Electron Microscopy

4. TEM

Electron diffraction

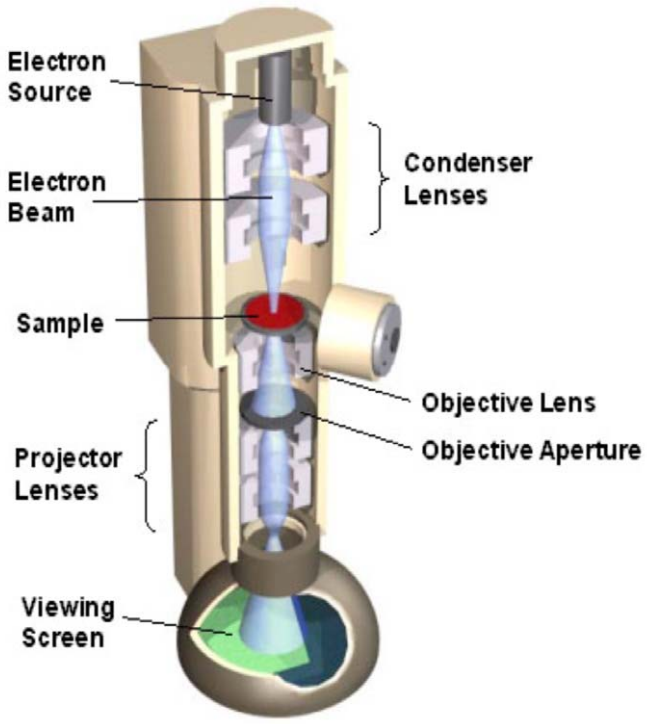
Basics: interactions, basic modes,
Diffraction: elastic scattering theory, reciprocal space, diffraction pattern,

Laue zones

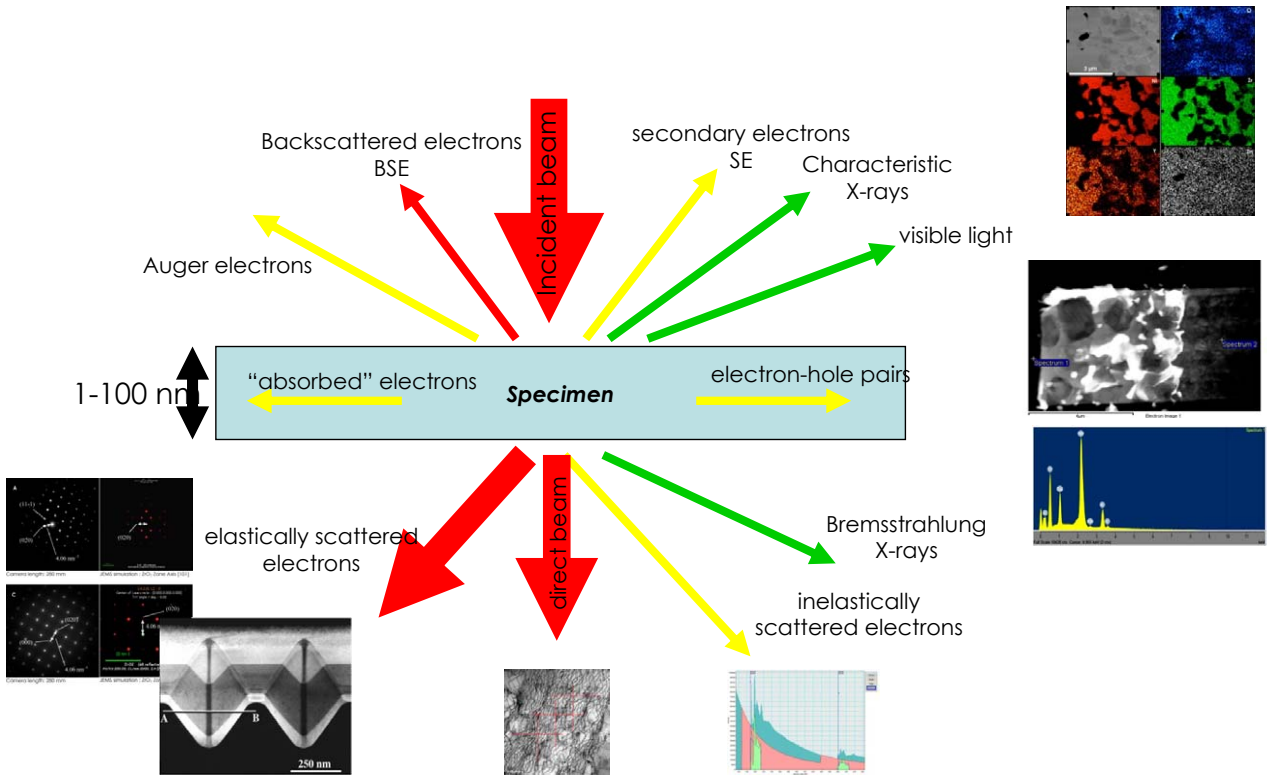
Diffraction phenomena

XRD x-ray diffraction

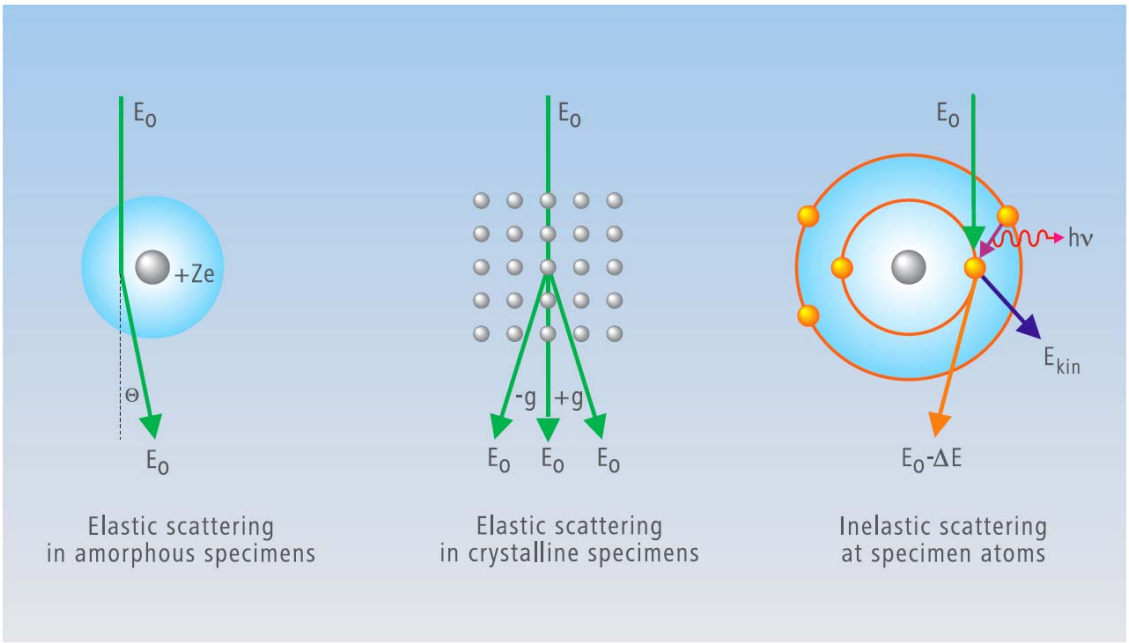
Typical TEM



Signals from a thin sample



Interaction of high energetic electrons with matter

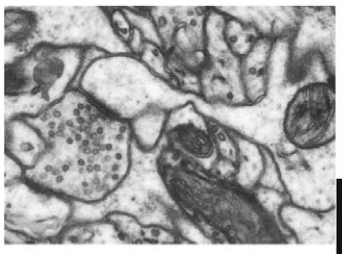


biological samples, polymers

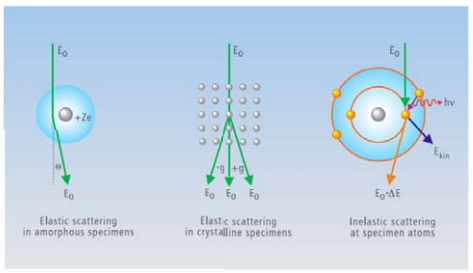
crystalline structure, defect analysis, high-resolution TEM

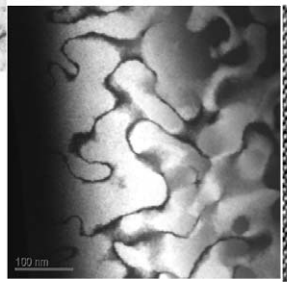
chemical analysis, spectroscopy

Interaction -> contrast

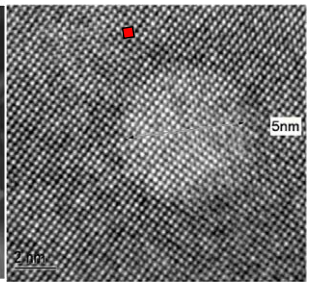


Thin section of mouse brain: mass contrast of stained membrane structures (G.Knott)

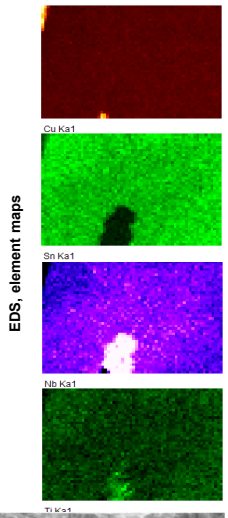


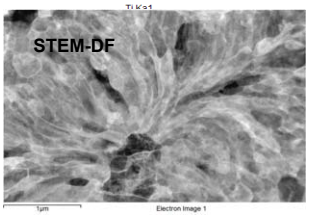


Dark field image of differently ordered domains: Diffraction contrast



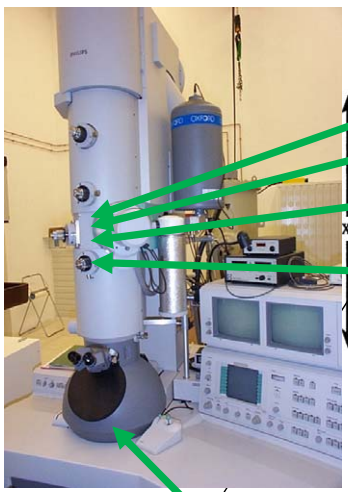
High-resolution image: Image contrast due to interference between transmitted and diffracted beam



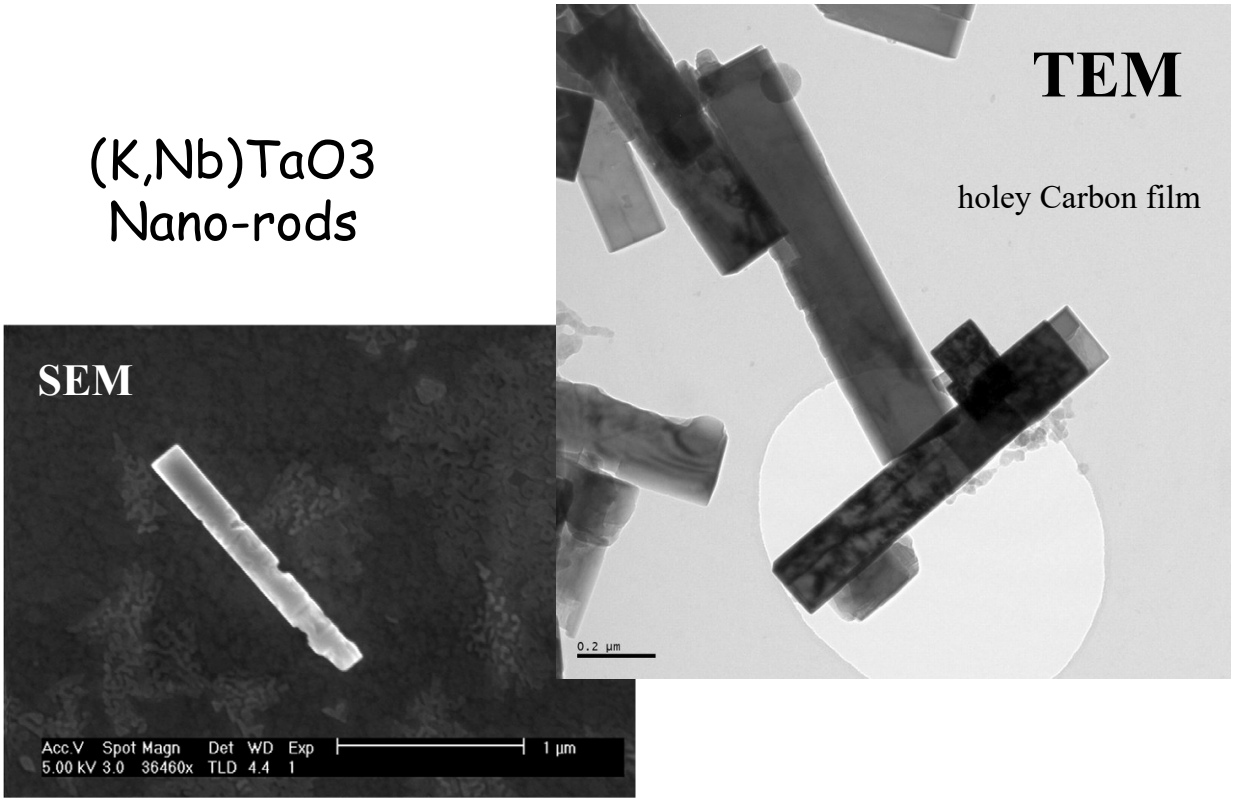


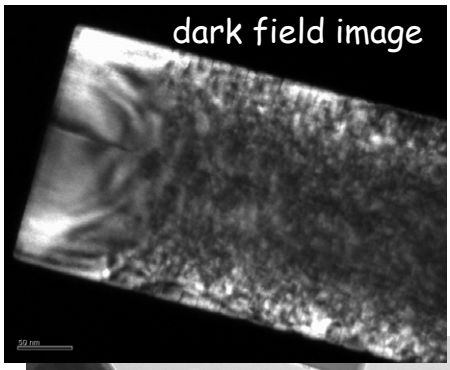
Element distribution maps Of Nb3Sn superconductor

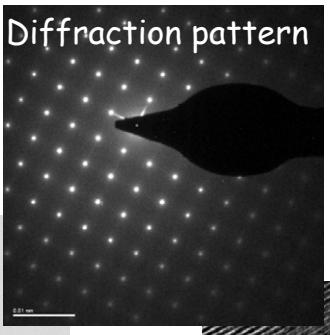
Two basic operation modes Diffraction <-> Image



(K,Nb)TaO3 Nano-rods

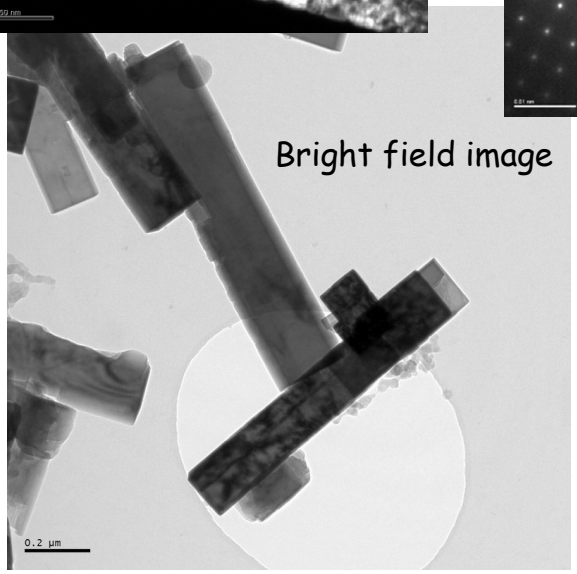


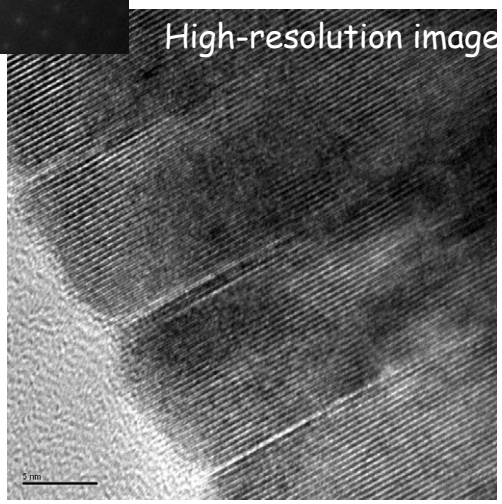




Shape, lattice parameters, defects, lattice planes

(K,Nb)O3 Nano-rods





Diffraction theory

- Introduction to electron diffraction
- Elastic scattering theory
- Basic crystallography & symmetry
- Electron diffraction theory
- Intensity in the electron diffraction pattern

Thanks to Dr. Duncan Alexander for slides

Why use electron diffraction?

Diffraction: constructive and destructive interference of waves

• wavelength of fast moving electrons much smaller than spacing of atomic planes
=> diffraction from atomic planes (e.g. 200 kV e^-, λ = 0.0025 nm)

• electrons interact very strongly with matter => strong diffraction intensity
(can take patterns in seconds, unlike X-ray diffraction)

• spatially-localized information
($\gtrsim$ 200 nm for selected-area diffraction;
2 nm possible with convergent-beam electron diffraction)

• close relationship to diffraction contrast in imaging

• orientation information

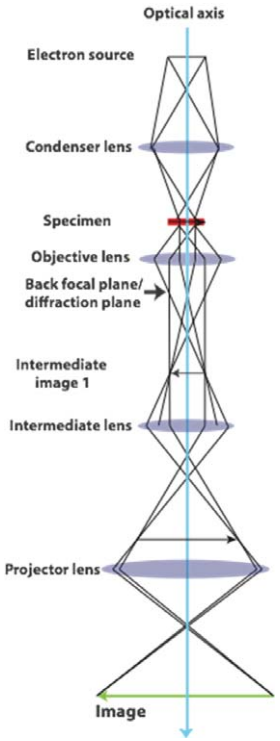
• immediate in the TEM!

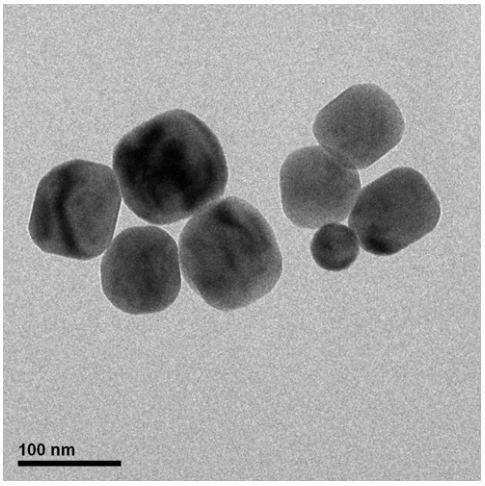
(diffraction from only selected set of planes in one pattern - e.g. only 2D information)

(limited accuracy of measurement - e.g. 2-3%)

(intensity of reflections difficult to interpret because of dynamical effects)

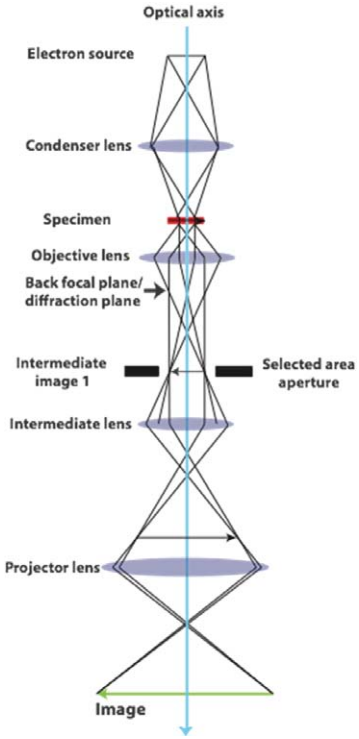
Image formation

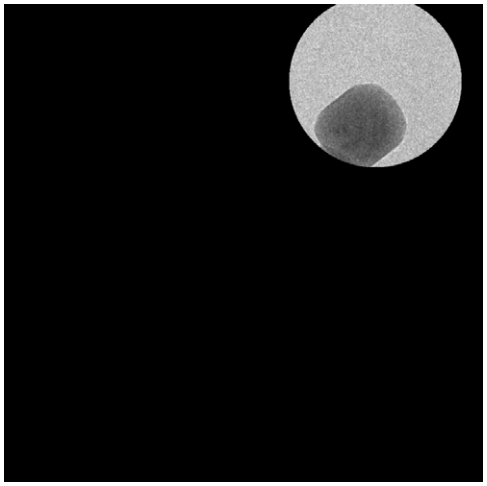




$BaTiO_3$ nanocrystals (Psaltis lab)

Area selection

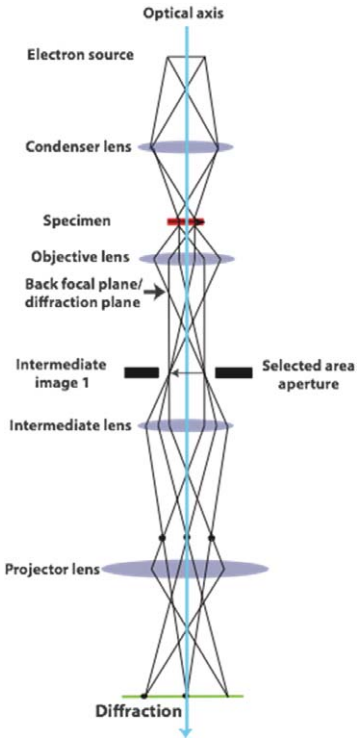


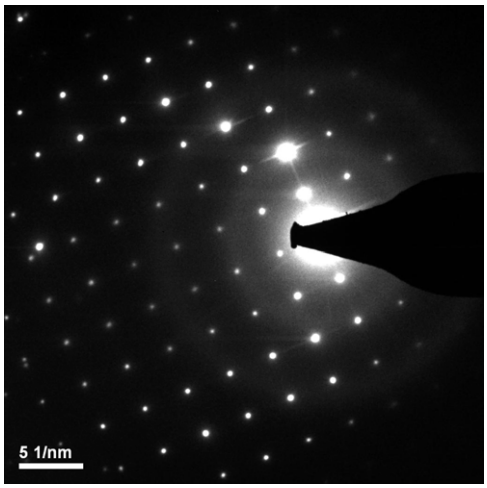


$BaTiO_3$ nanocrystals (Psaltis lab)

Insert selected area aperture to choose region of interest

Take selected-area diffraction pattern





Press "D" for diffraction on microscope console - alter strength of intermediate lens and focus diffraction pattern on to screen

Find cubic $BaTiO_3$ aligned on [0 0 1] zone axis

Scatter range of electrons, neutrons and X-rays

(99% of intensity lost)

Elément (masse spécifique)	4-Be 1.84 g/cm³	13-Al 2.7 g/cm³	29-Cu 8.93 g/cm³	82-Pb 11.3 g/cm³
Rayons X Cu-Kα λ=1.54 Å Mo-Kα λ=0.71 Å	16 mm 83 mm	0.35 mm 3.3 mm	0.10 mm 0.10 mm	0.017 mm 0.034 mm
Neutrons thermiques $\lambda \approx 1.08$ Å	89 m	6 m	0.26 m	14 m
Électrons λ=0.037 Å à 100 kV λ=0.020 Å à 300 kV	39 µm	42 µm ~330 µm	11 µm	0.6 µm

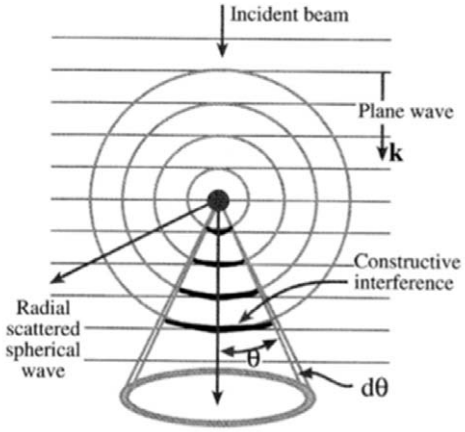
electron, neutron X-ray scattering

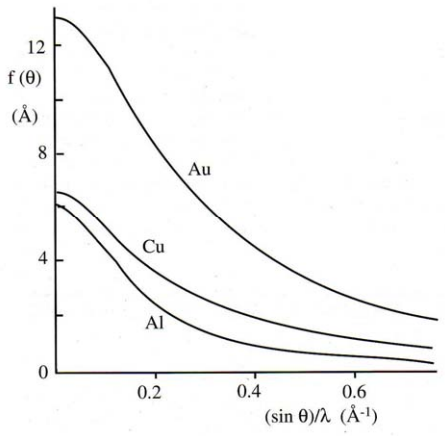
wave	Wavelength λ	Source	Scattering at	Differentiation of	Sample size
X-rays	0.07nm 0.15nm	X-ray tubes synchrotrons	Electron cloud	Lattice parameters Unit cell	0.1mm
Electrons	2pm @300keV	e guns (SEM/TEM)	Potential distribution (electrons & nucleus)	Lattice parameters, Orientations	0.1um
Neutrons (1)	~0.1nm	Nuclear reactors	Nuclear scattering (nucleus)	LP, isotopes	m
Neutrons (2)	"	"	Magnetic spin (outer electrons)	Oxidation states	m

Scattering power: n : X-ray : e = 1 : 10 : 10^4

Scattering theory - Atomic scattering factor

Consider coherent elastic scattering of electrons from atom





$$\psi(\mathbf{r}) = e^{ikz} + f(\theta)\frac{e^{ikr}}{r},$$

Atomic scattering factor for electrons

Differential elastic scattering cross section:

$$\frac{d\sigma(\theta)}{d\Omega} = |f(\theta)|^2$$

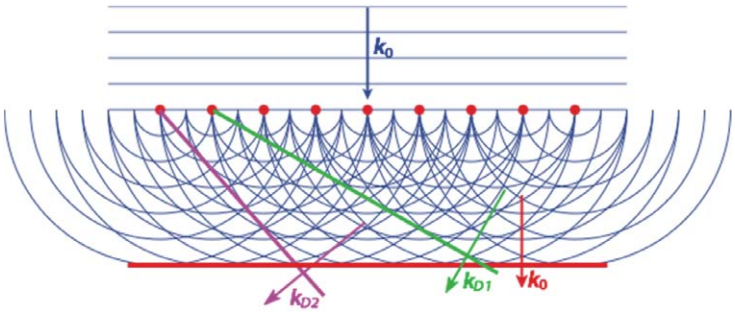
$$f(\theta) = \frac{\left(1 + \frac{E_0}{m_0 c^2}\right)}{8\pi}\left(\frac{\lambda}{\sin\frac{\theta}{2}}\right)(Z - f_x)$$

The **Mott-Bethe formula** is used to calculate electron form factors from X-ray form factors (f_x)

Scattering theory - Huygen's principle

Periodic array of scattering centres (atoms)

Plane electron wave generates secondary wavelets

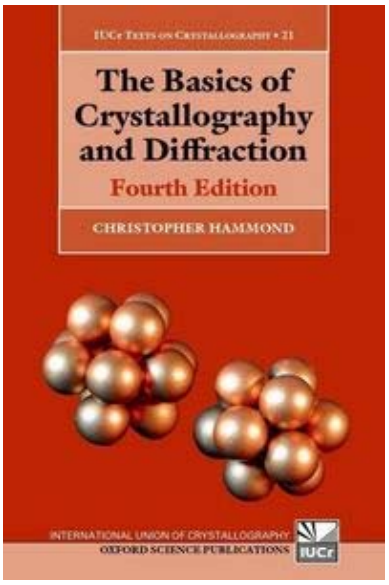


Secondary wavelets interfere =>
strong direct beam and multiple orders of diffracted beams from constructive interference

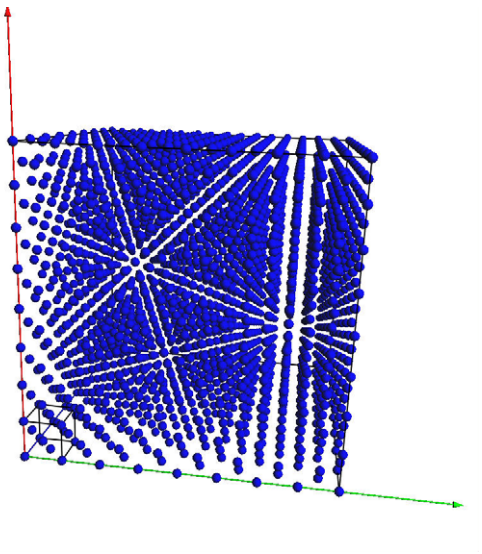
Atoms closer together => scattering angles greater

=> Reciprocity!

Basic crystallography & symmetry



Basic crystallography
Crystals: translational periodicity & symmetry

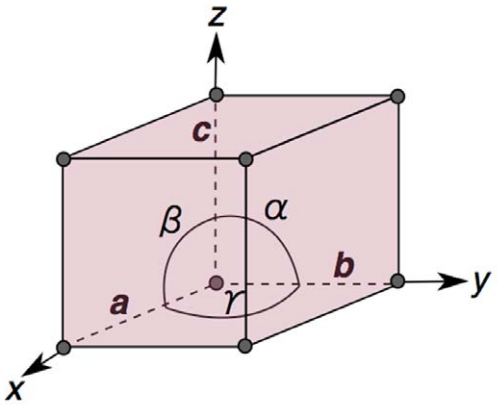


Repetition of translated structure to infinity

Crystallography: the unit cell

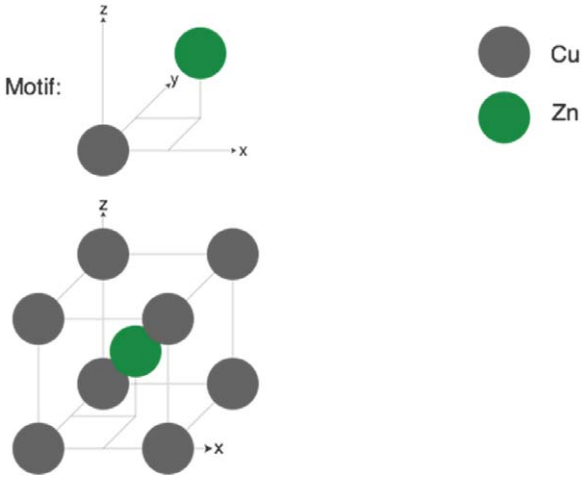
Unit cell is the smallest repeating unit of the crystal lattice
Has a lattice point on each corner (and perhaps more elsewhere)

Defined by lattice parameters *a*, *b*, *c* along axes *x*, *y*, *z*
and angles between crystallographic axes: $\alpha = b\hat{}c$; $\beta = a\hat{}c$; $\gamma = a\hat{}b$



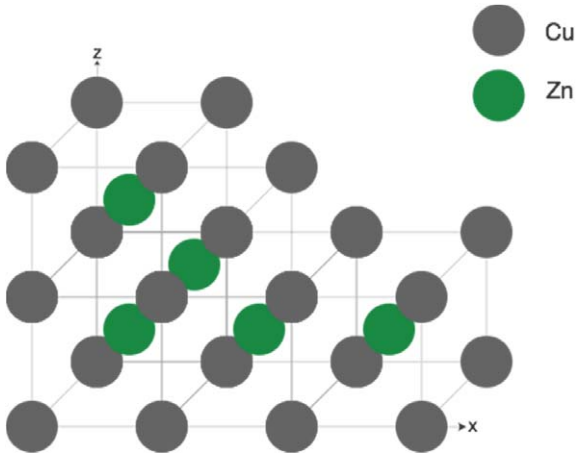
Building a crystal structure

Use example of CuZn brass
Choose the unit cell - for CuZn: primitive cubic (lattice point on each corner)
Choose the motif - Cu: 0, 0, 0; Zn: ½,½,½
Structure = lattice +motif => Start applying motif to each lattice point



Building a crystal structure

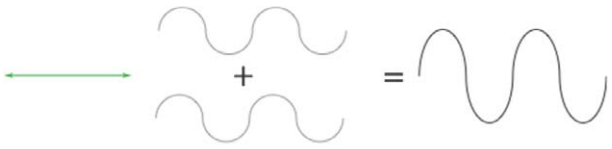
Use example of CuZn brass
Choose the unit cell - for CuZn: primitive cubic (lattice point on each corner)
Choose the motif - Cu: 0, 0, 0; Zn: ½,½,½
Structure = lattice +motif => Start applying motif to each lattice point
Extend lattice further in to space

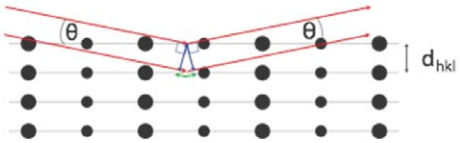


Diffraction theory - Bragg law

Path difference between reflection from planes distance d_{hkl} apart = $2d_{hkl}\sin\theta$

=> Bragg law:
$n\lambda = 2d_{hkl}\sin\theta$



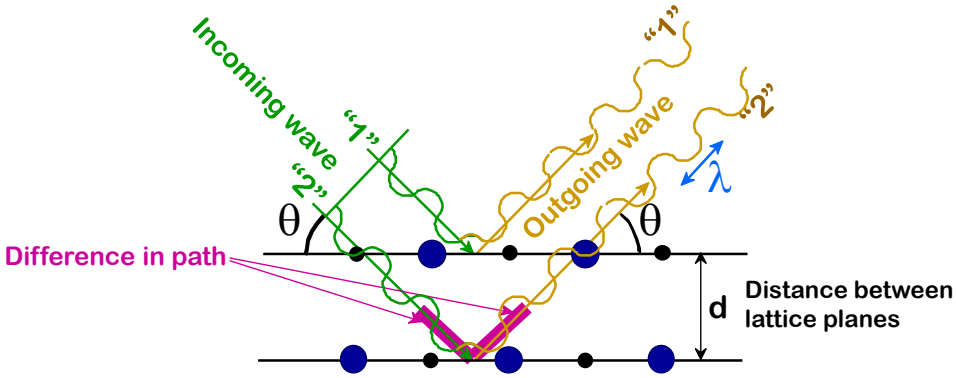


Electron diffraction: $\lambda \sim 0.001$ nm
therefore: $\lambda << d_{hkl}$
=> small angle approximation: $n\lambda \approx 2d_{hkl}\theta$
Reciprocity: scattering angle $\theta \sim d_{hkl}^{-1}$

Bragg's law

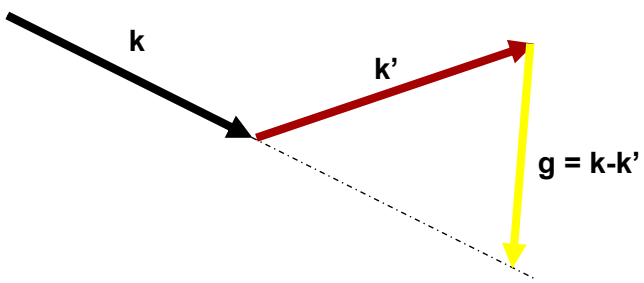
$2\sin\theta\, d_{hkl} = n\lambda$

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



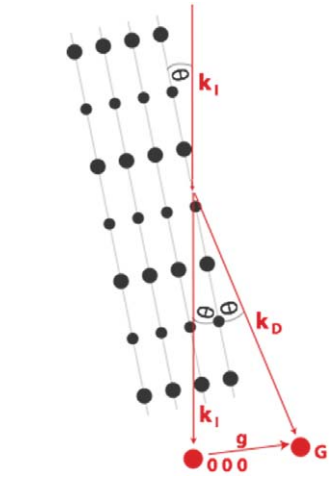
Elastic diffraction

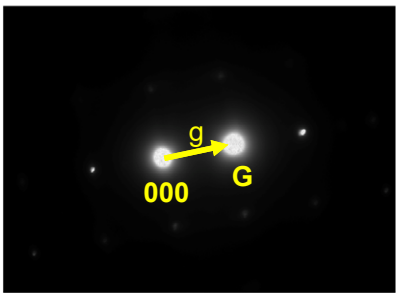
$|\mathbf{k}| = |\mathbf{k'}|$



Periodic arrangement of lattice planes:
g : reciprocal lattice vector

Diffraction theory - 2-beam condition





Observed diffraction pattern

Diffraction vector, $\mathbf{g}_{hkl}$

$$2\theta_B = \frac{\lambda}{d_{hkl}}$$

$$|g_{hkl}| = \frac{1}{d_{hkl}}$$

2-beam condition: strong scattering from single set of planes

Multi-beam scattering condition

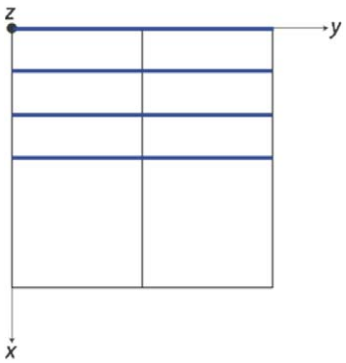
Electron beam parallel to low-index crystal orientation [U V W] = zone axis

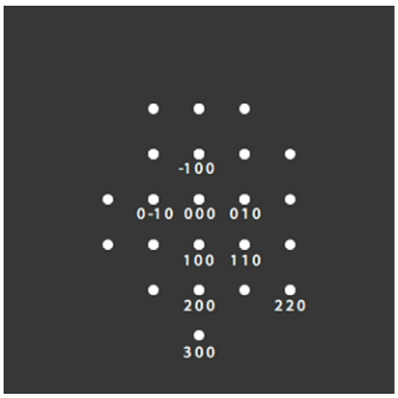
Crystal "viewed down" zone axis is like diffraction grating with planes parallel to e-beam

In diffraction pattern obtain spots perpendicular to plane orientation

Example: primitive cubic with e-beam parallel to [0 0 1] zone axis

2 x 2 unit cells

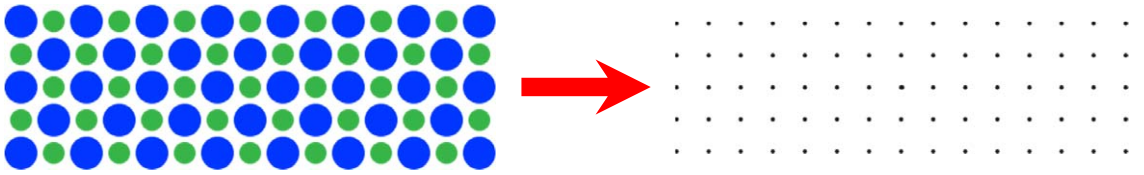




Note reciprocal relationship: smaller plane spacing => larger indices (*h k l*)
& greater scattering angle on diffraction pattern from (0 0 0) direct beam

The reciprocal lattice

In diffraction we are working in "reciprocal space"; useful to transform the crystal lattice in to a "reciprocal lattice" that represents the crystal in reciprocal space:



Real lattice vector: $\mathbf{r}_n = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$

Reciprocal lattice vector: $\mathbf{r}^* = m_1\mathbf{a}^* + m_2\mathbf{b}^* + m_3\mathbf{c}^*$

where:

$$\mathbf{a}^*.\mathbf{b} = \mathbf{a}^*.\mathbf{c} = \mathbf{b}^*.\mathbf{c} = \mathbf{b}^*.\mathbf{a} = \mathbf{c}^*.\mathbf{a} = \mathbf{c}^*.\mathbf{b} = 0$$

$$\mathbf{a}^*.\mathbf{a} = \mathbf{b}^*.\mathbf{b} = \mathbf{c}^*.\mathbf{c} = 1$$

i.e. $\mathbf{a}^* = (\mathbf{b} \wedge \mathbf{c})/V_C$ V_C: volume of unit cell

For scattering from plane (h k l) the diffraction vector:

$\mathbf{g}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

Plane spacing: $d_{hkl} = \frac{1}{|\mathbf{g}_{hkl}|}$

Ewald sphere

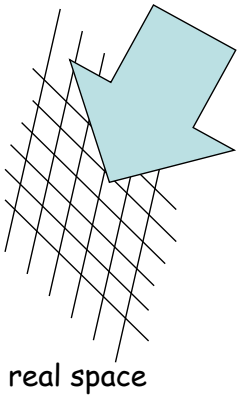
A vector in reciprocal space:

$\mathbf{g}_{hkl} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^*$

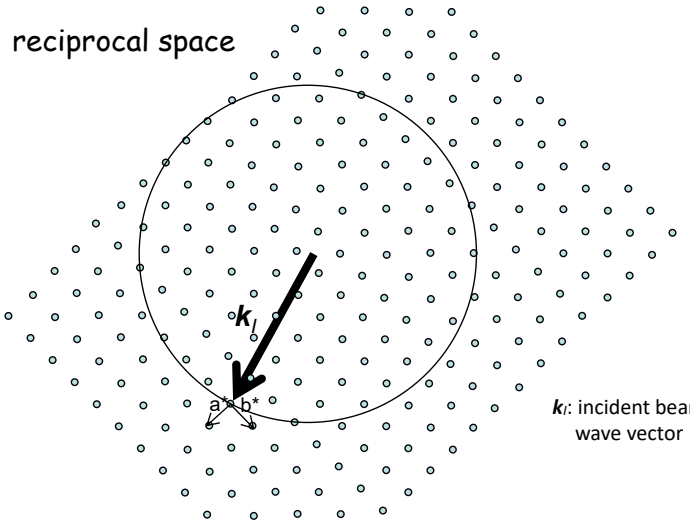
diffraction if :

$\mathbf{k}_I - \mathbf{k}_D = \mathbf{g}$ and $|\mathbf{k}_I| = |\mathbf{k}_D|$

Bragg and elastic scattering



real space



k_I: incident beam wave vector

Bragg: $d_{hkl} = \lambda/2 \sin\theta = 1/|\mathbf{g}|$

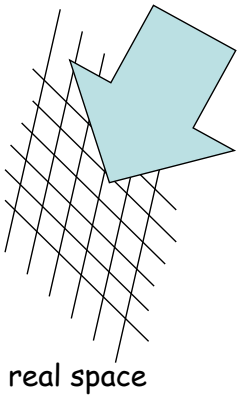
Reciprocal space: sphere radius 1/λ represents possible scattering wave vectors intersecting reciprocal space

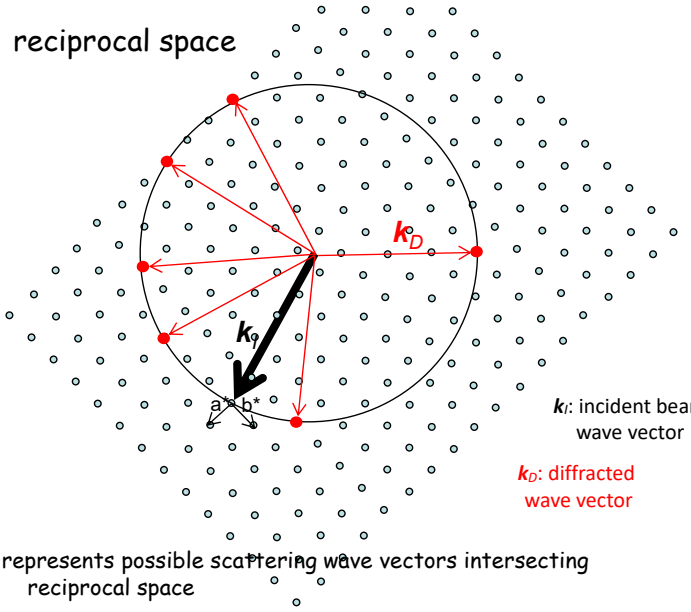
Electron diffraction: radius of sphere very large compared to reciprocal lattice
=> sphere circumference almost flat

Ewald sphere

A vector in reciprocal space:
$\mathbf{g}_{hkl} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^*$

diffraction if :
$\mathbf{k}_I - \mathbf{k}_D = \mathbf{g}$ **and** $|\mathbf{k}_I| = |\mathbf{k}_D|$
Bragg **and** elastic scattering





k_I: incident beam wave vector

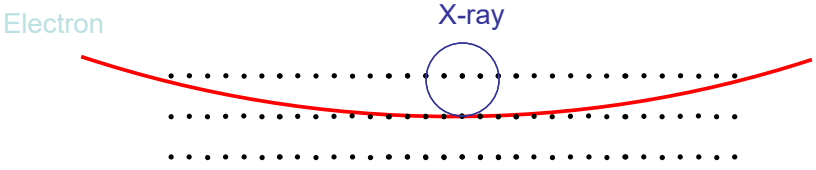
k_D: diffracted wave vector

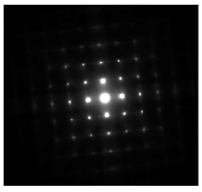
Reciprocal space: sphere radius 1/λ represents possible scattering wave vectors intersecting reciprocal space

Electron diffraction: radius of sphere very large compared to reciprocal lattice
=> sphere circumference almost flat

the reciprocal space
Almost flat Ewald sphere in electron diffraction

there are two main differences between x-ray and electron diffraction

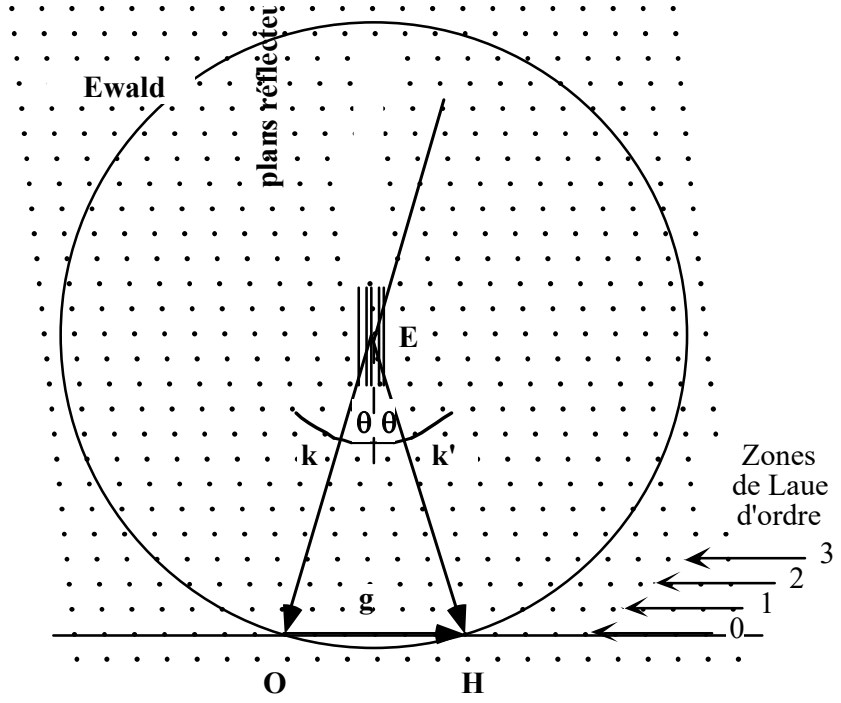




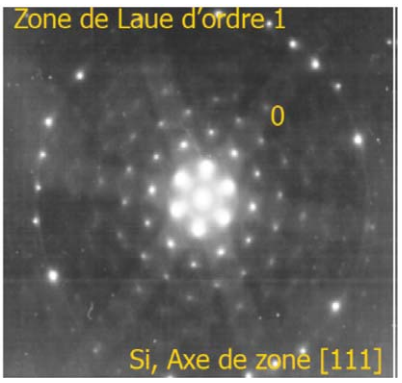
observed diffraction pattern

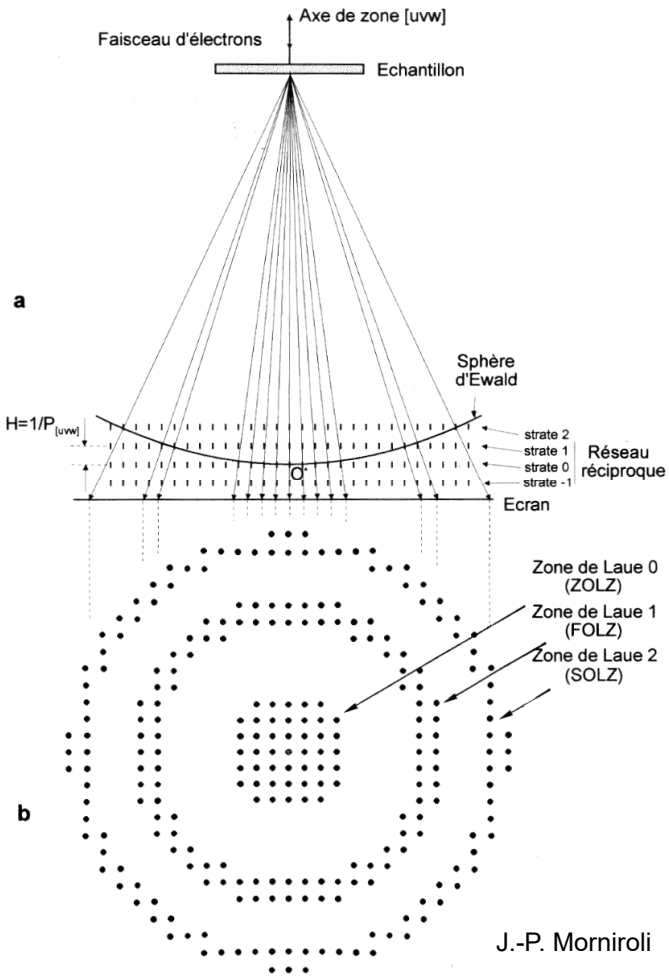
The energy of the electron beam (typically 80-300 keV) is far higher than that of a typical x-ray beam and so the wavelength of radiation is much smaller.
This means that the Ewald sphere radius (= 1/λ) is much larger for electron diffraction:
almost flat Ewald sphere

Laue Zones



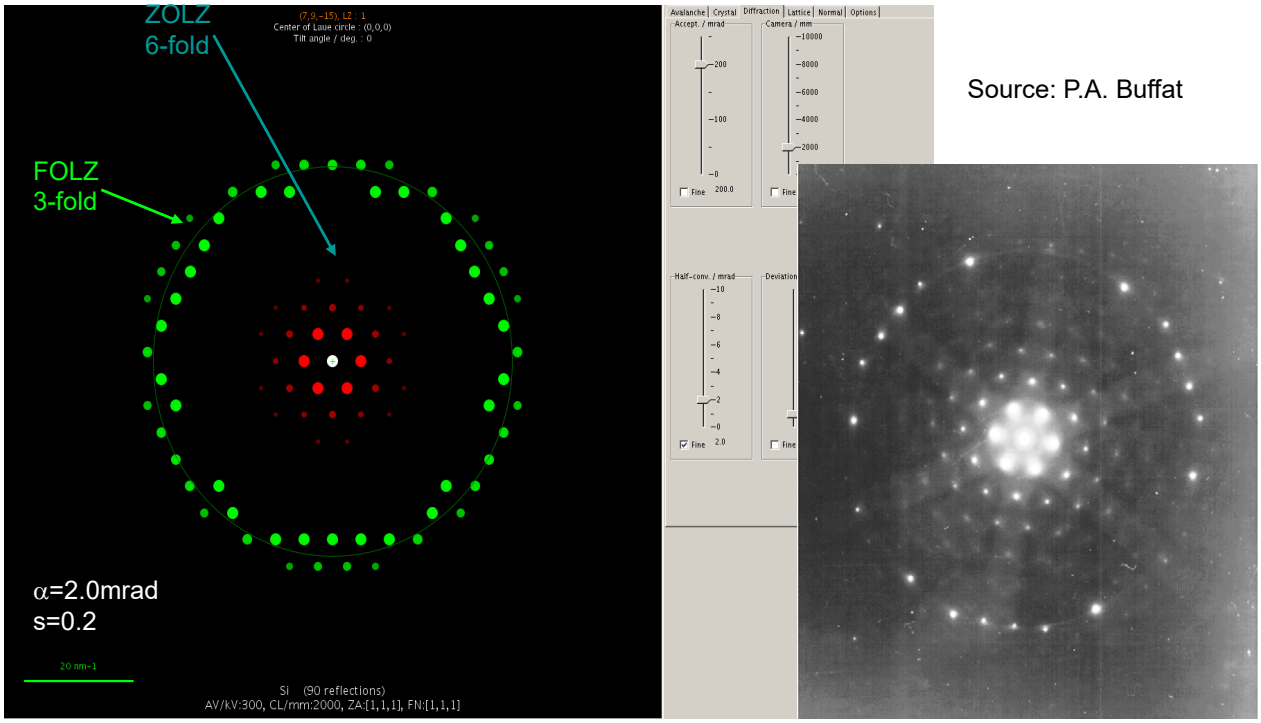
- Laue zones





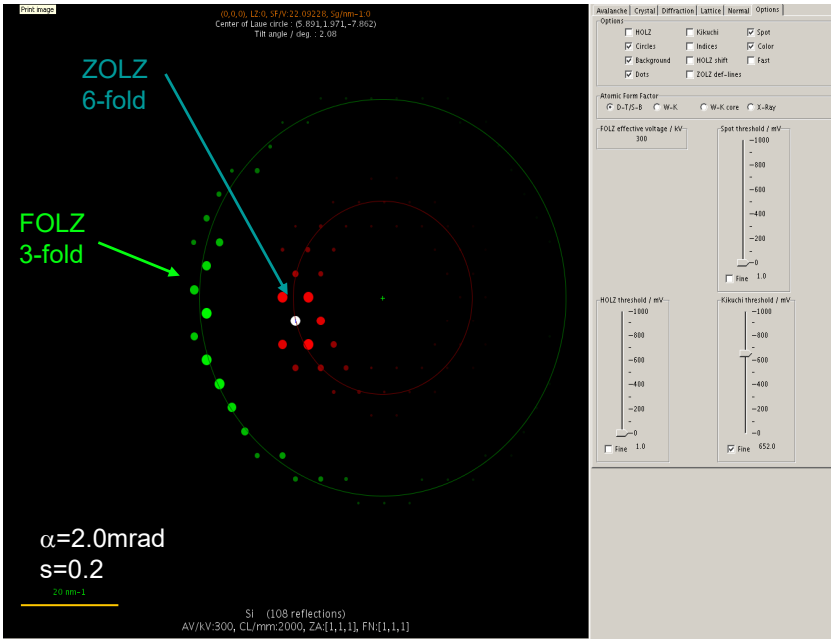
J.-P. Morniroli

Ewald Sphere : Laue Zones (ZOLZ+FOLZ)



Source: P.A. Buffat

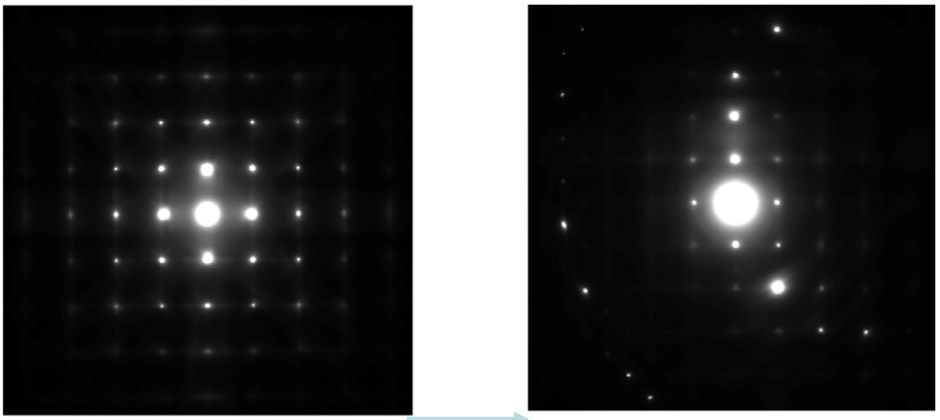
Ewald Sphere: Laue Zones (ZOLZ+FOLZ) tilted sample



the reciprocal space
tilting away from zone axis

Relaxation of Bragg condition due to the "rod" shape of reflections:

When we tilt the specimen away from a zone axis we still see reflections for planes that are not in exact Bragg condition.
The diffractions spots will not "move" with tilt. They will "fade away" as the Ewald sphere intersections change



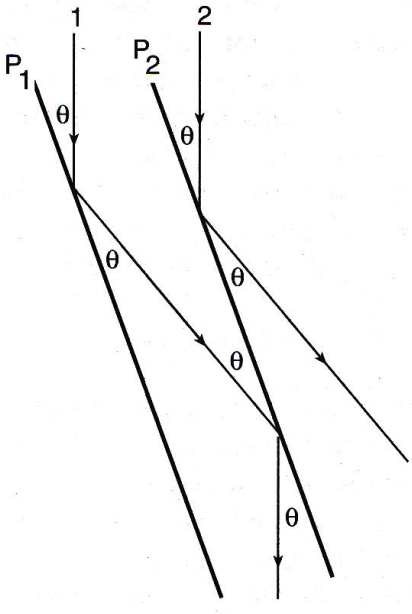
Dynamical scattering

For interpretation of intensities in diffraction pattern, single scattering would be ideal - i.e. "*kinematical*" scattering

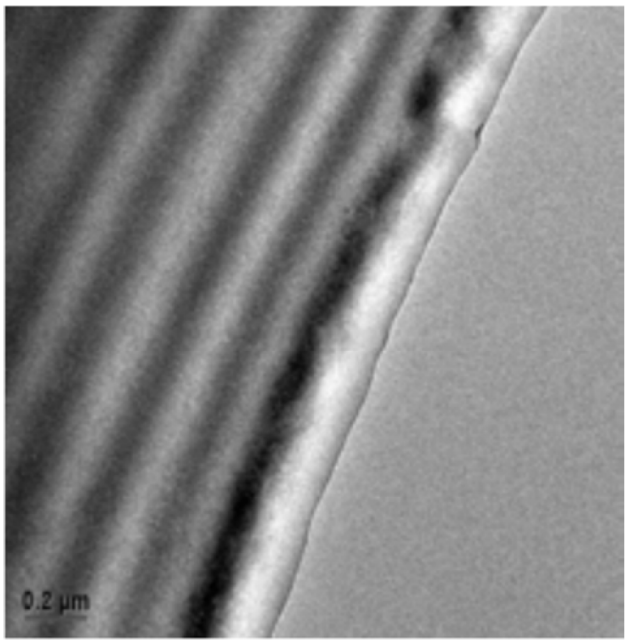
However, in electron diffraction there is often multiple elastic scattering: i.e. "*dynamical*" behaviour

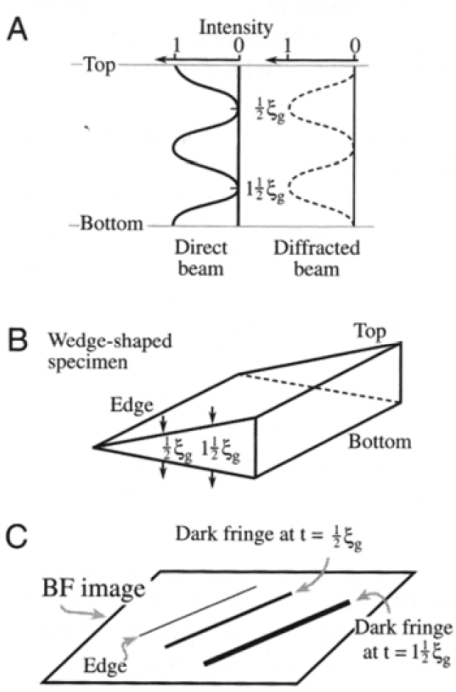
This dynamical scattering has a high probability because a Bragg-scattered beam is at the perfect angle to be Bragg-scattered again (and again...)

As a result, scattering of different beams is not independent from each other

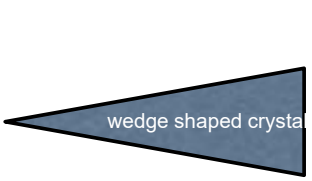


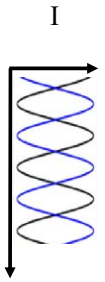
Dynamical scattering thickness fringes



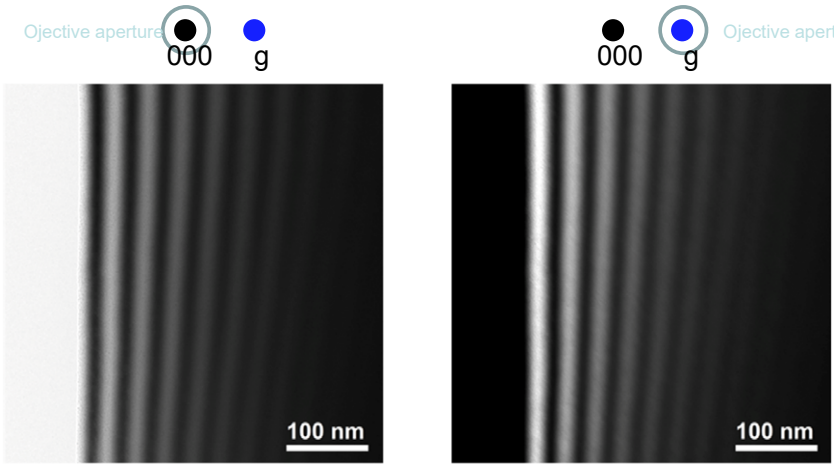


Dynamical scattering Thickness fringes





Intensity of (000) and g with thickness



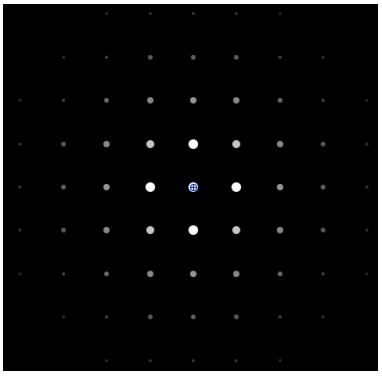
Bright-field Dark-field

Symmetry information

Zone axis SADPs have symmetry closely related to symmetry of crystal lattice

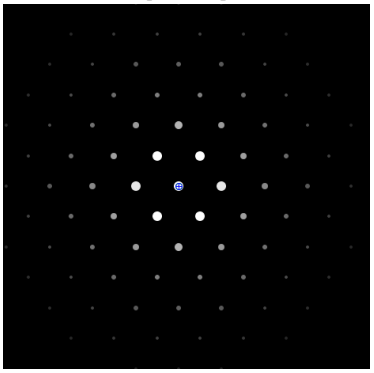
Example: FCC aluminium

[0 0 1]



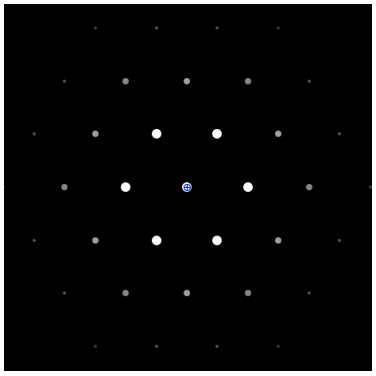
4-fold rotation axis

[1 1 0]



2-fold rotation axis

[1 1 1]



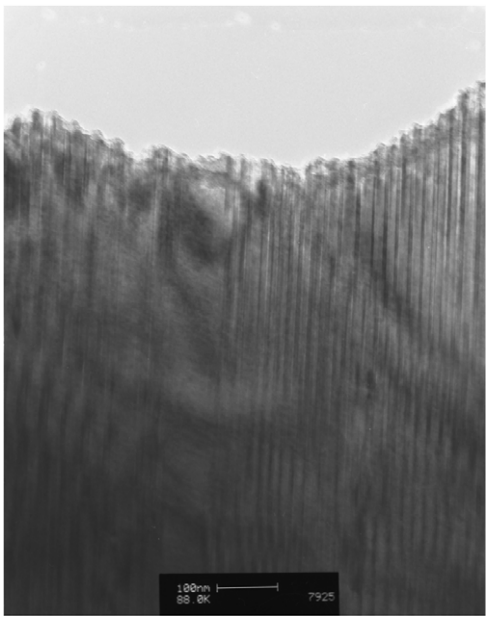
6-fold rotation axis - but [1 1 1] actually 3-fold axis

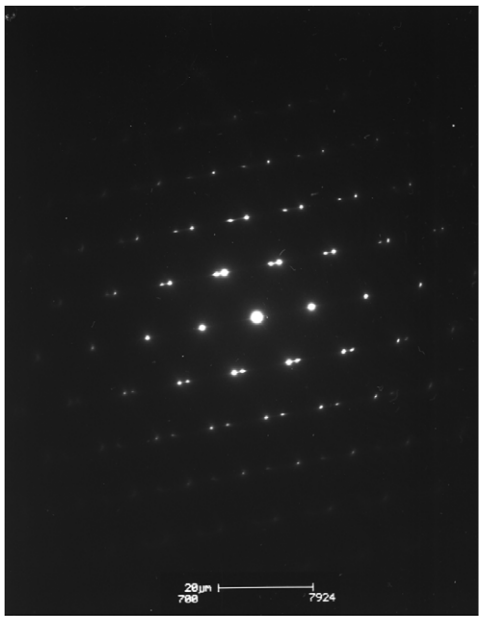
Need third dimension for true symmetry!

Twinning in diffraction

Example: Co-Ni-Al shape memory FCC twins observed on [1 1 0] zone axis

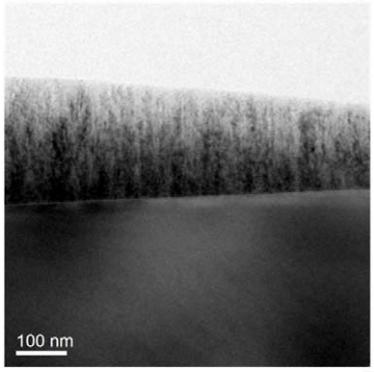
(1 1 1) close-packed twin planes overlap in SADP





Images provided by Barbora Bartová, CIME

Epitaxy and orientation relationships



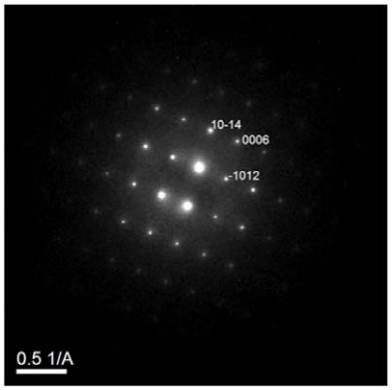
SADP excellent tool for studying orientation relationships across interfaces

Example: Mn-doped ZnO on sapphire

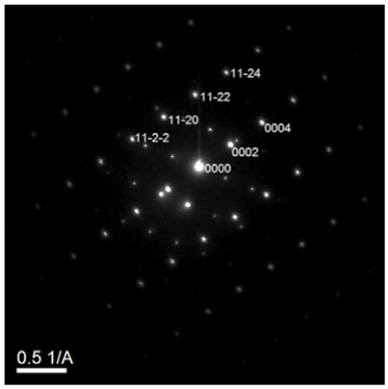
Zone axes:
$[1\ -1\ 0]_{ZnO}$ // $[0\ -1\ 0]_{sapphire}$

Planes:
c-plane$_{ZnO}$ // c-plane$_{sapphire}$

Sapphire substrate

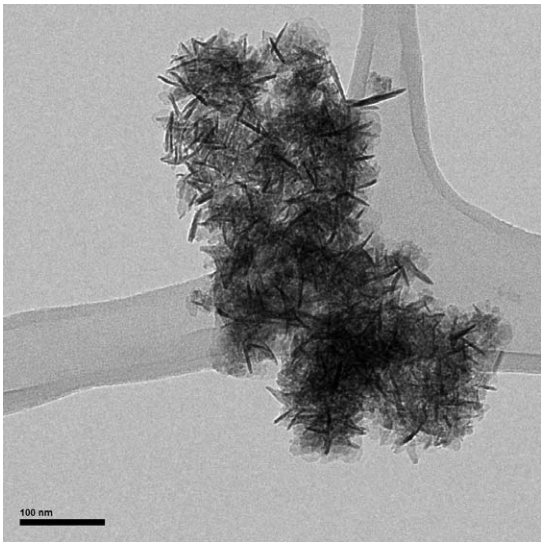


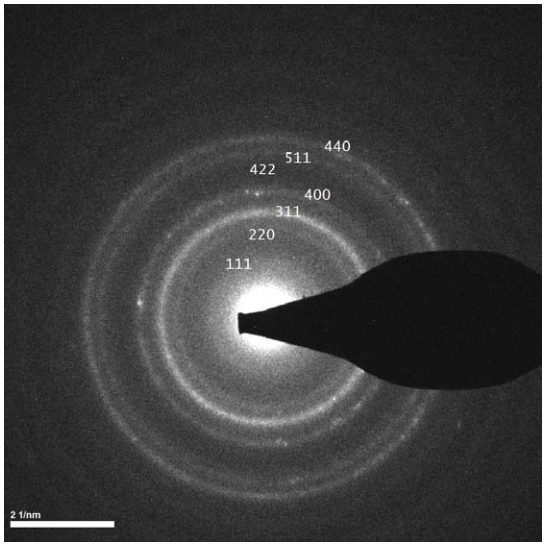
Sapphire + film



Ring diffraction patterns

If selected area aperture selects numerous, randomly-oriented nanocrystals, SADP consists of rings sampling all possible diffracting planes
- like powder X-ray diffraction



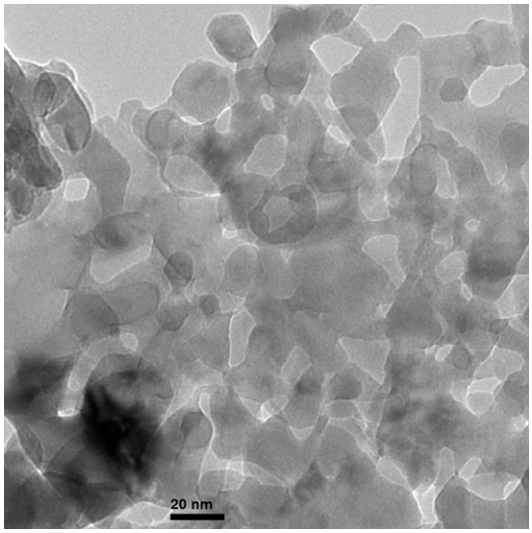


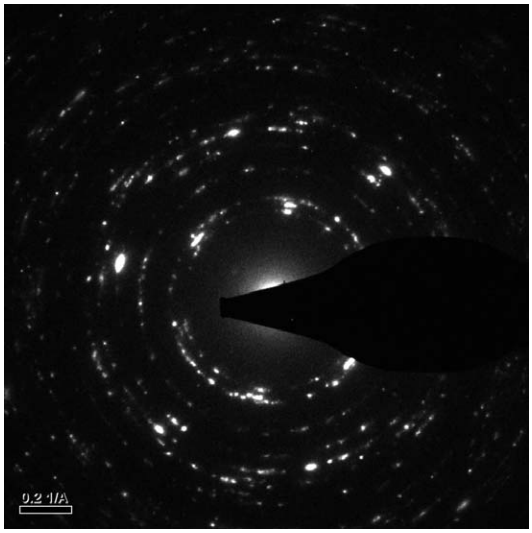
Example: "needles" of contaminant cubic $MnZnO_3$ - which XRD failed to observe!

Ring diffraction patterns

Larger crystals => more “spotty” patterns

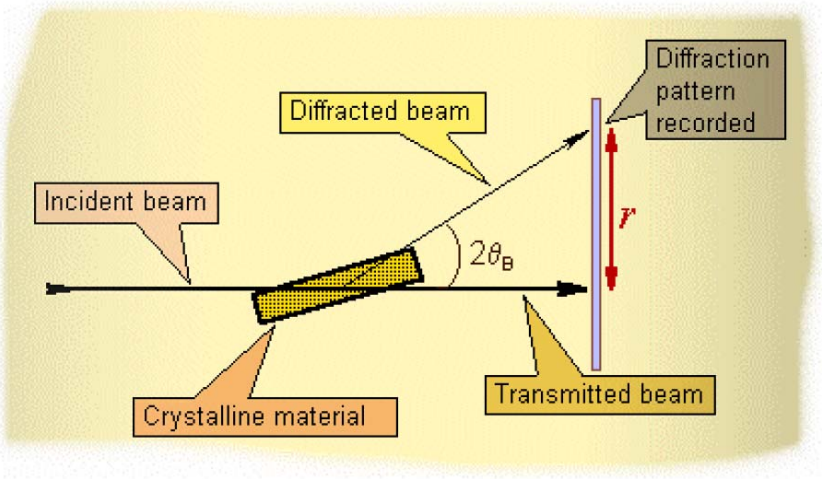
Example: ZnO nanocrystals ~20 nm in diameter





XRD

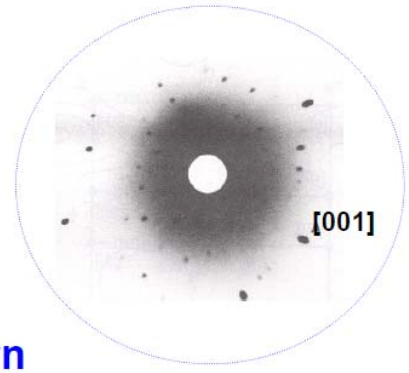
- X-ray diffraction



www.micro.magnet.fsu.edu/primer/java/interference/index.html

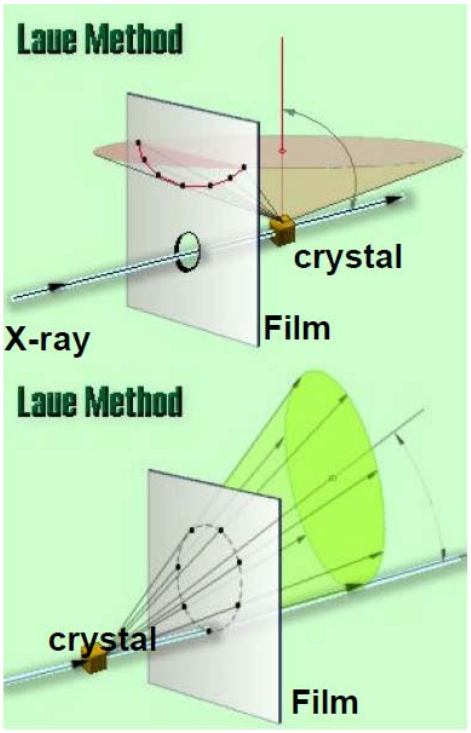
Laue Method

Back-reflection Laue



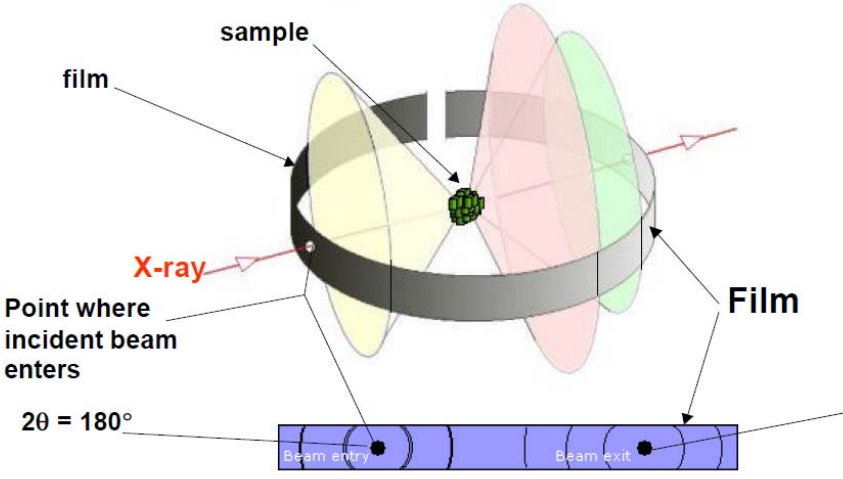
pattern

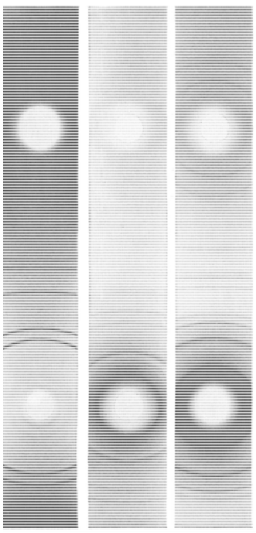
Transmission Laue



Debeye-Scherrer

Detection of Diffracted X-rays
by Photographic film





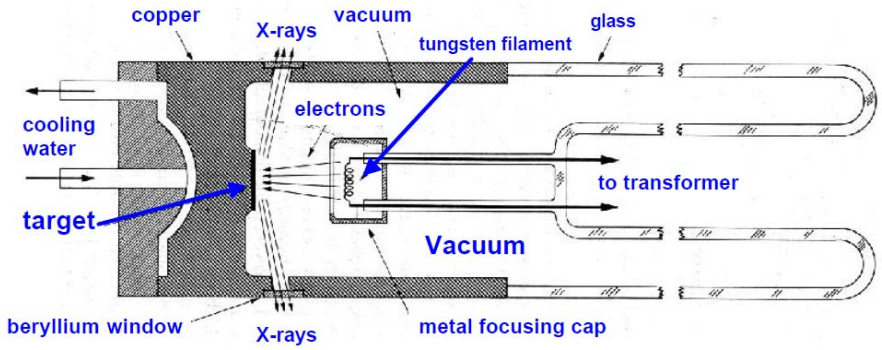
Debye - Scherrer Camera

A sample of some hundreds of crystals (i.e. a powdered sample) show that the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.

X-ray tube

3.0 Production of X-rays

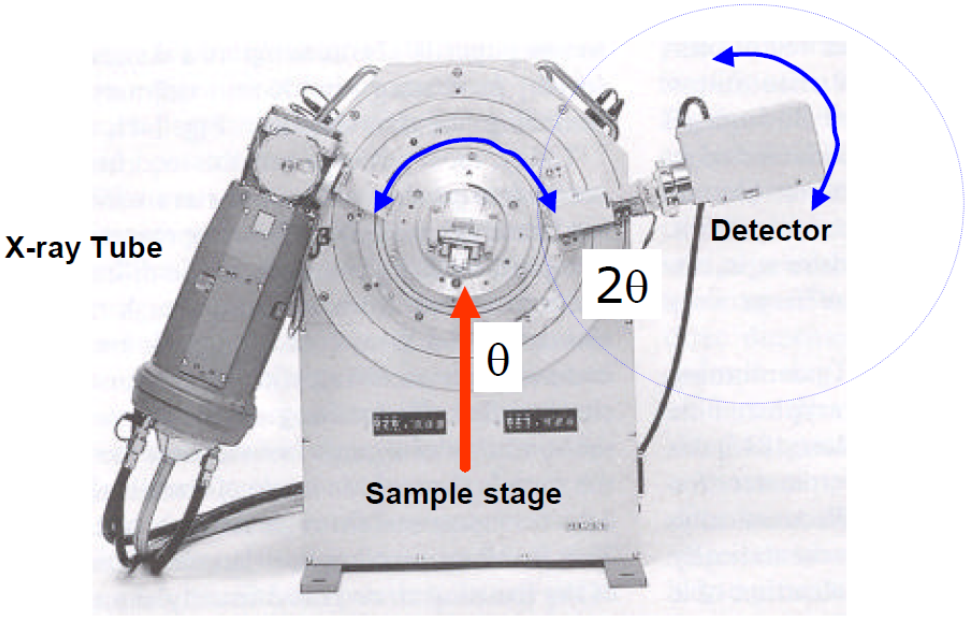
Cross section of sealed-off filament X-ray tube



X-rays are produced whenever high-speed electrons collide with a metal target. A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, *Cu*, Al, Mo, Mg. The anode is a water-cooled block of Cu containing desired target metal.

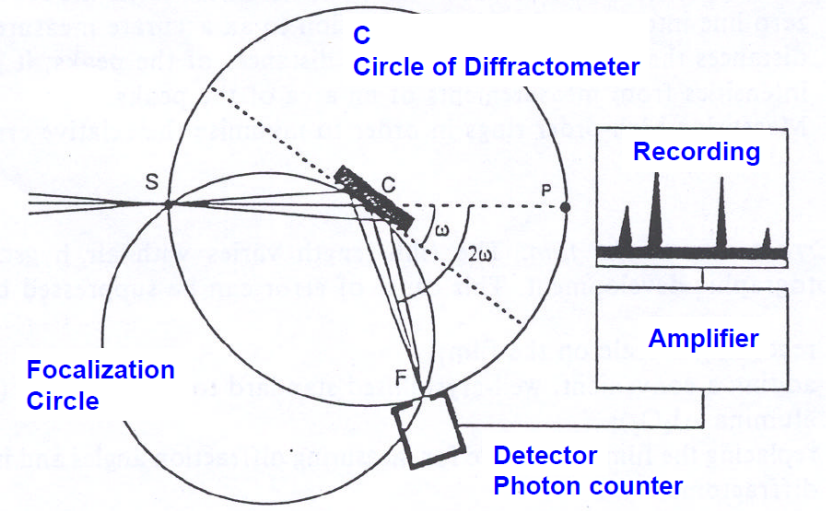
Diffractometer

A Modern Automated X-ray Diffractometer



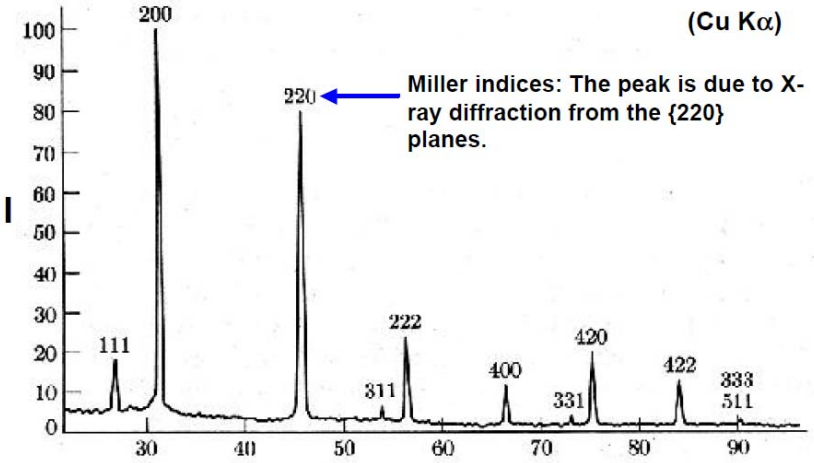
Cost: $560K to 1.6M

Detection of *Diffracted* X-rays
by a Diffractometer



Bragg - Brentano Focus Geometry, Cullity

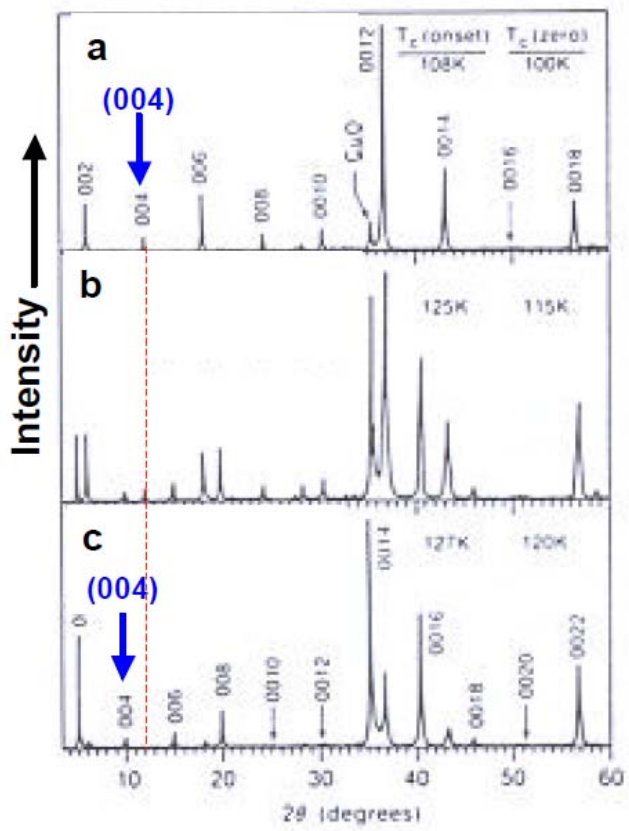
XRD Pattern of NaCl Powder



Diffraction angle 2θ (degrees)

One of the most important uses of XRD!!!

- Obtain XRD pattern
- Measure d-spacings
- Obtain integrated intensities
- Compare data with known standards in the JCPDS file, which are for random orientations (there are more than 50,000 JCPDS cards of inorganic materials).



Diffraction patterns of three Superconducting thin films annealed for different times.

a. $Tl_2CaBa_2Cu_2O_x$ (2122)
b. $Tl_2CaBa_2Cu_2O_x$ (2122) + $Tl_2Ca_2Ba_2Cu_3O_y$ (2223)
   b = a + c
c. $Tl_2Ca_2Ba_2Cu_3O_y$ (2223)

CuO was detected by comparison to standards

References

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"Transmission Electron Microscopy: Physics of Image Formation and Microanalysis (Springer Series in Optical Sciences)", Reimer, Springer Publishing

"Electron diffraction in the electron microscope", J. W. Edington, Macmillan Publishers Ltd

"Large-Angle Convergent-Beam Electron Diffraction Applications to Crystal Defects", Morniroli, Taylor & Francis Publishing

http://escher.epfl.ch/eCrystallography

http://www.doitpoms.ac.uk

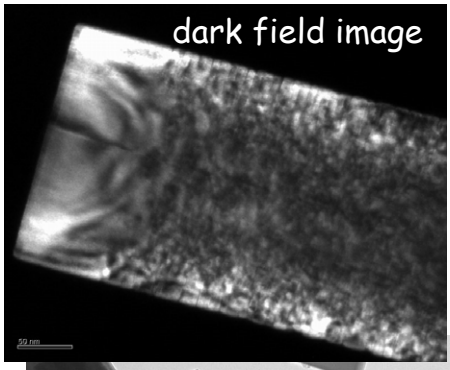
JEMS Electron Microscopy Software Java version
http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/jems.html

Web-based Electron Microscopy APplication Software (WebEMAPS)
http://emaps.mrl.uiuc.edu/

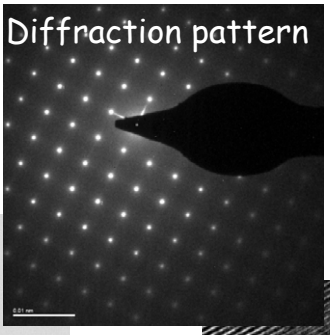
http://crystals.ethz.ch/icsd - access to crystal structure file database
Can download CIF file and import to JEMS

TEM
imaging with diffraction contrast

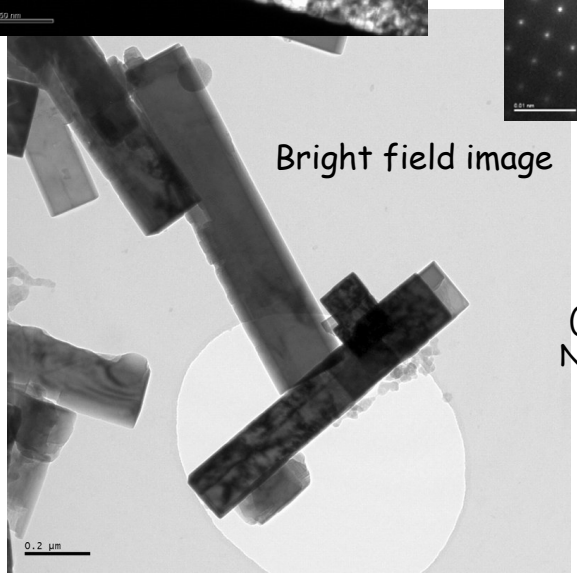
Bright Field / Dark Field



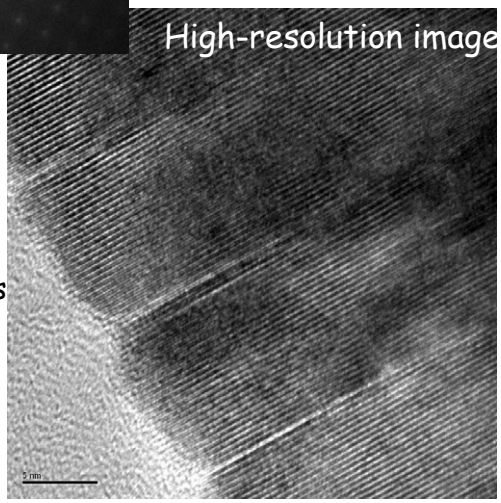
Diffraction induced image contrast
BF/DF Imaging, high-resolution TEM



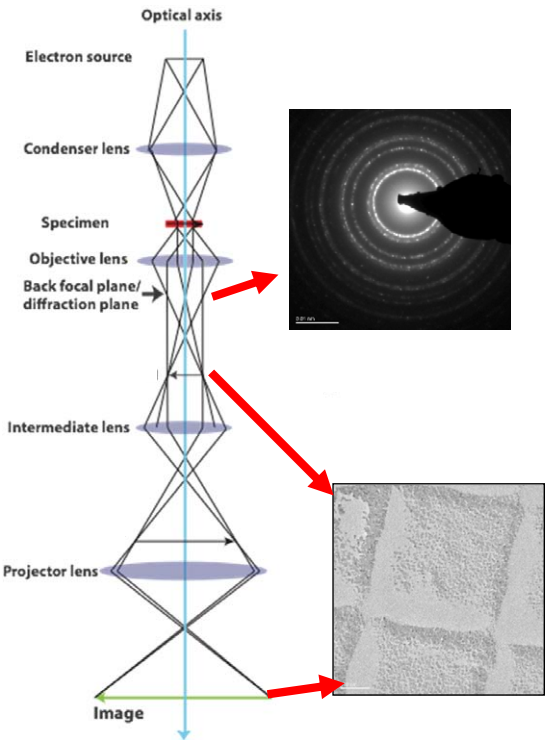
Shape, lattice parameters, defects, lattice planes

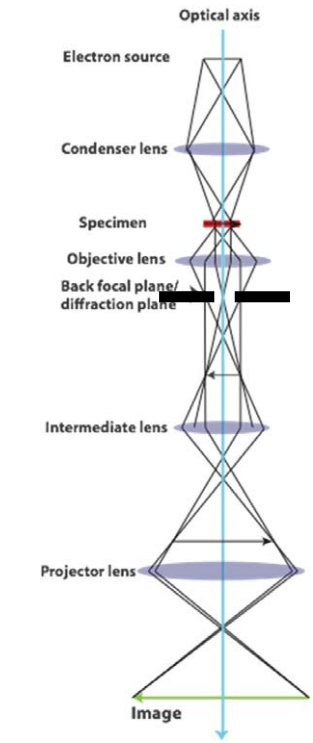


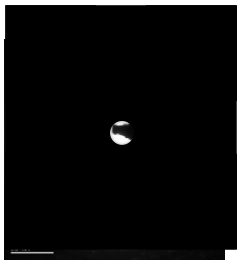
$(K,Nb)O_3$
Nano-rods

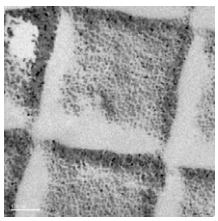


Bright Field Imaging
Diffraction Contrast
Au (nano-) particles on C film

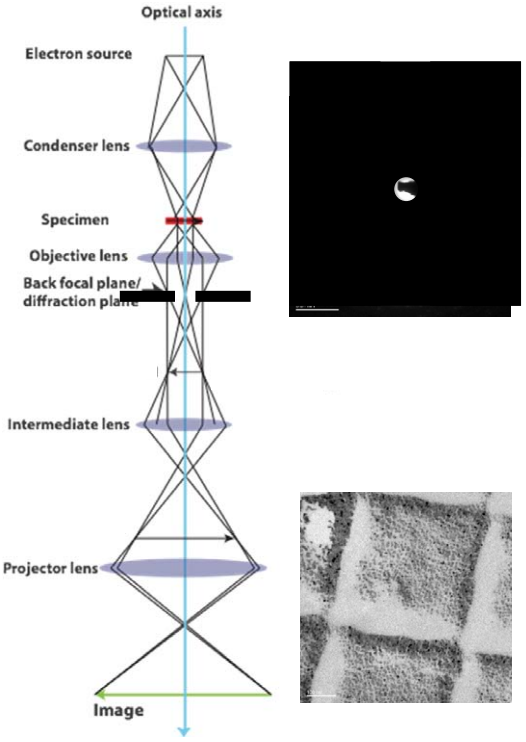


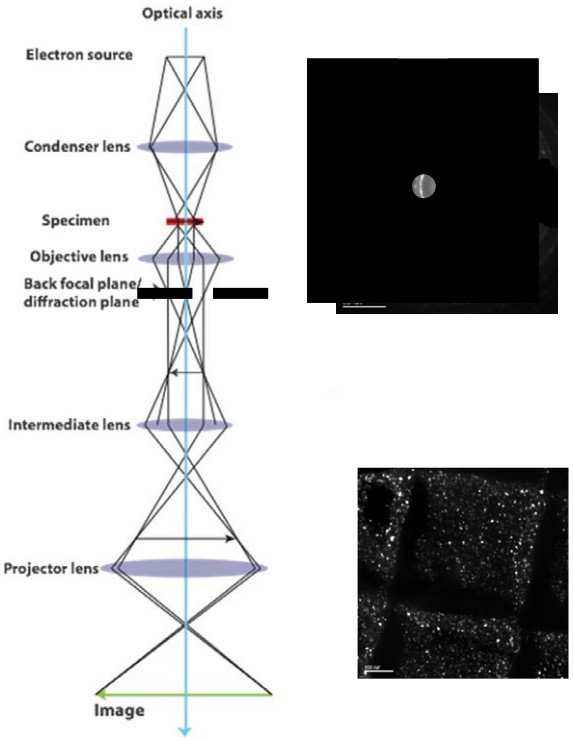




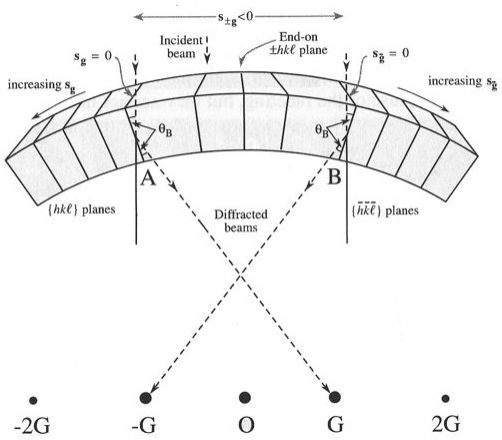


Bright Field / Dark Field





Bend Contours /Bragg Contours



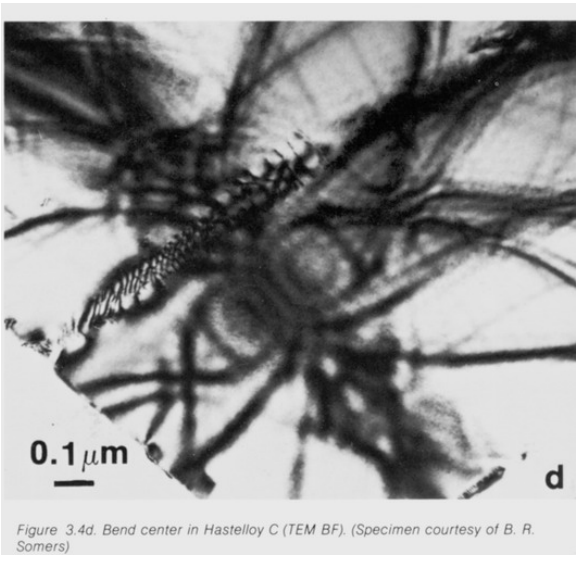
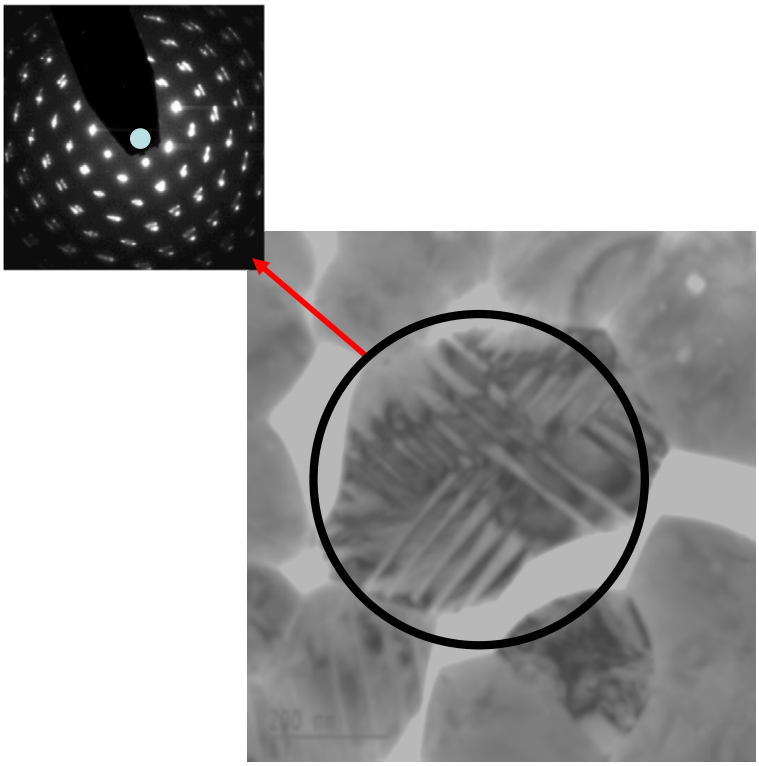


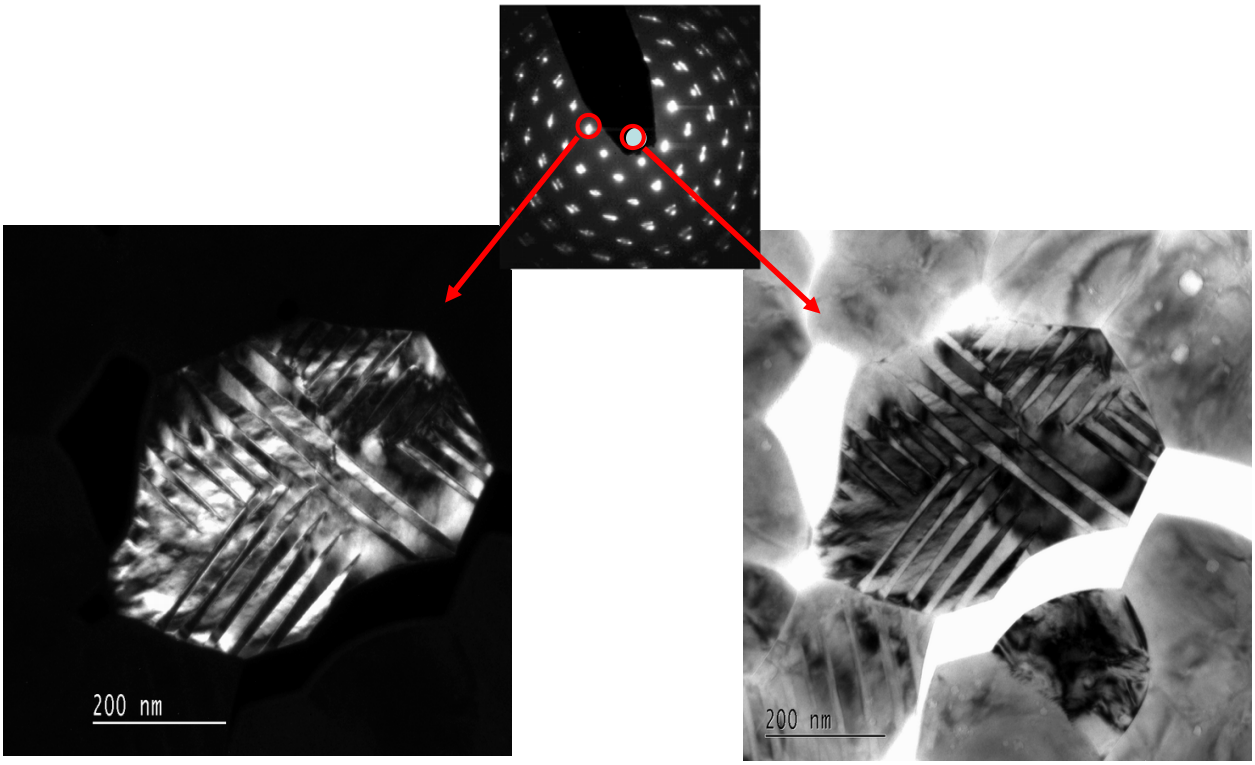
Figure 3.4d. Bend center in Hastelloy C (TEM BF). (Specimen courtesy of B. R. Somers)

Bragg conditions change across the bent sample

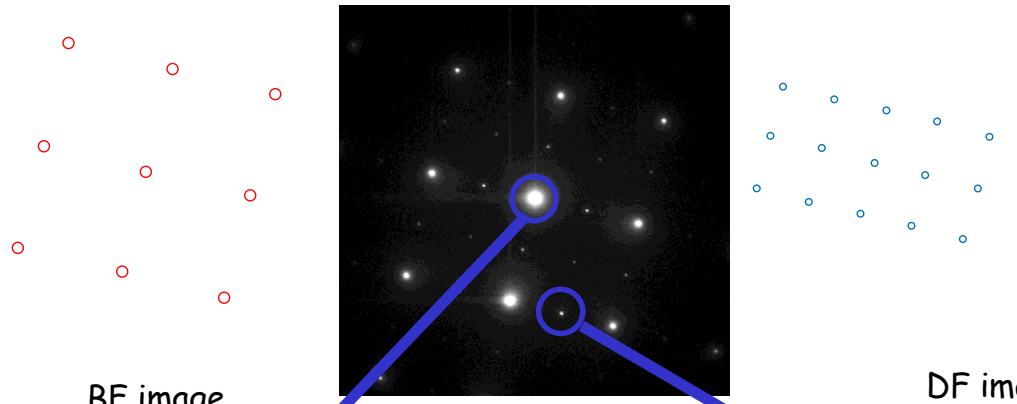
Twin lamellae in $PbTiO_3$



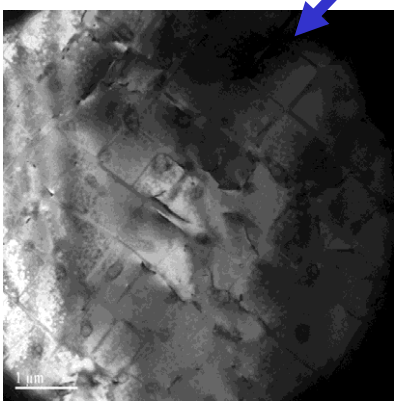
Twin lamellae in $PbTiO_3$



Ni based Superalloy



BF image



DF image