- Aberration corrected TEM
  - HREM imaging
  - STEM-HAADF imaging
  - EELS / XEDS mapping

High Resolution Imaging

How to improve the resolution ?

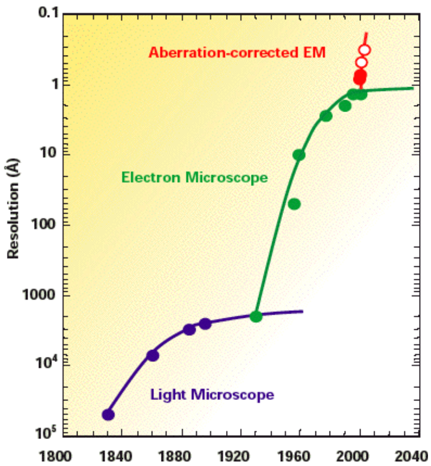


Jeol 2100F ***IMPMC***

- 200 kV → 0.19 nm
- 300 kV → 0.17 nm
- 400 kV → 0.16 nm

- Lowering λ
  E = 1250 kV, λ = 7.36 pm
  Resolution ≈ 0.095 nm

  8 M€ in 1990 !!!

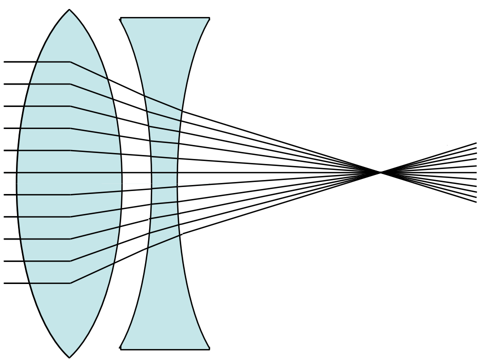


High Resolution Imaging

How to improve the resolution ?

Spherical aberration correction

- Lenses with rotational symmetric electromagnetic fields exhibit spherical aberration



For optic lenses, aberration correction may be easily obtained

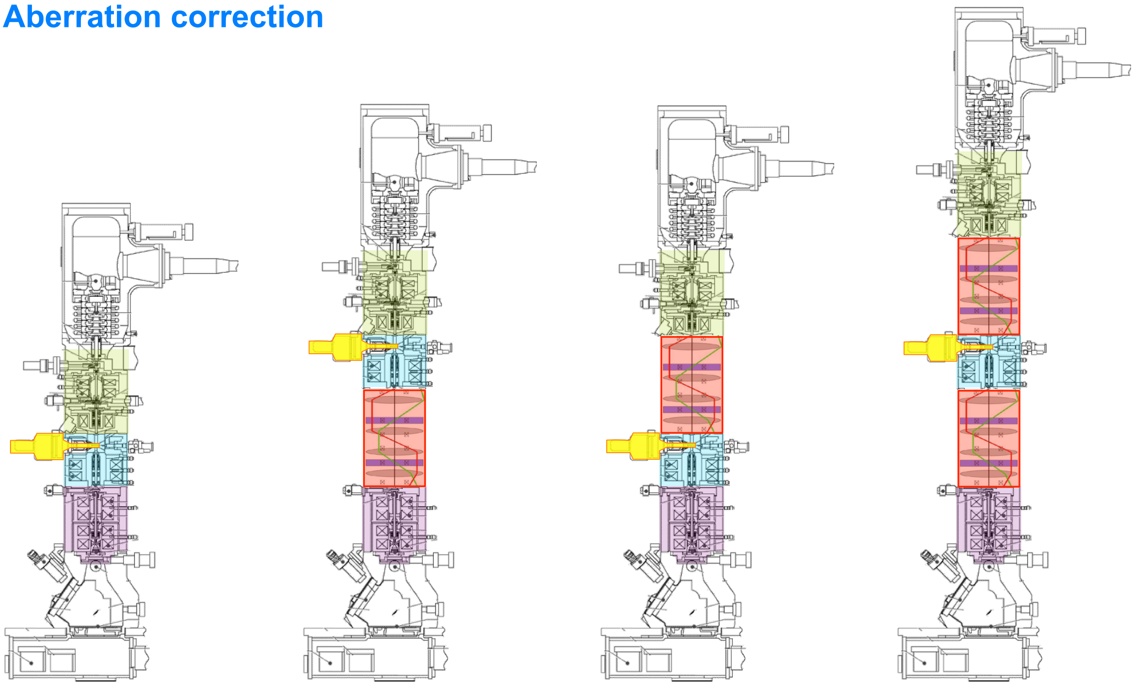
http://www.ceos-gmbh.de

lens aberrations can be corrected introducing non-rotational symmetry in the electron path

High Resolution Imaging

How to improve the resolution ?

Aberration correction



TEM

TEM
Cs-objective

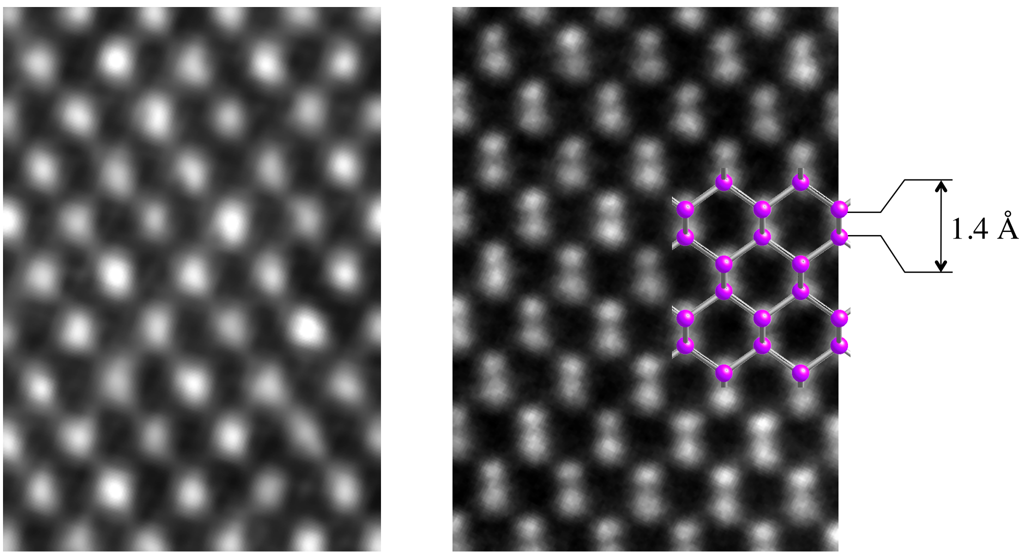
STEM
Cs-probe forming

TEM/STEM
double corrector

Aberration corrected HREM

Cs corrector objective lens

HREM image of Si [110]



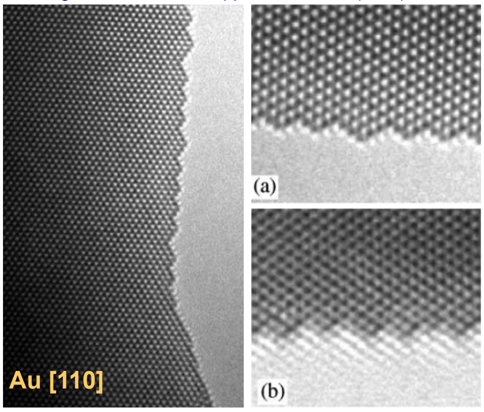
without Cs correction

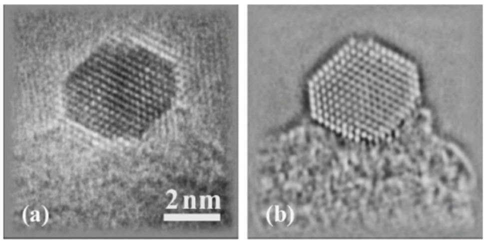
with Cs correction

Freitag *et al*,.*Ultramicroscopy* **102**, 209-214 (2005)

Aberration corrected HREM
Cs corrector objective lens

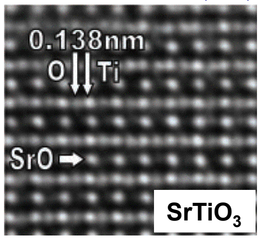
Freitag *et al*,.*Ultramicroscopy* **102**, 209-214 (2005)



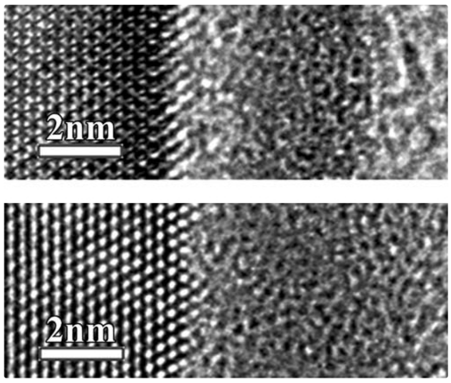


Takai, Y. and Y. Kimura. *Vac. Soc. Jpn.*, **51**: 707-713 (2008)

Jia et al, *Science*, **299**, 870 (2003)



- light atoms are visible

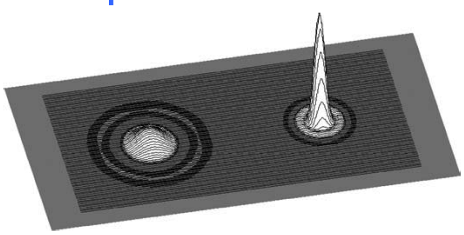


Inamoto et al. J.of Appl. Phys., 107: 124510 (2010)

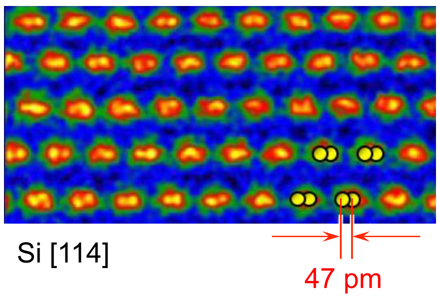
- Images are more easily interpretable
- No delocalisation effect : ⇒ study of interfaces

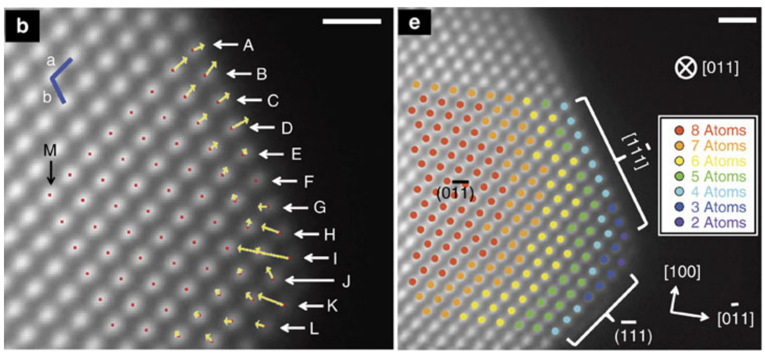
STEM-HAADF Imaging
Cs-probe forming corrector

Cs probe corrector



→ More intense and more focused probe
≈ 50 pm

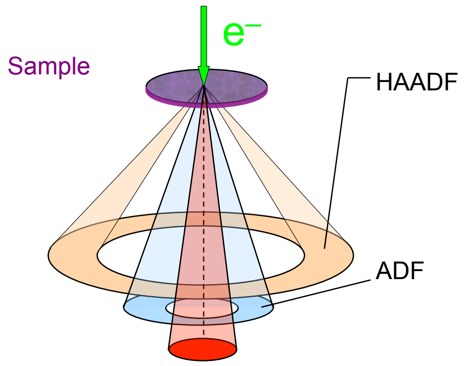


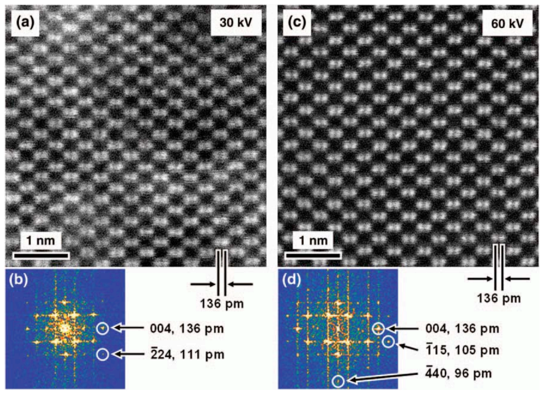


→ quantitative analysis of STEM-HAADF images

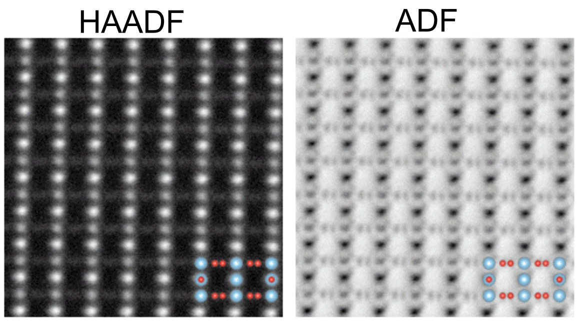
STEM-HAADF Imaging

Cs-probe forming corrector





→ Atomic resolution at low voltage



→ Visualization of light elements

Sasaki et al. *J Electron Microsc (Japan) (2010)*
doi: 10.1093/jmicro/dfq027

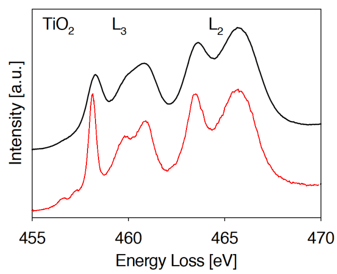
Electron sources

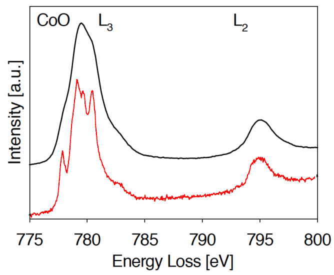
Monochromators / Spectrometer / Cold FEG

→ EELS resolution : 0.8 eV → 0.03 eV

- core loss – element speciation - redox

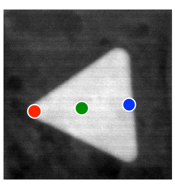
Mitterbauer et al. Ultramicroscopy 96 (2003) 469–480

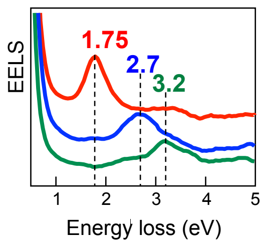


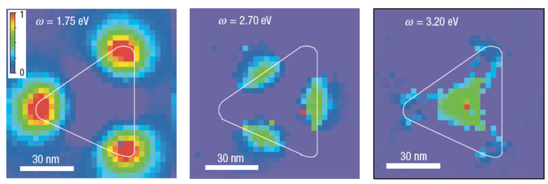


Energetic resolution comparable/better than XAS

- low loss spectroscopy – physical/optical properties measurements





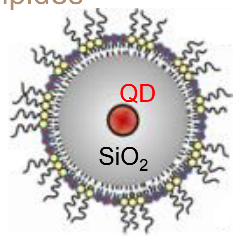


Nelayah *et al.*
Nat. Phys. (2007)
STEM group
Orsay

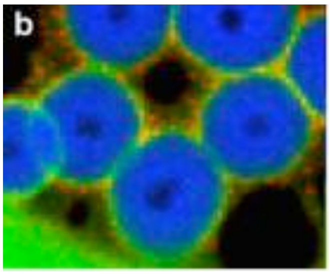
Physical properties at the atomic scale

Combination of Cs-corrected STEM-HAADF and EELS
Spatially resolved EELS

lipides



Hybride organic-inorganic nanoparticles

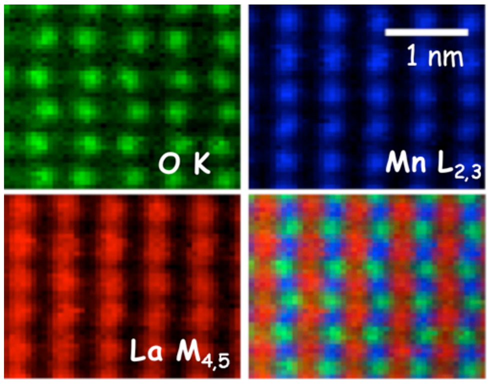


van Schooneveld *et al.*
Nature Nanotech;
5, 538–544 (2010)

STEM group, Orsay

- chemical composition
- spectroscopic signature of the lipidic layer
- lipidic layer thickness measurements

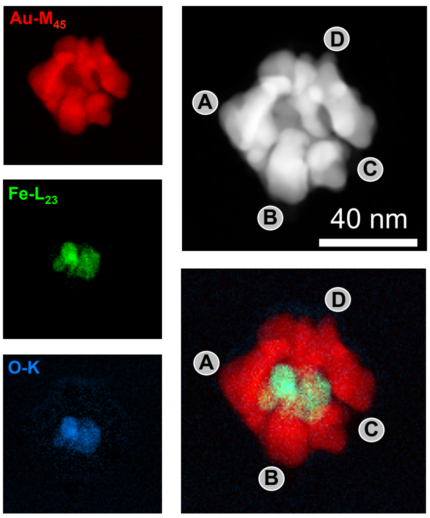
$LaMnO_3$ *Oak Ridge Nat. Lab*

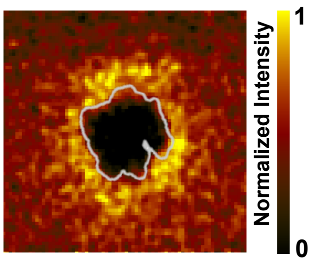


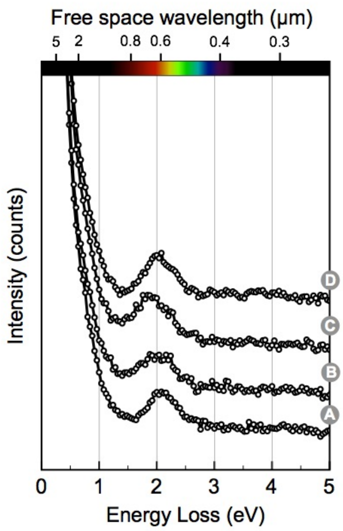
Chemical imaging at the atomic scale

Combination of Cs-corrected STEM-HAADF and EELS
Spatially resolved EELS

Fe_3O_4 / Au : system combining magnetic and plasmonic properties





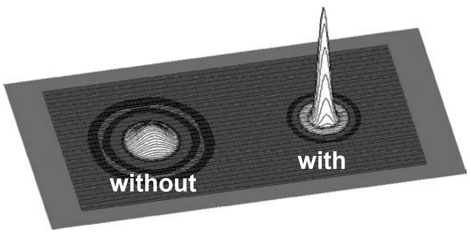


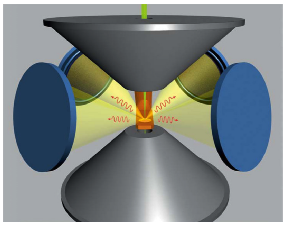
Wilhelm *et al. in press*

Chemical imaging and physical properties at the atomic scale

Combination of Cs-corrected STEM-HAADF and XEDS

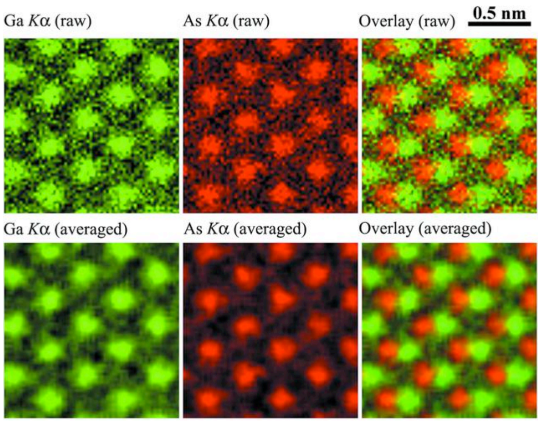
Spatially resolved XEDS





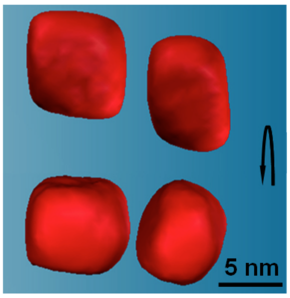
FEI®

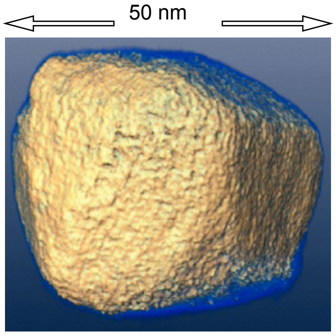
Detector efficiency



Electron tomography

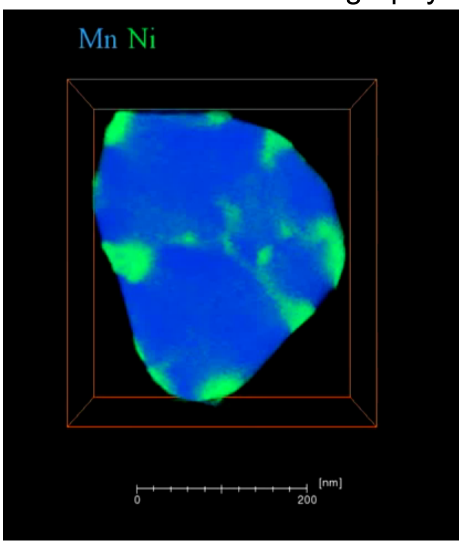
CeO_2





M. Posfai *et al.*
XX IUCR Congress, Firenze (2004)

3-D XEDS STEM Tomography

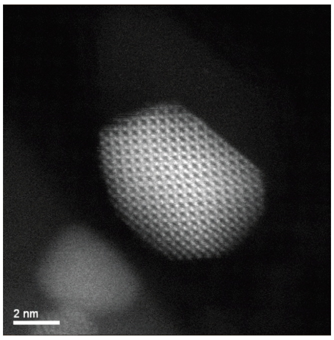


FEI website

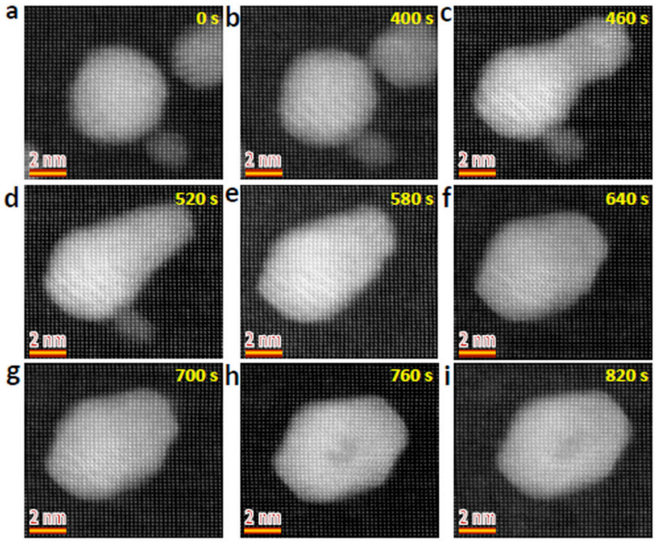
3D morphology of nano-objects

in situ heating sample holders

in situ heating



Pt nanoparticle catalyst at 1000 °C, (20 s scan)
Protochips® web site

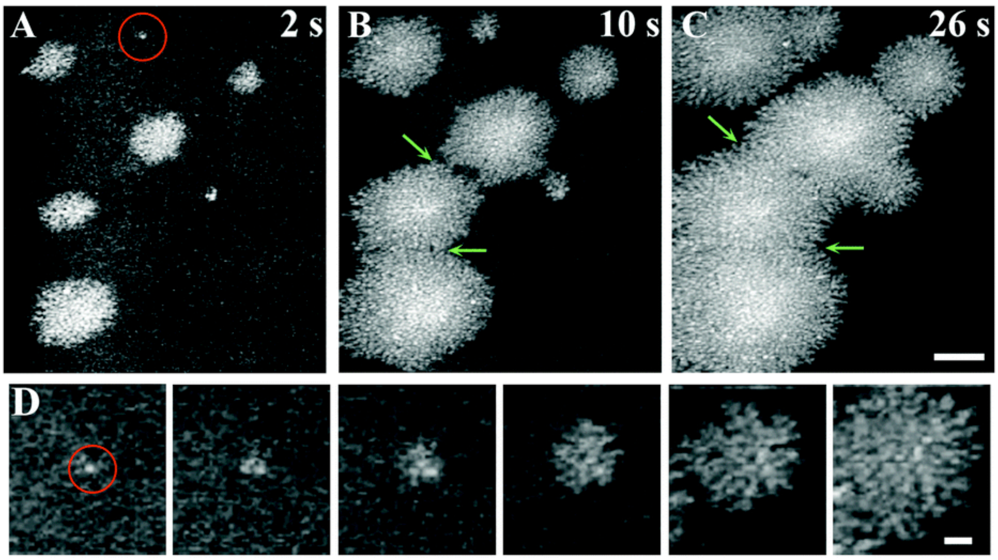


Evolution of Gold nano-clusters morphology onto Y:ZrO_2 surface at high temperature

in situ sample holders

Liquid TEM/STEM

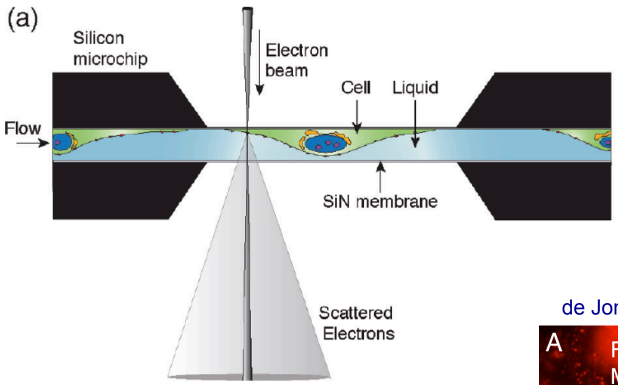
Zhu *et al. Chem. Commun.*, (2014), 50, 9447--9450



"diffusion-limited aggregation" type mechanism and direct atomic deposition can explain dendritic morphologies of Pt nanoparticles

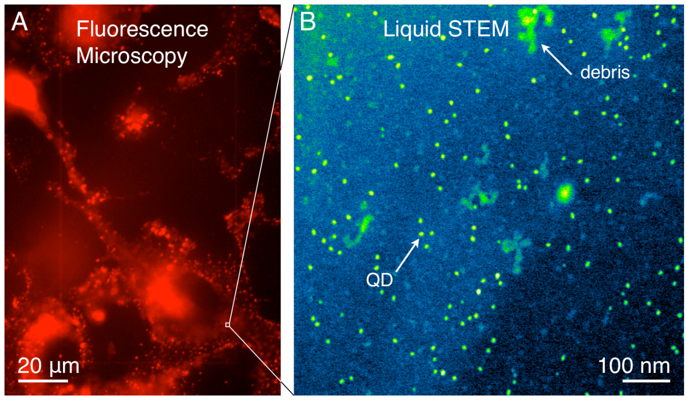
Bibliography about *in situ* liquid TEM provided by Protochips® :
http://www.protochips.com/app/bibliography-abstract-poseidon.html

in situ sample holders



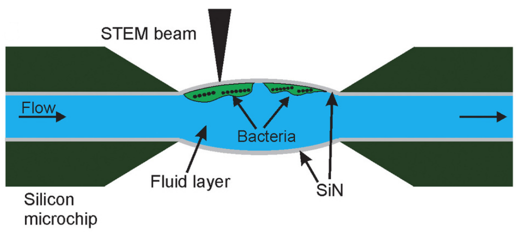
Liquid TEM/STEM

de Jonge et al. *Nat. Nanotech.* (2011) doi: 10.1038/NNANO.2011.161



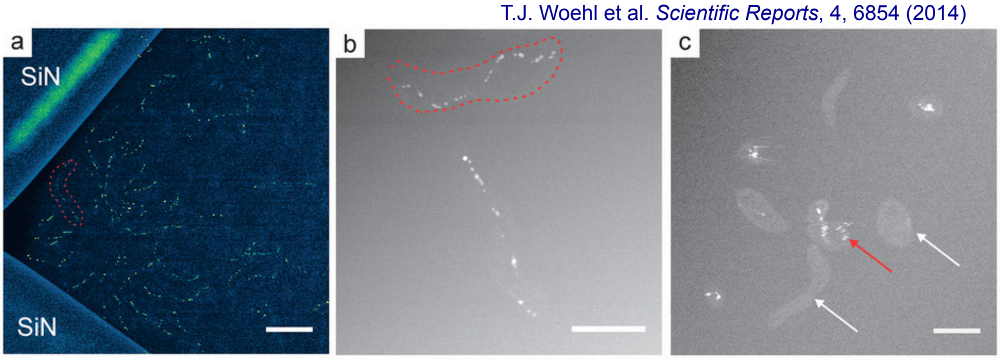
Correlative with Light Microscopy - Intact fixed eukaryotic cells in saline water.

in situ sample holders



Liquid TEM/STEM

T.J. Woehl et al. *Scientific Reports*, 4, 6854 (2014)



→ 50% bacteria are still alive after 1h irradiation

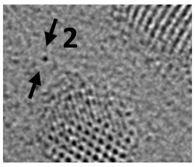
in vivo studies of bacteria ?

Conclusion

Recent progress in analytical methods associated with TEM/STEM

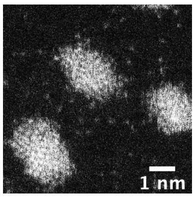
- **Imaging**

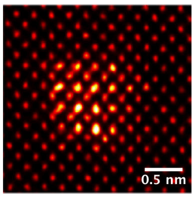
HREM



Alloyeau *et al.*, APL.(2012)

STEM-HAADF

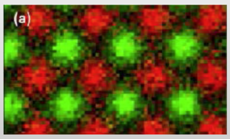




Couillardet *al.*, *PRL.*(2011)

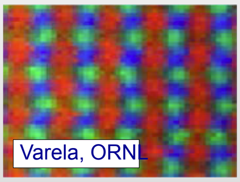
- **Atomic elemental mapping**

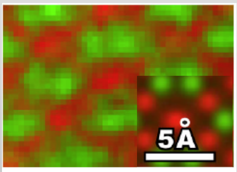
XEDS



Allen et al., MRS Bull.(2012)

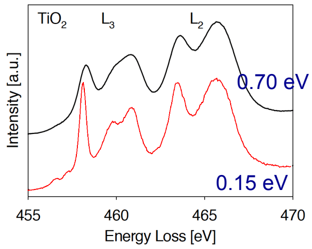
EELS – core loss





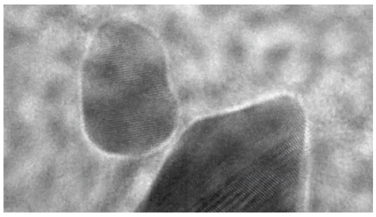
Tan *et al.PRL.*(2011)

- **EELS resolution → 0.03 eV**



Mitterbauer, *Ultramicroscopy* (2003)

- ***in situ* experiments**



Li *et al. Science* (2012)

→ useful tools for material science and Earth science