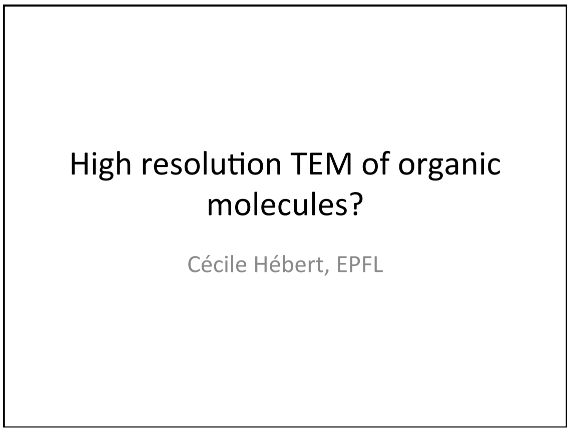
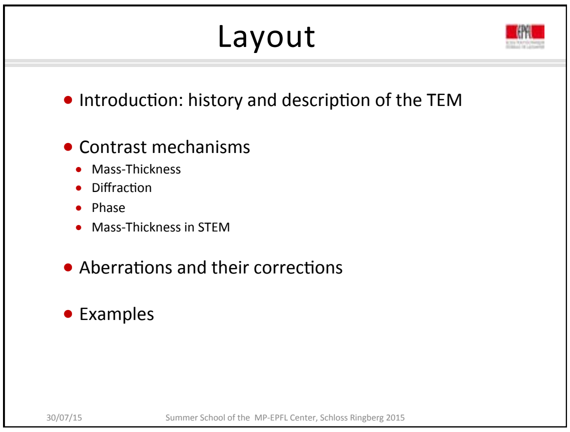


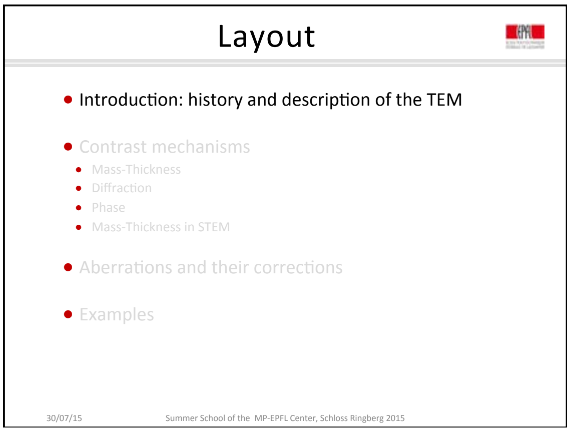
High resolution TEM of organic molecules?

Cécile Hébert, EPFL



Layout

- Introduction: history and description of the TEM
- Contrast mechanisms
  - Mass-Thickness
  - Diffraction
  - Phase
  - Mass-Thickness in STEM
- Aberrations and their corrections
- Examples



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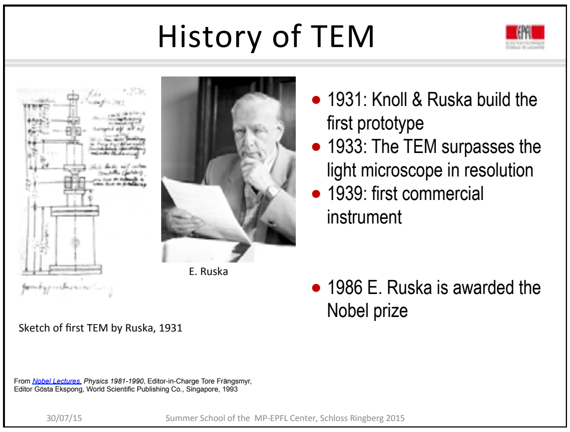


History of TEM

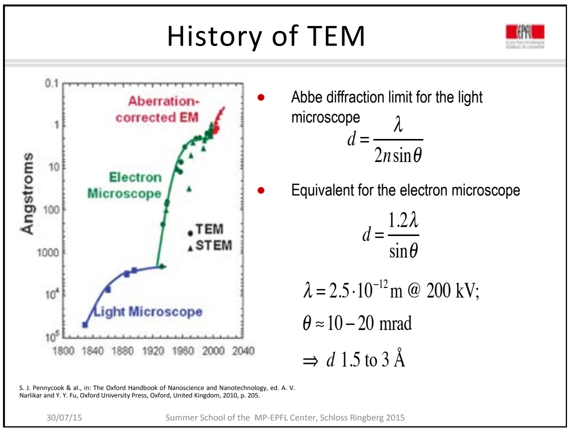
E. Ruska

Sketch of first TEM by Ruska, 1931

- 1931: Knoll & Ruska build the first prototype
- 1933: The TEM surpasses the light microscope in resolution
- 1939: first commercial instrument

- 1986 E. Ruska is awarded the Nobel prize

From *Nobel Lectures, Physics 1981-1990*, Editor-in-Charge Tore Frängsmyr, Editor Gösta Ekspong, World Scientific Publishing Co., Singapore, 1993



History of TEM

- Abbe diffraction limit for the light microscope

$$d = \frac{\lambda}{2n\sin\theta}$$

- Equivalent for the electron microscope

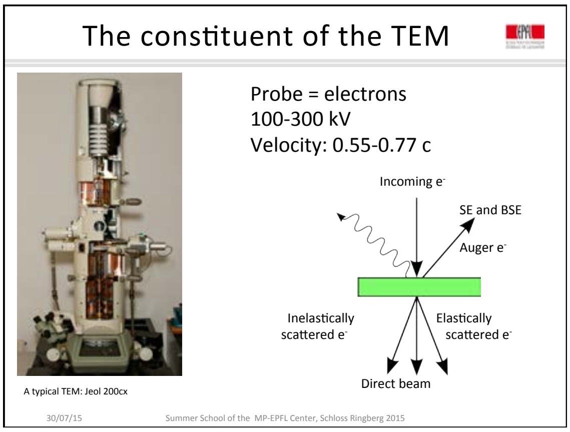
$$d = \frac{1.2\lambda}{\sin\theta}$$

$$\lambda = 2.5\cdot 10^{-12}\,\mathrm{m}\ @\ 200\ \mathrm{kV};$$

$$\theta \approx 10-20\ \mathrm{mrad}$$

$$\Rightarrow\ d\ 1.5\ \text{to}\ 3\ \text{Å}$$

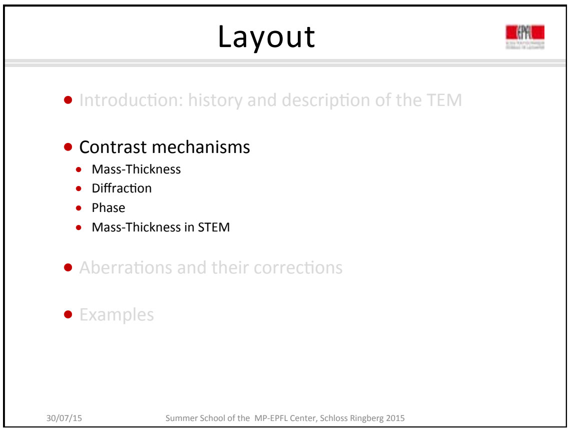
S. J. Pennycook & al., in: The Oxford Handbook of Nanoscience and Nanotechnology, ed. A. V. Narlikar and Y. Y. Fu, Oxford University Press, Oxford, United Kingdom, 2010, p. 205.



The constituent of the TEM

A typical TEM: Jeol 200cx

Probe = electrons
100-300 kV
Velocity: 0.55-0.77 c



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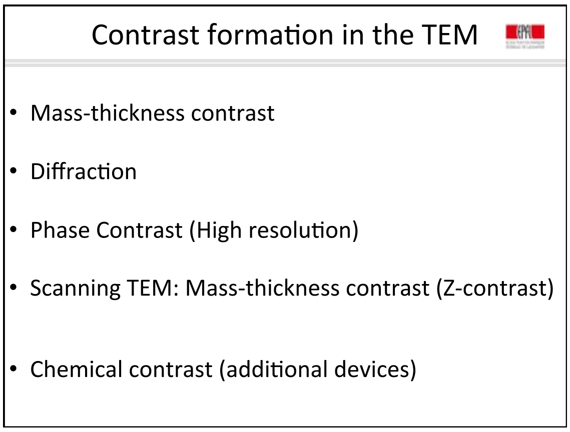
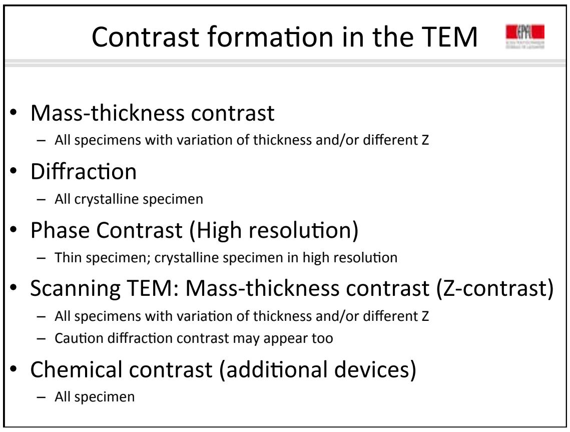


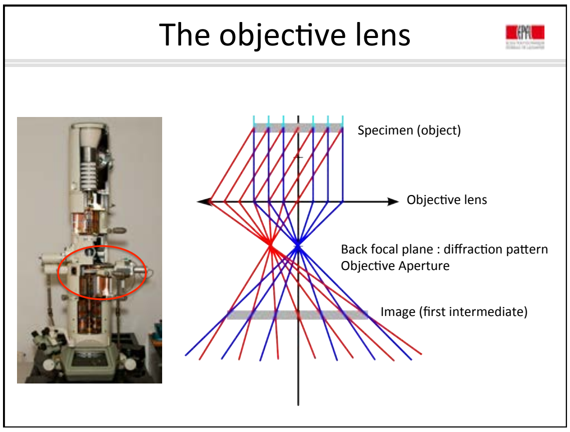
Contrast formation in the TEM

- Mass-thickness contrast
- Diffraction
- Phase Contrast (High resolution)
- Scanning TEM: Mass-thickness contrast (Z-contrast)
- Chemical contrast (additional devices)

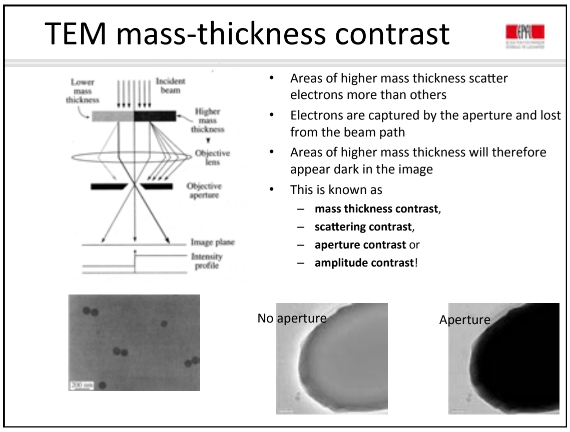


Contrast formation in the TEM

- Mass-thickness contrast
  - All specimens with variation of thickness and/or different Z
- Diffraction
  - All crystalline specimen
- Phase Contrast (High resolution)
  - Thin specimen; crystalline specimen in high resolution
- Scanning TEM: Mass-thickness contrast (Z-contrast)
  - All specimens with variation of thickness and/or different Z
  - Caution diffraction contrast may appear too
- Chemical contrast (additional devices)
  - All specimen

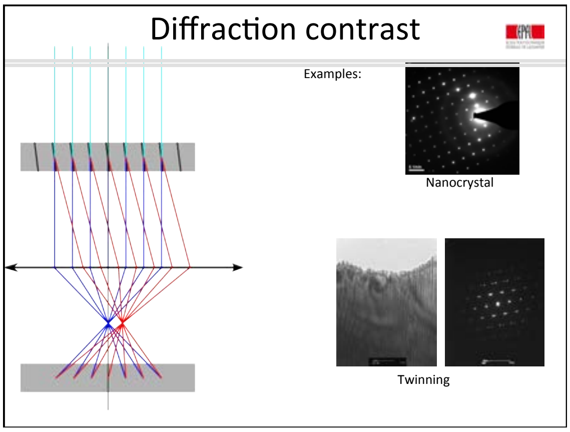


The objective lens



TEM mass-thickness contrast

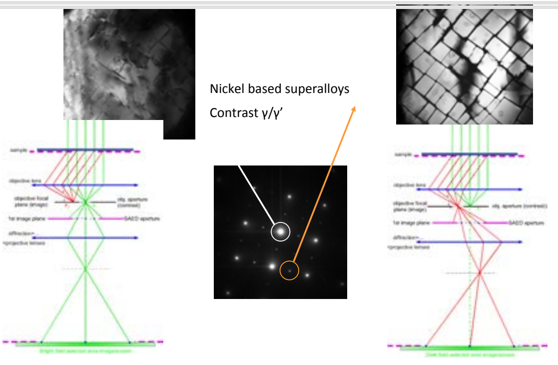
- Areas of higher mass thickness scatter electrons more than others
- Electrons are captured by the aperture and lost from the beam path
- Areas of higher mass thickness will therefore appear dark in the image
- This is known as
  - **mass thickness contrast**,
  - **scattering contrast**,
  - **aperture contrast** or
  - **amplitude contrast**!



Diffraction contrast

Examples:

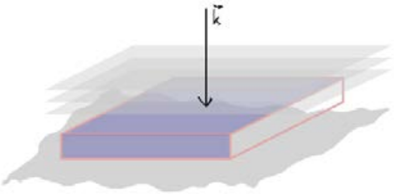
Bright-field/dark-field imaging



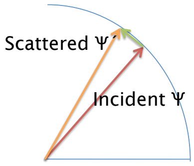
Nickel based superalloys

Contrast γ/γ'

Phase contrast



Phase contrast

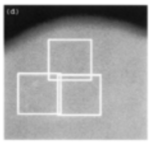


$$\Psi' = \Psi \exp[i f(\mathbf{r})]$$

$$\Psi' = \Psi [1 + i f(\mathbf{r}) - \tfrac{1}{2} f^2(\mathbf{r}) + \ldots]$$

$$\Psi' \approx \Psi [1 + i f(\mathbf{r})],\ f(\mathbf{r}) << 1$$

Detector: $\Psi'^{*}\Psi' = \Psi^2 [1 + f^2(\mathbf{r})]$



Virtually no contrast in the image plane

Phase contrast

- EM is an imperfect microscope:
  - Low coherence source
  - Chromatic aberration
  - Spherical aberration
  - Other problems…
- These ‘features’ result in the loss of resolution, but help to generate contrast
- Defocus can also generate contrast

Contrast transfer function

- The lens applies a phase shift χ, dependent on scattering angle θ

$$\chi(\theta) = 2\pi/\lambda\ (½\ \Delta f\ \theta^2 + ¼\ C_s\theta^4)$$

where C_s is the spherical aberration and Δf is the defocus, λ is the electron wavelength.

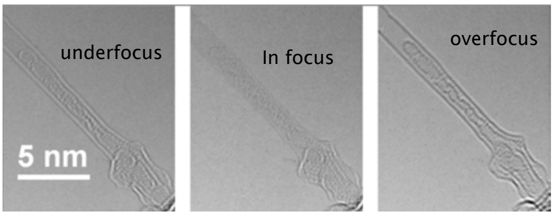
- The angle θ is related to the spatial frequency ν

$$\theta \approx \lambda\ \nu$$

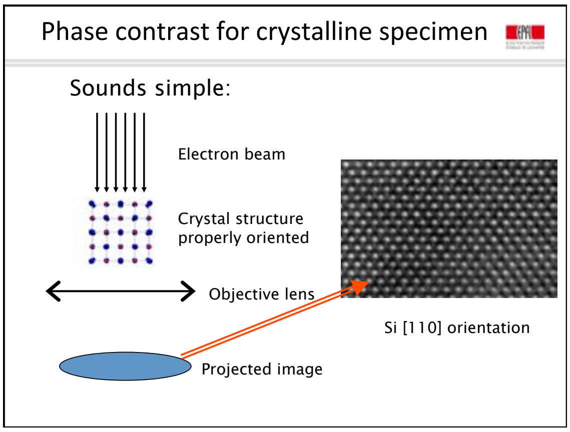
$$\chi(\nu) = \pi\lambda(\Delta f \nu^2 + ½\ C_s\ \lambda^2 \nu^4)$$

- The phase shift $\chi(\nu)$ leads to contrast enhancements at specific Δf.

Resolution / Contrast tradeoff



Carbon nanotubes filled with sexitiophene



Phase contrast for crystalline specimen

Sounds simple:

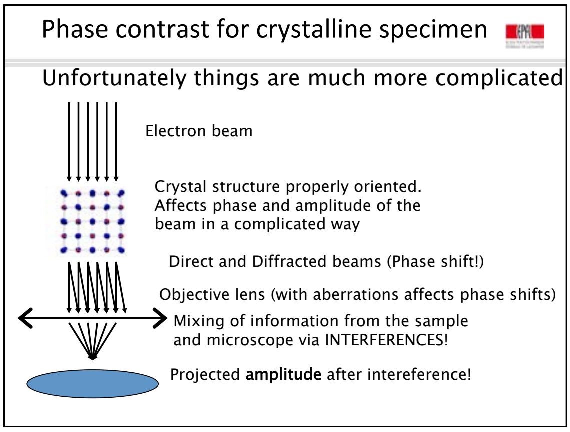
Electron beam

Crystal structure properly oriented

Objective lens

Projected image

Si [110] orientation



Phase contrast for crystalline specimen

Unfortunately things are much more complicated

Electron beam

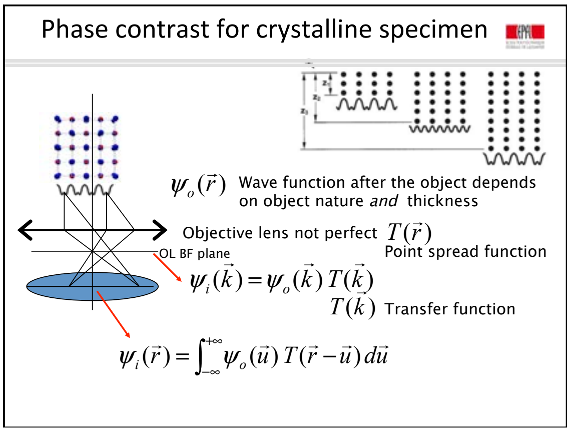
Crystal structure properly oriented. Affects phase and amplitude of the beam in a complicated way

Direct and Diffracted beams (Phase shift!)

Objective lens (with aberrations affects phase shifts)

Mixing of information from the sample and microscope via INTERFERENCES!

Projected **amplitude** after intereference!



Phase contrast for crystalline specimen

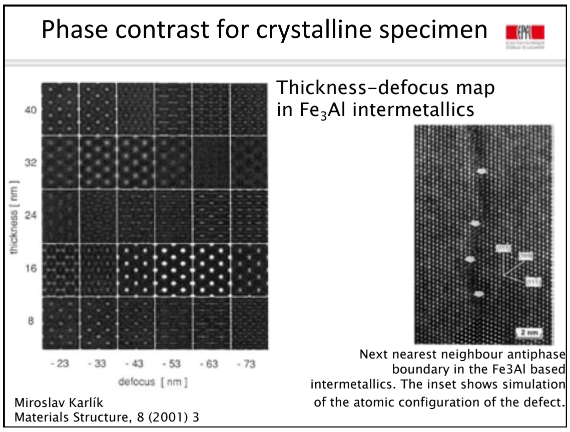
$\psi_o(\vec{r})$ Wave function after the object depends on object nature *and* thickness

Objective lens not perfect $T(\vec{r})$ Point spread function

$$\psi_i(\vec{k}) = \psi_o(\vec{k})\, T(\vec{k})$$

$T(\vec{k})$ Transfer function

$$\psi_i(\vec{r}) = \int_{-\infty}^{+\infty} \psi_o(\vec{u})\, T(\vec{r}-\vec{u})\, d\vec{u}$$

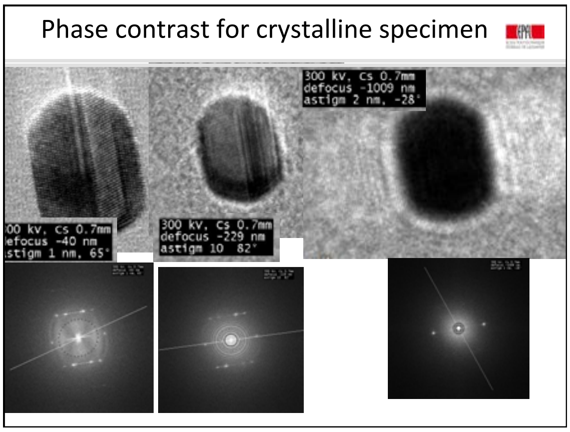


Phase contrast for crystalline specimen

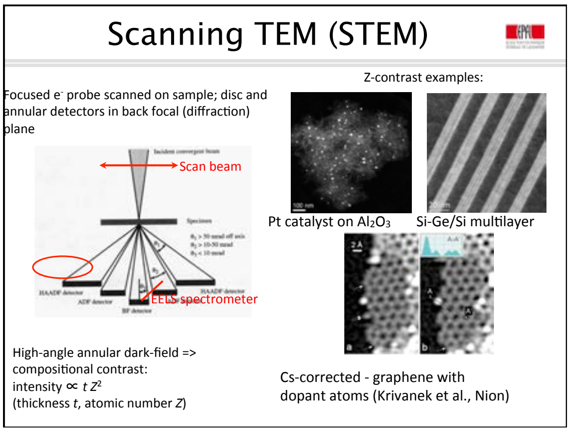
Thickness–defocus map in Fe$_3$Al intermetallics

Next nearest neighbour antiphase boundary in the Fe3Al based intermetallics. The inset shows simulation of the atomic configuration of the defect.

Miroslav Karlík
Materials Structure, 8 (2001) 3



Phase contrast for crystalline specimen



Scanning TEM (STEM)

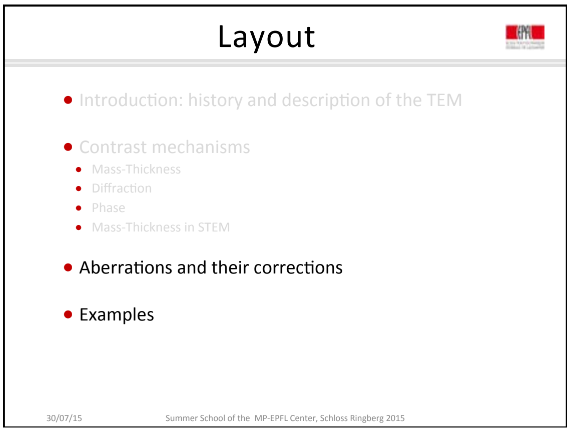
Focused e$^-$ probe scanned on sample; disc and annular detectors in back focal (diffraction) plane

High-angle annular dark-field => compositional contrast:
intensity ∝ $t Z^2$
(thickness *t*, atomic number *Z*)

Z-contrast examples:

Pt catalyst on Al$_2$O$_3$ Si-Ge/Si multilayer

Cs-corrected - graphene with dopant atoms (Krivanek et al., Nion)



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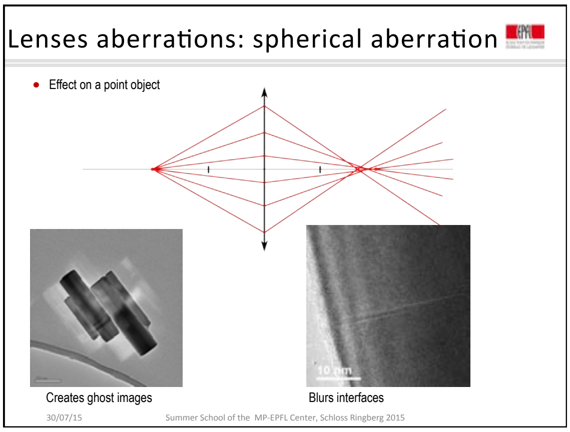

Lenses aberrations: spherical aberration

- Effect on a point object

Creates ghost images

Blurs interfaces

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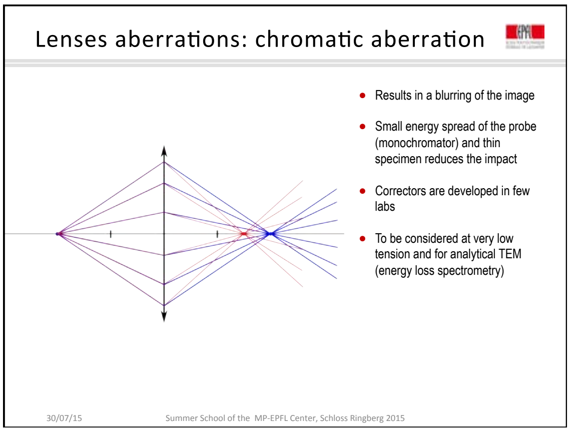

Lenses aberrations: chromatic aberration

- Results in a blurring of the image
- Small energy spread of the probe (monochromator) and thin specimen reduces the impact
- Correctors are developed in few labs
- To be considered at very low tension and for analytical TEM (energy loss spectrometry)

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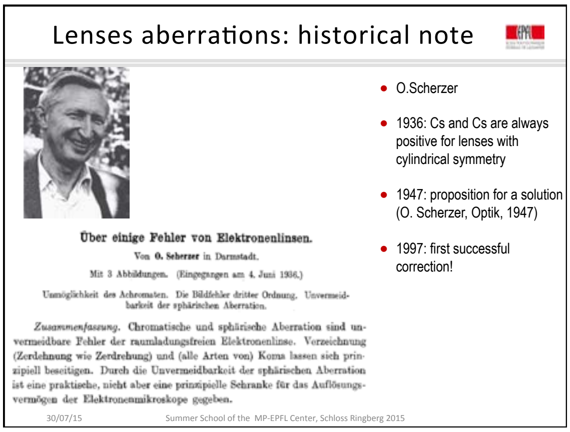

Lenses aberrations: historical note

- O.Scherzer
- 1936: Cs and Cs are always positive for lenses with cylindrical symmetry
- 1947: proposition for a solution (O. Scherzer, Optik, 1947)
- 1997: first successful correction!

Über einige Fehler von Elektronenlinsen.

Von **O. Scherzer** in Darmstadt.

Mit 3 Abbildungen. (Eingegangen am 4. Juni 1936.)

Unmöglichkeit des Achromaten. Die Bildfehler dritter Ordnung. Unvermeidbarkeit der sphärischen Aberration.

Zusammenfassung. Chromatische und sphärische Aberration sind unvermeidbare Fehler der raumladungsfreien Elektronenlinse. Verzeichnung (Zerdehnung wie Zerdrehung) und (alle Arten von) Koma lassen sich prinzipiell beseitigen. Durch die Unvermeidbarkeit der sphärischen Aberration ist eine praktische, nicht aber eine prinzipielle Schranke für das Auflösungsvermögen der Elektronenmikroskope gegeben.

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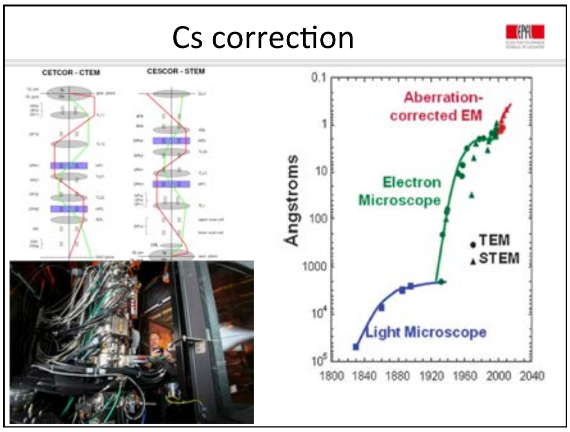
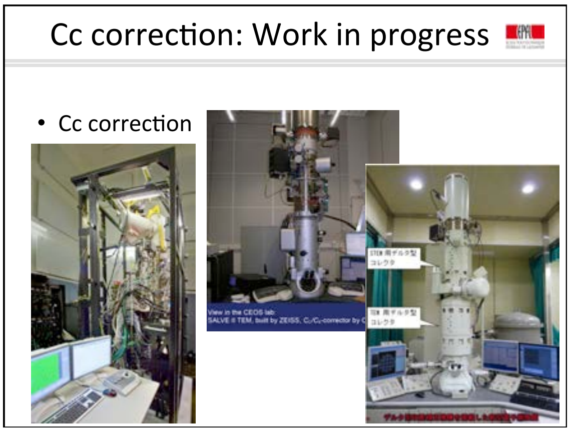


Cs correction



Cc correction: Work in progress

- Cc correction

View in the CEOS lab
SALVE II TEM, built by ZEISS, Cc/Cs-corrector by C

The advantages

- Improved resolution
  - At lower voltage! (beam sensitive materials)
  - For large pole piece gap (in-situ experiments possible)
- Higher precision (better contrast)
  - Lower dose possible
  - Higher frame rate (video)
- Less delocalisation

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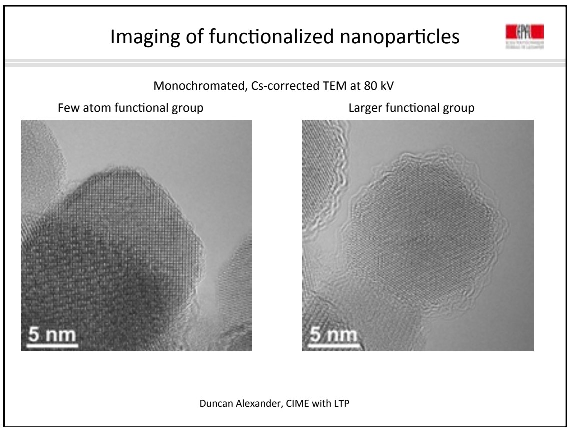


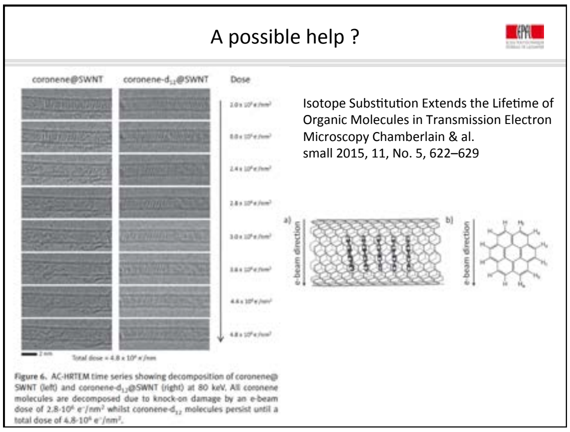
Imaging of functionalized nanoparticles

Monochromated, Cs-corrected TEM at 80 kV

Few atom functional group

Larger functional group

Duncan Alexander, CIME with LTP



A possible help ?

Figure 6. AC-HRTEM time series showing decomposition of coronene@SWNT (left) and coronene-d_{12}@SWNT (right) at 80 keV. All coronene molecules are decomposed due to knock-on damage by an e-beam dose of $2.8 \cdot 10^6$ e^-/nm^2 whilst coronene-d_{12} molecules persist until a total dose of $4.8 \cdot 10^6$ e^-/nm^2.

Isotope Substitution Extends the Lifetime of Organic Molecules in Transmission Electron Microscopy Chamberlain & al.
small 2015, 11, No. 5, 622–629