EPFL

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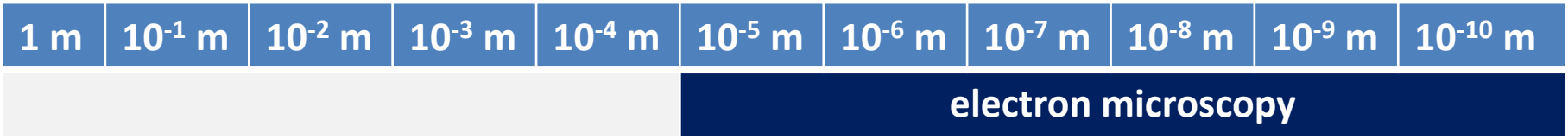
Physical and Chemical Analyses of Materials

TEM: basics

Introduction

⇨ Transmission Electron Microscopy TEM is related to electron microscopy. The principle of TEM was demonstrated by Ernst Ruska and Max Knoll in 1931 and the first prototype was built around 1935. The invention was awarded by the Nobel Prize in physics in 1986.

⇨ Conventional microscopes use an electron beam from 10 to 100 keV. These electron energies allow the studies of samples from 10^{-5} to 10^{-10} meter size.



⇨ Increasing the electron beam energy increases the resolution power of the microscopy through the decrease of the wavelength of the electrons. High Resolution Transmission Electron Microscopy HRTEM is obtained for an electron energy greater than 200 keV and below 1 MeV.

⇨ TEM is widely used in material sciences, metallurgy, nanotechnologies medical and life sciences, forensic analysis, gemmology…

⇨ TEM focuses on the electrons passing through the analysed sample and provides mostly structural analyses of materials. Topography, morphology, thickness measurements and chemical information (XRMA) can also be accessible.

⇨ TEM is dedicated to thin samples ≈ 100 nm at the maximum which can exhibit a big relief.

⇩ Increasing the electrons energy allows the study of thicker samples. It brings then new constraints regarding the stability of the material towards such an electron beam.

⇨ Due to its thickness, the sample is deposited on a conducting grid made of Cu, Ni, Ag, Au, Pt…

⇨ TEM requires the use of a high vacuum (10^{-5} to 10^{-7} mBar) that brings additional constraints to the sample nature.

⇨ The analysis is based on both scattered and non-scattered transmitted electrons.

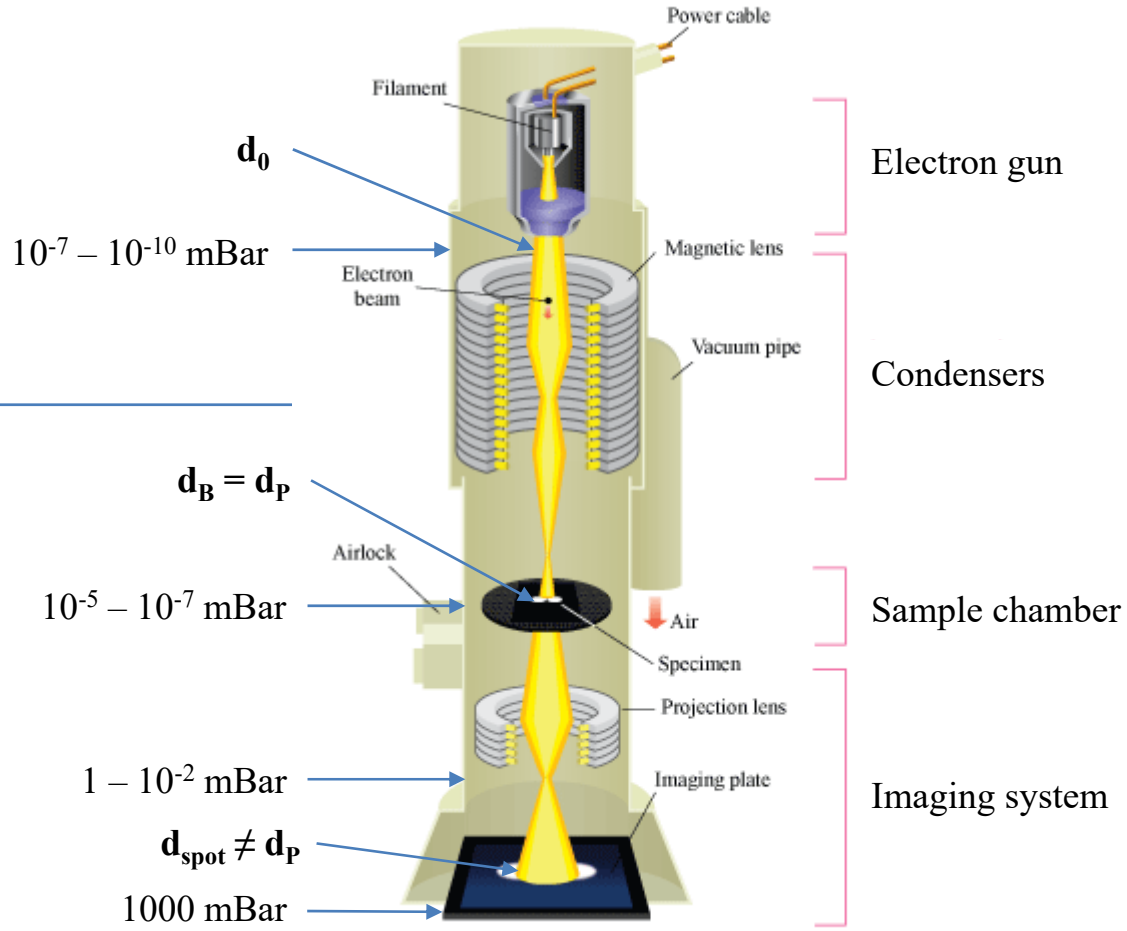
⇨ The analysis is realised in a static mode. To obtain some information on bigger surfaces a scanning mode is also available: STEM

⇨ The study of the topography of a surface in TEM requires a specific preparation of the material sample.

TEM overview

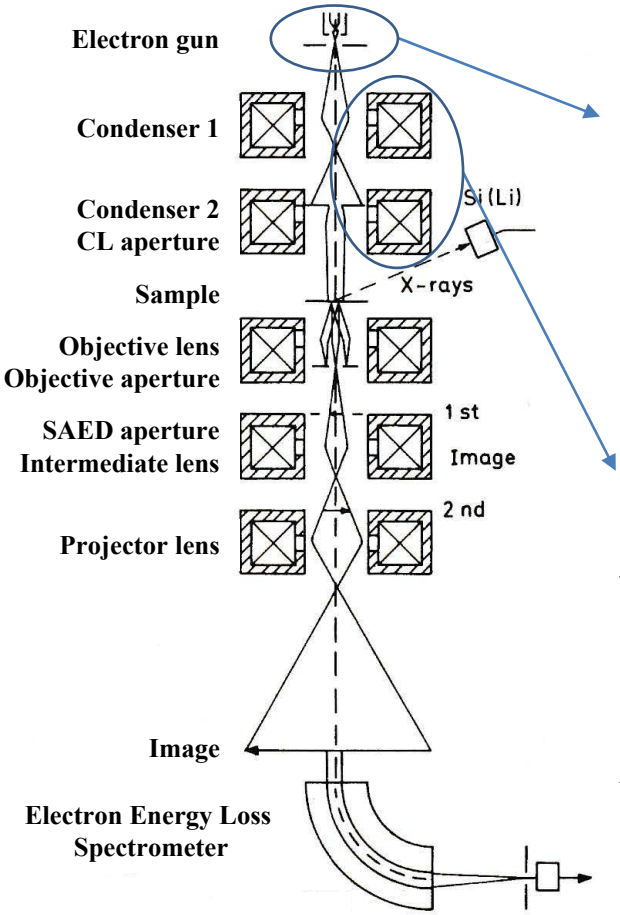
TEM instruments

TEM Jeol JEM-2100 Plus



simplified TEM scheme

Electron source



⇨ The electron source is constituted by an electron gun and some condensers.

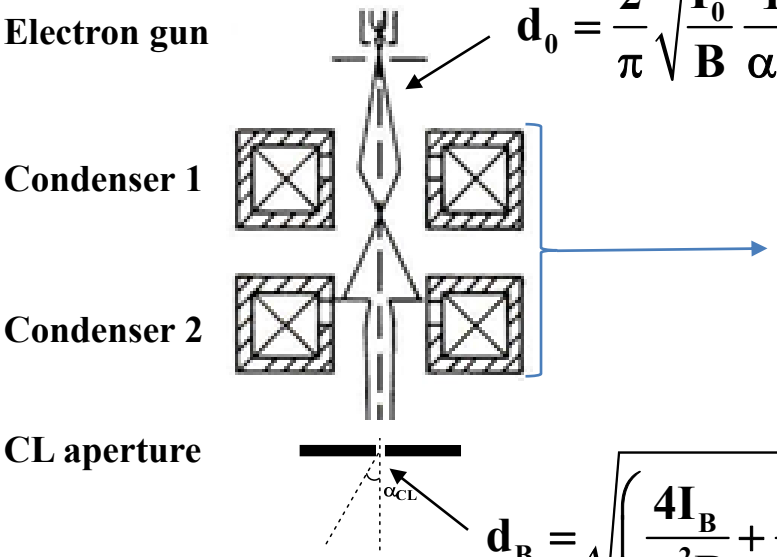
⇨ The electron gun is made of a thermionic (W or LaB_6) or field-emission source (S-FEG or C-FEG).

↳ The best microscope resolution is achieved with the electron gun which provides the best brightness *i.e.* FEG sources.

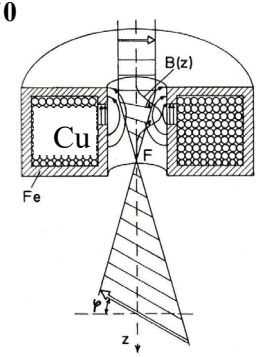
⇨ The electron beam produced by the electron gun is further focused thanks to a series of tuneable electromagnetic lenses which constitute the condenser (*i.e.* condenser 1 and 2).

↳ Condenser 1 defines the beam size $\mathbf{d_B}$. Condenser 2 controls the illumination area, *i.e.* the intensity $\mathbf{I_B}$ shone on the sample. The diameter of the probe $\mathbf{d_P}$ shone on the sample is equal to $\mathbf{d_B}$.

↳ In recent TEMs, a third "mini" condenser is used to control the convergence angle of the electron beam.



$$d_0 = \frac{2}{\pi}\sqrt{\frac{I_0}{B}}\frac{1}{\alpha_0}$$



↳ Increased lens current = increased focusing power = decreased beam current $\mathbf{I_B}$ = decreased $\mathbf{d_B}$.

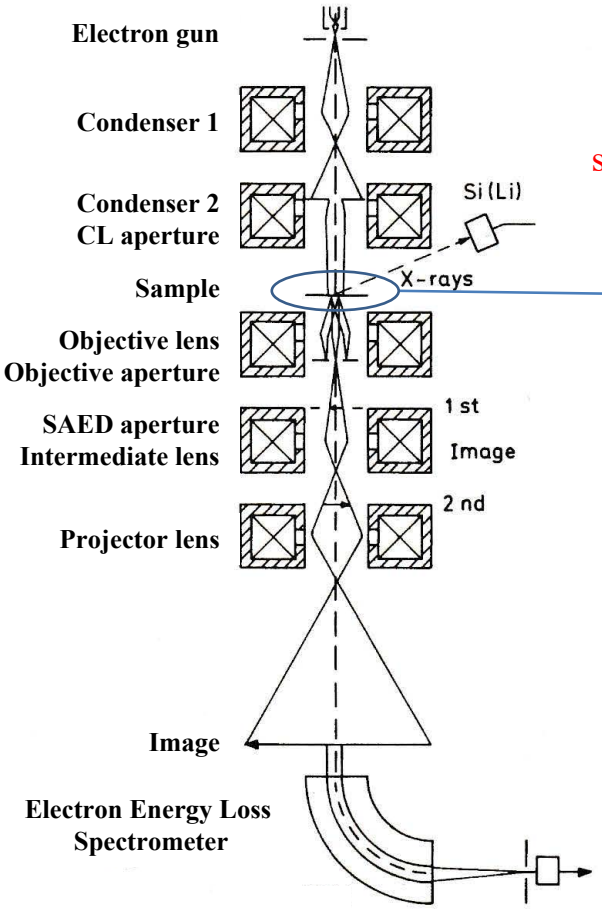
$$d_B = \sqrt{\left(\frac{4I_B}{\pi^2 B} + \frac{2.28}{E_0}\right)\frac{1}{\alpha_{CL}^{\ 2}} + \frac{1}{4}C_s^{\ 2}\alpha_{CL}^{\ 6} + \left(\frac{\Delta E}{E_0}\right)^2 C_c^{\ 2}\alpha_{CL}^{\ 2}}$$

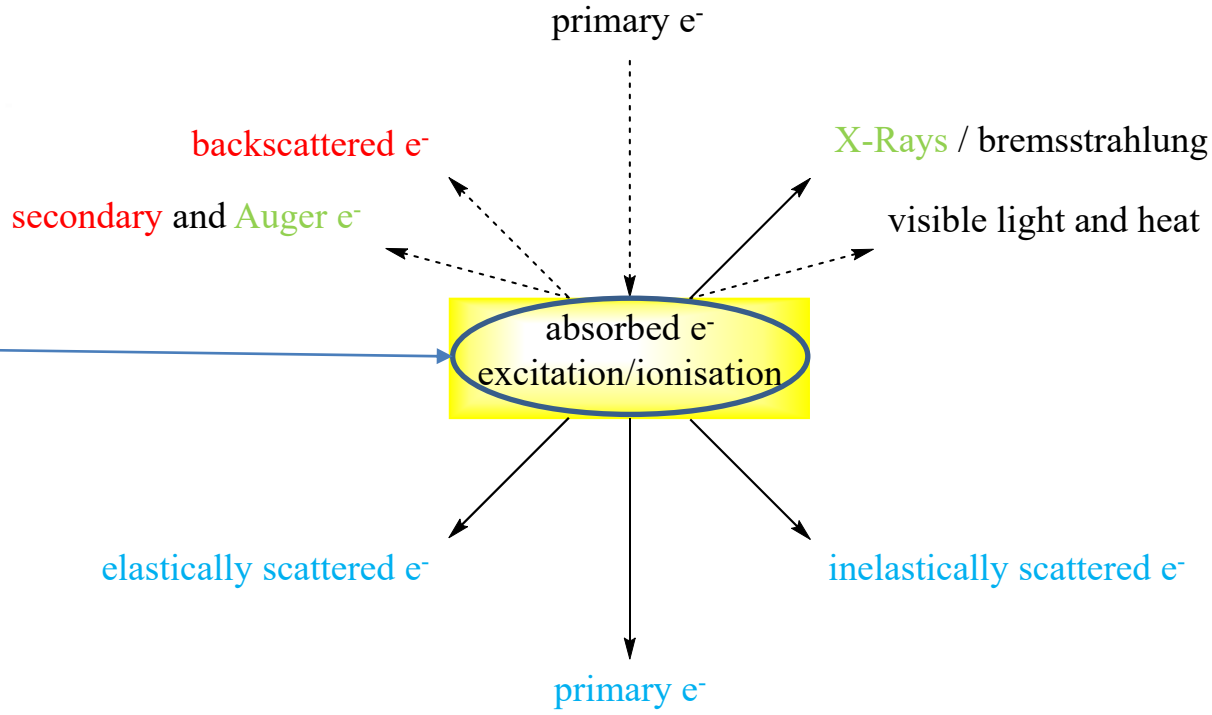
↳ The diameter of the beam $\mathbf{d_B}$ (m) is related to the electron gun and suffers from the aberrations inherent to the electromagnetic lenses used to focus the electron beam.

↳ In these equations, $\mathbf{I_0}$ is the beam current of emission (A), $\boldsymbol{\alpha_0}$ is the divergence half-angle of the emitted beam (rad), $\mathbf{d_0}$ is the initial cross-over (m), **B** is the electron gun brightness ($A \cdot m^{-2} \cdot sr^{-1}$), $\mathbf{I_B}$ is the beam current (A), $\boldsymbol{\alpha_{CL}}$ is the half-angle of the condenser lens aperture (rad), $\mathbf{C_S}$ (nm) and $\mathbf{C_C}$ (nm) are the coefficients for spherical and chromatic aberrations respectively. $\Delta\mathbf{E}$ represents the energy peak broadening of the electron beam (see the chapter on electron sources).

Beam-sample interactions

⇨ The thin sample is deposited on a conductive grid: Cu, Ni, Ag, Au, Pt…

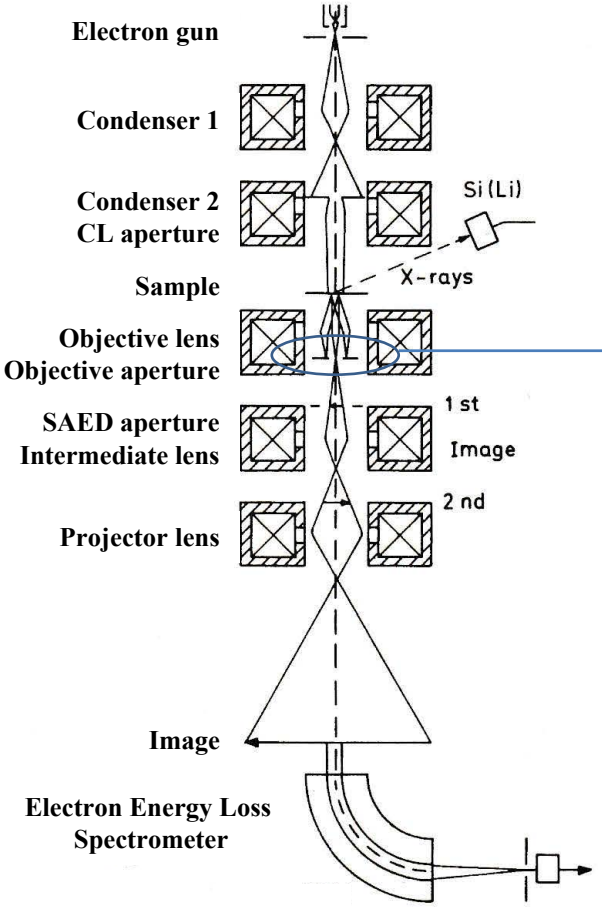




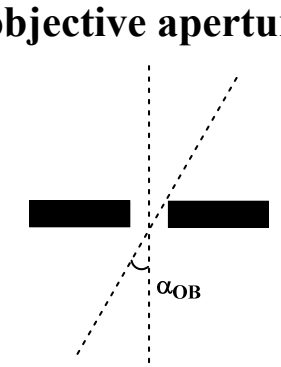
In this scheme the dash lines represent the non-recorded events.

⇩ TEM can be coupled to XRMA and/or EELS (Electron Energy-Loss Spectrometry). Cathodoluminescence rely on the study of the visible light emitted by the sample.

The objective and objective aperture



⇨ The objective forms the image and the objective aperture fixes the microscopic resolution:

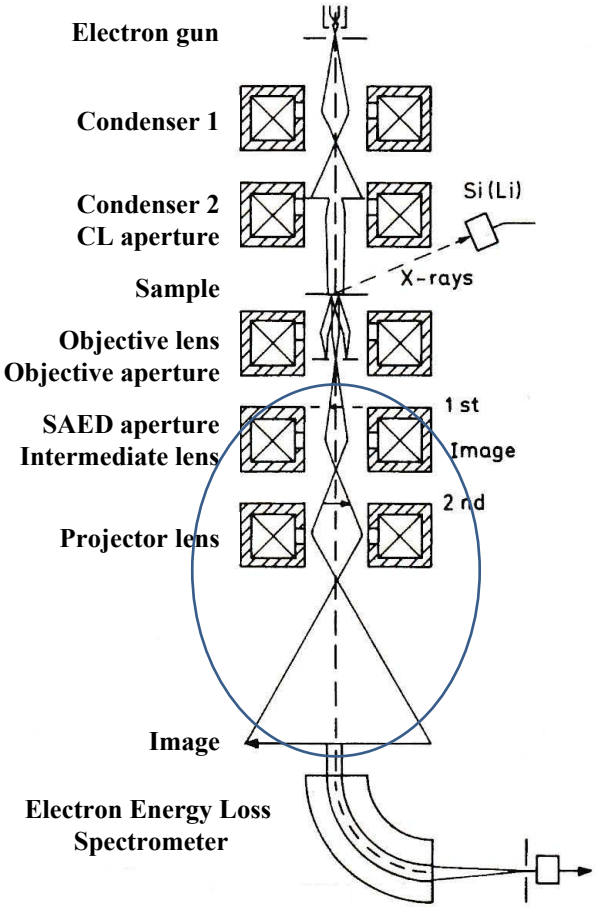


↳ The lateral resolution **d** is in theory: $\mathbf{d} = \frac{\mathbf{0.61\lambda}}{\mathbf{n \sin \alpha_{OB}}}$

↳ **λ** is the wavelength (m), **n** is the refractive index between the objective lens and the observed object and $\boldsymbol{\alpha_{OB}}$ is the half-angle of the objective aperture.

↳ at 100 keV: **λ** = 0.037 Å, $\boldsymbol{\alpha_{OB}} = 5\times10^{-3}$ rd, **n** = 1, **d** ≈ 4.5 Å

The imaging system



⇨ TEM can provided diffraction studies or imaging.

↳ Diffraction is a scattering process which occurs when the wavelength of the beam is similar to the size of the observed object. Diffraction is used for structural studies like the determination of the distance between vicinal atoms in crystals. The Selected Area Electron Diffraction (SAED) aperture is used for this purpose.

⇨ Intermediate lenses (3 lenses) select the TEM mode: diffraction or imaging. In addition there are used to change the magnification.

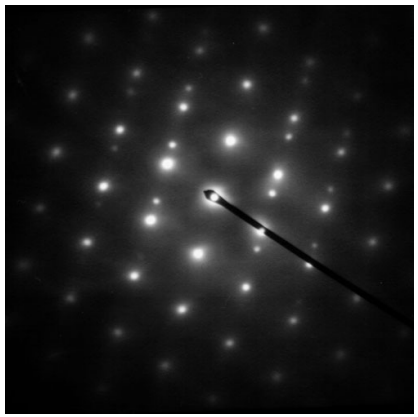
⇨ The projector lens is used to greatly magnify the last intermediate image and also ensures that the latest is plane when projected onto the detector.

⇨ The last element of this chain is the detector, generally made of either a phosphor screen (direct observation) and/or a film made of undoped or doped YAG (Yttrium Aluminium Garnet) deposited on a CCD system (camera).

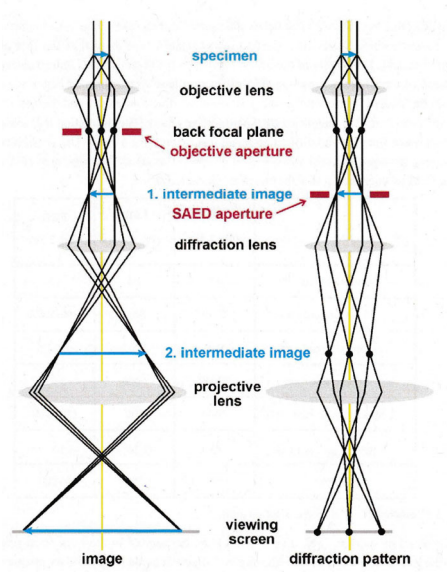
⇨ The imaging system offers different operating modes:

↳ Diffraction mode: the intermediate and projector lenses magnify and project the back focal plane of the objective lens onto the detector.

↳ Image mode: the intermediate and projector lenses magnify and project the image plane of the objective lens onto the detector.



diffraction pattern:
structural studies



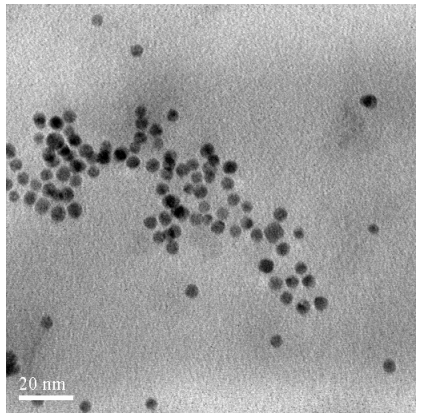


image:
morphological studies

⇨ The resolution is both limited by spherical and chromatic aberrations of the objective lens. Both errors can be corrected by using a suitable combination of lenses. The microscope must also be aligned to gain in accuracy.

TEM principle

⇨ TEM deals with scattered and non-scattered electrons.

⇨ Scattered electrons interact with the sample across elastic and inelastic interactions.

⇨ An electron passing through a solid can be subjected to a single, plural or multiple scattering(s).

↳ Plural scatterings describe scattering events from 2 to 20 and multiple scatterings concern more than 20 events.

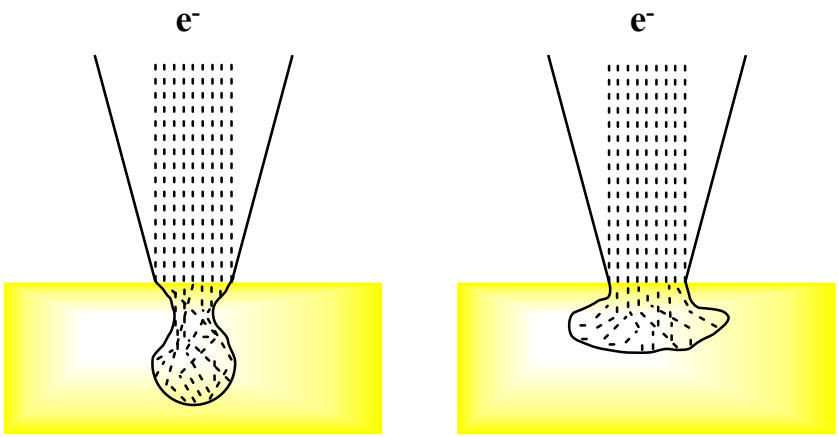
↳ The electron mean path is linked to the number of scattering events underwent by the latest.

↳ The number of scattering events underwent by an electron depends on its interaction cross-section $\boldsymbol{\sigma_t(\overrightarrow{k_1})}$ and its **LET**.

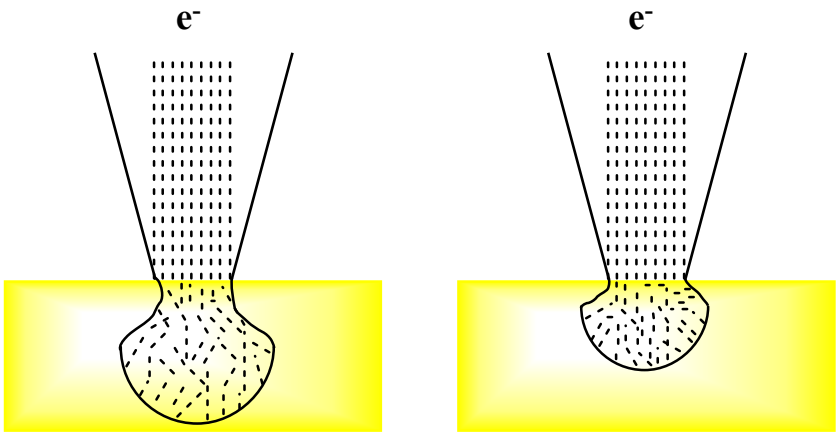
⇨ The interaction volume of the electrons with a material depends on their energy (**keV**) and on the nature of the target atoms (number of protons **Z**).

⇨ The choice of the thickness of the sample is strongly dependent on the interaction volume of the electrons. The material thickness must be lower than the free mean path of the electrons.

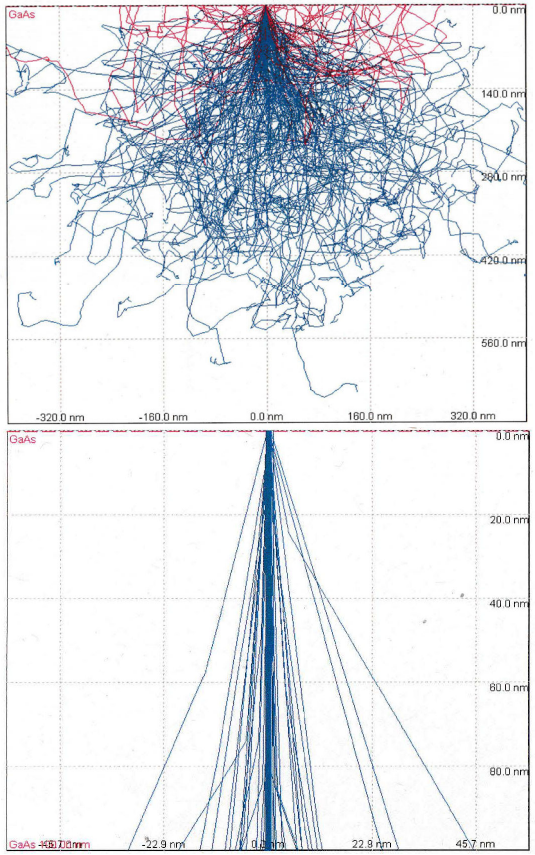
⇨ Below is represented the interaction volume of the electrons as a function of their energy (**keV**) and as a function of the material nature (**Z**):



low **keV** and low **Z** | low **keV** and high **Z**



high **keV** and low **Z** | high **keV** and high **Z**



e- at 10 **keV** / GaAs

e- at 100 **keV** / GaAs

Monte Carlo simulation
University of Sherbrook (Canada)

Sample preparation

General features

⇨ TEM is dedicated to thin samples ≈ 100 nm which can exhibit a big relief. When moving toward HRTEM, the sample thickness must not exceed 10 nm to observe scattered and non-scattered transmitted electrons.

⇨ As TEM requires the use of a high vacuum (10^{-5} to 10^{-7} mBar) that brings additional constraints to the sample nature and so orientates toward a dedicated sample preparation (see the review on the preparation of TEM samples).

⇨ Due to its thickness, the sample must be deposited on a support. The support must meet specific features:

⇩ be transparent to electrons

⇩ must support the interactions imposed by the electron beam

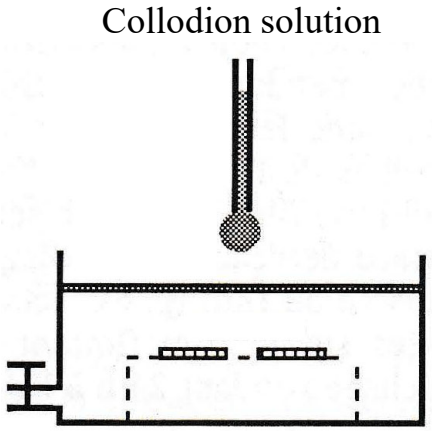
⇩ must not introduce image or diffraction artefacts

⇨ The sample must be as clean as possible, without contaminants.

Sample support

⇨ The sample preparation requires the deposition of an amorphous membrane at the surface of a grid of 3 mm diameter made of Cu, Ni, Ag, Au, Pt…

⇨ Membrane made of Collodion:



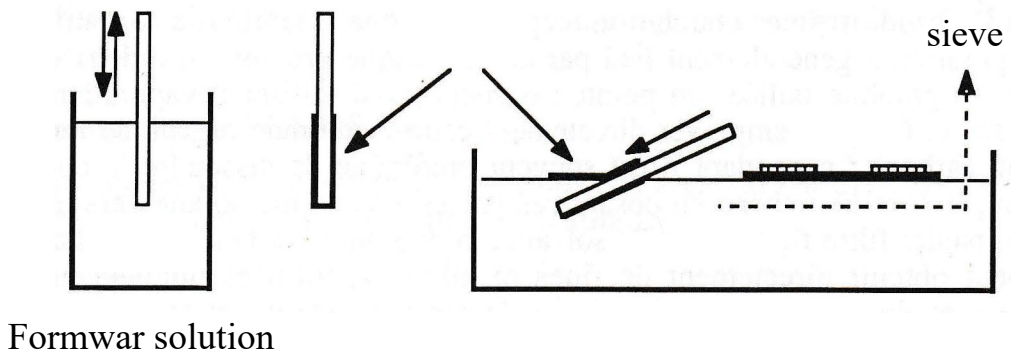
↳ The grid is deposited on a support in a vessel filled with distillated water

↳ A Collodion solution is deposited dropwise onto the water. The Collodion solution is made of nitrocellulose dissolved in amyl- or butyl-acetate at 1 - 3%.

↳ A Collodion membrane (hydrophobic) is developed at the water surface after solvent evaporation. This first membrane is removed to clean the water surface. Another membrane is generated using the same process.

↳ The vessel is gently purge until the membrane deposition onto the grid.

⇨ Membrane made of Formwar:



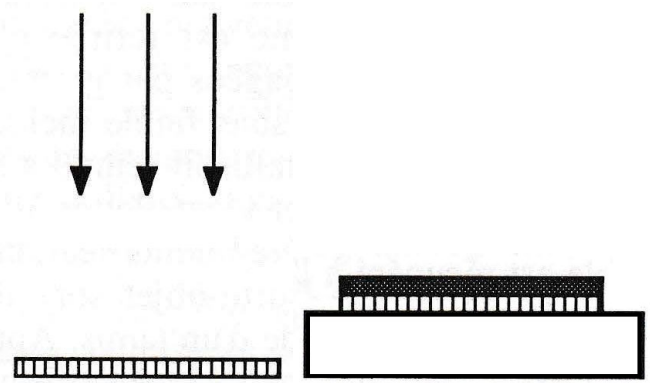
↳ An ultra-cleaned glass slide is dip-coated in a Formwar solution. Formwar is a copolymer made of PVA and Formaldehyde mixed with PVAC. This resin is dissolved at 1-3% in 1,2-dichloroethane.

↳ The modified glass slide is dried and immersed in a vessel filled with distillated water to peel the film.

↳ A grid is dropped on the floating Formwar film.

↳ The modified grid is removed from the vessel using a sieve.

⇨ Membrane made of carbon:



↳ The carbon membrane is deposited by carbon evaporation under vacuum (**a**).

↳ The carbon membrane can be deposited by carbon evaporation under vacuum on a glass slide which will undergo the same coating process than the one described with Formwar (**b**).

↳ Carbon coating is indicated when the membrane must be rigid and resistant to intense electron bombardment (HRTEM).

⇨ micro-grids:

↳ Micro-grids are prepared by drilling organic membranes with a laser for example. A micro-hole array is obtained. Tiny holes are necessary for astigmatism correction.

↳ Membranes are coated either by carbon or by metal deposition. Very thin membranes can be used (thickness < 20 nm). When using thicker membranes, an electrolytic metal deposition of Ag or Cu can also be performed. The supporting membrane is dissolved when producing grids of 1 µm thick.

Sample conditioning

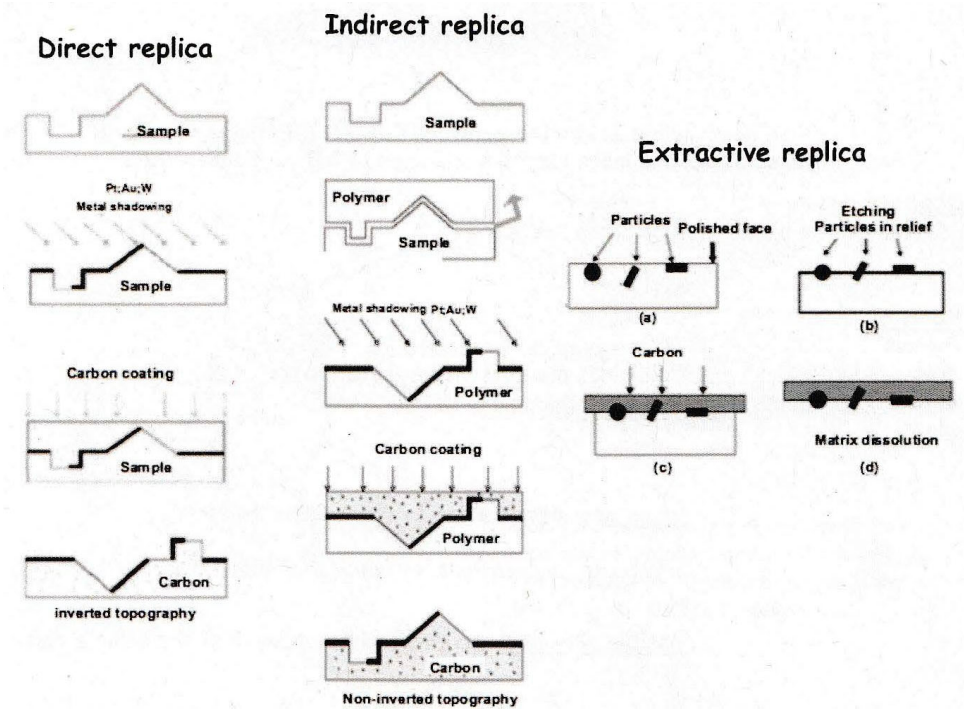
⇨ According to the sample thickness (10 - 100 nm) and size (grid of 3mm of diameter), it requires a special conditioning.

⇨ The sample conditioning includes numerous processes such as grinding, thinning polishing, ion-milling, embedding, ultra-microtome slicing… Most of conditioning methods are gathered in a literature review (see the additional file).

⇨ For topographical studies, the method of replicas is the most suitable.

↳ In this method one can either make a direct or an indirect replica of the material surface.

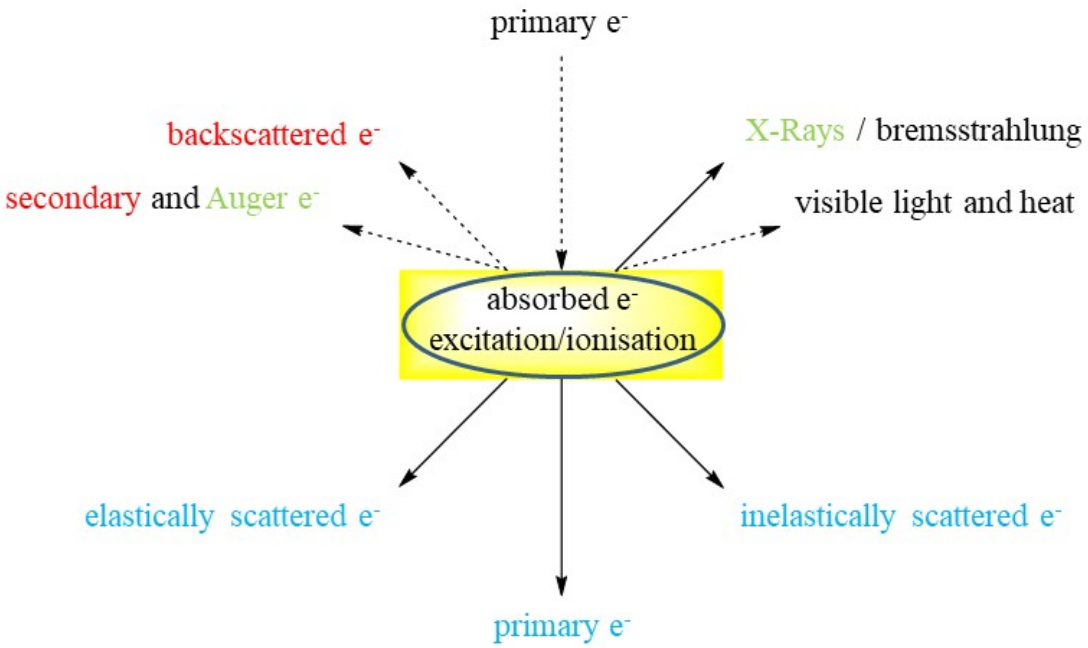
↳ Extractive replicas can be use to extract and study chemical species located at the surface or in the bulk of a material.



Sample modification

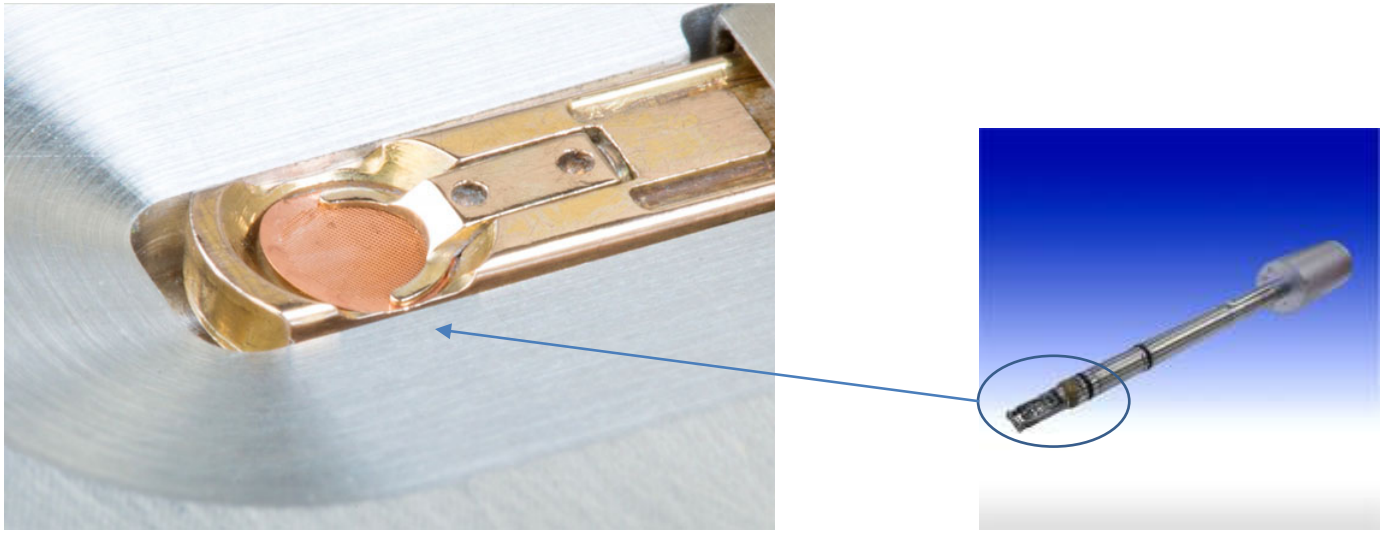
⇨ Electron microscopy is not an non-invasive method because of the inelastic (excitation/ionisation) and the elastic scattering processes (thermal and chemical effects, atomic displacements) underwent by the sample.

⇨ All these inelastic scattering events give rise to the sample relaxation that provides some chemical information about the studied material. XRMA will be described in details in a further chapter.



Sample holder

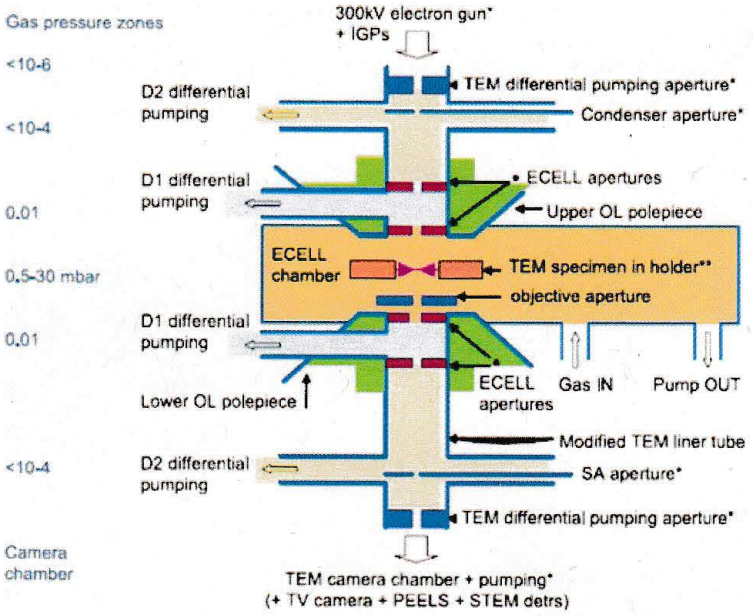
⇨ Here is presented a classic holder for TEM, showing also a magnification of the sample grid location. This type of holder allows the tilting of the studied sample along the perpendicular axis of the microscope:



⇨ This simple holder can be replaced by a special holder enabling to orientate the sample along 2 D-axes and/or to perform in-situ heating, cooling…

Special sample chamber

⇨ When a sample is sensitive to the high vacuum of the sample chamber (10^{-5} – 10^{-7} mBar) or for studies which require an atmospheric pressure and/or the need of a gas environment, specifically designed chambers are available:



⇨ This technique relates to ETEM: Environmental TEM.

Image formation

Lens aberration corrections

⇨ There are five possible isotropic aberrations as in light optics: spherical aberration, astigmatism, field curvature, distortion and coma. There is also anisotropic aberrations, the most important one is chromatic aberration.

⇩ Technical progresses in lens fabrication allow to reduce both lens aberrations and the size of the electron column.

⇨ The correction of spherical aberration of lenses, based on a corrector design proposed by H. Rose, was achieved in 2000.

⇩ The system consists of two hexapoles and two transfer lenses placed before the objective lens.

⇨ Astigmatism and field curvature are compensated by applying two orthogonal correction **B** fields in the **x** and **y** axes.

⇩ The correction is achieved thanks to the use of two quadrupoles along the **z** axis tuned by an adjustable current.

⇨ Distortion and coma are mainly due to the spherical aberration of the lens projector and can be corrected, if necessary, using the same approach than the one for the spherical aberration of the objective lens.

⇨ The emergence of electron energy filtration devices favour the reduction of chromatic aberration. Chromatic aberration is simultaneously corrected with spherical aberration by the system proposed by H. Rose.

⇩ Aberration-corrected TEMs found a place of importance in structural studies and in investigations at low electron energies to study sensitive materials.

⇩ They allow structural investigations without the disturbing effect of the delocalisation of information due to spherical aberration.

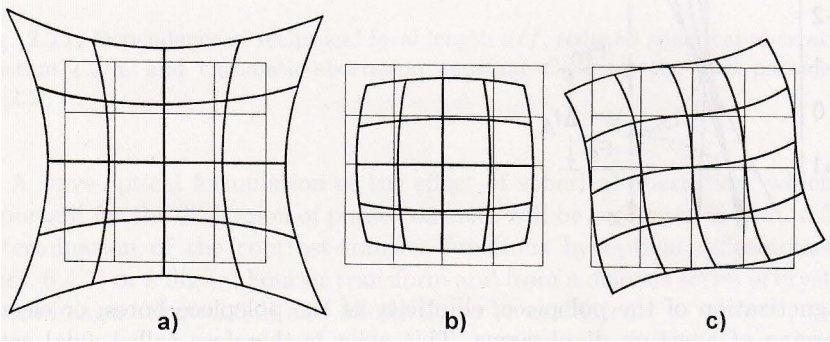
⇨ The microscope must also be aligned to gain in accuracy.

Microscope alignment

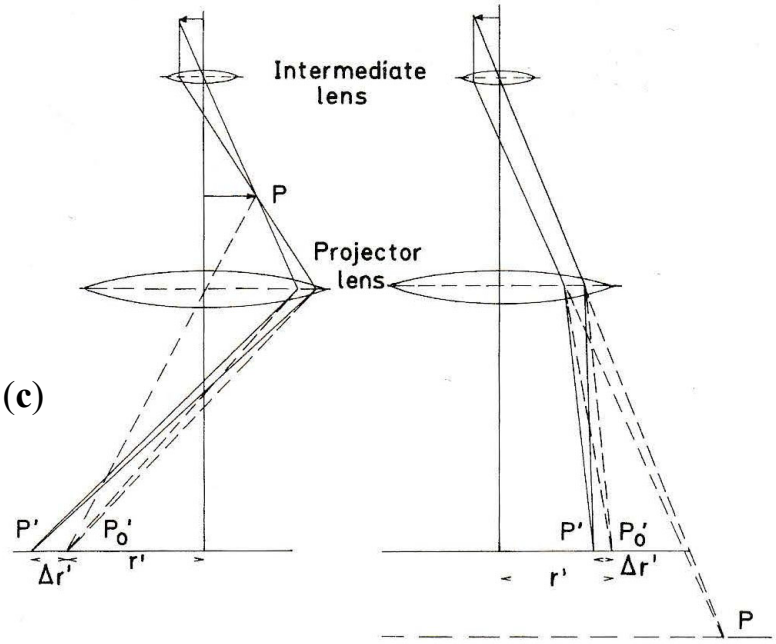
⇨ Microscope alignment involves the centring of the CL aperture around the optical axis **z**.

⇩ If the CL aperture is off-centered, the beam is displaced away from the optical axis given by the condenser lenses.

- This problem of alignment will cause the distortion of the recorded image:



Distortion of a square: pin cushion (**a**), barrel (**b**) spiral distortion (**c**)



Examples of distortion caused by
the spherical aberration of a projector lens

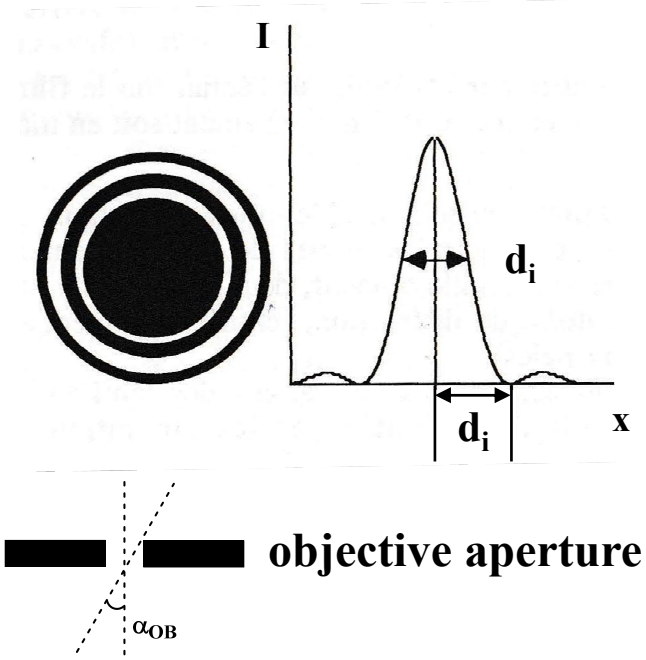
- Distortion causes a displacement in the Gaussian image plane.
- Distortion can also be indirectly due to the spherical aberration of the projector lens.

Resolution, magnification and depth of field

Resolution

⇨ The resolution of a microscope stems from its ability to separate two points vicinal points.

⇩ In the following schemes, are represented the diffraction pattern corresponding to the image of a point of diameter $\mathbf{d_i}$ (left side), also named an Airy pattern and its corresponding signal intensity **I** as a function of the distance **x** also called the intensity distribution.

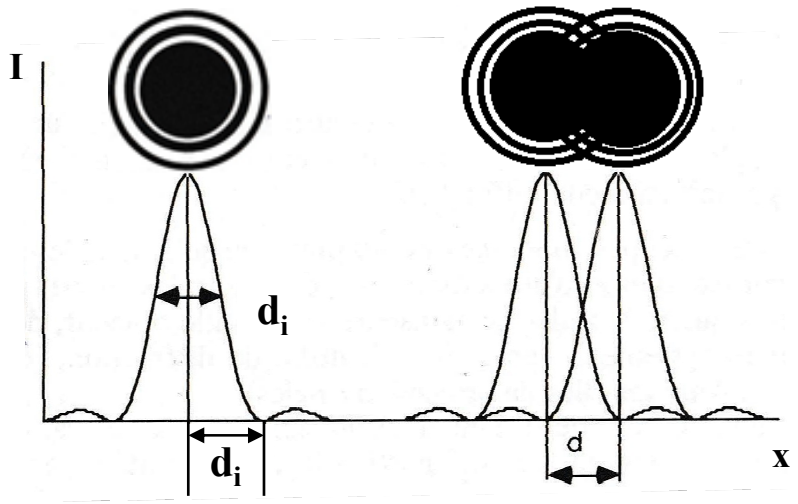


⇩ The width of the principal disk of confusion $\mathbf{d_i}$ (nm) at small $\boldsymbol{\alpha_{OB}}$ half-angles in vacuum is given by:

$$\mathbf{d_i = \frac{0.61\lambda M}{\alpha_{OB}}}$$

⇩ The width $\mathbf{d_i}$ depends on the beam wavelength $\boldsymbol{\lambda}$ (nm), the objective magnification **M** and the half-angle $\boldsymbol{\alpha_{OB}}$ of the objective aperture.

⇨ The resolution **d** of a microscope is the lowest distance needed to obtain a resolved system. It is associated to the diameter $\mathbf{d_i}$ of the image of a point: $\mathbf{d = d_i}$.

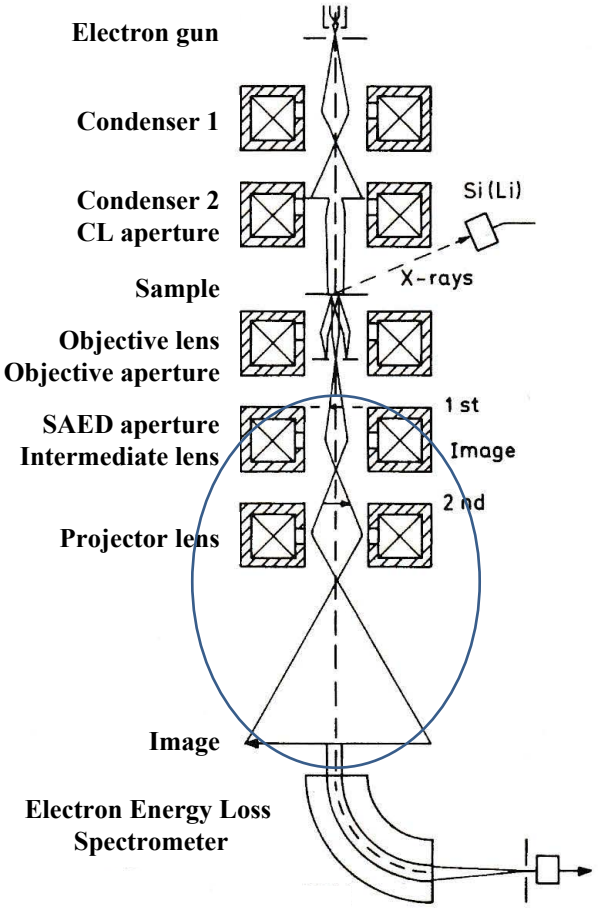


⇩ With the help of the correction of spherical aberration of the objective lens, and thanks to the use of FEG sources, a lateral resolution **d** of 0.5 Å is now achieved:

$$\mathbf{d = 0.66 C_s^{1/4} \lambda^{3/4}}$$ ($\mathbf{C_s}$ (nm) is the coefficient of spherical aberration)

⇩ The resolution **d** decreases when the thickness of the sample increases.

Magnification



⇨ The projector lens is used to greatly magnify the last intermediate image and also ensures that the latest is plane when projected onto the detector.

⇨ The magnification is defined by two practical limits between which an image is clear.

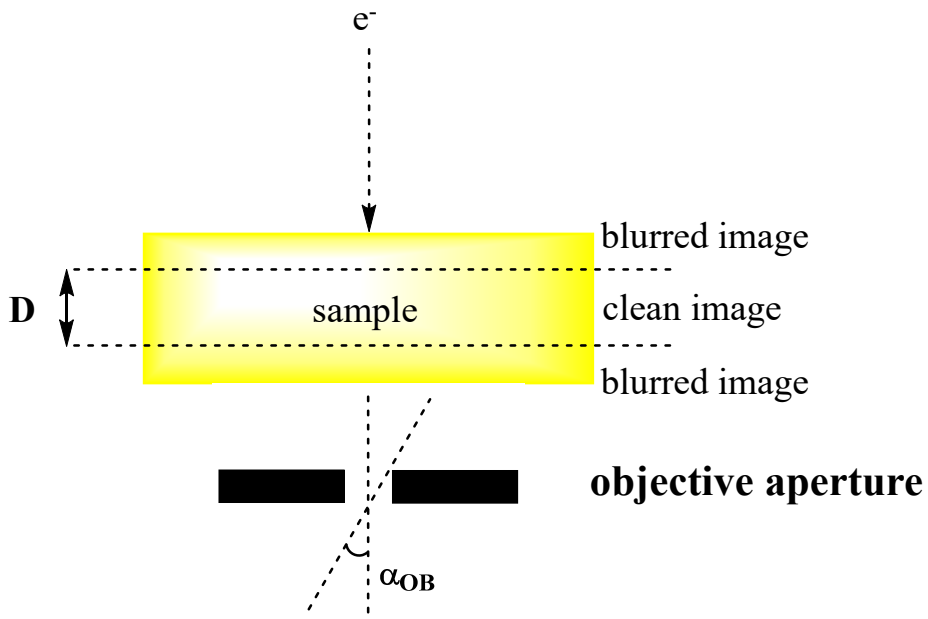
⇨ The magnification is obtained by tuning the strength of the projector lens and the intermediate lenses (3 lenses).

↳ The strength of an electromagnetic lens, that is its focal distance, is tuned thanks to the current passing in the electromagnet.

↳ The magnification can be varied from 50x to up to 50 000 000x.

Depth of field

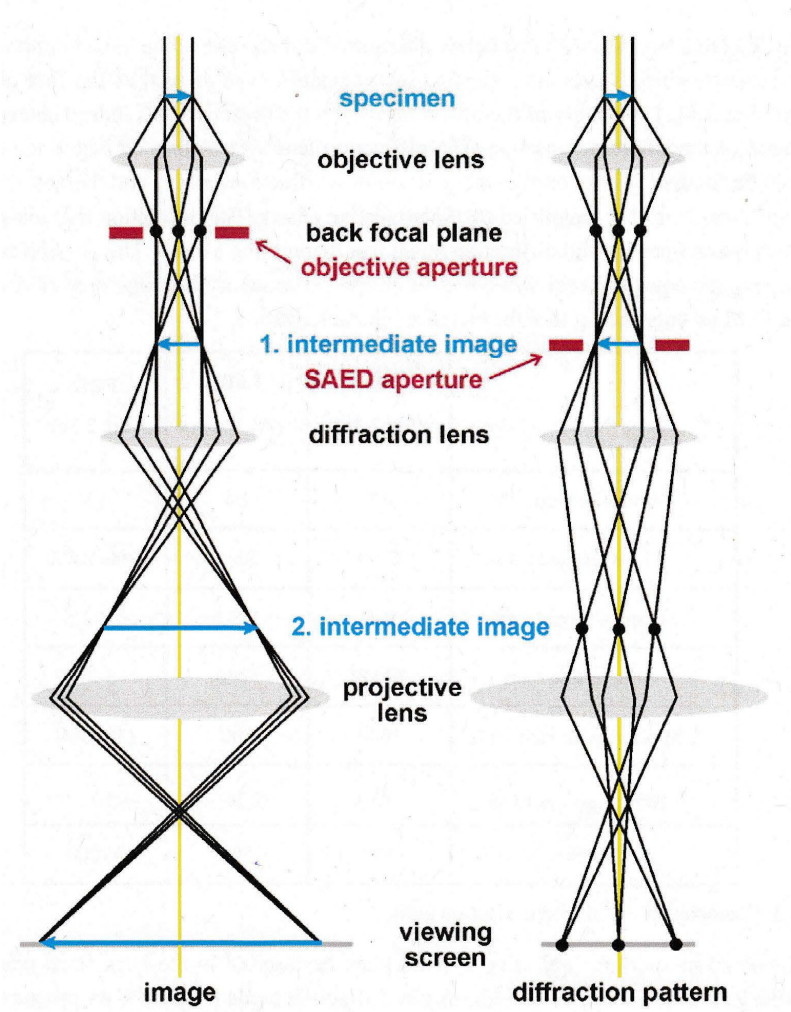
⇨ The depth of field **D**, without altering the resolution **d**, can be estimated as: $\mathbf{D = d\alpha_{OB}^{-1}}$



↳ The thickness of the studied sample must be lower than **D** to provide a representative image analysis of the overall sample for a given resolution **d**.

TEM imaging modes

⇨ TEM provides two modes: the TEM image mode and the diffraction image mode.

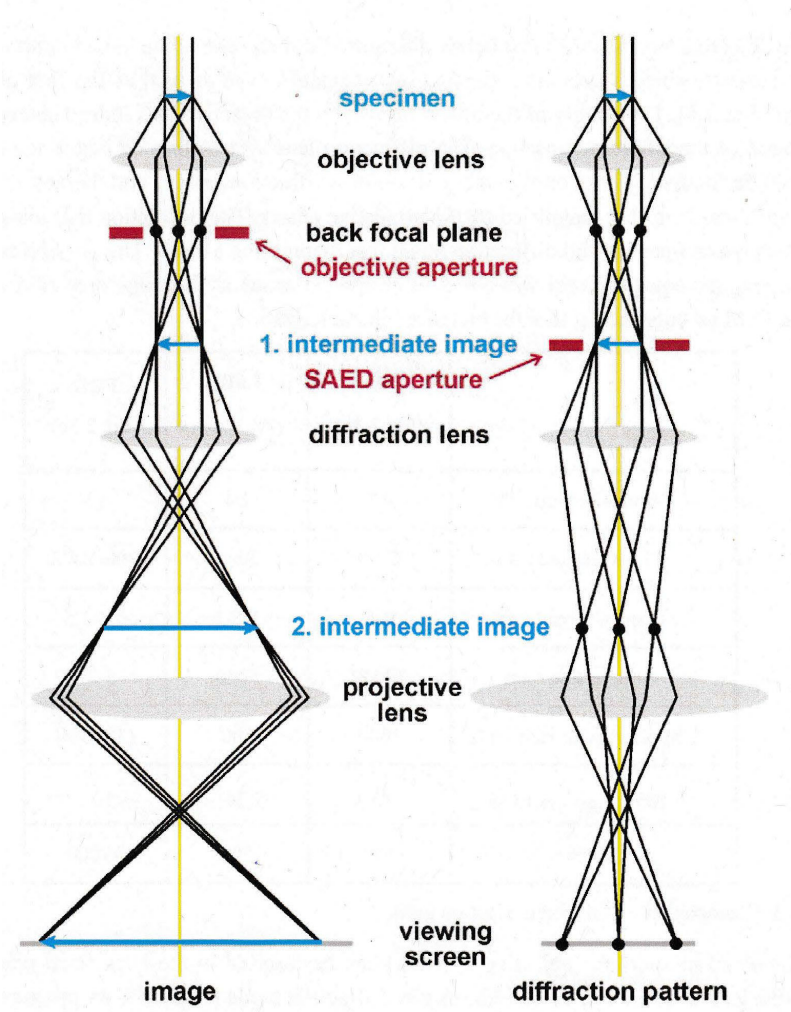


⇨ The objective lens represents the most important lens as it generates the first intermediate image as well as the first diffraction pattern.

⇨ The quality of the image or diffraction pattern formed by the objective lens determines the resolution of the whole microscope (see lens aberration corrections).

⇨ The diffraction lens system can be focused either on TEM imaging or on diffraction imaging.

↳ This system thus determines which mode will be magnified by the projective lens.

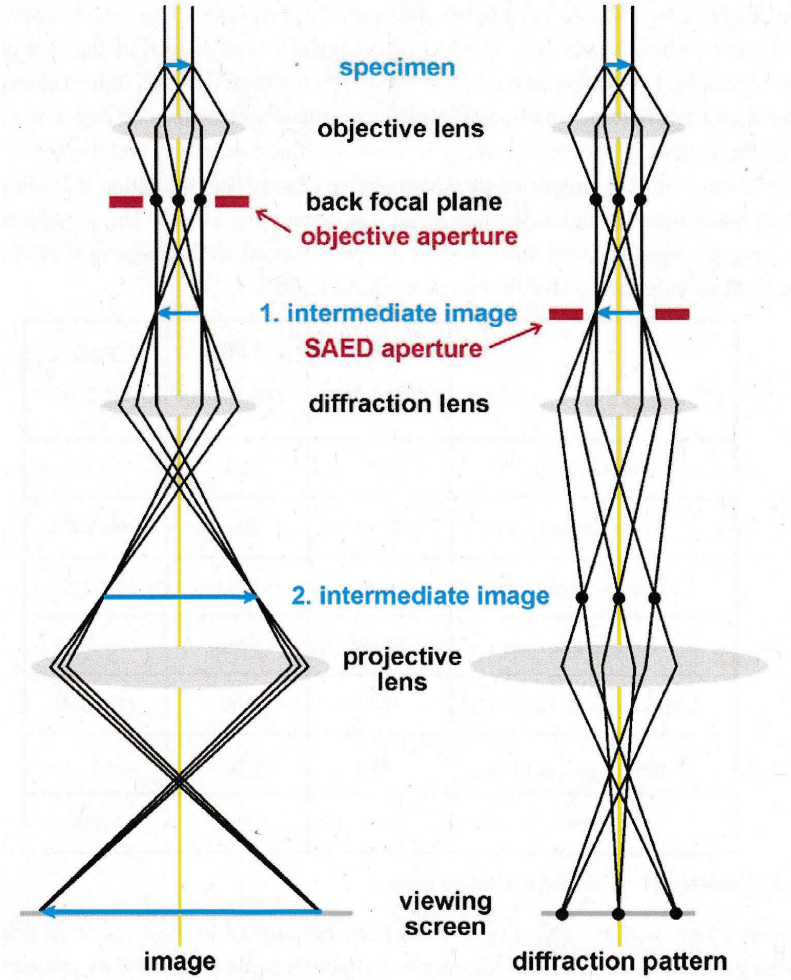


⇨ It is possible to switch automatically from the TEM image mode to the diffraction image mode to get both information simultaneously.

⇨ In the image mode, the objective aperture (made of several hole sizes), is inserted in the back focal plane of the objective lens.

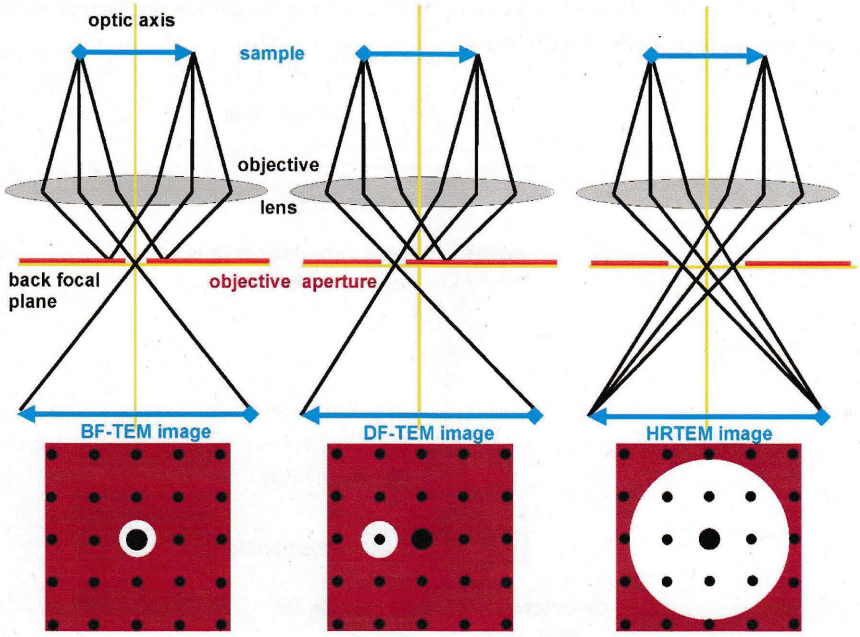
↳ The size of the selected holes of the aperture and the aperture position will give rise to different types of image as explained below.

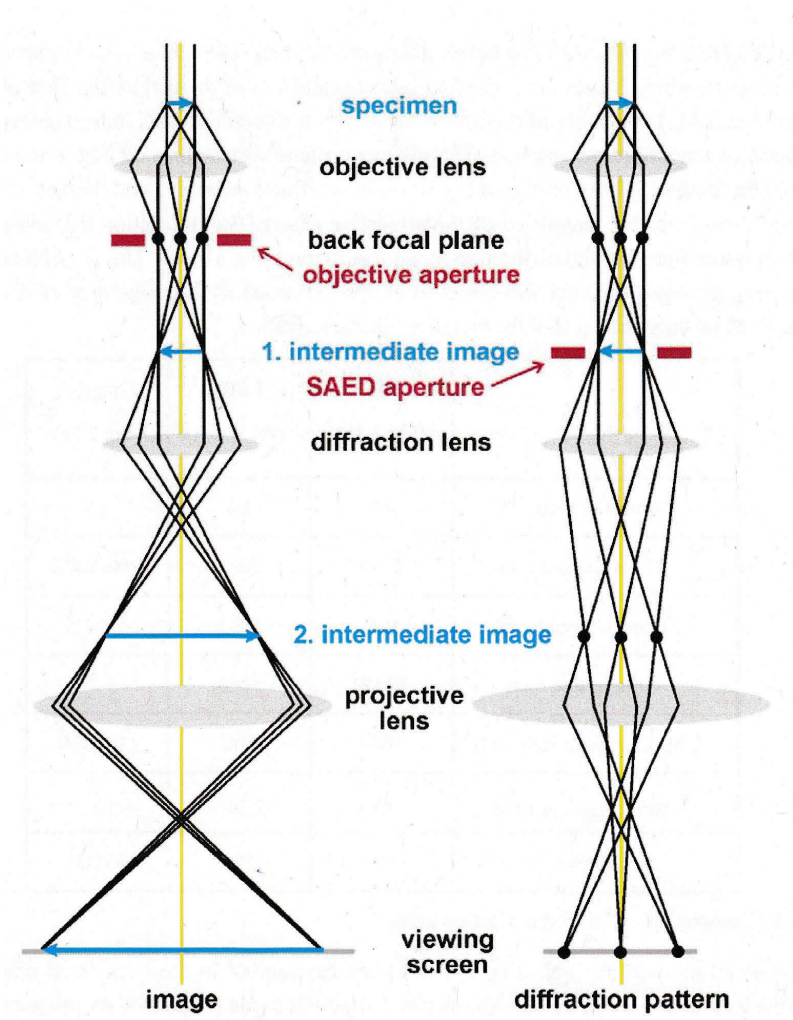
↳ With a small aperture (small holes), if only the transmitted beams (*i.e.* parallel to the optical axis) are allowed to pass through the objective aperture, a Brigth-Field image is formed: BF-image.



↳ The objective aperture can be moved to select the scattered beams, so all the transmitted beams are blocked, thus a Dark-Field Image is obtained: DF-image.

⇨ If a large aperture is selected, the transmitted and scattered beams are collected and interfere in the image plane. This is the setup for HRTEM.





⇨ In the diffraction mode, the objective aperture is removed and the Selected Area Electron Diffraction (SAED) aperture is inserted in the plane of the first intermediate image. It allows to select the region from which the electron pattern is derived: SAED mode.

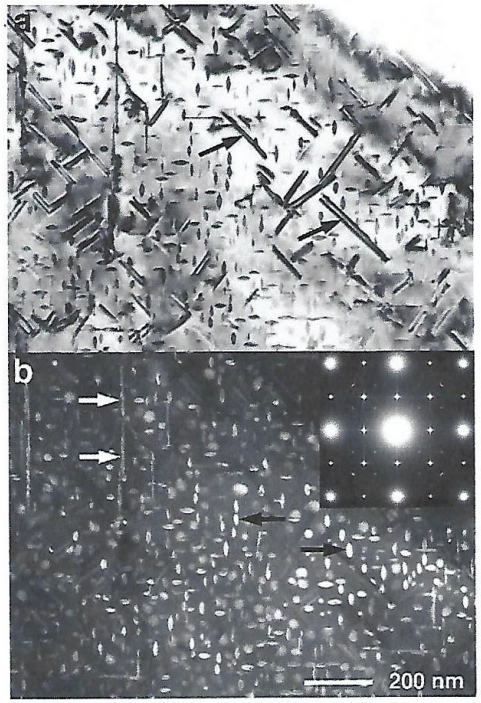
⇨ The contrast in TEM is mainly due to the diffraction/scattering processes and the mass-thickness contrast.

⇨ The contrast depends on the scattering cross-section of the chemical elements of the sample and on the number of scattering elements along the electrons path.

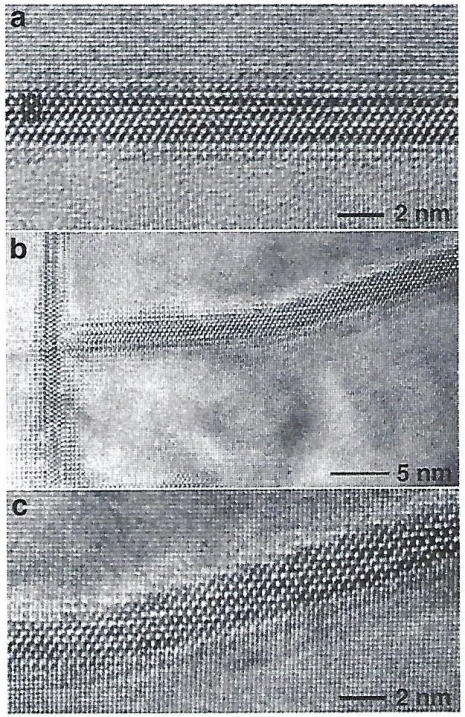
⇨ The detector is generally made of either a phosphor screen (direct observation) and/or a film made of undoped or doped YAG (Yttrium Aluminium Garnet) deposited on a CCD system (camera).

⇨ Strongly scattering regions of the sample will appear darker compared to weakly scattering ones in a BF image.

⇨ The examples below are presenting several images from Al-Li-Cu alloys: R. Yoshimura et al., *Acta Materialia*, **2003**, *51*, 4251-4266.



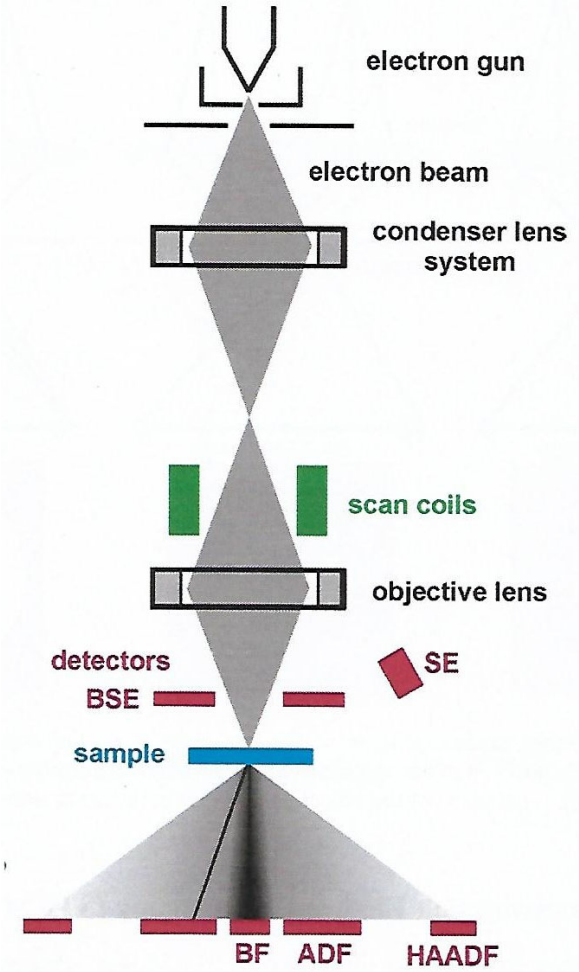
TEM BF (a) and DF (b) images of 2.4 % (m/m) Al-Li-Cu alloy annealed at 220°C. The Insert depicts the SAED image.



HRTEM images of atypical θ' precipitate in the 2.4 % (m/m) Al-Li-Cu alloy annealed at 220°C.

STEM

⇨ Scanning TEM (STEM) provides a surface information of a studied material. It requires a FEG source.



⇨ Whereas TEM works with a parallel illumination, STEM, as for SEM, uses a tiny convergent electron beam. The beam can be scanned across a surface.

⇨ The transmitted electrons generate a signal recorded by selected detectors spot by spot which forms an image on a screen, pixel by pixel.

⇨ To obtain a STEM image, three detectors are needed.

⇨ The Bright Field Detector (BF-Detector) is placed along the optical axis.

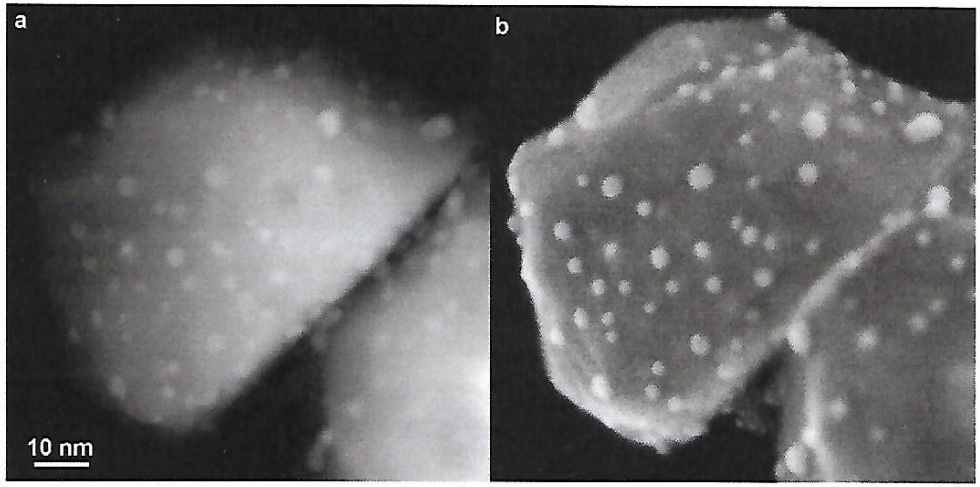
⇨ The Annular Dark Field Detector (ADF-Detector) is a ring-shape semi-conductor device. This detector analyses scattered and diffracted electrons at small angles: a DF-image is formed.

↳ The measured contrast results from electrons diffracted in crystalline areas further superimposed to incoherent scattering events.

⇨ The High-Angle Annular Dark Field Detector (HAADF-Detector) is a semiconductor disk with a hole. Its inner diameter is much larger than the ADF-Detector one.

↳ It detects electrons scattered at high angles arising mostly from incoherent scattering events.

⇨ It is also possible to install some additional detectors to analyse secondary and back scattered electrons (SE and BSE) as it is the case in SEM. With this configuration, one can obtain supplementary morphological and topographical information of a given sample.



↳ On the left side is presented STEM images of Au nanoparticles on TiO_2 (from ETHZ).

↳ The picture **a** is a HAADF-STEM image and the picture **b** shows a SE-STEM image (secondary electrons SE).

HT-TEM

⇨ High Tension TEM (HT-TEM) was developed to improve the imaging resolution.

⇨ In HT-TEM, the acceleration tension delivered at the electron gun spreads from 1 to 3.5 MV (*i.e.* an electron energy from 1 to 3.5 MeV).

⇩ With such electron energies, which improve a lot the lateral resolution **d** of the microscope, the damages caused to the sample are huge and the energy of the emitted X-Rays (bremsstrahlung) imposes a special protection for the operator of the microscope.

⇨ HT-TEM allows to observe some massive sample with thickness up to 1 µm.

⇨ HT-TEM is still in development for advanced research but is not useful for routine analyses.