Master sciences et technologies
Mention Physique et Applications

Transmission Electron Microscopy

Part #1
Diffraction
Conventional Imaging

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Outline

- **Part 1 : Conventional TEM**
    - - Transmission Electron Microscope
    - - TEM sample
    - - conventional imaging : bright field / dark field
    - - electron diffraction

- **Part 2 : Advanced TEM**
    - - high resolution imaging
    - - STEM HAADF imaging
    - - XEDS spectroscopy
    - - EELS spectroscopy
    - - advanced aberration-corrected TEM/STEM

Part 1 : Conventional TEM

- Introduction

- Transmission Electron Microscope
    - gun, lens

- TEM sample
    - specificity
    - preparation,
    - Focused Ion Beam (FIB)

- conventional imaging in TEM
    - image formation
    - origin of contrast
    - bright field, dark field

- electron diffraction
    - principle
    - applications

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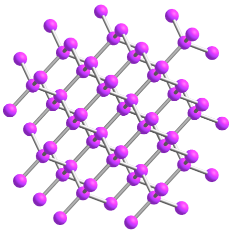
Introduction

how to see atomic structure of condensed matter ?

- to see an object with a size d you need a wavelength λ such as : $\lambda < d$

  example : visible light → 0.5 µm



- in general, to get information about the atomic structure, you need a wavelength $\lambda \leq 0.1$ nm

⇒ Electromagnetic radiation with $\lambda \approx 0.1$ nm : X-rays

problem : best x-ray microscope ≈ 10 nm

→ X-ray diffraction (not a direct image)

Introduction

how to see atomic structure of condensed matter ?

⇒ Electron radiation

- de Broglie's relation (1924) for relativistic electron ($U > 100$ keV):

$$\lambda = \frac{h}{\sqrt{2\, m_0\, e\, U}} \frac{1}{\sqrt{1 + \frac{e\, U}{2\, m_0\, c^2}}}$$

$\lambda = 2.51$ pm for $U = 200$ kV

- electron beams can be focused
  - → electrostatic lenses
  - → magnetic lenses

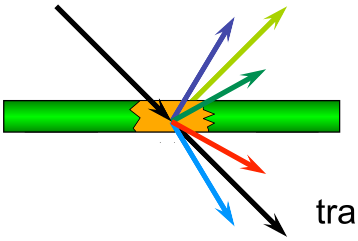
→ first transmission electron microscope build in 1931

Ernst Ruska (1986 Nobel Prize)

E. Ruska et M. Knoll 1931

Introduction

general principle of material analysis



Incident beam
(probe)

secondary, scattered
beams

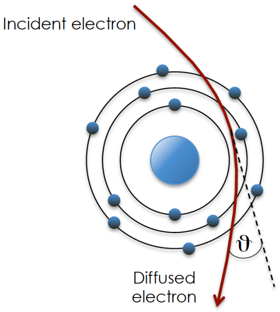
transmitted, scattered
beams

Required :

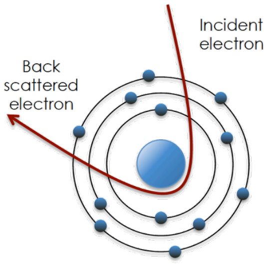
- knowledge of the incident beam (nature, intensity)
- knowledge of the radiation / matter interaction (at the quantum level)
- identification/quantification of secondary/scattered radiations

Introduction

Elastic electron - matter interaction



Low angle diffusion :
$\theta < 20$ mrad @ 200 keV
Coulomb interaction with the electron cloud

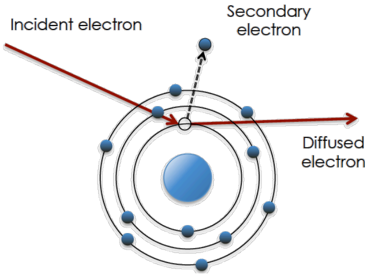


High angle diffusion / back scattering :
$\theta > 70$ mrad @ 200 keV
Coulomb interaction with the atom nucleus
(Rutherford diffusion)

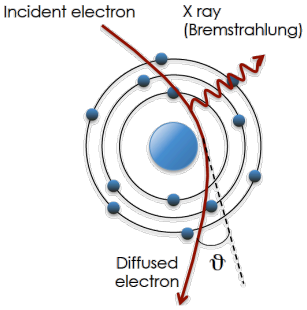
Elastic interaction : → no energy transfer
→ the atom is not ionized

Introduction

Inelastic electron - matter interaction



Atom ionization :
The incident electron ejects a bound electron and then changes direction with an energy loss



Brehmstrahlung :
Incident electron can loss energy by Coulomb interaction with atom nucleus

+ phonons, plasmons, …

Inelastic interaction : → energy transfer: the incident electron losses energy
→ atom may be ionized

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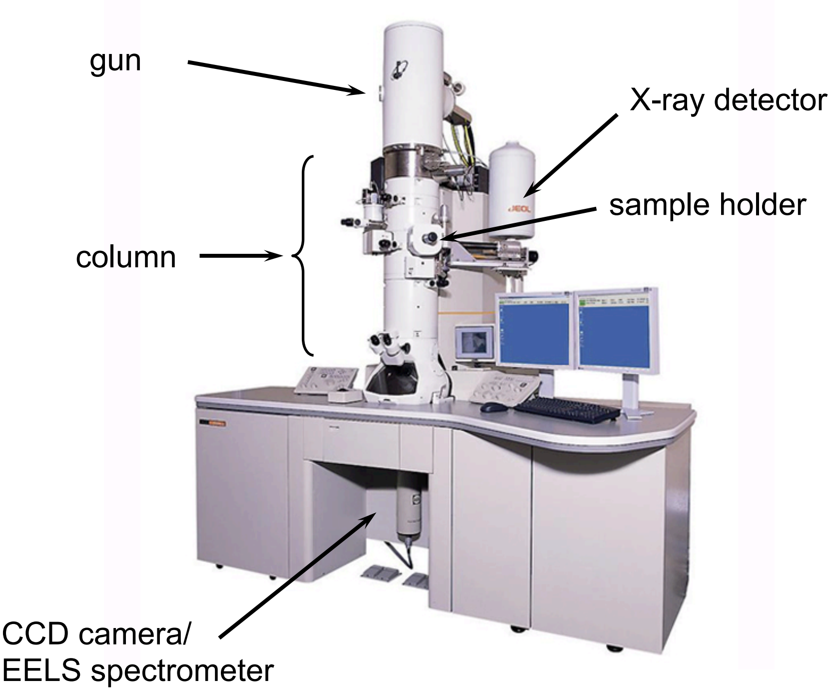
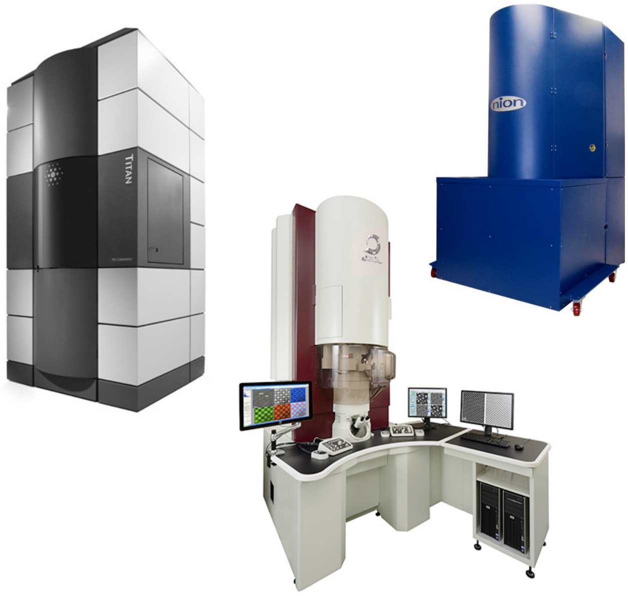
TEM



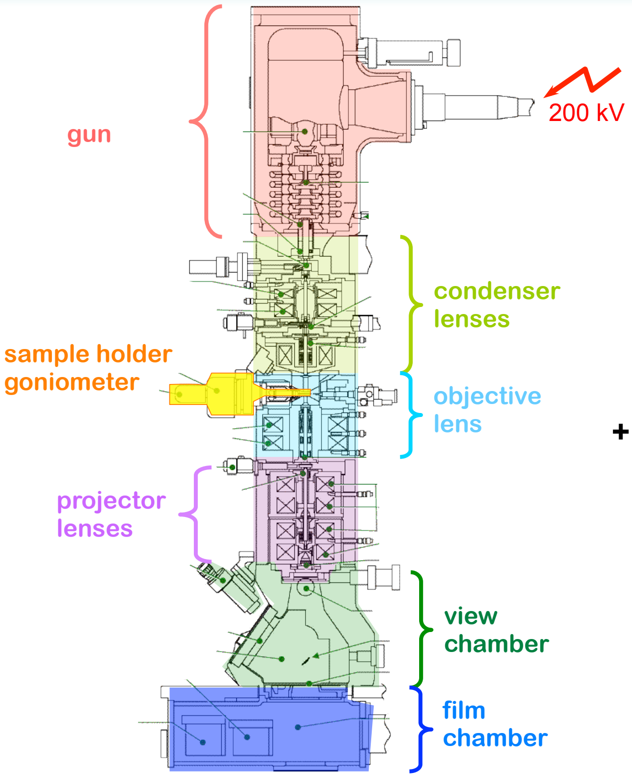
TEM through the ages

1933



2015

TEM

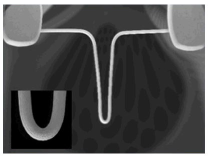


+ several detectors:

- CCD camera
- X-rays detector
- EELS spectrometer
- HAADF detector
- …

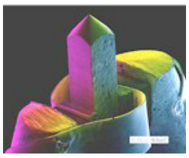
Electron sources

1930



W filament

1970

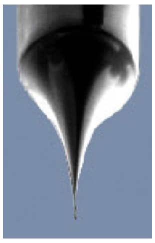


LaB_6 tip

1990

Schottky emitter (FEG)

1970, 2015



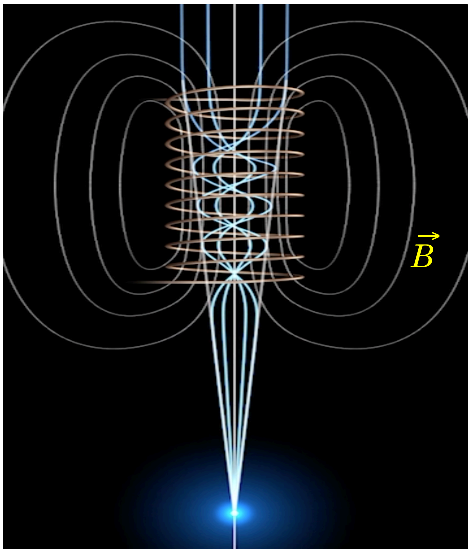
cold field emitter (CFEG)

	W	LaB6	W-ZrO (FEG)	W (CFEG)
Work temperature [K]	2800	2000	1800	300
Work pressure [Pa]	10^{-5}	10^{-6}	$< 10^{-8}$	10^{-9}
Brightness [$A\ cm^{-2}\ sr^{-1}$]	$10^4 – 10^5$	$3\ 10^5$	10^8	10^9
Cross-over diameter [μm]	20 – 50	10 – 20	0.015	0.01 ≤
Energy spread [eV]	1 – 2	0.5 – 2	0.6	0.2 – 0.4

analytical at the atomic scale

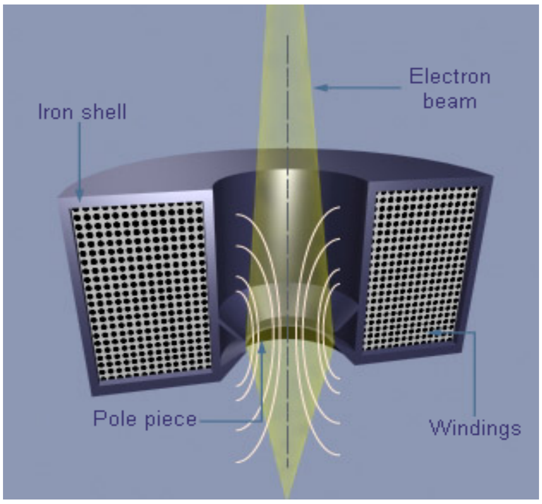
Electromagnetic lenses

Rotational symmetric electromagnetic fields



Lorentz force

$$\vec{F} = q\,\vec{v} \times \vec{B}$$



acts on electrons
as an optical lens acts on light
→ focusing

http://www.jst.go.jp/first/tonomura/e/commentary/mechanism/index.html

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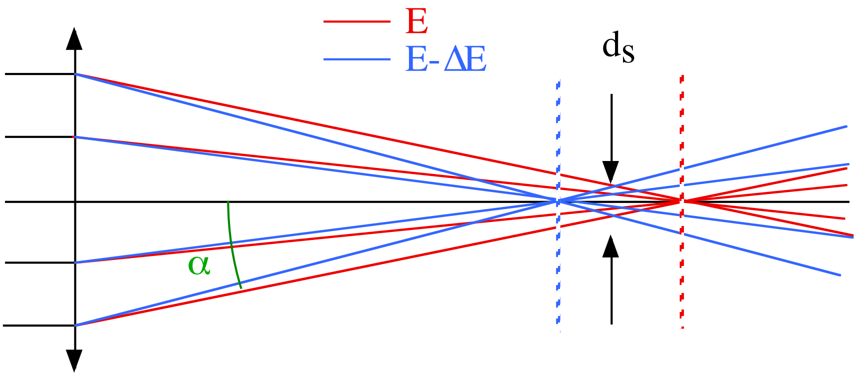
Defects of electromagnetic lenses

Chromatic aberration

Chromatic aberration

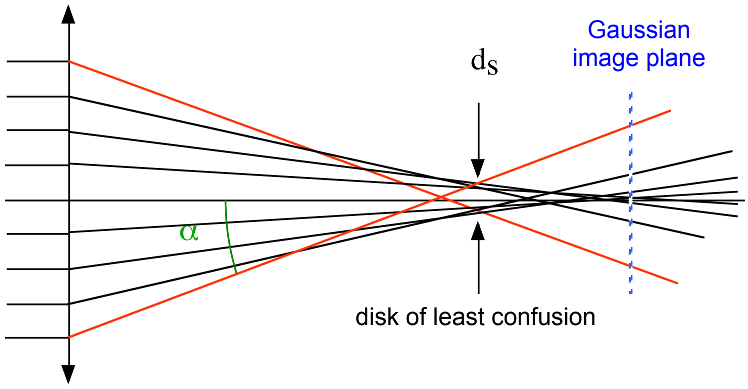


$$d_s = c_c \,\frac{\Delta E}{E}\,\alpha$$

Defects of electromagnetic lenses

Spherical aberration **(1)**

Spherical aberration

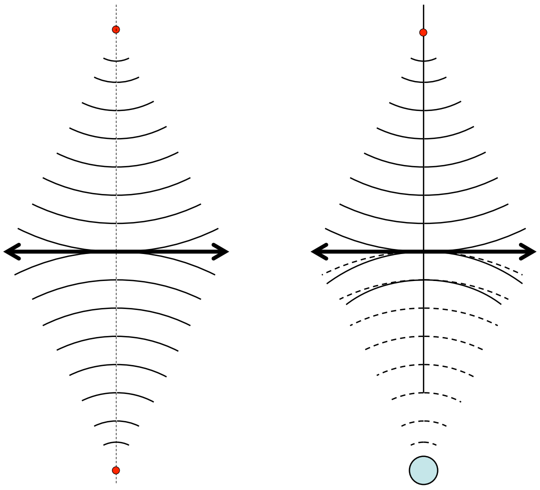


$$d_s = \frac{1}{2} c_s \alpha^3$$

The focus depends on the axial distance of the electron path

Defects of electromagnetic lenses

Spherical aberration **(2)**



ideal lens

real lens

- the image of a point is not a point
- a phase shift appears between diffracted beams

⇒ lowering the resolution (→ 1.5 Å)

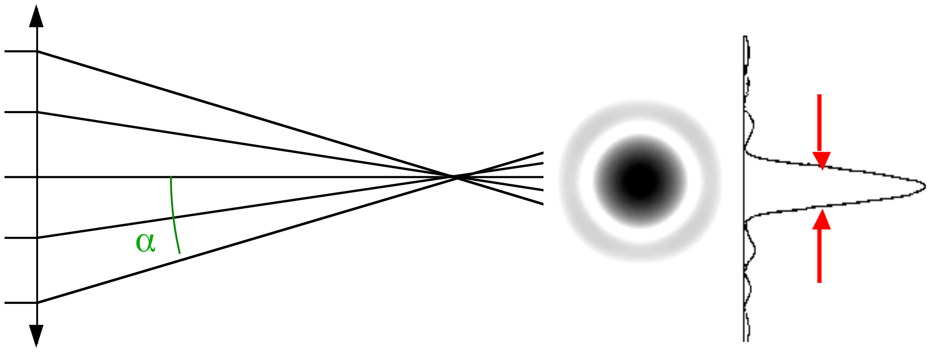
⇒ images may be difficult to interpret

Defects of electromagnetic lenses

diffraction

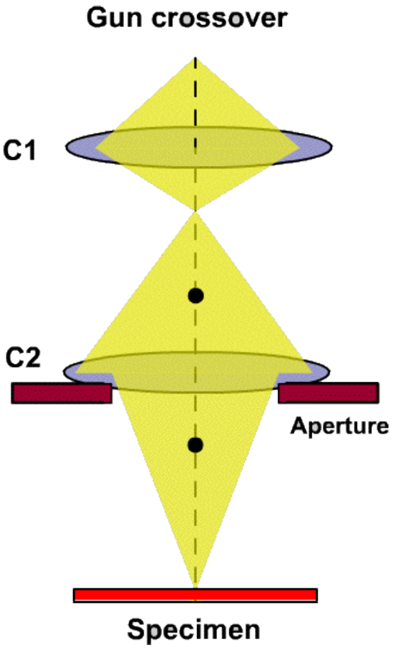
Diffraction

May appear, due to the contrast aperture



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

Condenser system



Three main components :

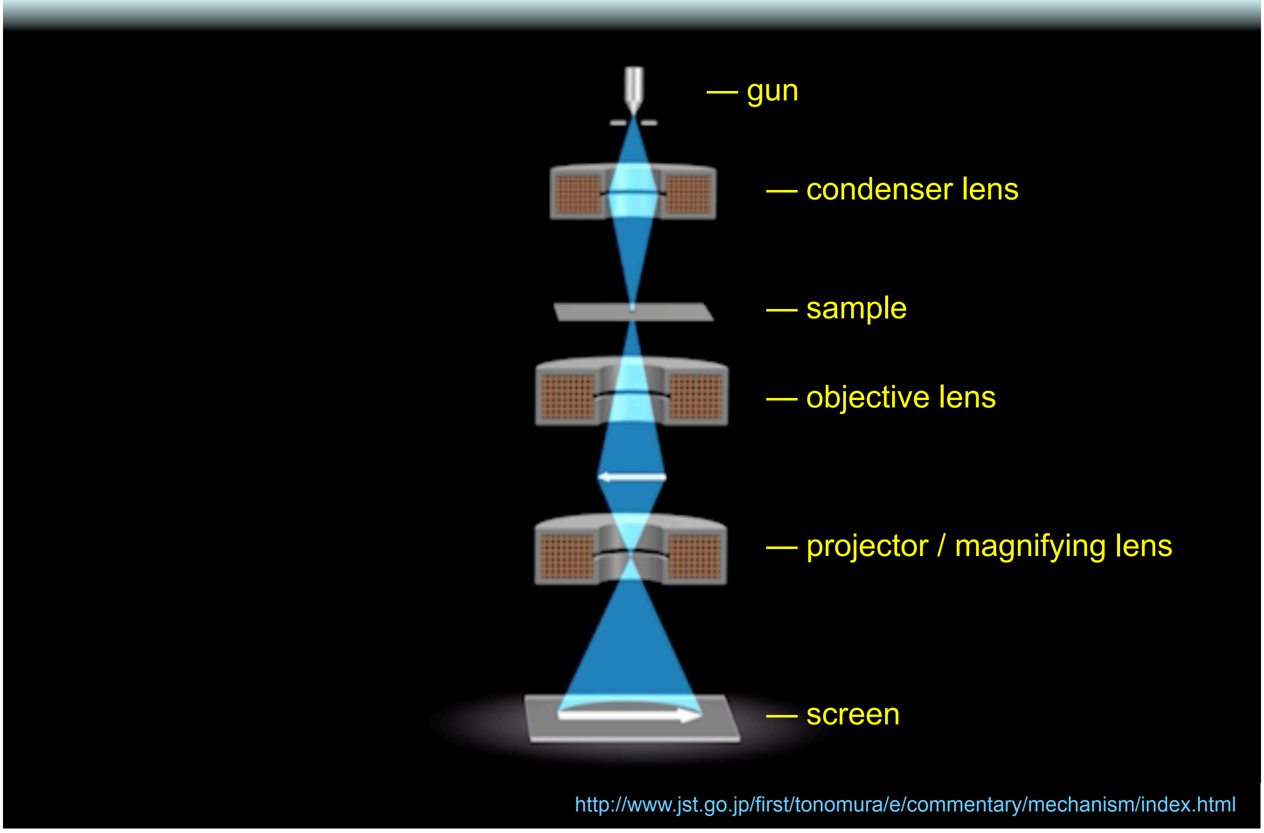
- C1 condenser
- C2 condenser
- condenser aperture

To control:

- spot size
- beam intensity
- beam convergence

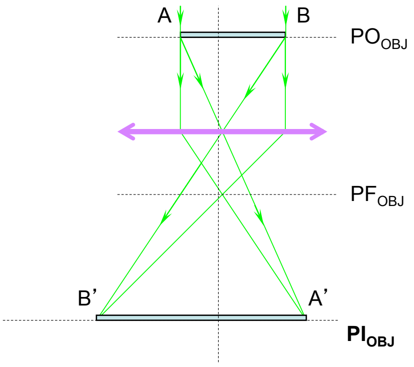
http://www.matter.org.uk/tem/default.htm

TEM optics



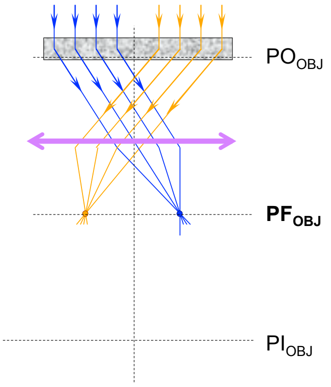
http://www.jst.go.jp/first/tonomura/e/commentary/mechanism/index.html

Objective lens



an image is formed
in the "image" plane

**objective
lens**



a diffraction pattern
is visible in the back focal plane

→ **reciprocal space**

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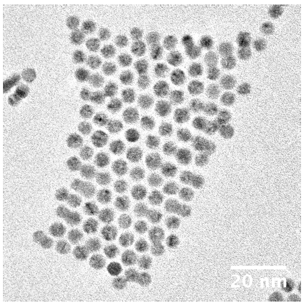
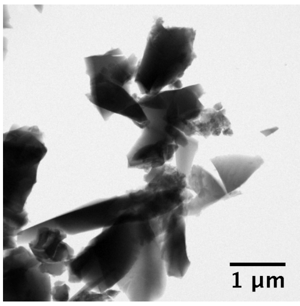
TEM sample

- must be "transparent" to high energy electrons (100 - 200 keV)
- thickness < 100 nm mandatory
- 20 nm : ideal

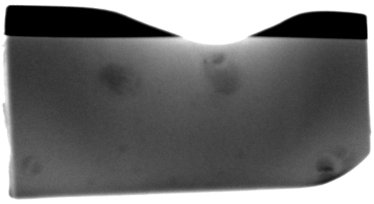
Nanoparticles



Particles



Thin foils
FIB

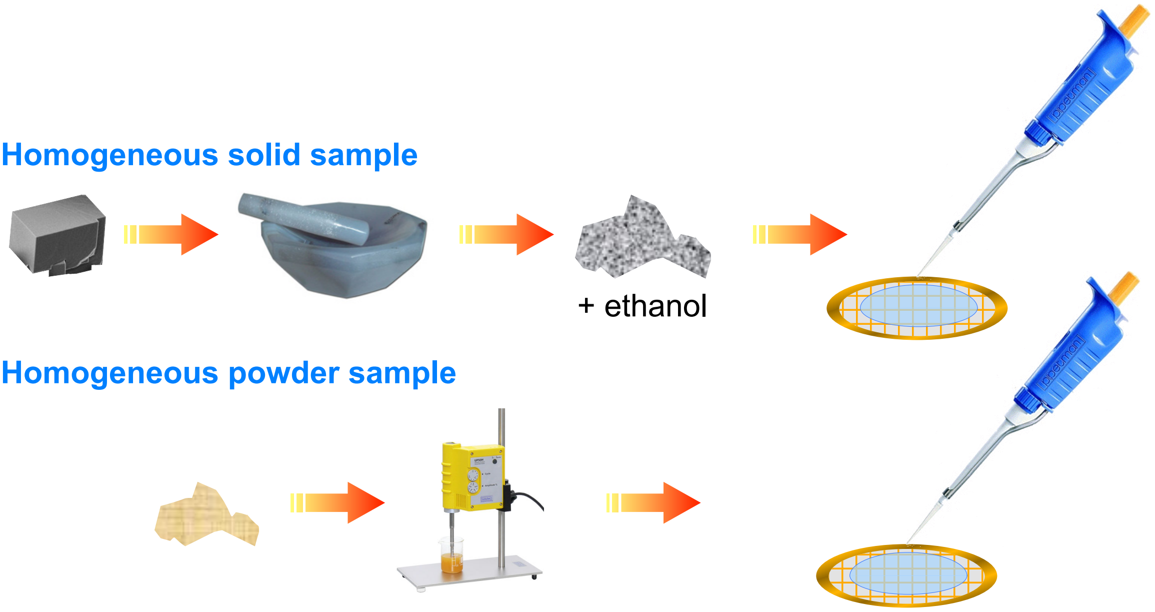


TEM sample preparation

nanoparticles

Homogeneous solid sample

Homogeneous powder sample

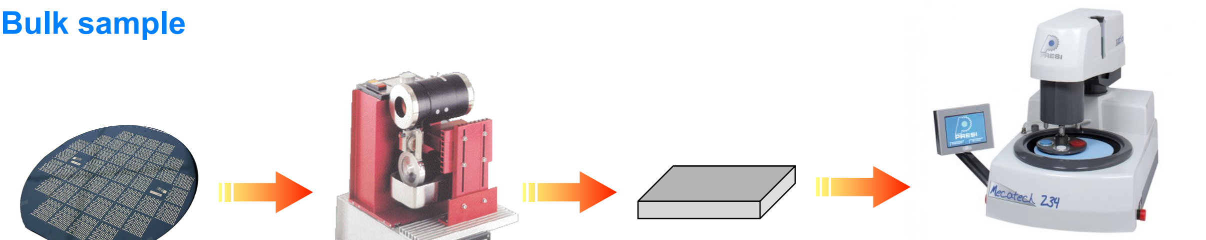


Preliminary glow discharge exposition of the carbon grid may help particles spread

TEM sample preparation

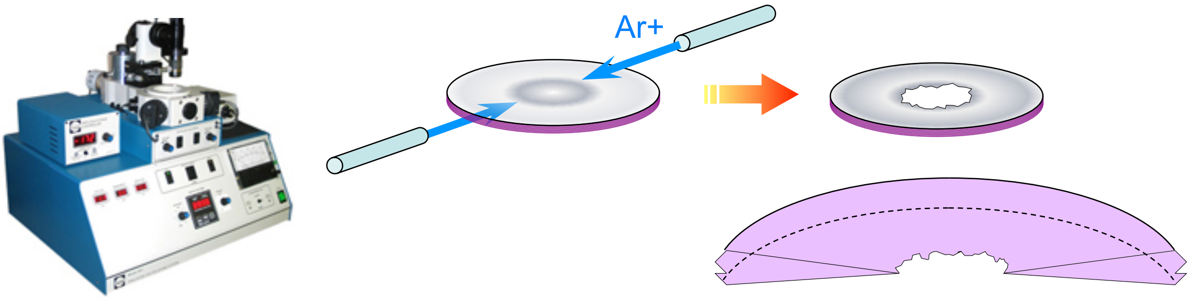
thin foil

Bulk sample


→ 1 mm

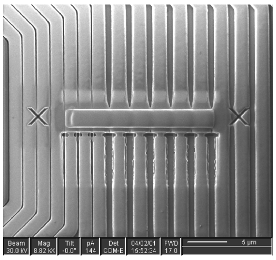
Mechanical polishing
→ 30 µm

ion polishing

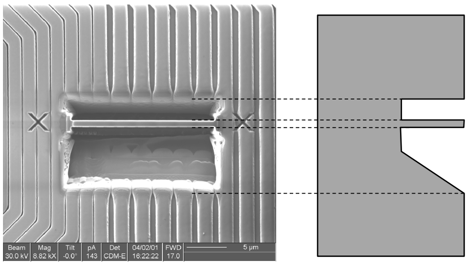


Thin foil preparation

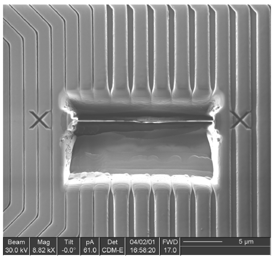
Focused Ion Beam – ***ex situ*** lift out



Pt protective layer



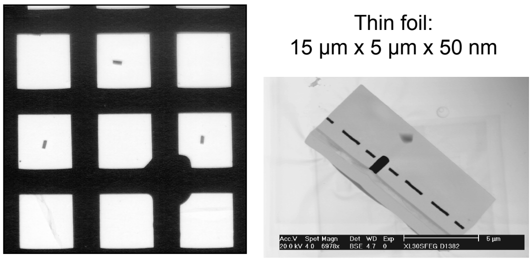
Parallel trenches are made around
the region of interest using ionic abrasion



Foil thinning
→ 50 nm

Thin foil is cut

micromanipulator



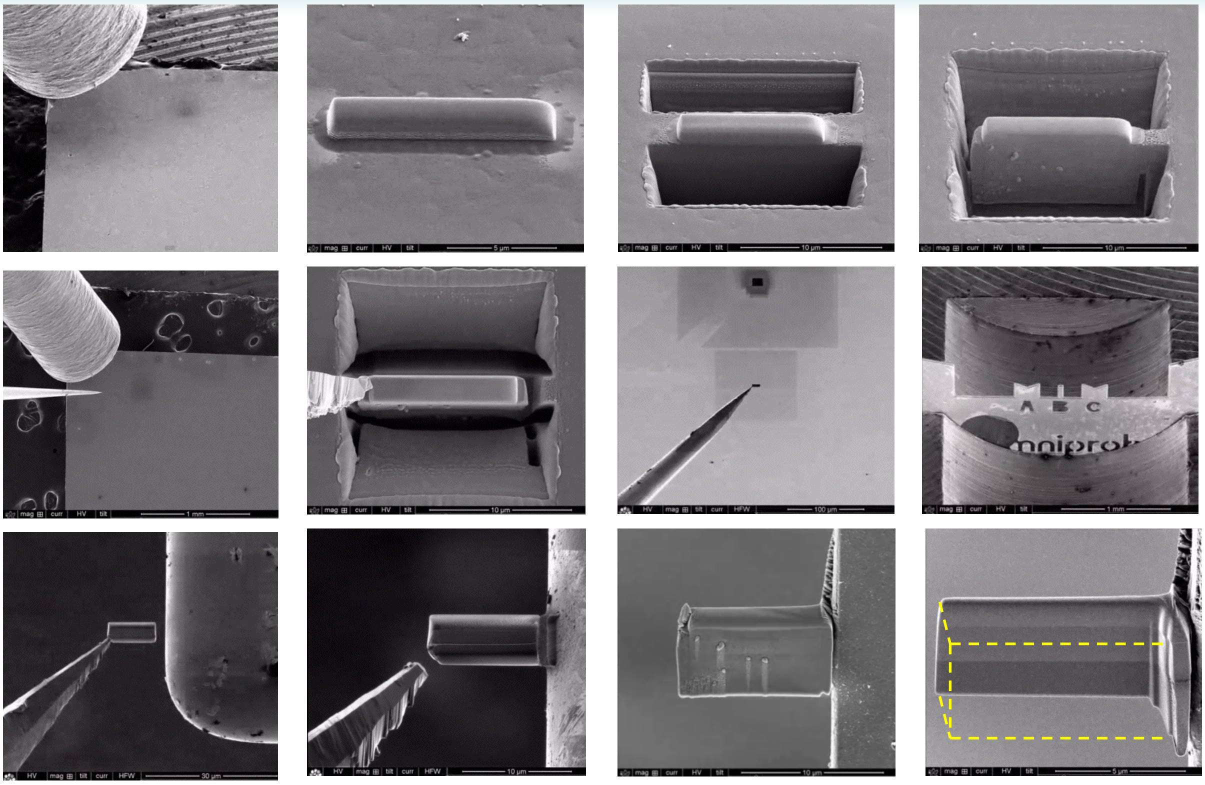
Thin foil:
15 µm x 5 µm x 50 nm

Transfer of the thin foil onto a TEM grid

http://temsamprep.in2p3.fr/fiche/fiche.php?lang=eng&fiche=20

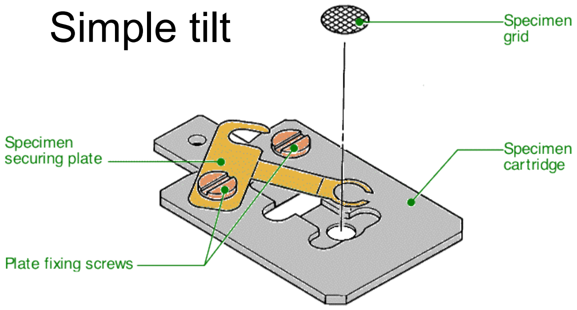
Thin foil preparation

Focused Ion Beam – ***in situ*** lift out

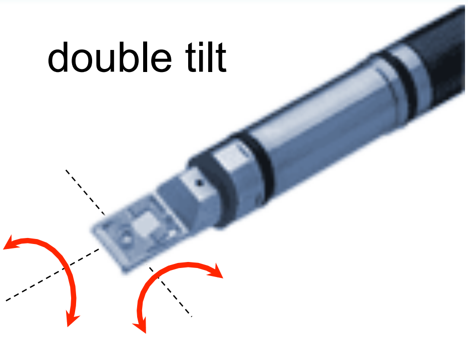


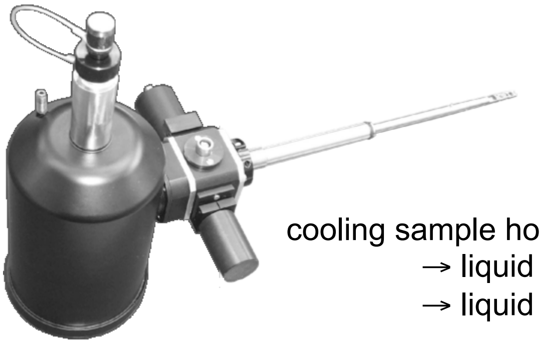
TEM sample holder

Simple tilt

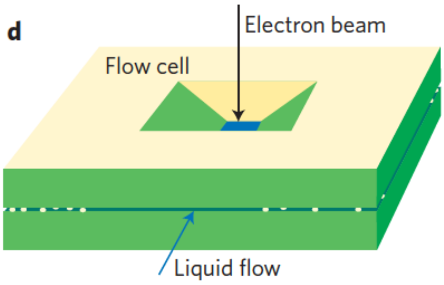


double tilt





cooling sample holder
→ liquid N_2
→ liquid He



in situ liquid/gaseous cell

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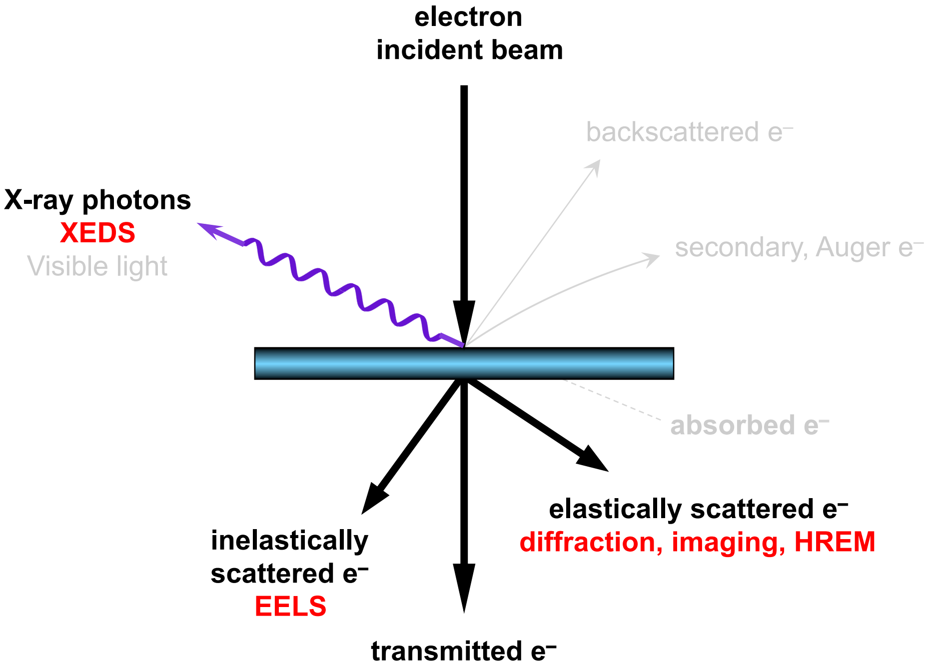
Electron – Matter interactions
thin sample



electron incident beam

backscattered e^-

X-ray photons
XEDS
Visible light

secondary, Auger e^-

absorbed e^-

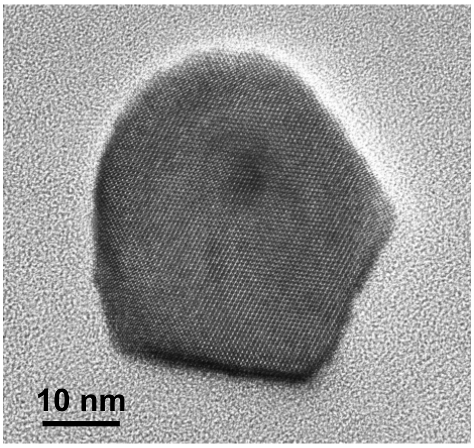
elastically scattered e^-
diffraction, imaging, HREM

inelastically scattered e^-
EELS

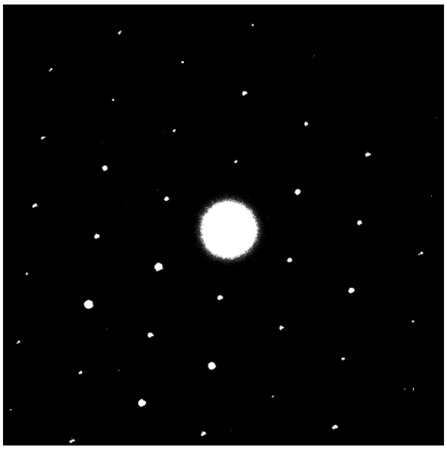
transmitted e^-

IMAGE and **DIFFRACTION** modes

With TEM, you can get (almost) simultaneously an image or a diffraction pattern of your sample :



Magnetite Fe_3O_4



<110> zone axis diffraction pattern

IMAGE and **DIFFRACTION** modes

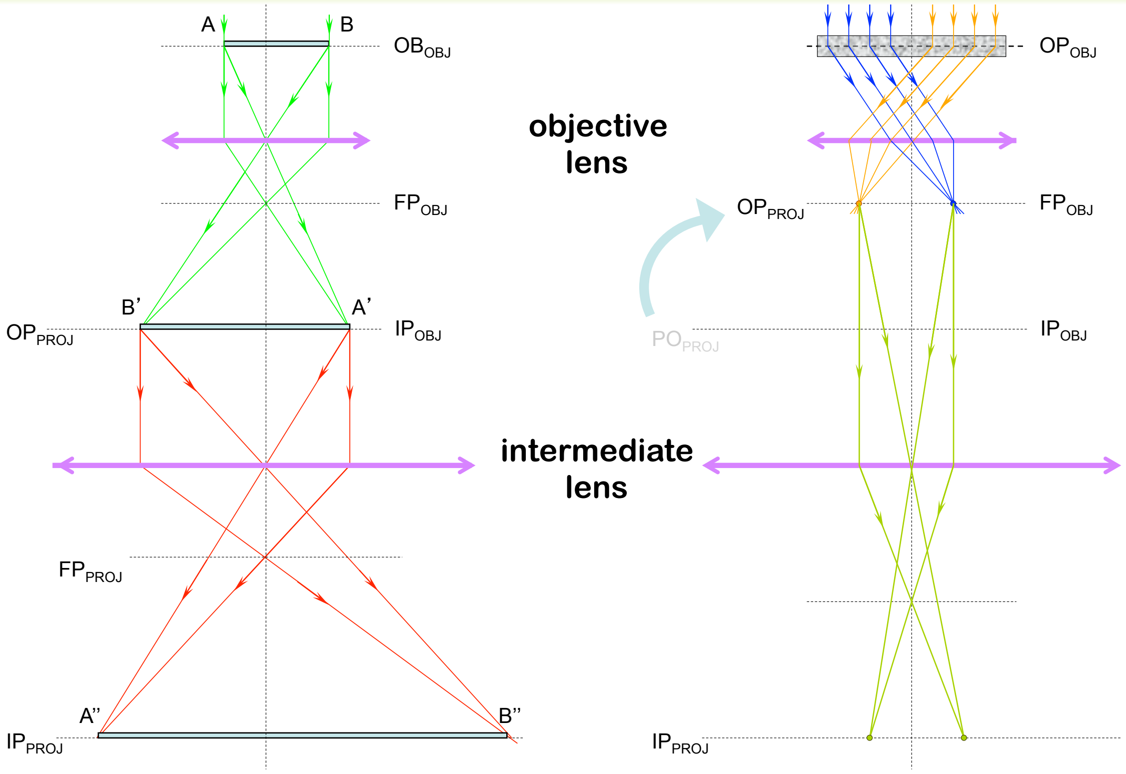
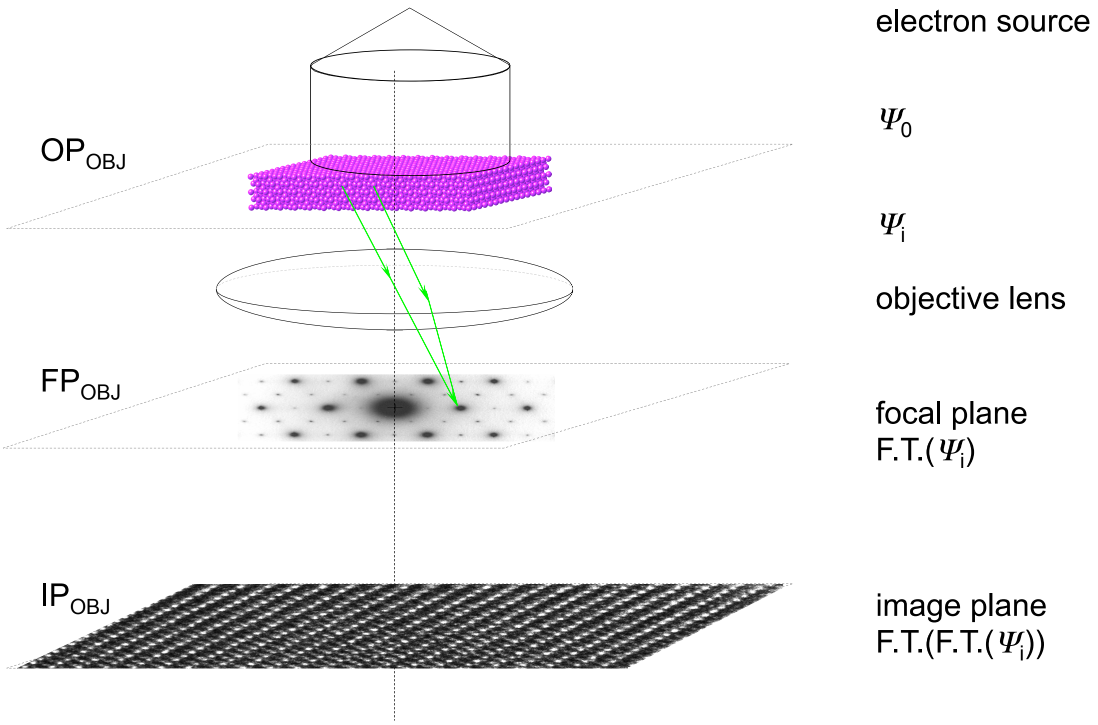


IMAGE and **DIFFRACTION** modes



Conventional TEM : origin of contrast

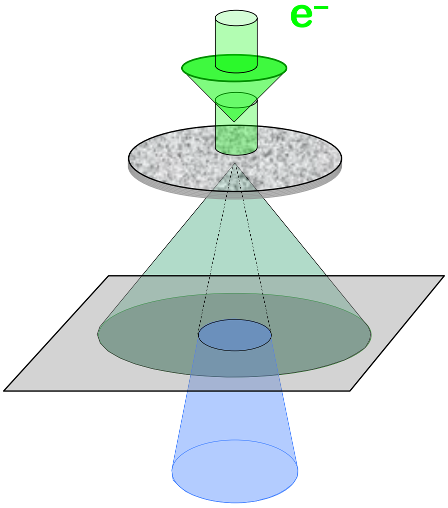
Thickness-Mass contrast – Diffraction contrast

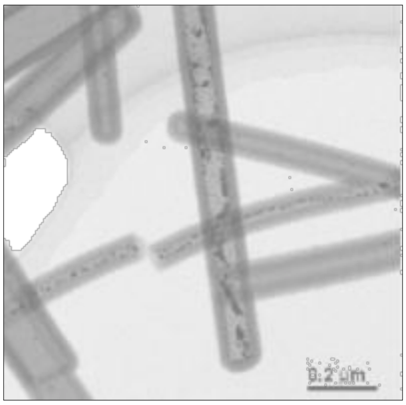
Incident electrons are :
- scattered by atoms of the sample
- absorbed by the sample

→ increasing with atomic number *Z*

→ increasing with sample thickness
- diffracted by crystals

High angle scattered electrons do not arrive onto the screen/camera :
- high Z materials appear darker than low Z materials
- thick parts of the sample appear darker than thin ones
- crystallized parts may appear darker than amorphous



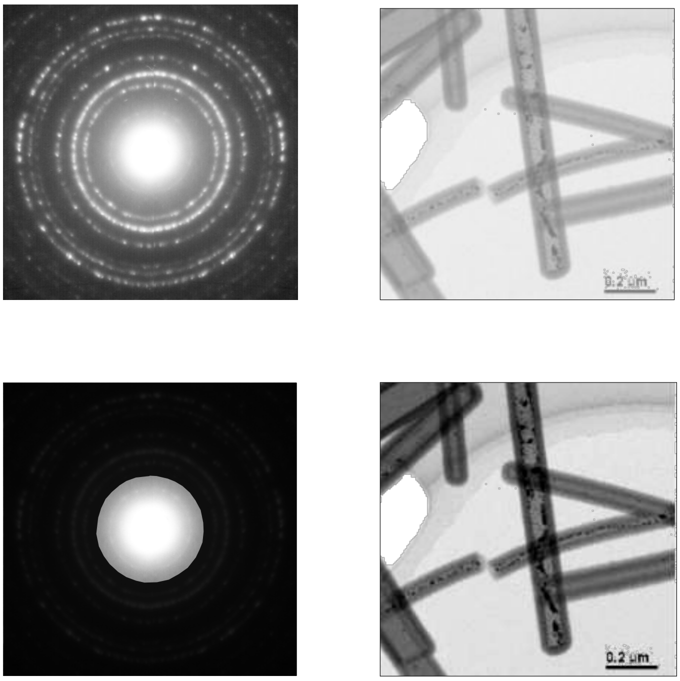


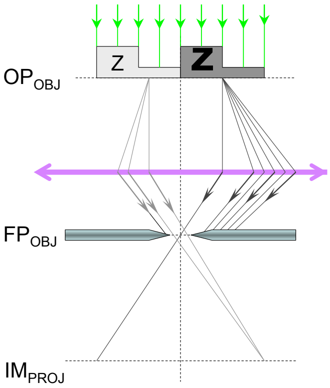
amorphous SiO_2 nano-tubes containing Pt particles

http://www.microscopy.ethz.ch/

Conventional TEM : Bright Field contrast

interest of the contrast aperture



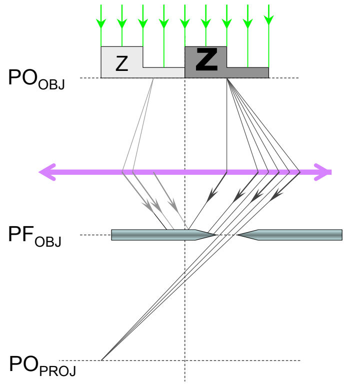


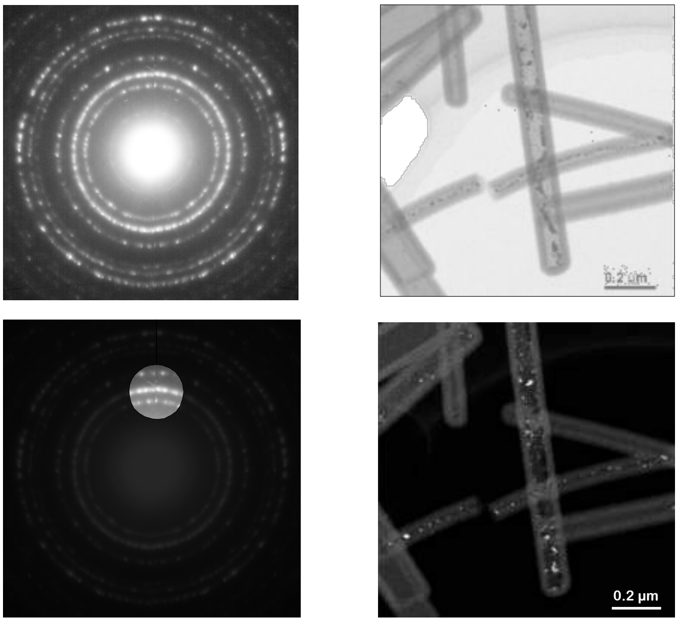
The "contrast" aperture in the back focal plane stops diffracted and high angle scattered electrons

→ contrast enhancement

http://www.microscopy.ethz.ch/

Conventional TEM : Dark Field contrast





http://www.microscopy.ethz.ch/

The objective aperture can select only diffracted or off axis diffused beam

⇒ non/weakly scattering areas are no more visible

⇒ crystallized particles and diffusing particles may be visible (bright contrast)

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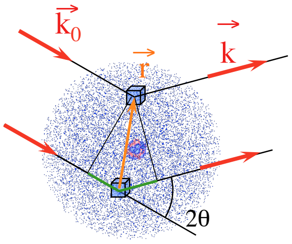
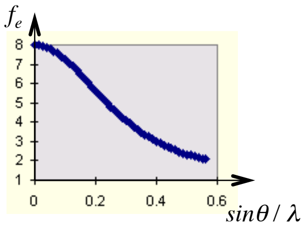
Electron scattering
comparison with x-ray, neutrons

elastic interaction between x-ray and matter :
Thomson scattering

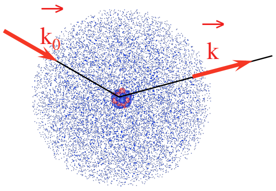
X-rays interact with electron

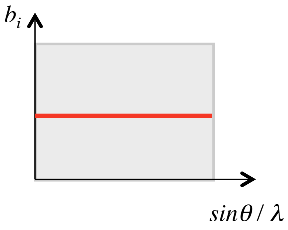




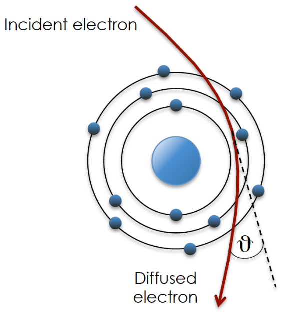
elastic interaction between neutron and matter :
nuclear interaction

Neutrons interact with nucleus

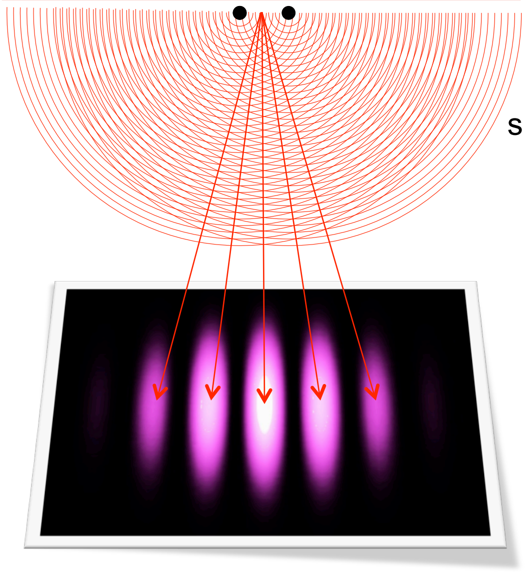




Coherent elastic electron scattering
interferences



monochromatic
plane wave



Young's experiment

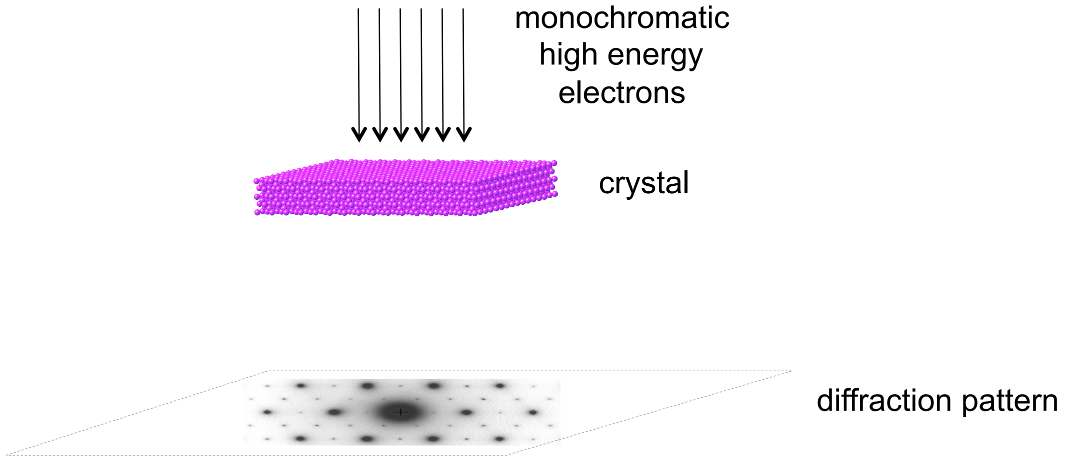
spherical wavelets

Interferences between scattered waves lead to diffraction pattern:

→ Young's fringes

Coherent elastic electron scattering

diffraction



monochromatic
high energy
electrons

crystal

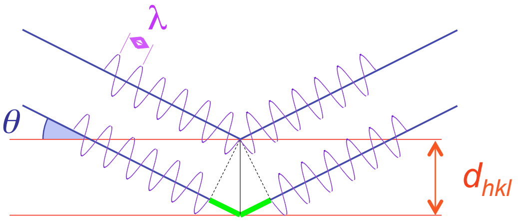
diffraction pattern

Electron diffraction

Ewald description for x-rays

The diffraction condition may be described:

in real space :

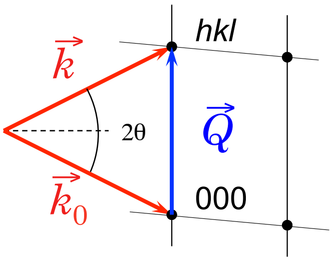


diffraction exits if optical path difference
is equal to $n \cdot \lambda$:

$$2\ d_{hkl}\ \sin\theta = n\ \lambda$$

Bragg's law

in reciprocal space :



The diffusion vector $\vec{Q}$ must be a reciprocal
lattice vector :

$$\vec{Q} = \vec{k} - \vec{k}_0 = \vec{G}^*_{hkl}$$

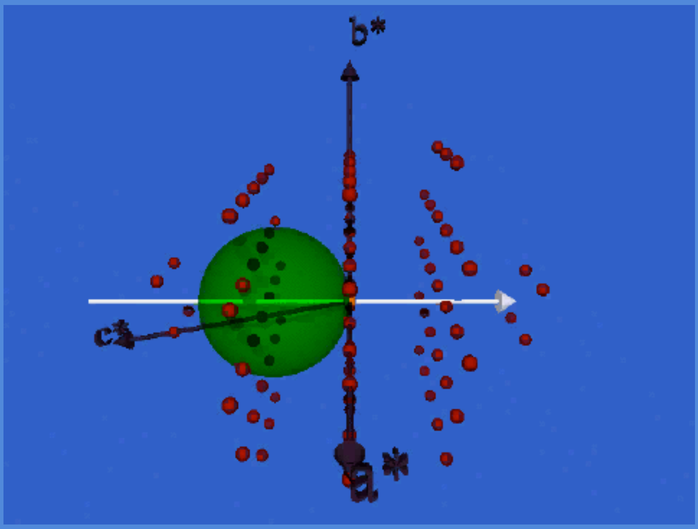
$$\left|\vec{G}^*_{hkl}\right| = \left|\vec{k} - \vec{k}_0\right| = 2\ \sin\theta \times \left|\vec{k}_0\right|$$

$$\frac{1}{d_{hkl}} = 2\ \sin\theta \times \frac{1}{\lambda}$$

Electron diffraction

Ewald description for x-rays

X-ray diffraction occurs when a reciprocal lattice node intercept the Ewald sphere



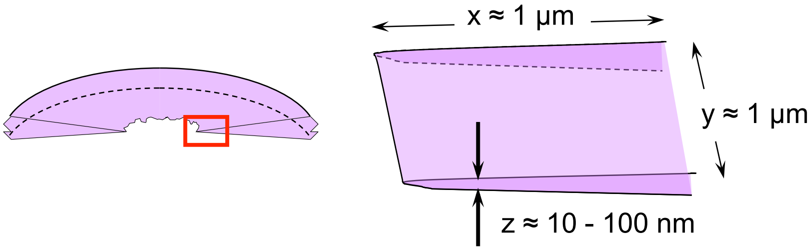
$\lambda \approx d_{hkl}$ $\Rightarrow k \approx 1/d_{hkl}$ ⇒ only one node may intercept the Ewald sphere at each time

---

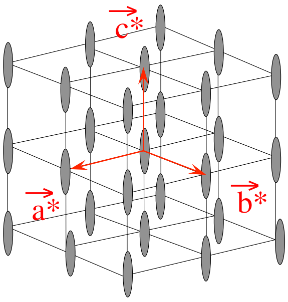
Electron diffraction in TEM (1)

influence of the sample size

TEM thin foil (prepared by ion polishing or FIB)



$$D(\vec{q}) = \int_{\Omega} \phi(\vec{r}) \cdot \mathrm{e}^{-2i\pi\, \vec{q} \cdot \vec{r}}\, d^3\vec{r}$$



Reciprocal lattice nodes are elongated in the direction for which the sample is the thinnest

Electron diffraction in TEM (2)

influence of the electron wavelength

Bragg's Law

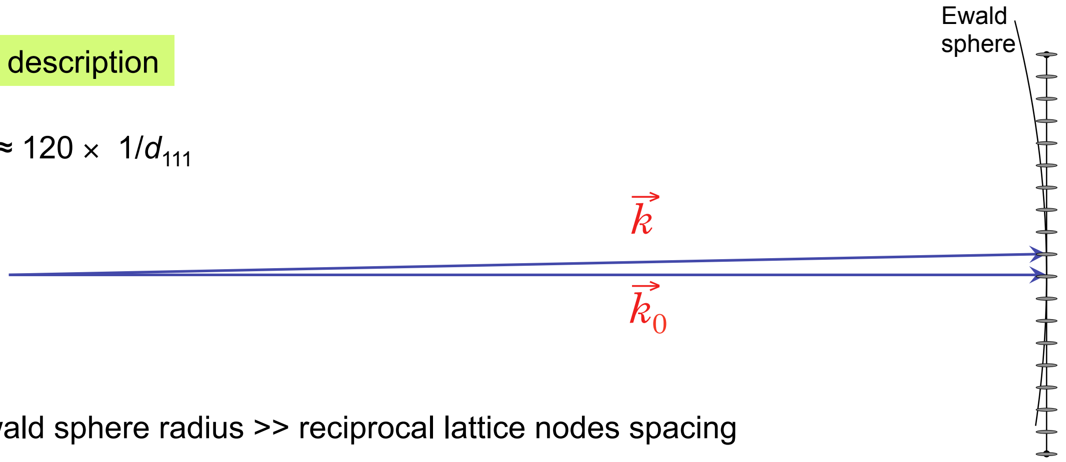
- at 200 kV, $\lambda = 0.0251$ Å
- for silicon: $d_{111} = 3.13$ Å

$\Rightarrow$ Si (111) diffraction occurs for $\theta \approx 0.22° \approx 4$ mrad

$\Rightarrow$ For high energy electron, diffraction angles are very small : **$\leq 1°$**

Ewald description

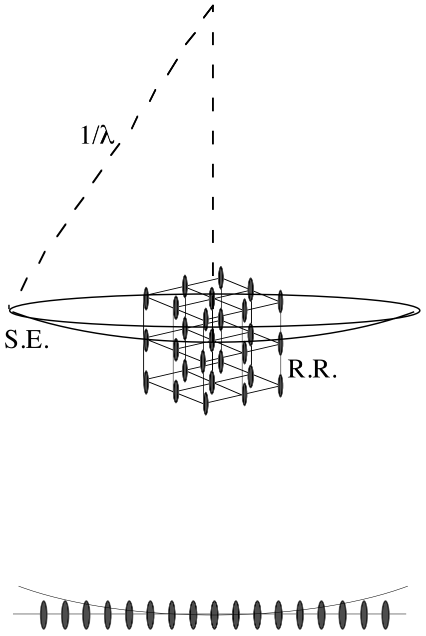
- $1/\lambda \approx 120 \times 1/d_{111}$

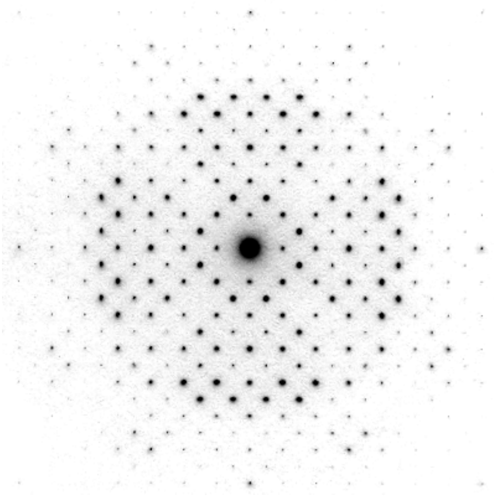


$\Rightarrow$ Ewald sphere radius >> reciprocal lattice nodes spacing

Electron diffraction in TEM

consequences of (1) and (2)

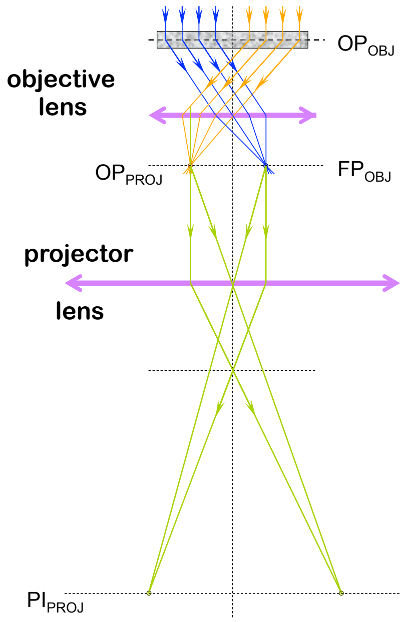


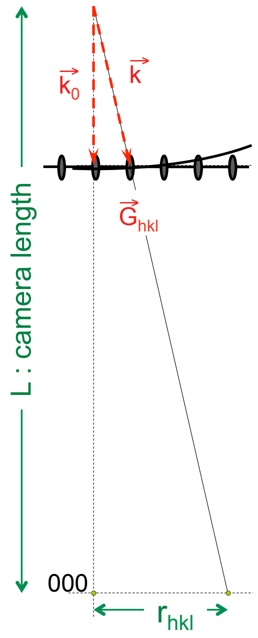


Selected Area Electron Diffraction (SAED)

Electron diffraction in TEM

determination of interplanar distances





$$\frac{|\vec{k}_0|}{L} = \frac{|\vec{G}_{hkl}|}{r_{hkl}}$$

$$\boxed{d_{hkl} = \frac{\lambda\ L}{r_{hkl}}}$$

- not very precise method : +/- 0.05 Å

Electron diffraction in TEM

Applications

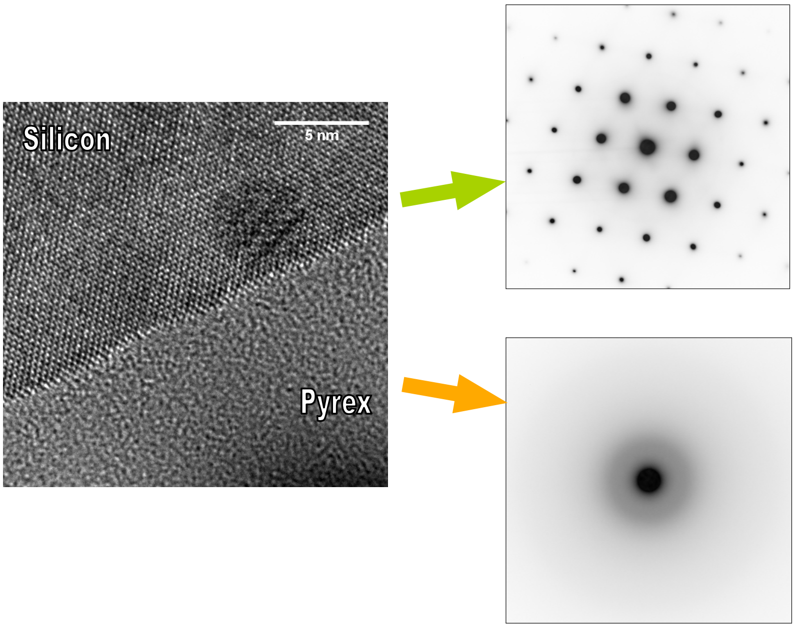
Applications

- Distinction between amorphous and crystalline materials
- Crystallography of nano-particles
- Study of multi-phases materials
- Phases identification
- Interface, defects analyses
- … so many applications !

Applications

amorphous vs crystalline materials

Silicon – Pyrex® interface



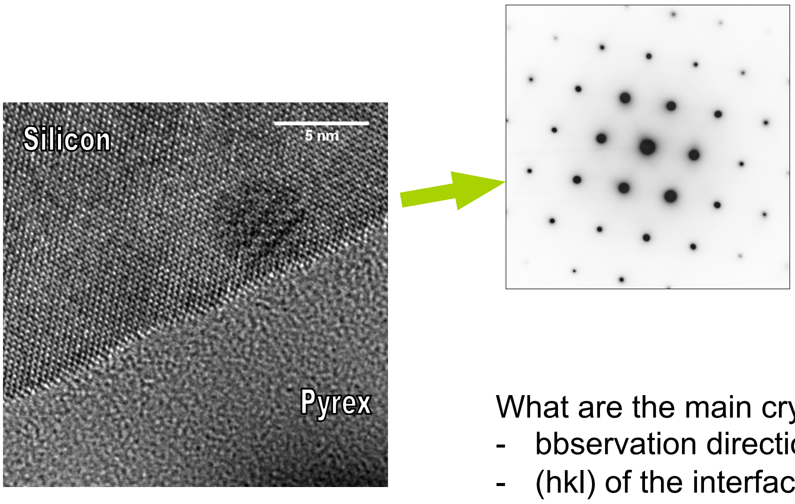
Diffraction pattern of
a crystallized material

Diffuse rings typical of
amorphous material

Applications

Identification of zone axis

Silicon – Pyrex® interface



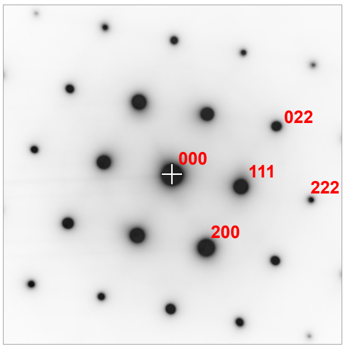
What are the main crystallographic directions ?

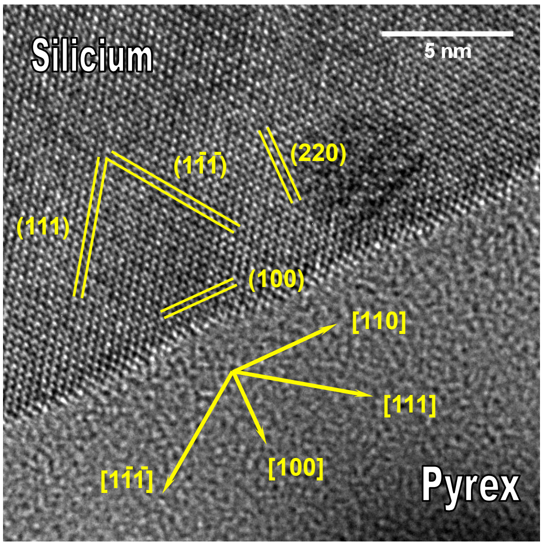
- bbservation direction ?
- (hkl) of the interface ?

→ indexation of the diffraction pattern

Applications

Identification of crystallographic features



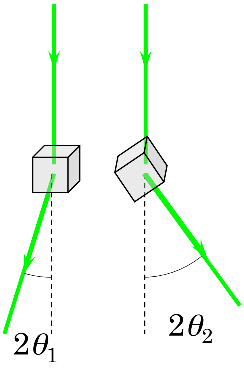


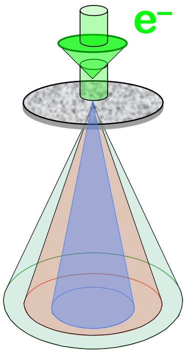
le plan d'interface entre le silicium et le pyrex est donc un plan {100}

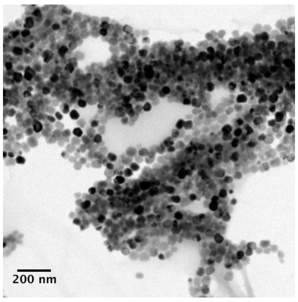
Applications

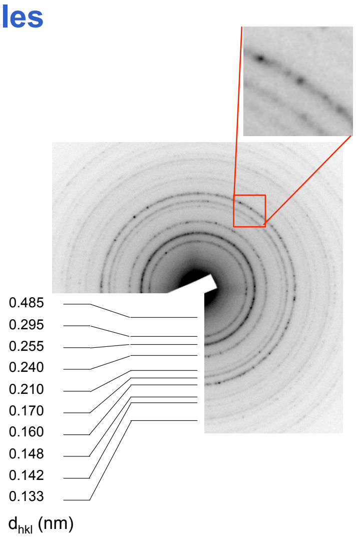
Cristallographic study of nano-particles

Electron diffraction pattern of an assembly of nanoparticles







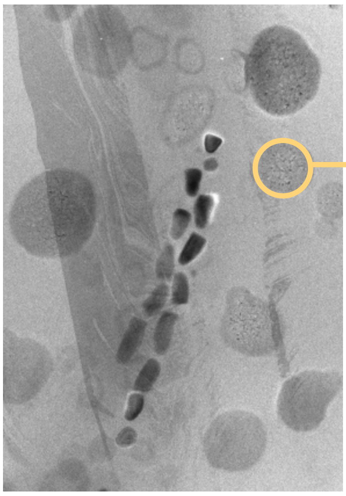


Similar to the Debye-Scherrer powder x-ray diffraction method

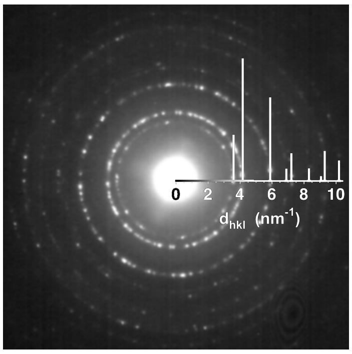
- The precision of electron diffraction lower than for x-ray diffraction

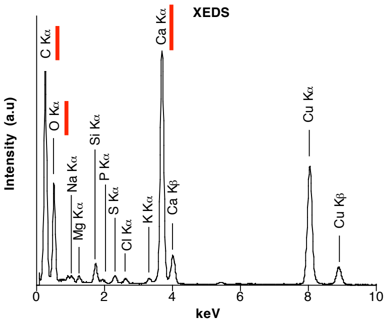
Applications
Identification of nano-crystalline phases

Identification of unknown phases



Isambert et al. *Am. Min.* (2007)





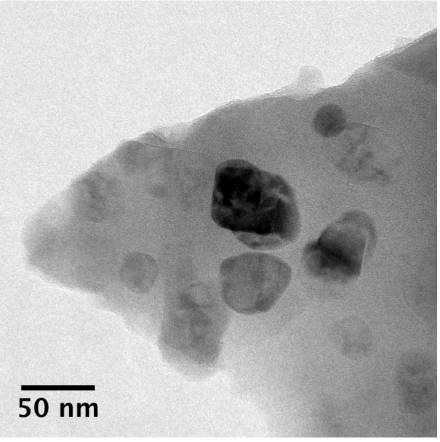
Diffraction :
compatible with CaO

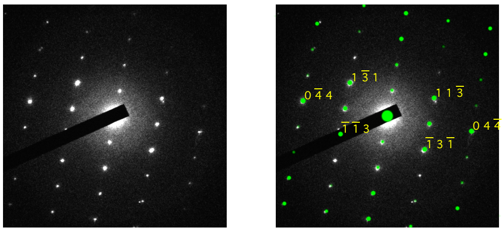
XEDS :
C - Ca - O
major elements

- For an unambiguous identification: composition analysis is mandatory !
- The precision of electron diffraction is not sufficient (≠ x-ray diffraction)

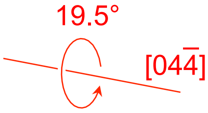
Applications
Identification of nano-(single) crystalline phases

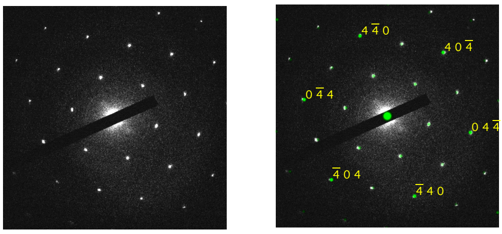
Study of a single crystal embedded in a amorphous glass
→ Electron diffraction





cubic F [112] zone axis





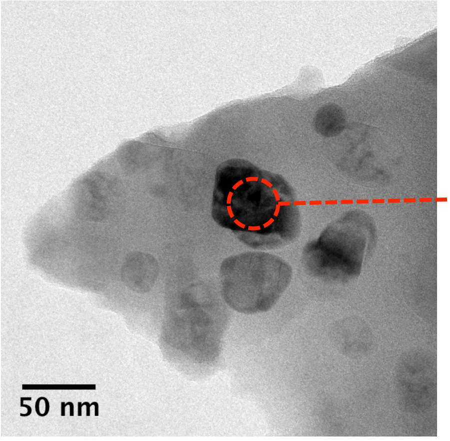
cubic F [111] zone axis

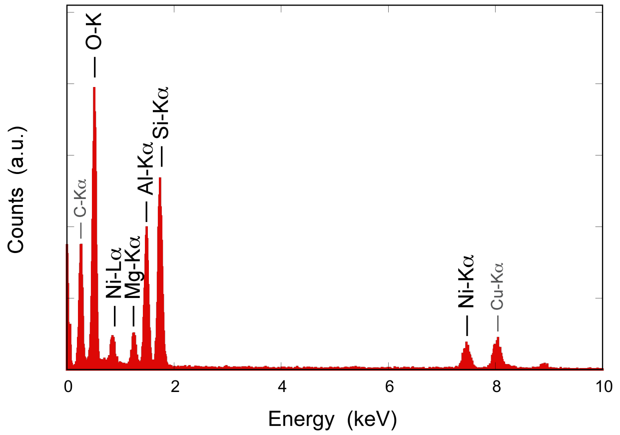
→ diffractions are compatible with a spinelle phase, *a* ≈ 8.05 Å

Several diffraction pattern are required to obtain an unambiguous identification
→ chemical analysis is highly recommended !!!

Applications
Identification of nano-(single) crystalline phases

Study of a single crystal embedded in a amorphous glass
→ chemical analysis

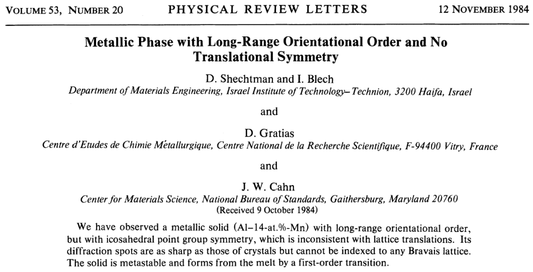




→ composition compatible with spinelle phase $NiAl_2O_4$

Mineralogical idenditification : - diffraction(s)
- chemical analysis

Applications
Discovery of new phases



VOLUME 53, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1984

Metallic Phase with Long-Range Orientational Order and No Translational Symmetry

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and

D. Gratias
Centre d'Etudes de Chimie Métallurgique, Centre National de la Recherche Scientifique, F-94400 Vitry, France

and

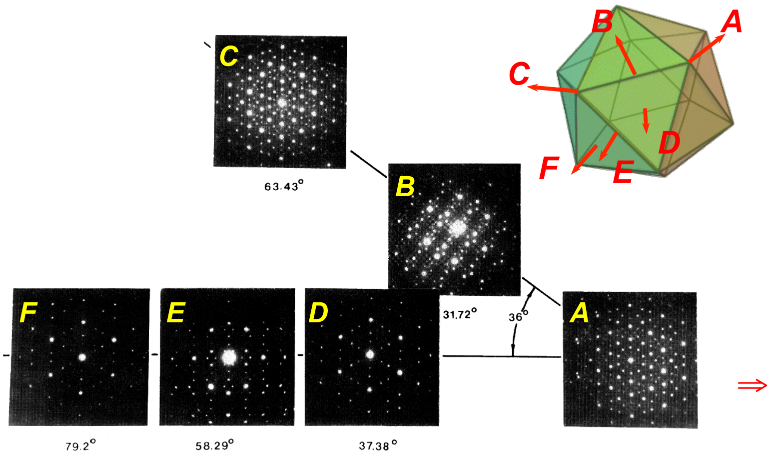
J. W. Cahn
Center for Materials Science, National Bureau of Standards, Gaithersburg, Maryland 20760
(Received 9 October 1984)

We have observed a metallic solid (Al–14-at.%-Mn) with long-range orientational order, but with icosahedral point group symmetry, which is inconsistent with lattice translations. Its diffraction spots are as sharp as those of crystals but cannot be indexed to any Bravais lattice. The solid is metastable and forms from the melt by a first-order transition.

1984 : discovery of an ordered
non-periodic phase

- $Al_{86}Mn_{14}$ alloy
- icosahedral symmetry ($m\bar{3}5$)

⇒ QUASI-CRYSTALS



D. Shechtmann
2011 Chemistry Nobel Prize

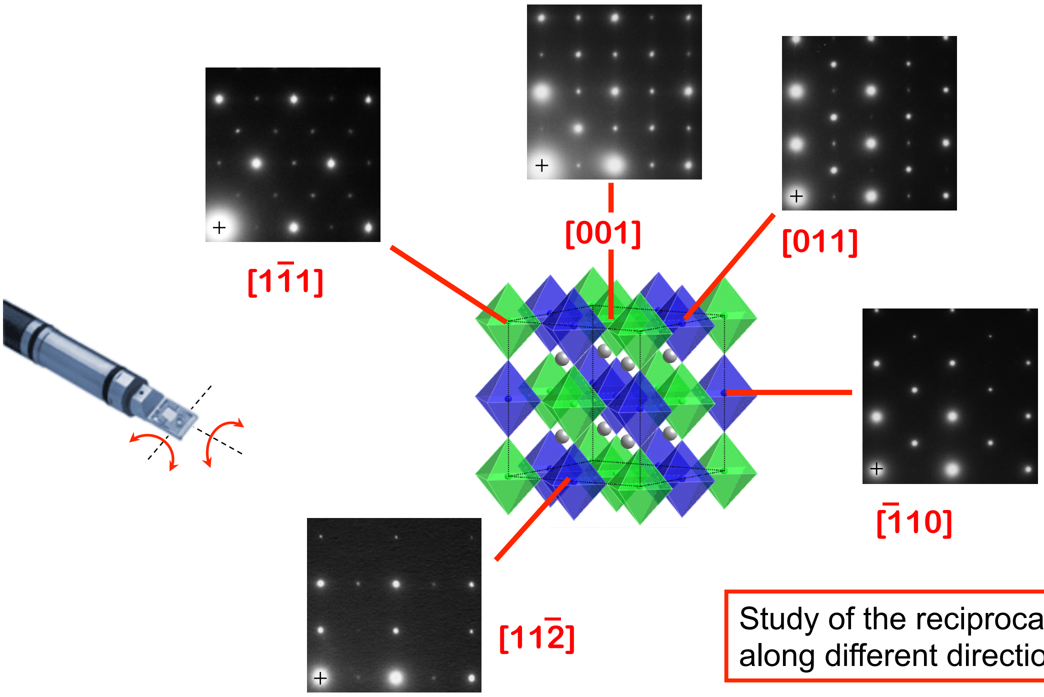
- $Al_{86}Mn_{14}$ alloy constituted of µm-sized quasi-crystals

⇒ Electron Diffraction mandatory !!!

Applications

Study of local ordering in Pb_2ScNbO_6 complex perovskite

Interest of a double-tilt specimen holder



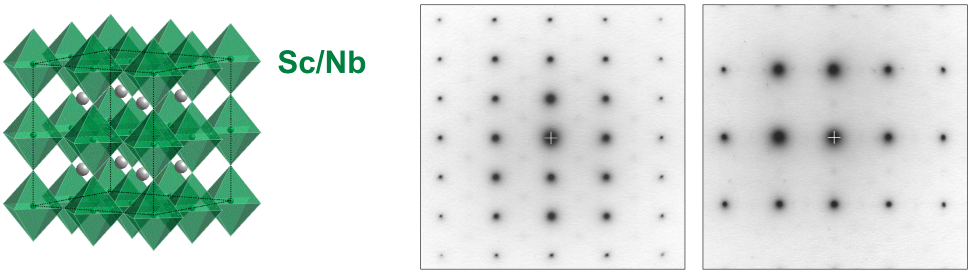
Study of the reciprocal space along different directions

Applications

Study of local ordering in Pb_2ScNbO_6 complex perovskite

Evidence of cation ordering with electron diffraction

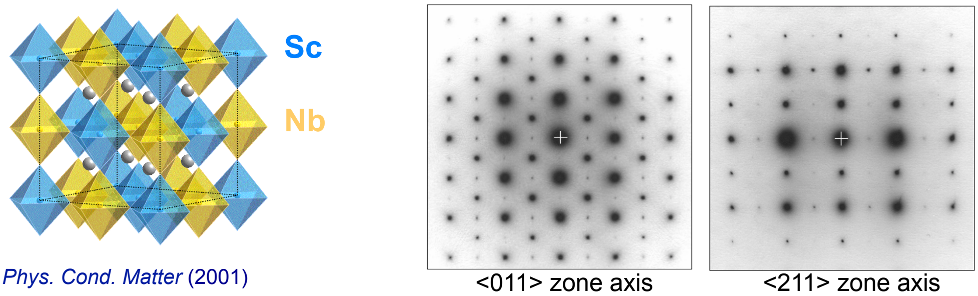
Short Range Order : no superstructure reflection



<011> zone axis <211> zone axis

$Pm\bar{3}m$

Long Range Order : intense superstructure reflections



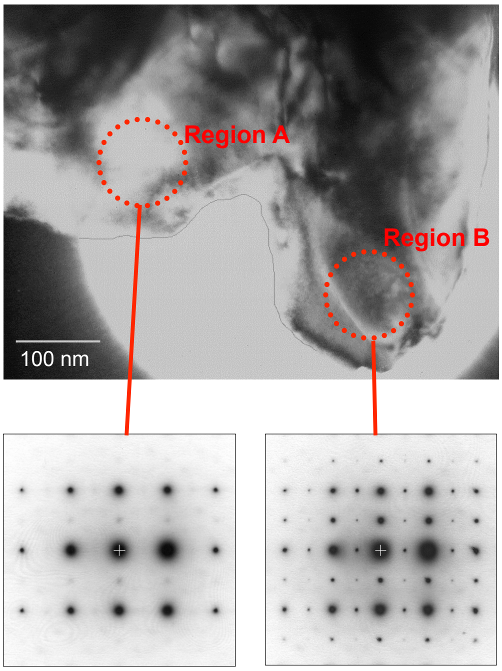
<011> zone axis <211> zone axis

$Fm\bar{3}m$

Perrin *et al.*, *J. Phys. Cond. Matter* (2001)

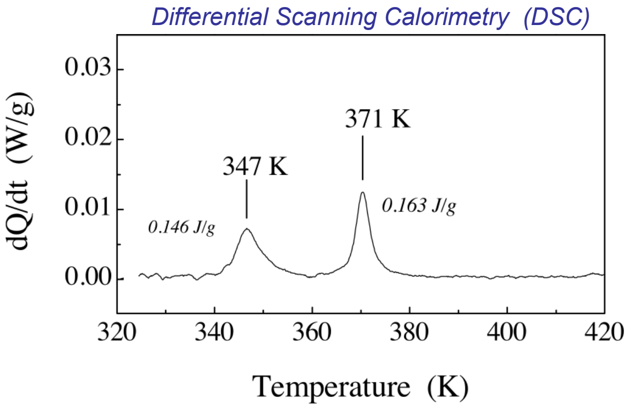
Applications

Study of local ordering in Pb_2ScNbO_6 complex perovskite



- coexistence of ordered and disordered phases in the same sample

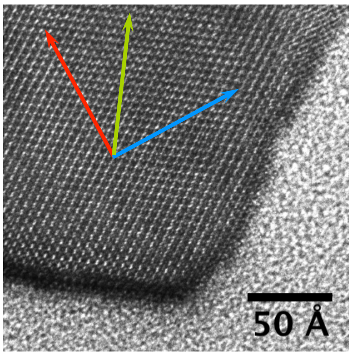
⇒ Sc^{3+}/Nb^{5+} ordering : 1st order transition

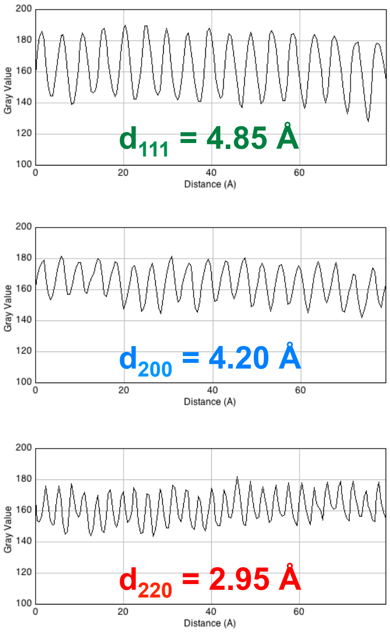


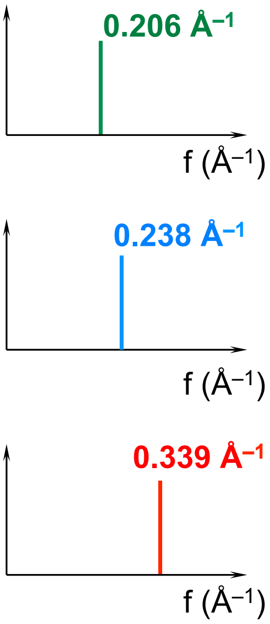
Perrin *et al.*, *J. Phys. Cond. Matter* (2001)

Electron Diffraction and Fourier Analysis

Local analysis from High Resolution images (HREM)



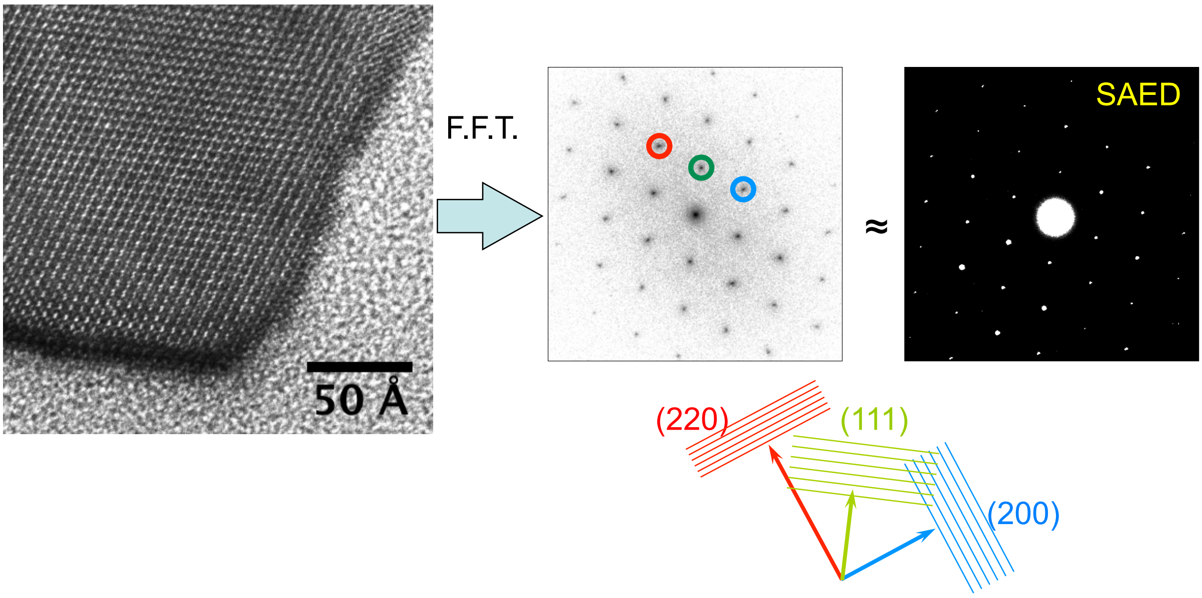




Analysis of the spatial frequencies of the image

Electron Diffraction and Fourier Analysis

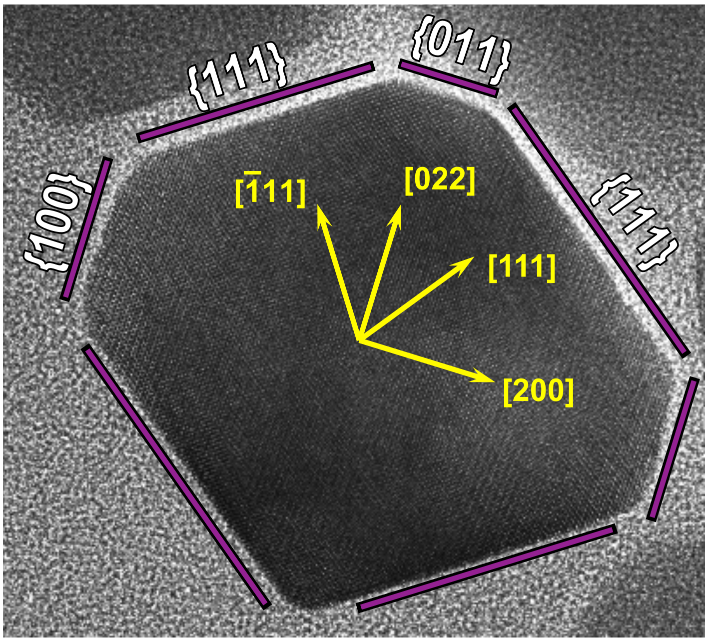
Local analysis from High Resolution images (HREM)



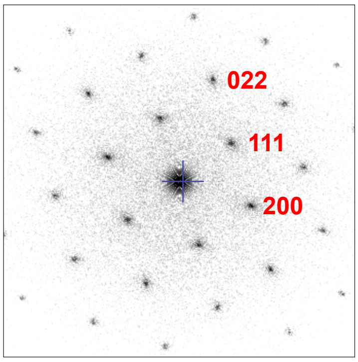
Numerical diffraction using FFT may be useful for nano-particles study

Electron Diffraction and Fourier Analysis

Local analysis from High Resolution images (HREM)



Crystallographic analysis
using Fast Fourier Transform



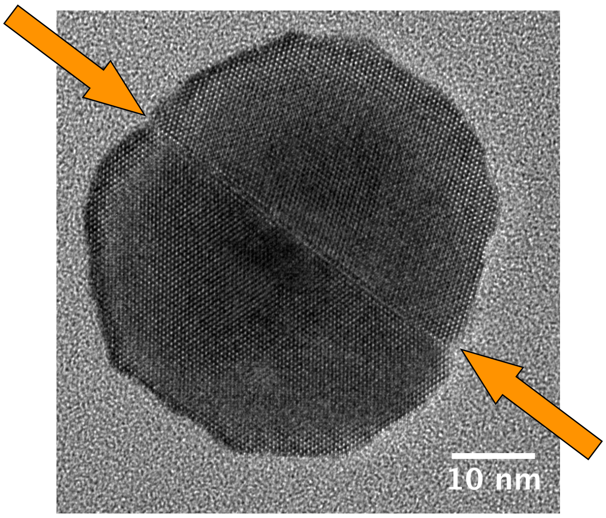
The 3-D morphology cannot be deduced from this image

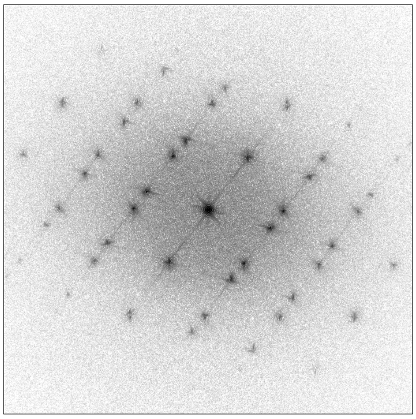
this is a projection !!! → ELECTRON TOMOGRAPHY

Electron diffraction applications

Study of defects

Planar defects in biogenic nano-magnetites

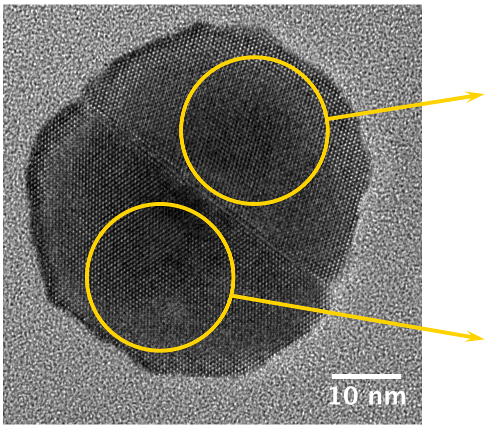


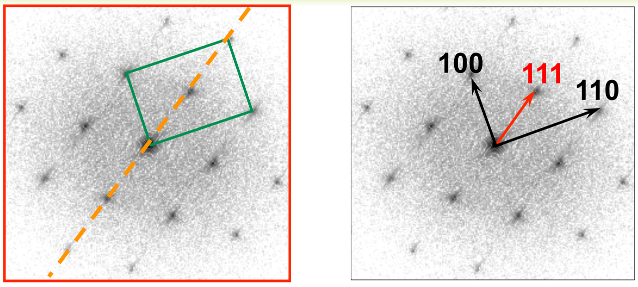


Unusual diffraction !!!

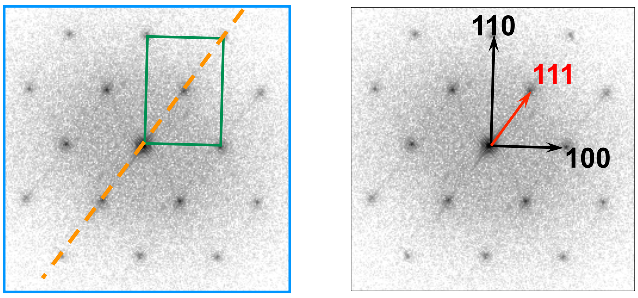
Electron diffraction applications

Study of defects





[110] zone axis

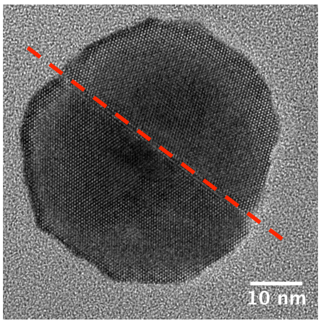


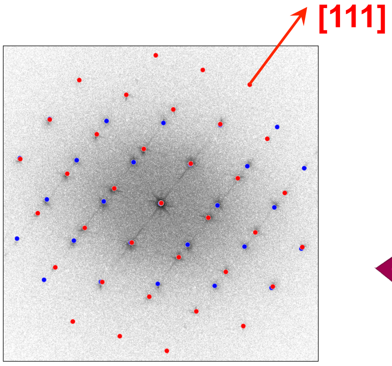
[110] zone axis

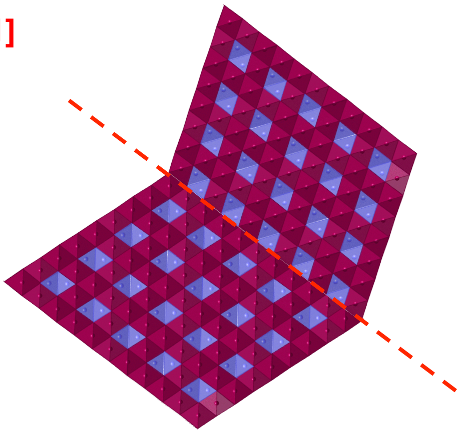
Two crystals share a common orientation : [111]
→ **twinning**

Electron diffraction applications

Study of defects





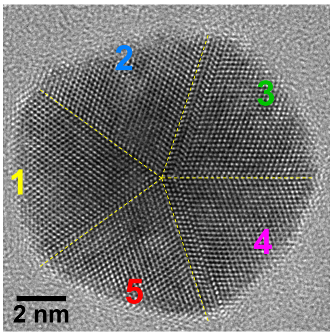


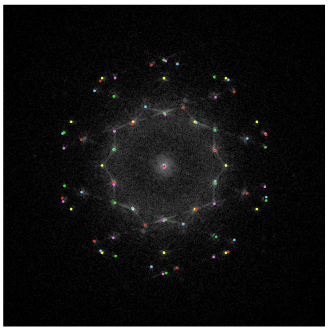
(111) twinning plane

Electron diffraction applications

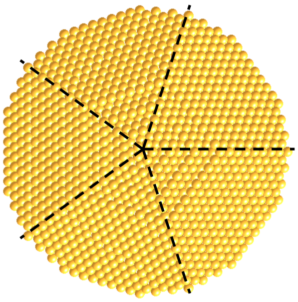
Study of defects

multiple-twinned Gold nano-particles

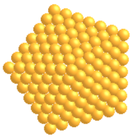


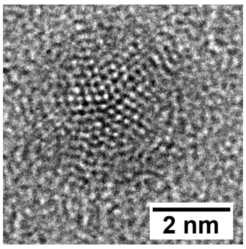


The overall diffraction pattern is the superimposition of 5 individual <110> zone axis diffraction patterns rotated by 72° one with respect to the other



→ penta-twinned Gold nanoparticles

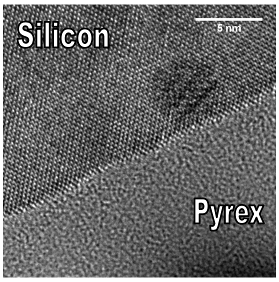


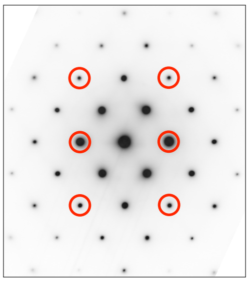


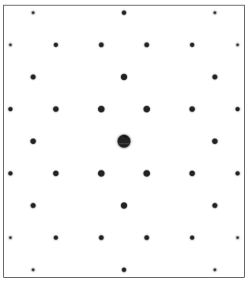
Gold clusters are also twinned

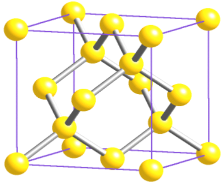
Electron Diffraction

experimental artifact : multiple diffraction




experimental


theoretical


Si : Fd$\bar{3}$m

According the Fd$\bar{3}$m spacegroup of silicon,

reflections for which $h + k + l = 4n + 2$ are forbidden

⇒ they shouldn't be observed !

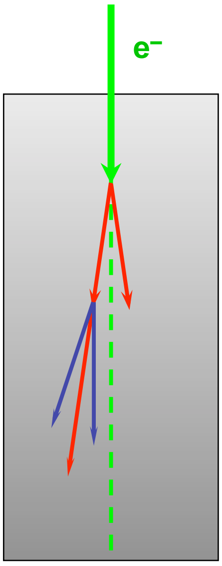
- This phenomenon is almost systematic for zone axis electron diffraction pattern
- There is no direct relationship between structure factor and observed intensities

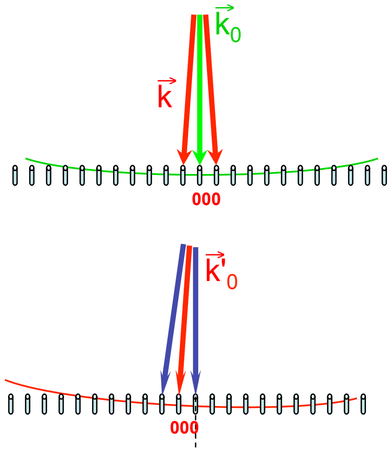
origin : multiple scattering

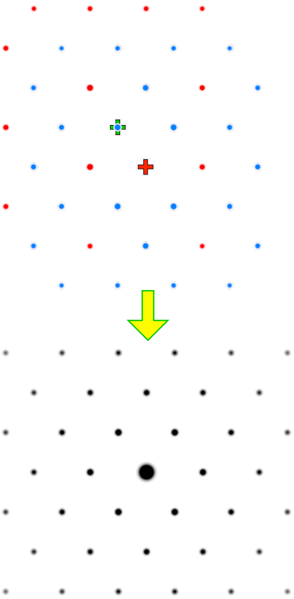
Electron Diffraction

experimental artifact : multiple diffraction

- Multiple scattering of electron occurs through the sample thickness



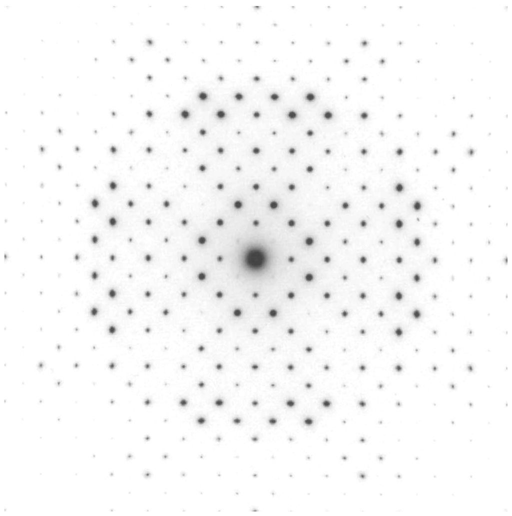




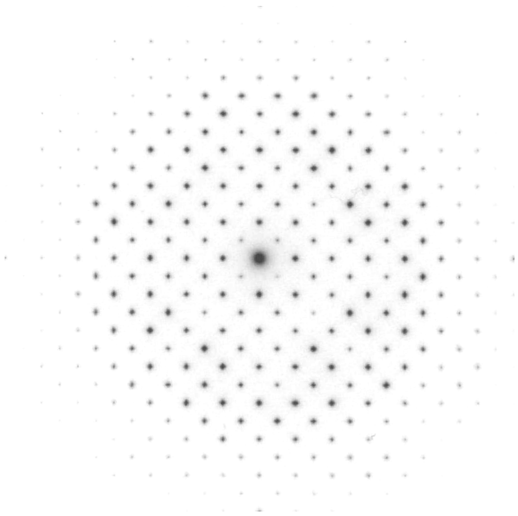
- electron diffraction is generally not quantitative
- multiple scattering is amplified by sample thickness

Electron Diffraction
experimental artifact : multiple diffraction

Influence of the sample thickness



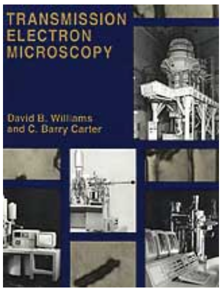
Thin part of the sample



Thick part of the sample

- multiple scattering is amplified by sample thickness

References



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