Diffraction from crystals

- A crystal is a three dimensional diffraction grating
- The lattice periodicity of the crystal determines the sampling regions of the diffraction pattern
- The unit cell contents give you the envelope function

Laue equations

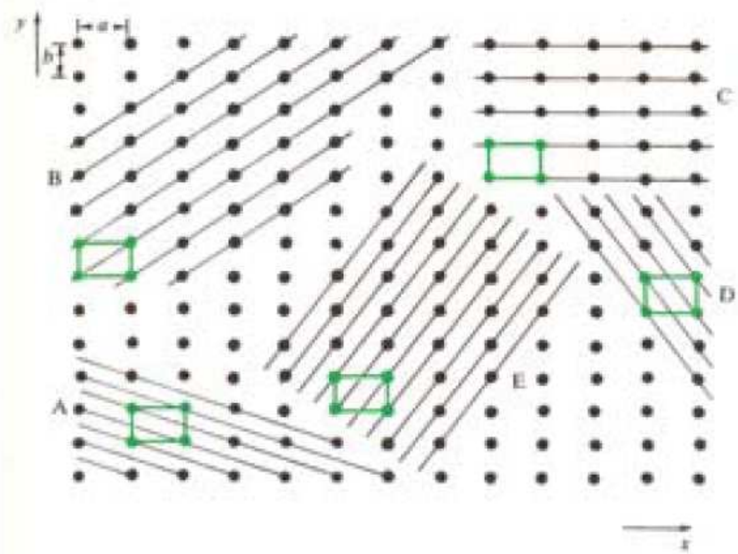
- Laue first mathematically described diffraction from crystals
  - consider X-rays scattered from every atom in every unit cell in the crystal and how they interfere with each other
  - to get a diffraction spot you must have constructive interference
  - Laue equations:
    - » $PD_1 = h_1\lambda$, $PD_2 = h_2\lambda$, $PD_3 = h_3\lambda$

The Bragg equation

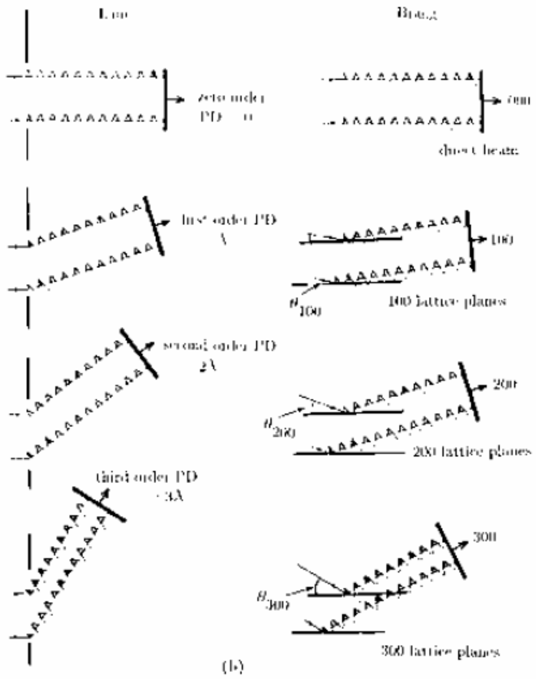
- Bragg discovered that you could consider the diffraction to have arisen from reflection from lattice planes
- Reformulated Laue equations
  - $2d_{hkl}\sin\theta_{hkl} = n\lambda$

The orientation of lattice planes

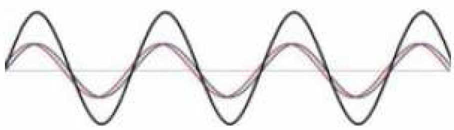
- It is possible to describe certain directions and planes with respect to the crystal lattice using a set of three integers referred to as Miller Indices



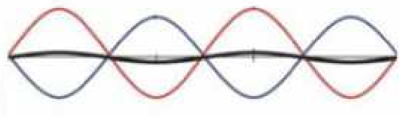
Laue and Bragg diffraction



Interference of Waves



Resulting wave
Wave 1
Wave 2

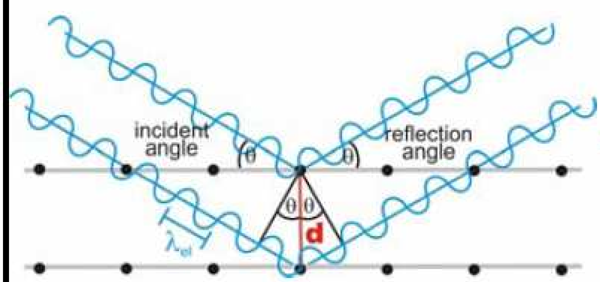


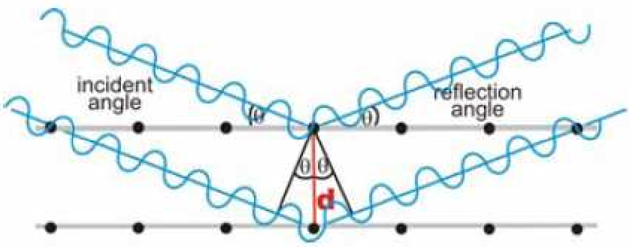
waves in phase

⇒ constructive interference

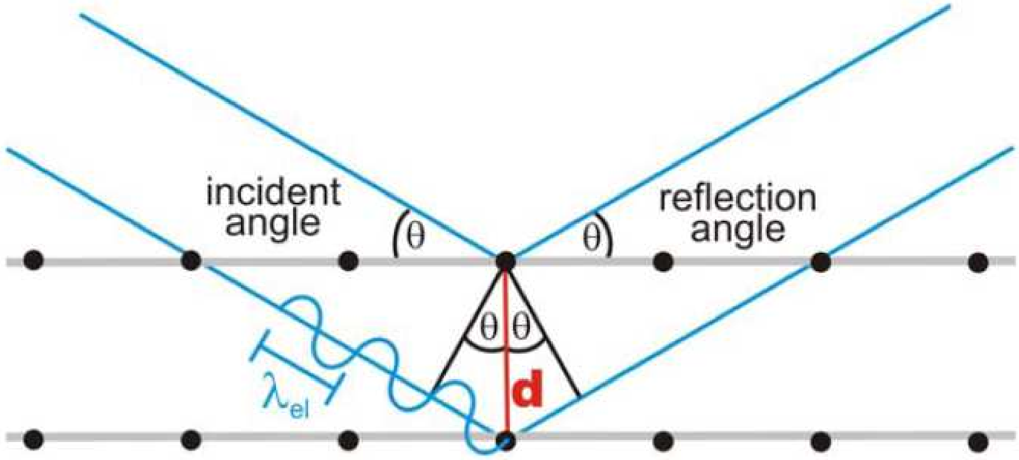
waves out of phase

⇒ destructive interference





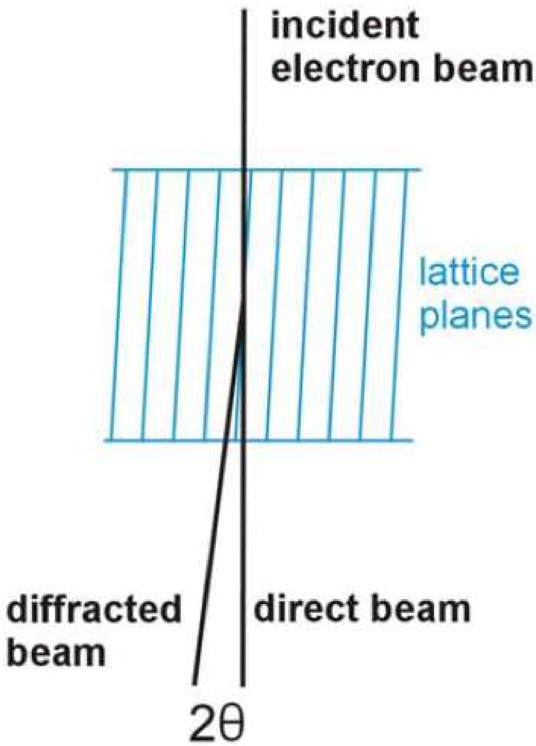
Bragg Description of Diffraction



Constructive interference between the waves reflected with an angle θ at atom planes of spacing d occurs if the path difference between the two waves is 2d sinθ.

Bragg law: $2d\sin\theta = n\lambda$

Electron Diffraction



Bragg law:

$$2d\sin\Theta = n\lambda$$

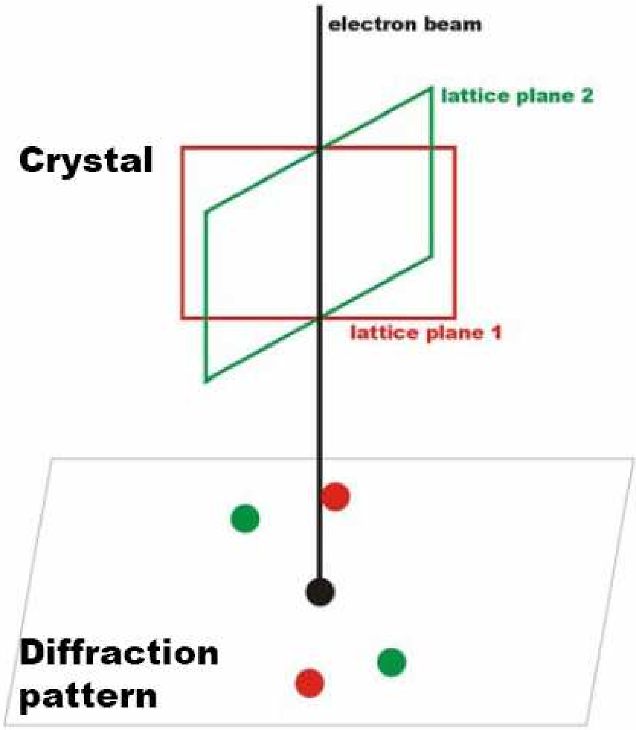
λ_{el} = 0.00197 nm (1.97 pm) for 300 kV

If d = 0.2 nm $\Rightarrow \Theta = 0.28°$

$\Rightarrow \quad 0 > \Theta > 1$

$\Rightarrow$ Reflecting lattice planes are almost parallel to the direct beam

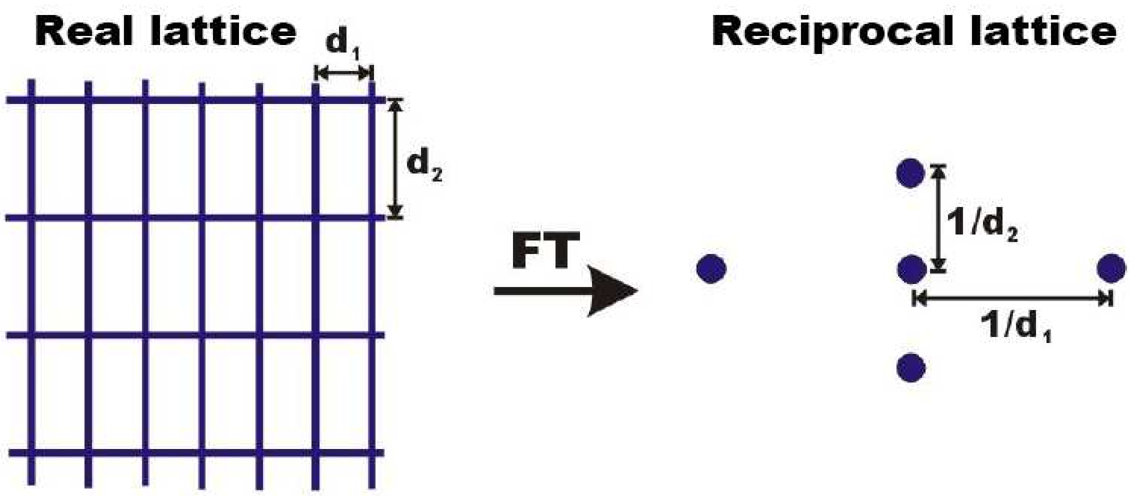
Electron Diffraction on a lattice



Electron beam is parallel to the zone axis of the diffracting lattice planes

Electron Diffraction

Diffraction of a lattice

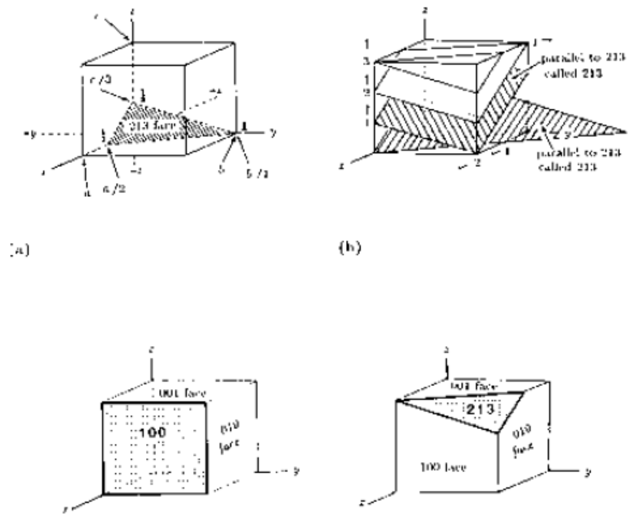


Each set of parallel lattice planes in real space causes a pair of reflections in reciprocal space, as mathematically described by the Fourier Transform (FT).

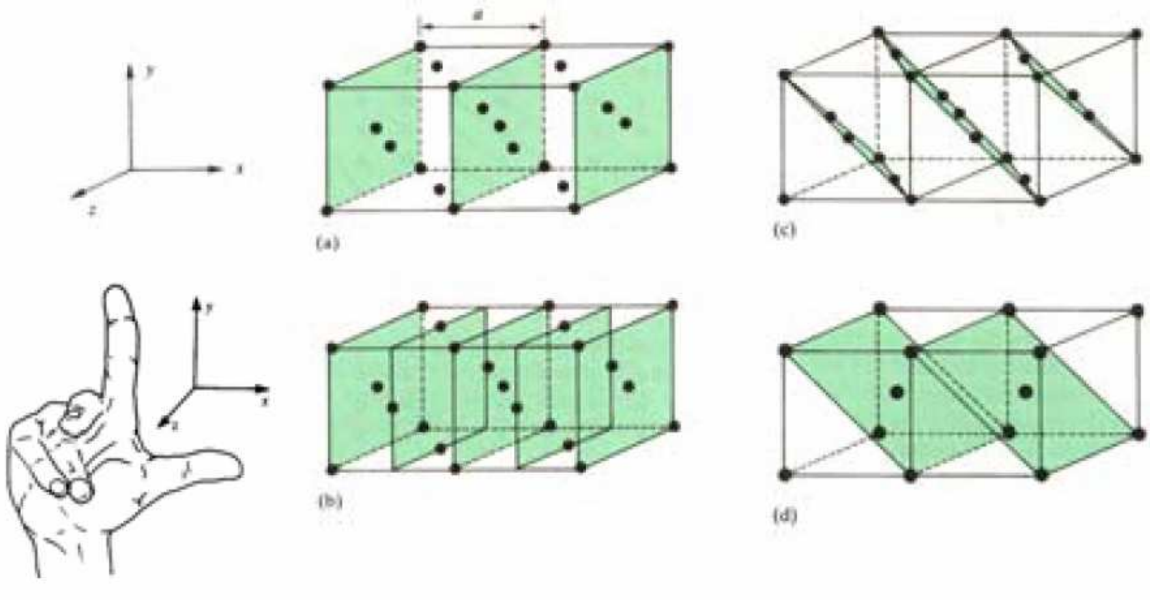
Electron Diffraction

Miller indices (hkl)

- Miller Indices are the reciprocal intercepts of the plane on the unit cell axes
- Identify plane adjacent to origin
  - can not determine for plane passing through origin
- Find intersection of plane on all three axes
- Take reciprocal of intercepts
- If plane runs parallel to axis, intercept is at ∞, so Miller index is 0



Examples of Miller indices

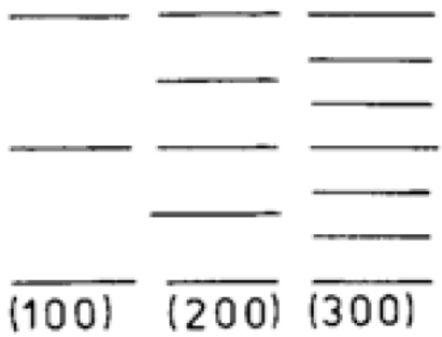


Families of planes

- Miller indices describe the orientation and spacing of a family of planes
  - The spacing between adjacent planes in a family is referred to as the "d-spacing"

Three different families of planes

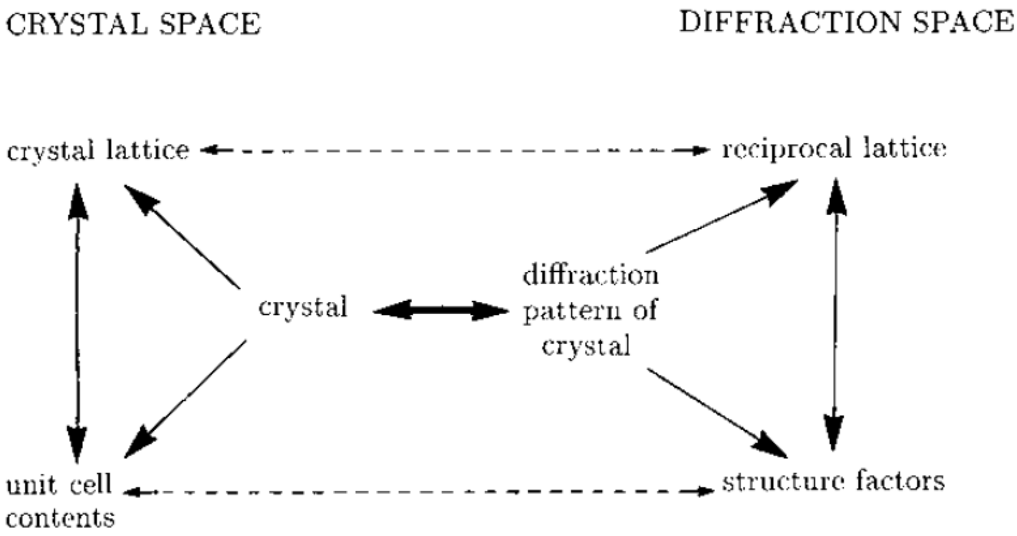
d-spacing between (300) planes is one third of the (100) spacing



Note all (100) planes are members of the (300) family

RASMOL demo here

Real space and reciprocal space



The reciprocal lattice

- It is convenient when talking about diffraction to use the concept of a reciprocal lattice
- The reciprocal lattice is related to the real space lattice by:

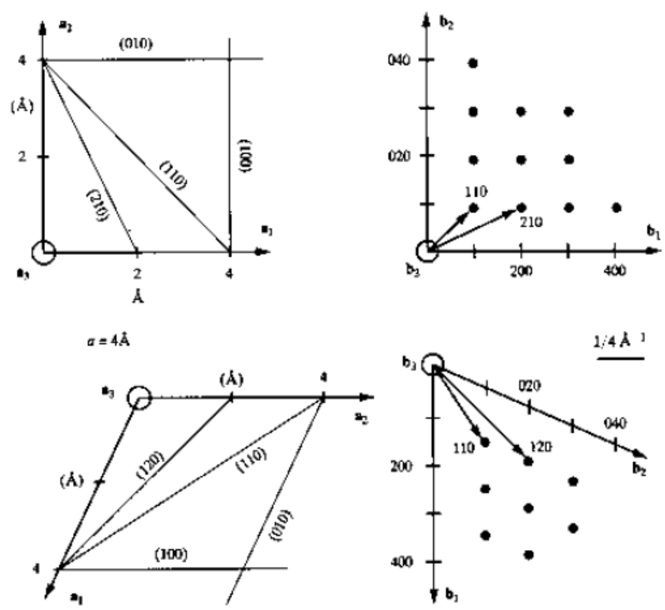
$$b_1 = \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3} \qquad b_2 = \frac{a_3 \times a_1}{a_1 \cdot a_2 \times a_3} \qquad b_3 = \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3}$$

- $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the vectors of the real space lattice (alternatively **a**,**b**,**c**) and $\mathbf{b}_1$,$\mathbf{b}_2$,$\mathbf{b}_3$ are the vectors of the reciprocal lattice (alternatively **a***,**b***,**c***).
- Note $a_1.a_2 x a_3$ is the unit cell volume

Properties of the reciprocal lattice

- Note $a_i.b_j=\delta_{ij}$
- So $a_1.b_1 = 1$, but $a_1.b_2 = 0$ and $a_1.b_3 = 0$ etc.
  - This is the origin of the term reciprocal lattice.
  - The reciprocal lattice and real space lattice are orthonormal
- Any point on the reciprocal lattice can be specified by a vector $\mathbf{H}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ (hkl are integers)
  - This vector is perpendicular to the plane in real space with Miller indices (hkl)
  - The length of this vector $H_{hkl} = 1/d_{hkl}$ where d_{hkl} is the interplanar spacing in real space
  - We get to represent a whole family of planes in real space by a single point in reciprocal space

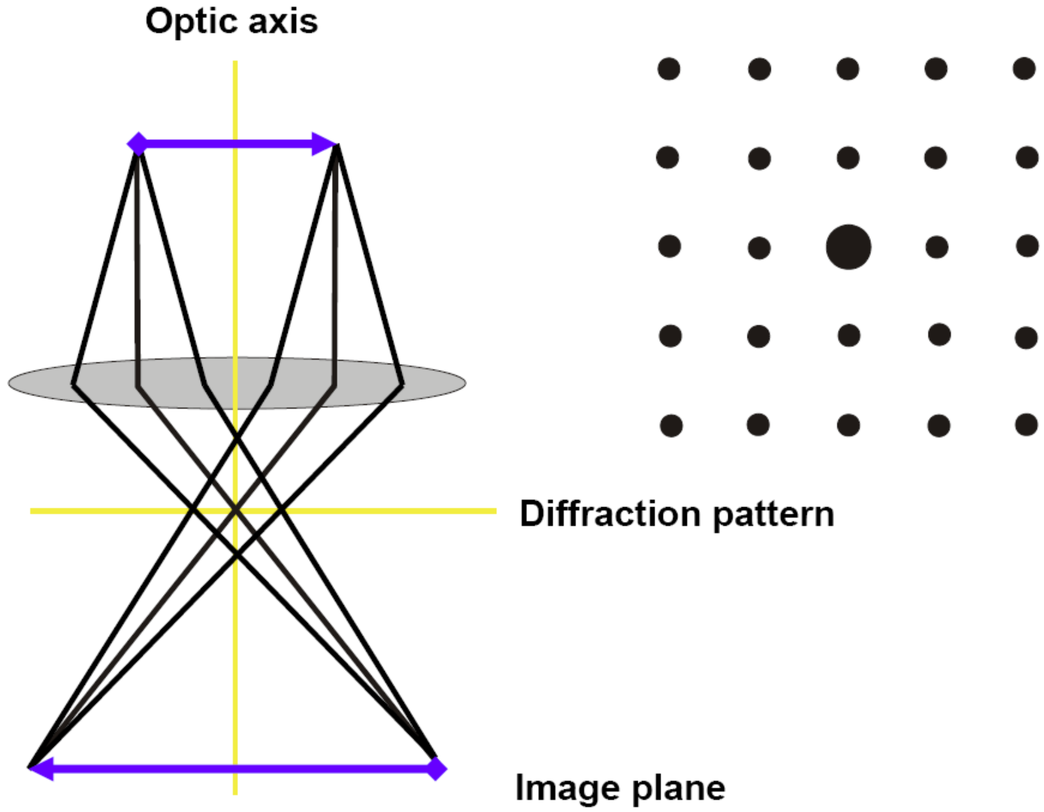
Geometrical relationship between real and reciprocal space



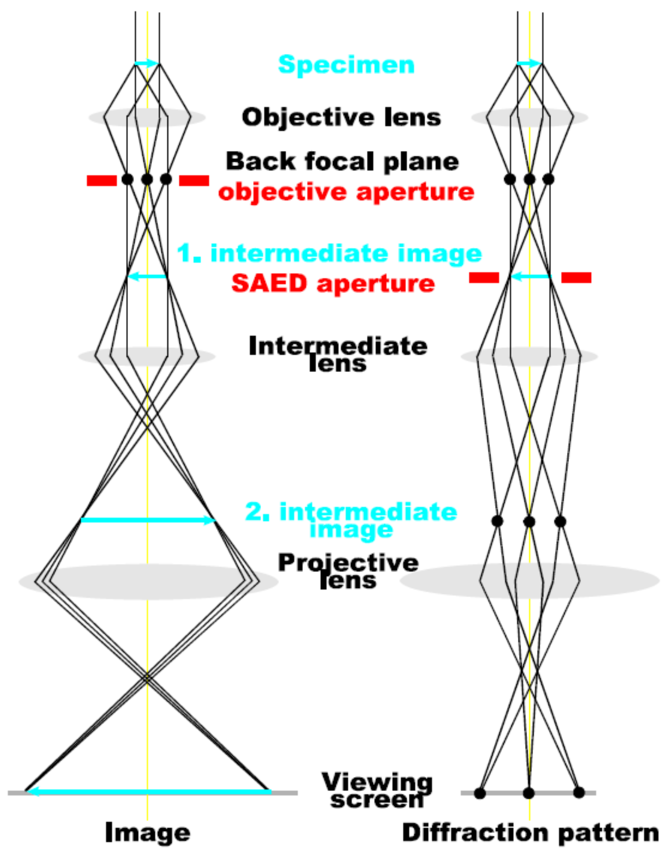
Note reciprocal lattice vector is always perpendicular to the corresponding real space plane

Only in orthogonal axis systems are the real and reciprocal lattice vectors parallel

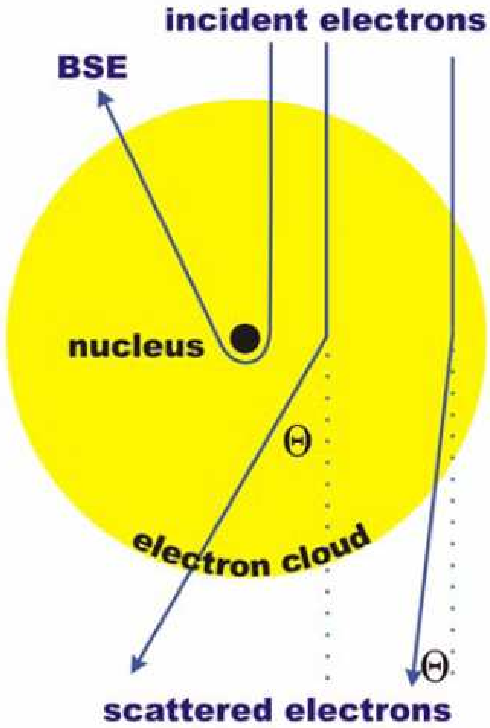
TEM – Imaging and Diffraction



Diffraction and Imaging Mode



Elastic Scattering of Electrons by an Atom



Weak Coulomb interaction within the electron cloud

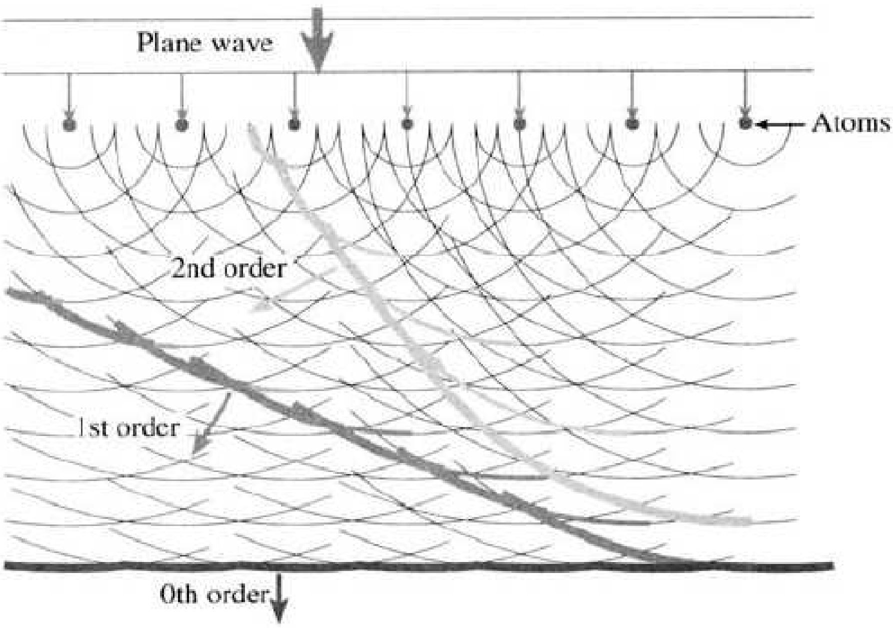
⇒ low-angle scattering

Strong Coulomb interaction close to the nucleus

⇒ Scattering into high angles or even backwards (Rutherford scattering)

⇒ atomic-number (*Z*) contrast

Coherent scattering

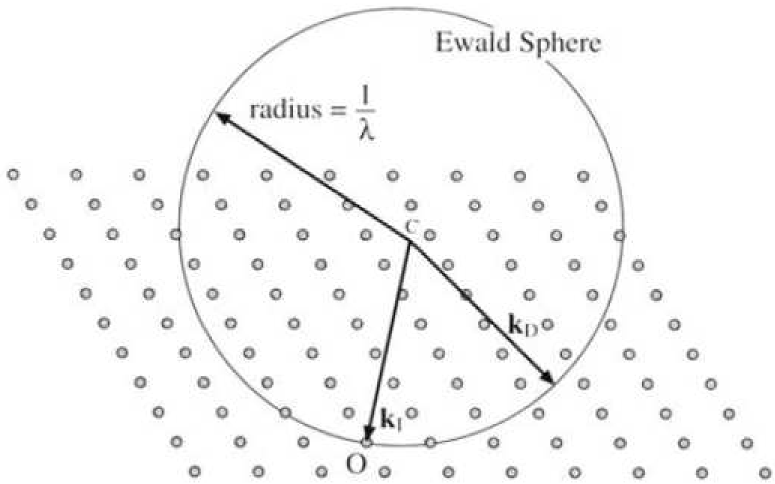


Plane electron wave generates secondary wavelets from periodically ordered scattering centers (atoms in a crystal lattice). Constructive interference of these wavelets leads to scattered beams.

The Ewald construction

- A crystal at a random orientation in an X-ray beam will not necessarily give a diffraction spot
- Ewald construction allows the prediction of the orientation required for diffraction
  - widely used in diffraction books

Description of Diffraction in Reciprocal Space: Ewald Sphere of Reflection



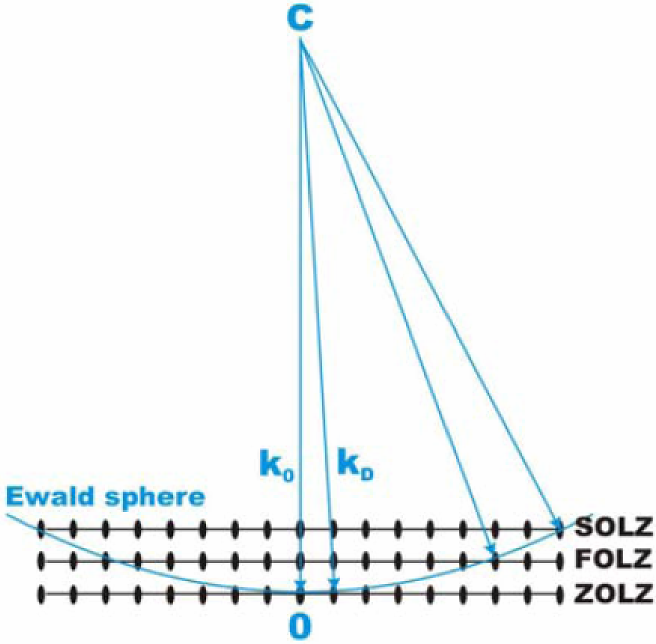
Radius of Ewald sphere $r = 1/\lambda$

k_1: wave vector of incident wave

k_D: wave vector

Bragg condition is satisfied if the Ewald sphere cuts through a reciprocal lattice point

Electron Diffraction: Description in Reciprocal Space by the Ewald Sphere of Reflection



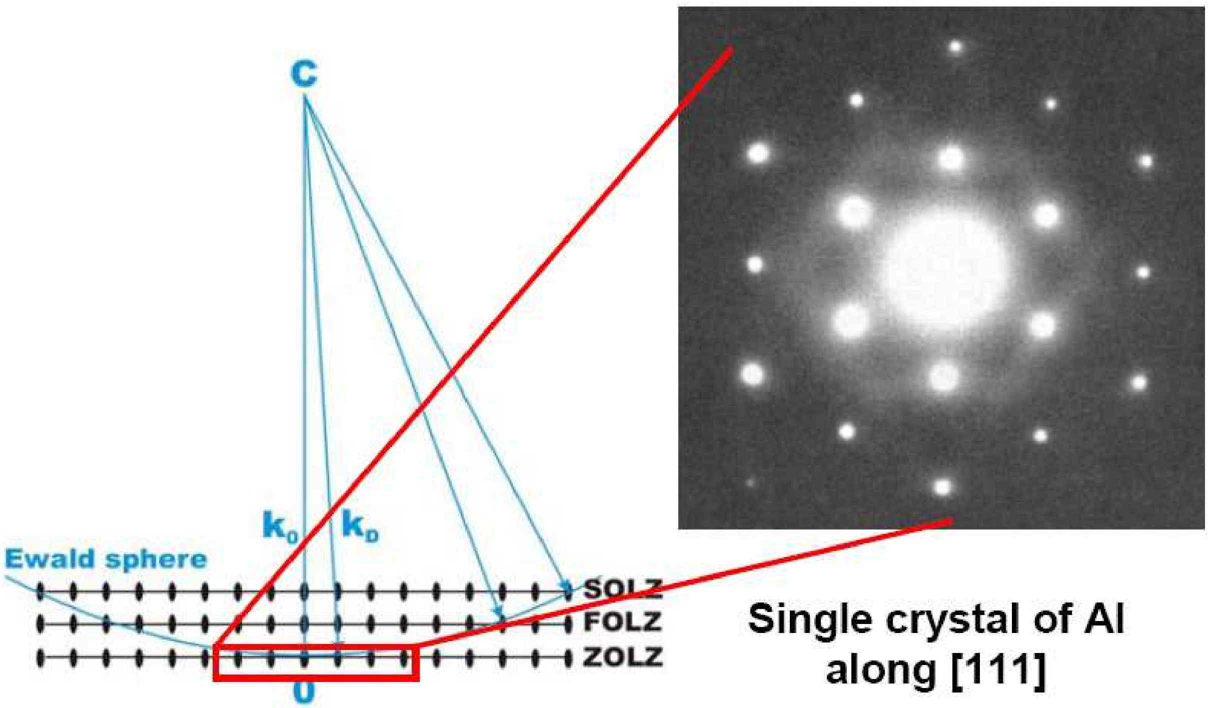
Radius of Ewald sphere r = $1/\lambda$ is large for electrons

$\Rightarrow$ Many reciprocal lattice points are intersected.

Due to the thin sample, the lattice points are transformed into rods (excitation error)

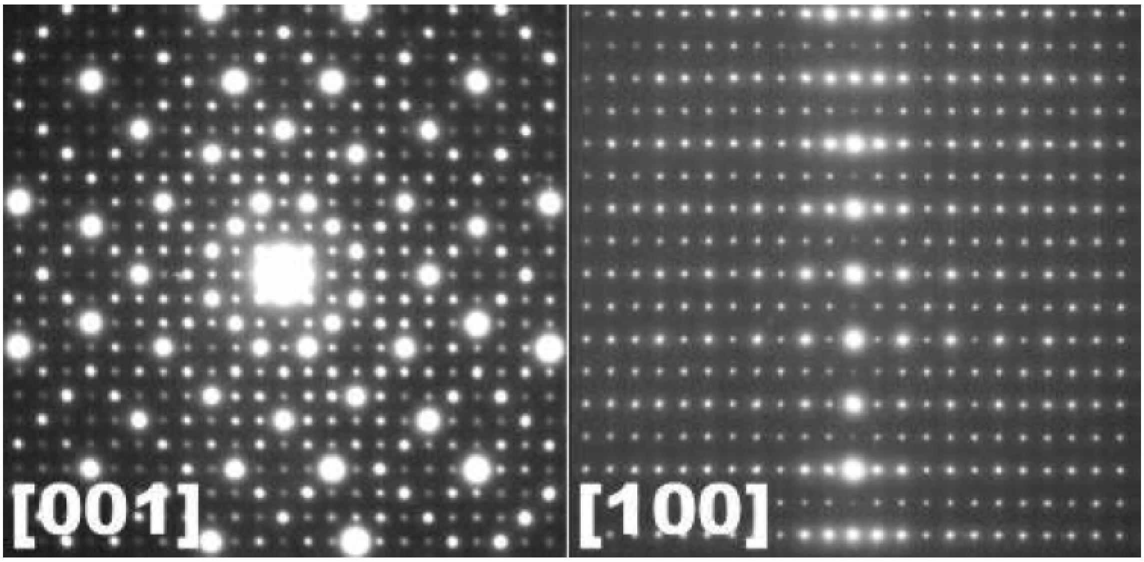
$\Rightarrow$ Reflections appear even if the Bragg condition is not exactly fulfilled.

Electron Diffraction: Examples



Single crystal of Al along [111]

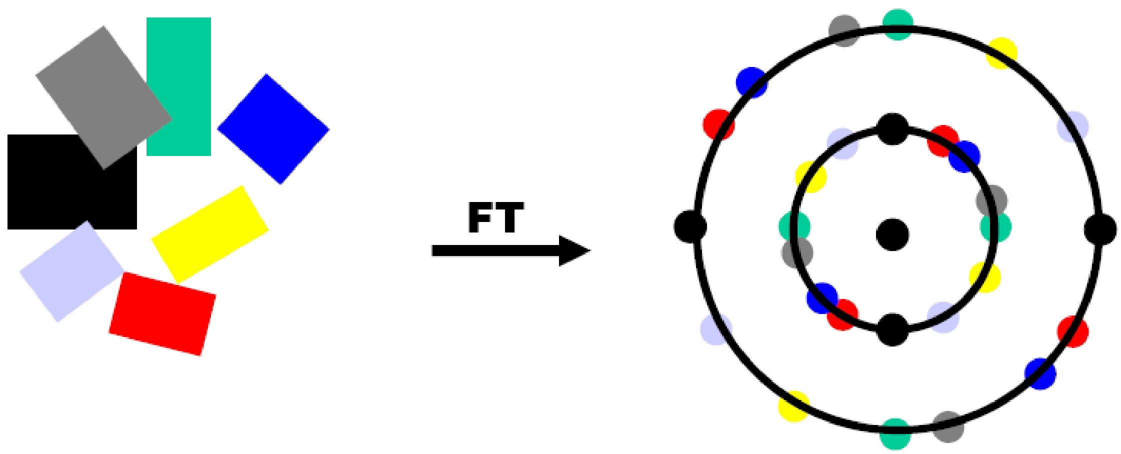
Electron Diffraction: Examples



SAED patterns of single micro-crystals of $Ta_{97}Te_{60}$ (tetragonal; a = 2.76 nm, c = 2.06 nm)

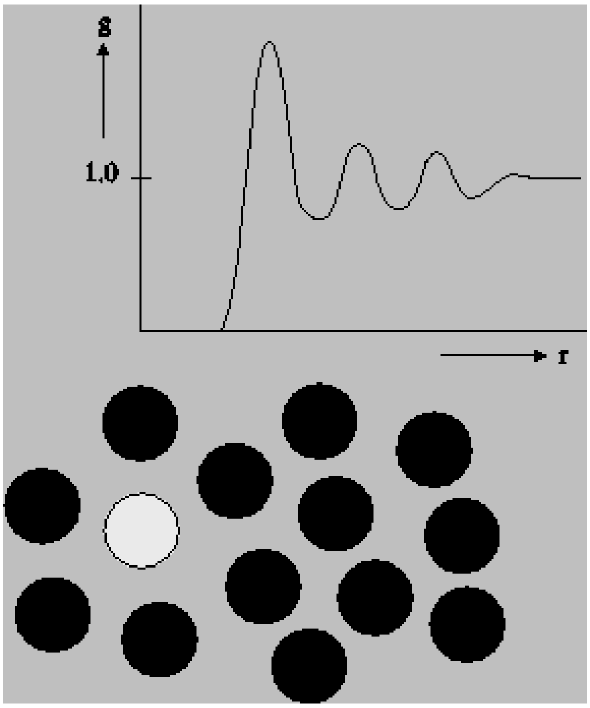
Diffraction of crystals

Crystals **Reciprocal lattice**



Superposition of the diffractograms of many small crystals gives rise to a ring pattern (powder diffractogram).

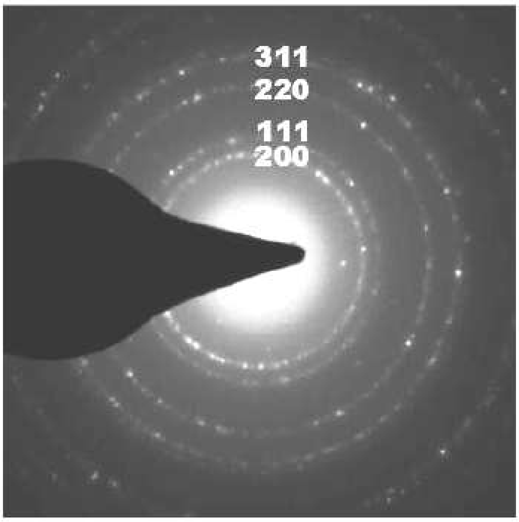
Radial Distribution Functions

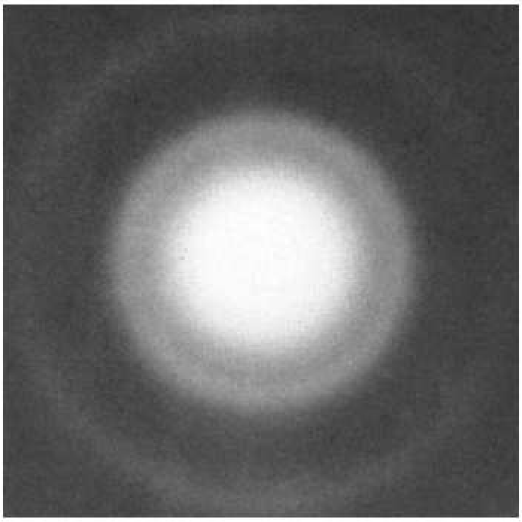


Probability that an atom lies r away
From another atom

Good for even fluids!

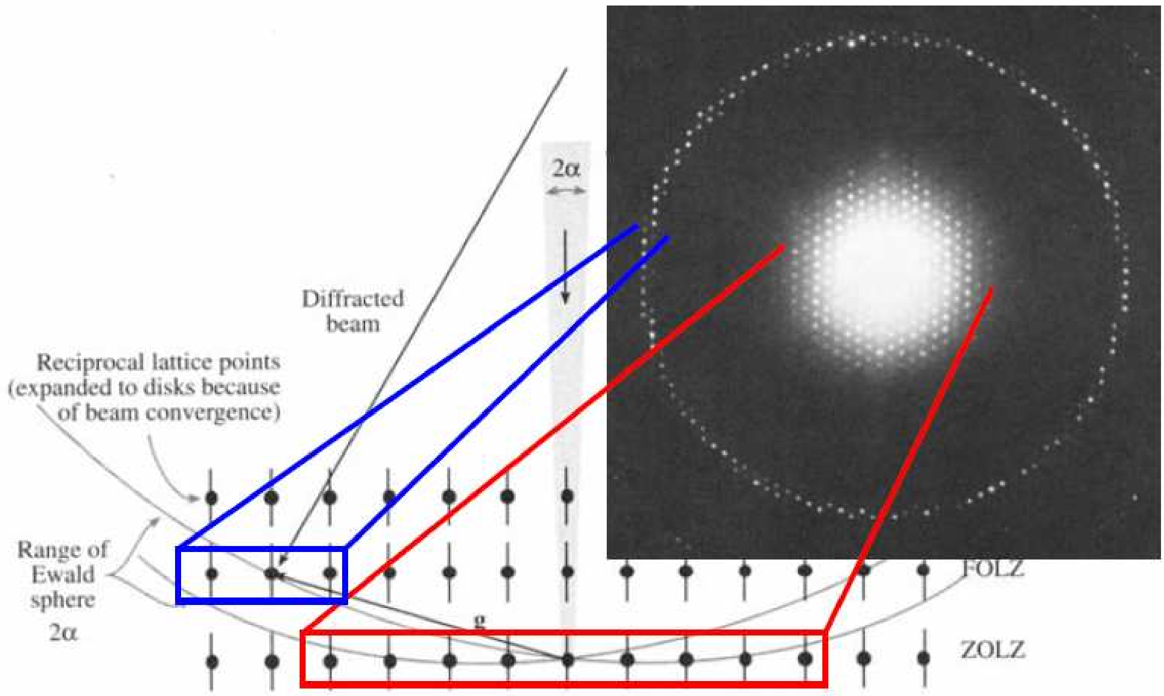
Electron Diffraction: Examples





SAED patterns of polycrystalline platinum (left) and of amorphous carbon (right).

Convergent Beam Electron Diffraction (CBED)



Comparison of electron (ED) and X-ray (XRD) Diffraction

What ED and XRD have in common:

- generated by interference (Bragg law, extinction rules…)
- single crystal and powder diffractograms

Differences:

- X-rays interact with the electron cloud, electrons are scattered by the positive potential inside the electron cloud
- electrons interact with matter much stronger than X-rays
  $\Rightarrow$ intensity of ED reflections is 10^6-10^7x those of XRD
  $\Rightarrow$ exposure times in ED: ~ sec; in XRD: ~ min - h
  $\Rightarrow$ problem: multiple scattering in ED
- wavelength of electrons (λ ~ 2 pm) much shorter than that of X-rays (λ~ 100 pm)
- diffraction angles: ED 0-2°; XRD 0-180°
- penetration depth: ED ~ 1 μm; XRD ~ 100 μm
- investigated sample volumes: ED ~ 1 μm^3 (CBED ~ 10 nm^3); XRD ~ 0.1-10 mm^3

Electron Diffraction

Methods:
- Selected Area Electron Diffraction (SAED)
- Convergent Beam Electron Diffraction (CBED)

Determination of
- Phases
- Sample crystallinity
- Lattice parameters
- Crystal symmetry

TEM Modes

Bright Field Imaging

Dark Field Imaging

Diffraction

Analysis

STEM

EFTEM

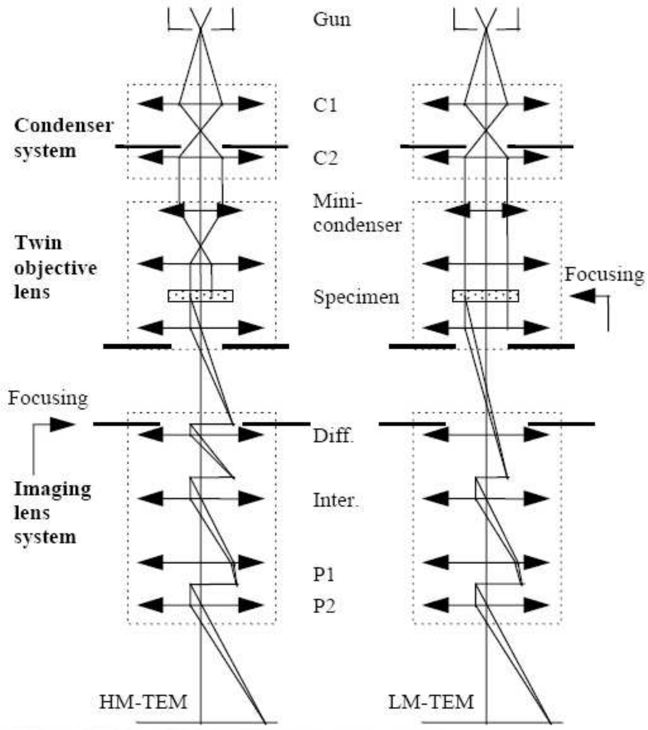
Bright Field TEM

Standard method for making images with the transmitted beam

Imaging modes

- LM (objective lens nearly off)
- HM (objective lens on)

Bright Field TEM (LM/HM)



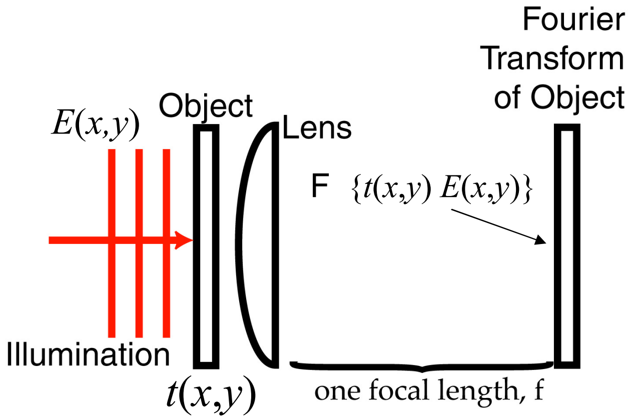
Different Focus of Lens Imaging System

A lens brings the far field in to its focal length.

This yields:

$$E(x_1, y_1) \propto \iint \exp\left\{-i\frac{k}{f}(x_0 x_1 + y_0 y_1)\right\} t(x_0, y_0) E(x_0, y_0)\, dx_0\, dy_0$$

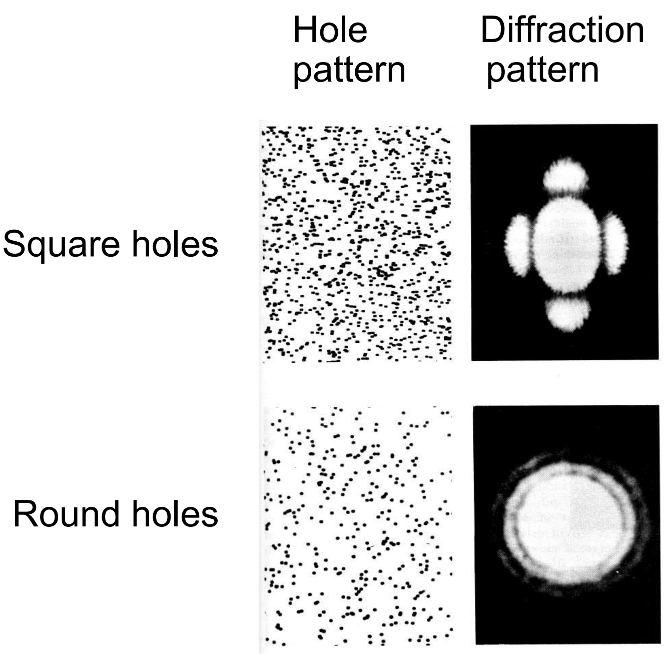
If we look in a plane one focal length behind a lens, we are in the Fraunhofer regime, even if it isn't far away! So we see the Fourier Transform of any object immediately in front of the lens!



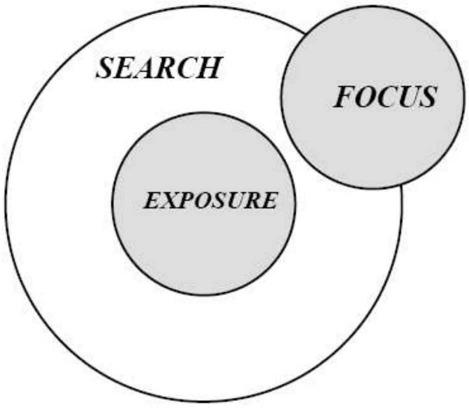
A lens in this configuration is said to be a Fourier-transforming lens.

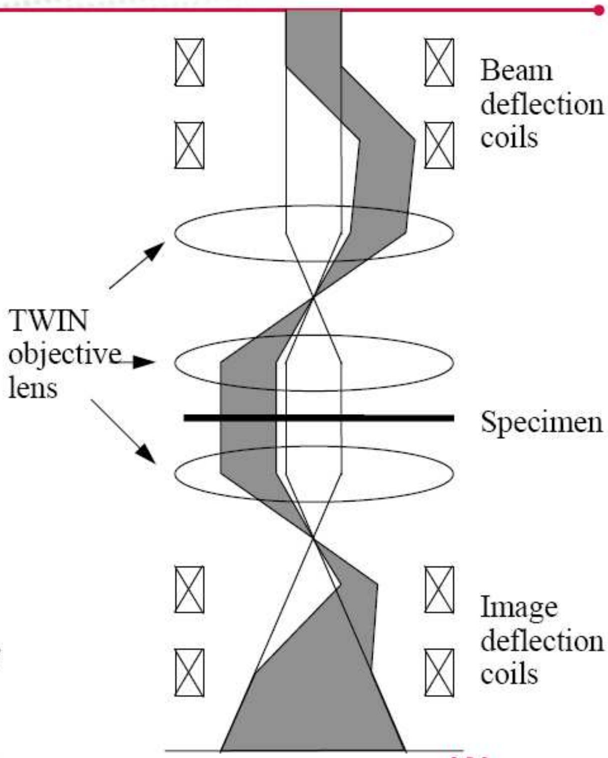
Fraunhofer Diffraction: interesting example

Randomly placed identical holes yield a diffraction pattern whose gross features reveal the shape of the holes.



Bright Field TEM: Low Dose





Beam-sensitive specimens

FEI

Dark Field TEM

Standard method for making images with deflected or diffracted beams

Imaging modes

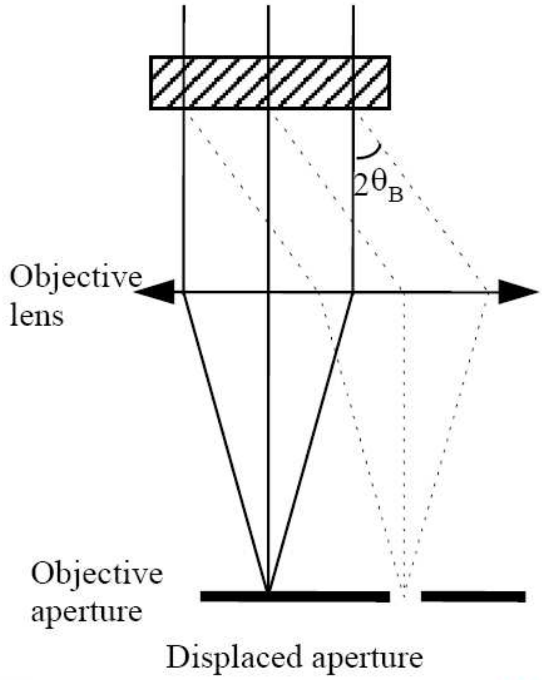
- Off-axis method
- Tilted Beam method

FEI

Dark Field TEM

Off-axis imaging

Loss of resolution due to higher C_s at off-axis positions

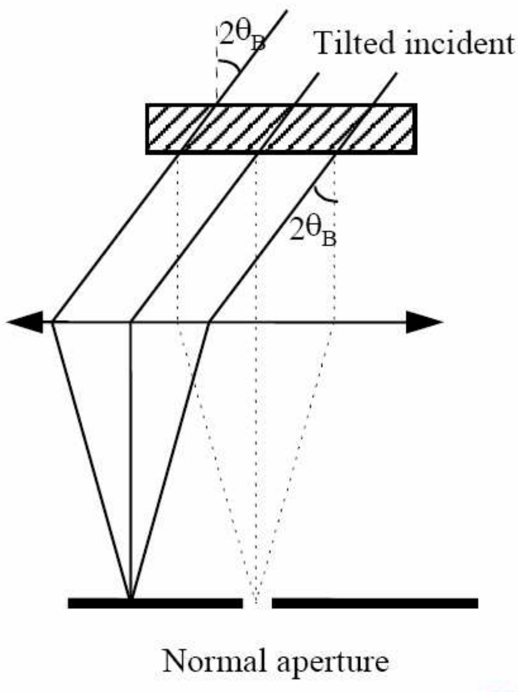


Dark Field TEM

Tilted Beam Method

Centred Dark Field Imaging

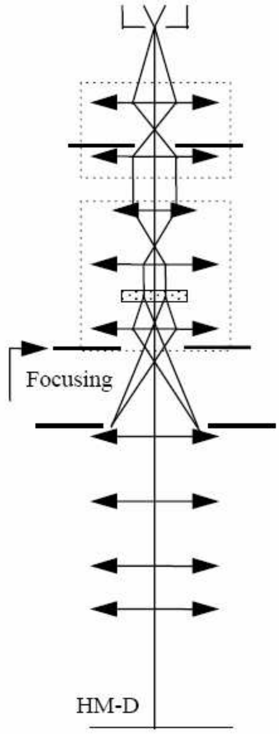
Normal resolution



Diffraction

The imaging lens system is focusing at the back focal plane of the objective lens

- Selected Area Diffraction (SAD)
- Micro-diffraction
- Convergent Beam Diffraction (CBED)



Diffraction: SAD

Specimen area for diffraction pattern can be selected with SA aperture

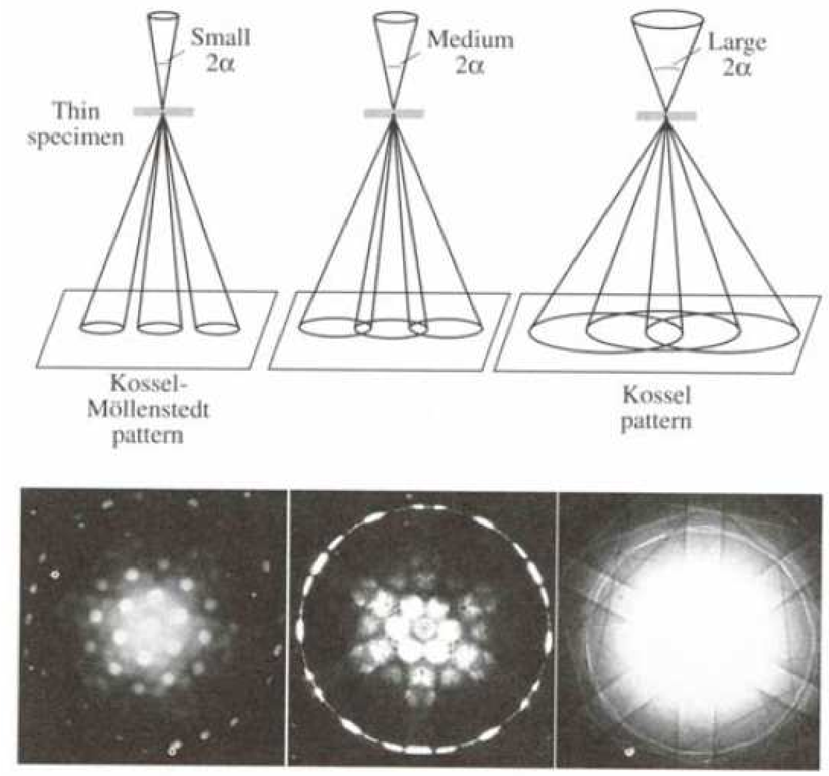
- effects in a virtual insertion of an aperture in the specimen plane with size M time smaller (M: 20-40x)

Diffraction: micro-diffraction and CBED

Specimen area for diffraction pattern can be selected by locating beam on area of interest

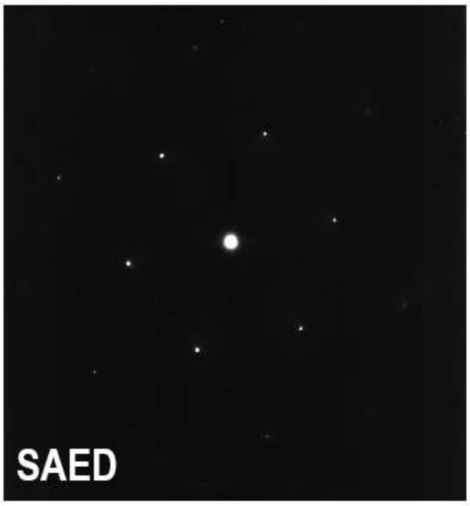
- convergent-beam
  - microprobe
  - nanoprobe (down to 0.3 nm)

Convergent Beam Electron Diffraction (CBED)



Diffraction

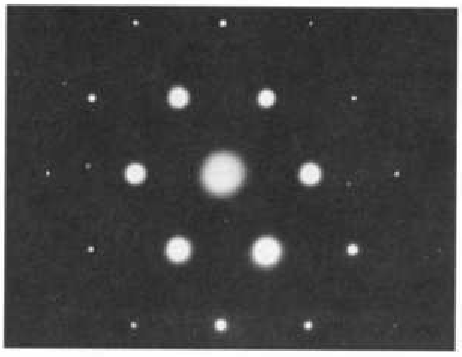
Range in diffraction



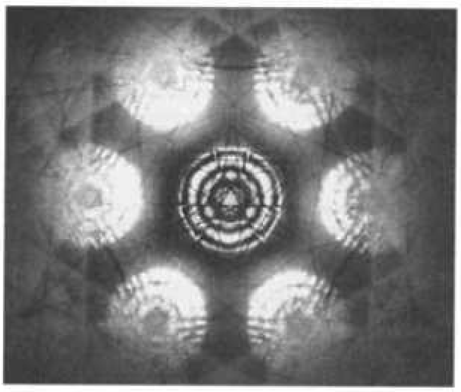
Diffraction patterns of Si [111]

Convergent Beam Electron Diffraction (CBED)

Si [111]



SAED



CBED

The Fourier Transform of a random array of identical tiny objects

Define a random array of two-dimensional delta-functions:

$$Rand(x,y) = \sum_{i=1}^{n} \delta(x - x_i, y - y_i)$$

Shift Theorem

$$\mathcal{F}\{Rand(x,y)\} = \sum_{i=1}^{n} \exp[-i(k_x x_i + k_y y_i)]$$

Sum of rapidly varying sinusoids (looks like noise)

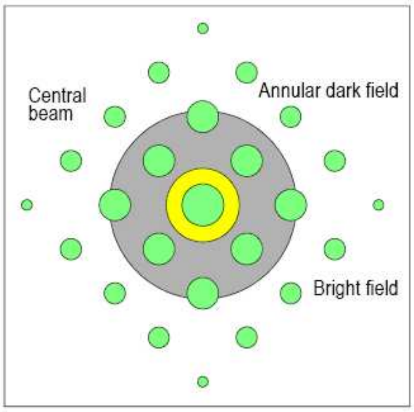
If *Hole(x,y)* is the shape of an individual tiny hole, then a random array of identically shaped tiny holes is:

$$Holes(x,y) = Rand(x,y) * Hole(x,y)$$

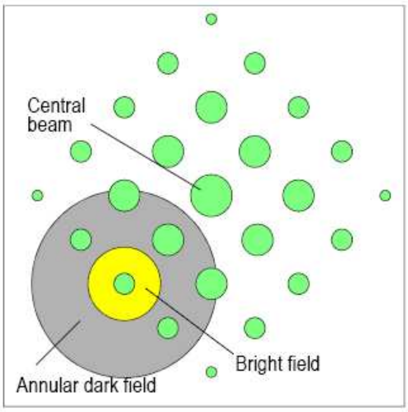
The Fourier Transform of a random array of identically shaped tiny holes is then:

$$\mathcal{F}\{Holes(x,y)\} = \underbrace{\mathcal{F}\{Rand(x,y)\}}_{\uparrow\ \text{Rapidly varying}}\ \underbrace{\mathcal{F}\{Hole(x,y)\}}_{\uparrow\ \text{Slowly varying}}$$

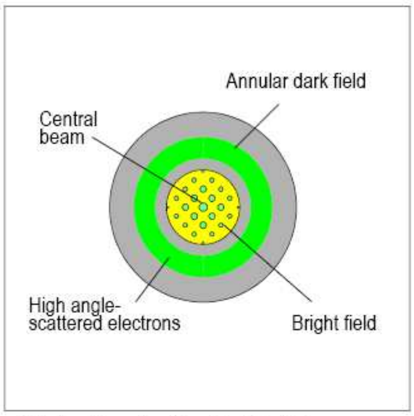
Scanning Bright Field / Dark Field



Standard BF/DF
Central beam on BF
Diffracted beams on DF



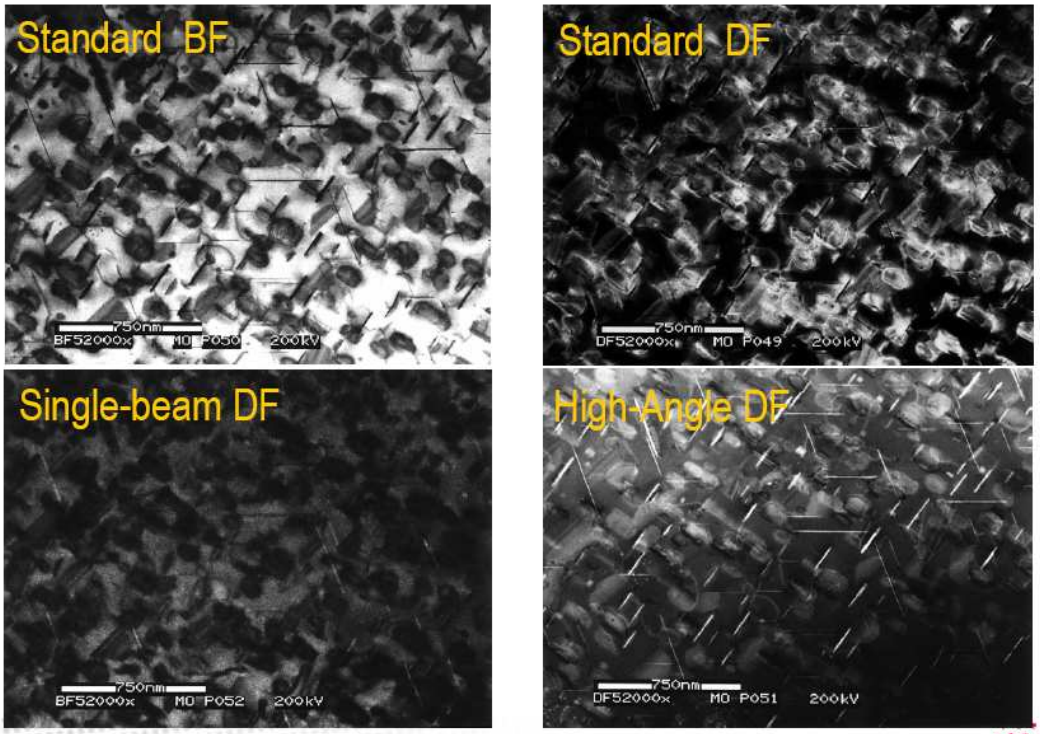
Single-beam DF
One diffracted beam on DF



High-Angle Dark Field
Central and diffracted beams on BF
High-angle electrons on DF

FEI

Scanning Bright Field / Dark Field



Al-Cu alloy

FEI