TEM Crystallography and Diffraction

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Contents

Introduction to electron diffraction

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
(≳ 200 nm for selected-area diffraction; 2 nm possible with convergent-beam electron diffraction)

✔ close relationship to diffraction contrast in imaging

✔ orientation information

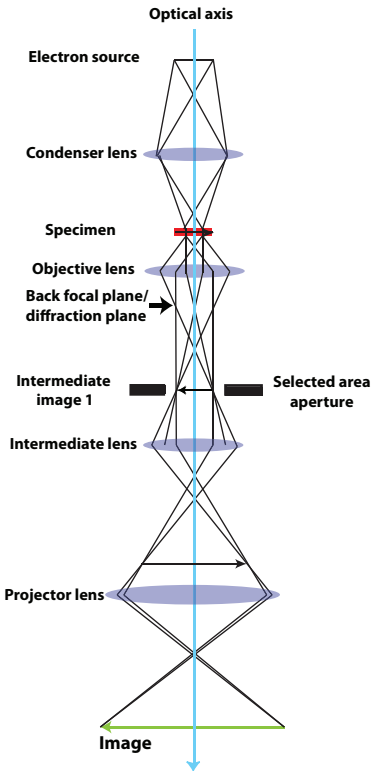
✔ immediate in the TEM!

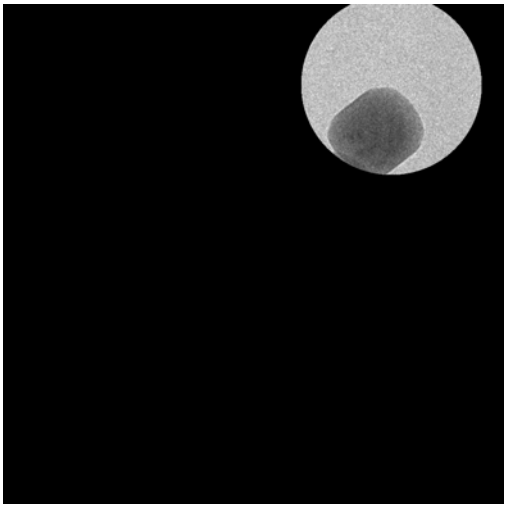
(✘ diffraction from only selected set of planes in one pattern - e.g. only 2D information)

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

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

Image formation

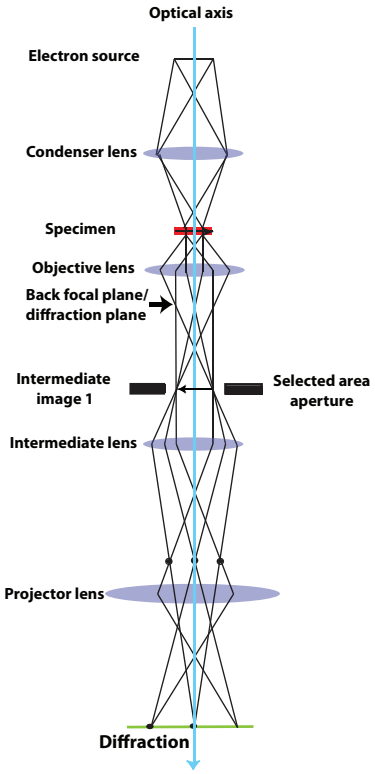


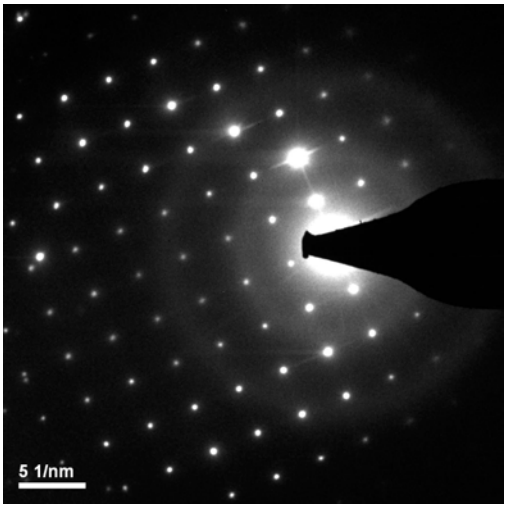


$BaTiO_3$ nanocrystals (Psaltis lab)

Insert selected area aperture to choose region of interest

Take selected-area diffraction pattern



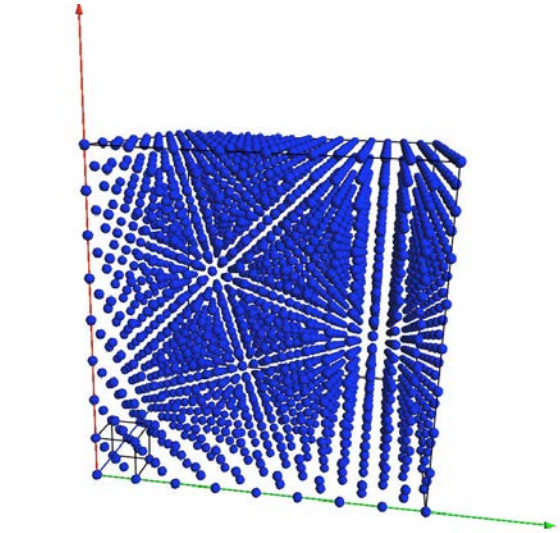


Press "D" for diffraction on microscope console - alter strength of intermediate lens and focus diffraction pattern on to screen

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

Basic crystallography & symmetry

Crystals: translational periodicity & symmetry

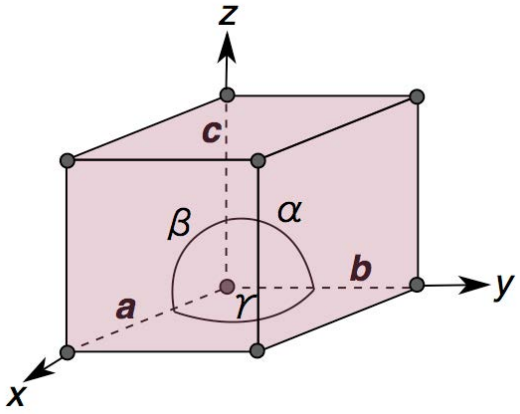


Repetition of translated structure to infinity

Crystallography: the unit cell

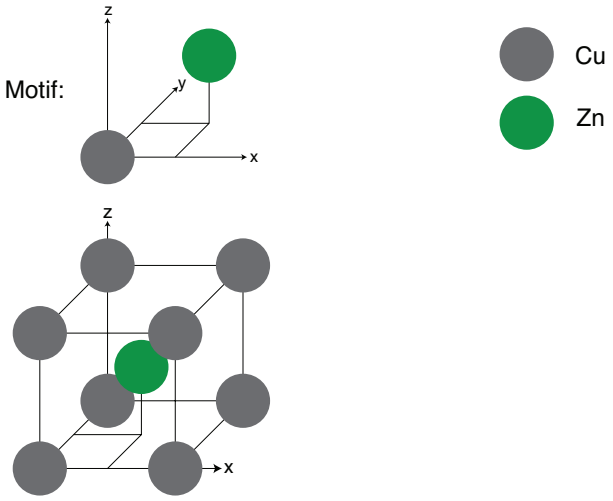
Unit cell is the smallest repeating unit of the crystal lattice
Has a lattice point on each corner (and perhaps more elsewhere)

Defined by lattice parameters *a*, *b*, *c* along axes *x*, *y*, *z*
and angles between crystallographic axes: α = *b*^*c*; β = *a*^*c*; γ = *a*^*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)

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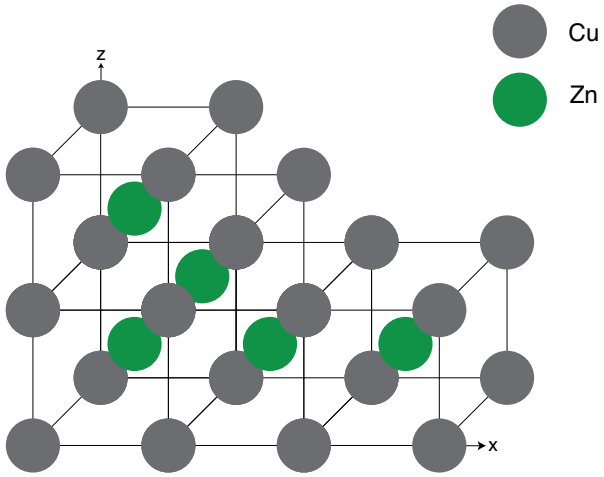
Structure = lattice +motif => Start applying motif to each lattice point

Extend lattice further in to space



Introduction to symmetry

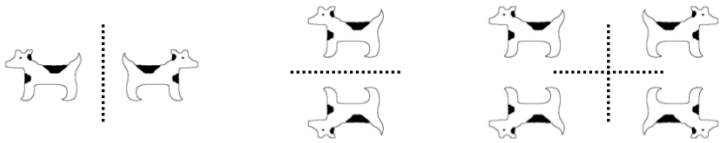
Excerpt from Bruno Munari's "Zoo", First Chronical Books

Introduction to symmetry

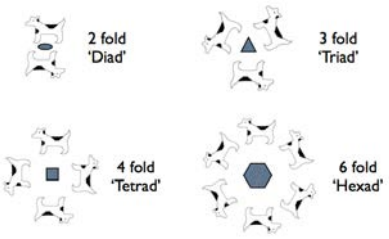
As well as having translational symmetry, nearly all crystals obey other symmetries - i.e. can reflect or rotate crystal and obtain exactly the same structure

Symmetry elements:

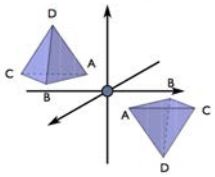
Mirror planes:



Rotation axes:



Centre of symmetry or inversion centre:



Inversion axes: combination of rotation axis with centre of symmetry

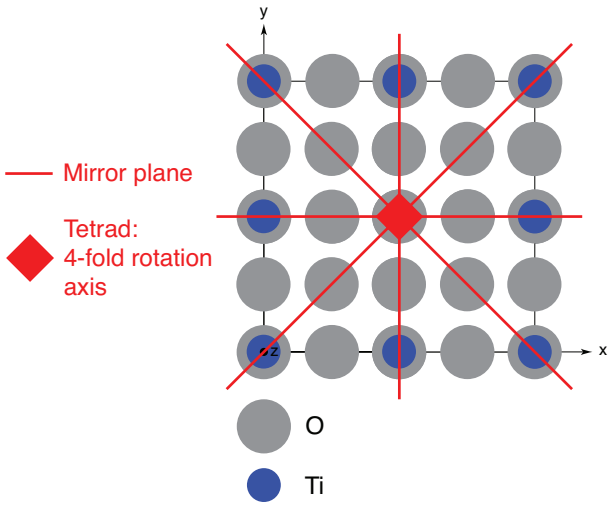
Introduction to symmetry

Example - Tetragonal lattice: $a = b \neq c$; $\alpha = \beta = \gamma = 90°$

Anatase TiO_2 (body-centred lattice) view down [0 0 1] (z-axis):

Identify mirror planes

Identify rotation axis: 4-fold = defining symmetry of tetragonal lattice!



More defining symmetry elements

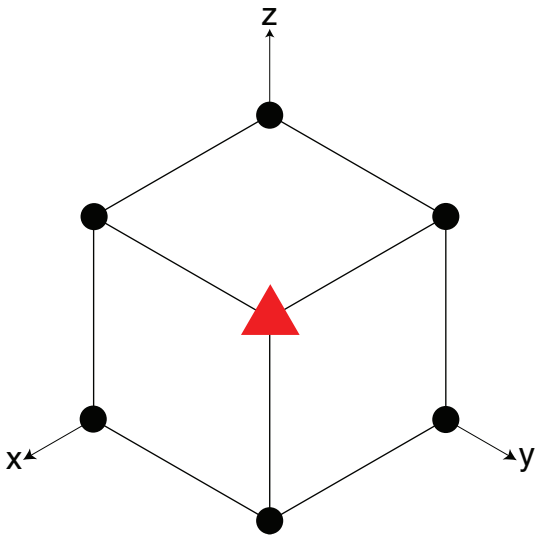
Cubic crystal system: $a = b = c$; $\alpha = \beta = \gamma = 90°$

View down body diagonal (i.e. [1 1 1] axis)

Choose Primitive cell (lattice point on each corner)

Identify rotation axis: 3-fold (triad)

Defining symmetry of cube: four 3-fold rotation axes (not 4-fold rotation axes!)



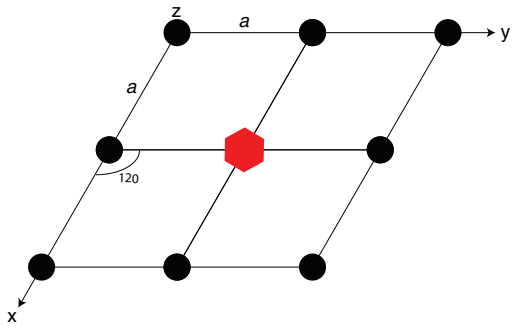
More defining symmetry elements

Hexagonal crystal system: $a = b \neq c$; $\alpha = \beta = 90°, \gamma = 120°$

Primitive cell, lattice points on each corner; view down z-axis - i.e.[1 0 0]

Draw 2 x 2 unit cells

Identify rotation axis: 6-fold (hexad) - defining symmetry of hexagonal lattice



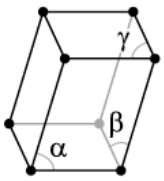
The seven crystal systems

7 possible unit cell shapes with different symmetries that can be repeated by translation in 3 dimensions

=> 7 crystal systems each defined by symmetry

Triclinic

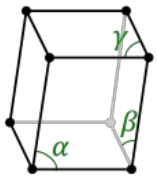
$\alpha,\beta,\gamma \neq 90°$



Monoclinic

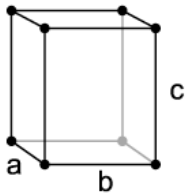
$\alpha \neq 90°$

$\beta, \gamma = 90°$



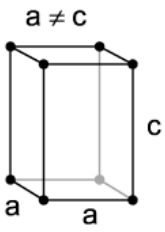
Orthorhombic

$a \neq b \neq c$



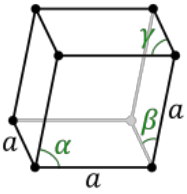
Tetragonal

$a \neq c$

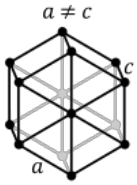


Rhombohedral

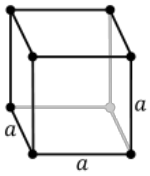
$\alpha, \beta, \gamma \neq 90°$



Hexagonal



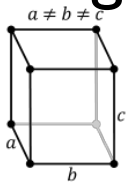
Cubic



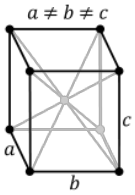
Diagrams from www.Wikipedia.org

Four possible lattice centerings

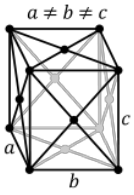
P: Primitive - lattice points on cell corners



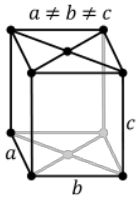
I: Body-centred - additional lattice point at cell centre



F: Face-centred - one additional lattice point at centre of each face



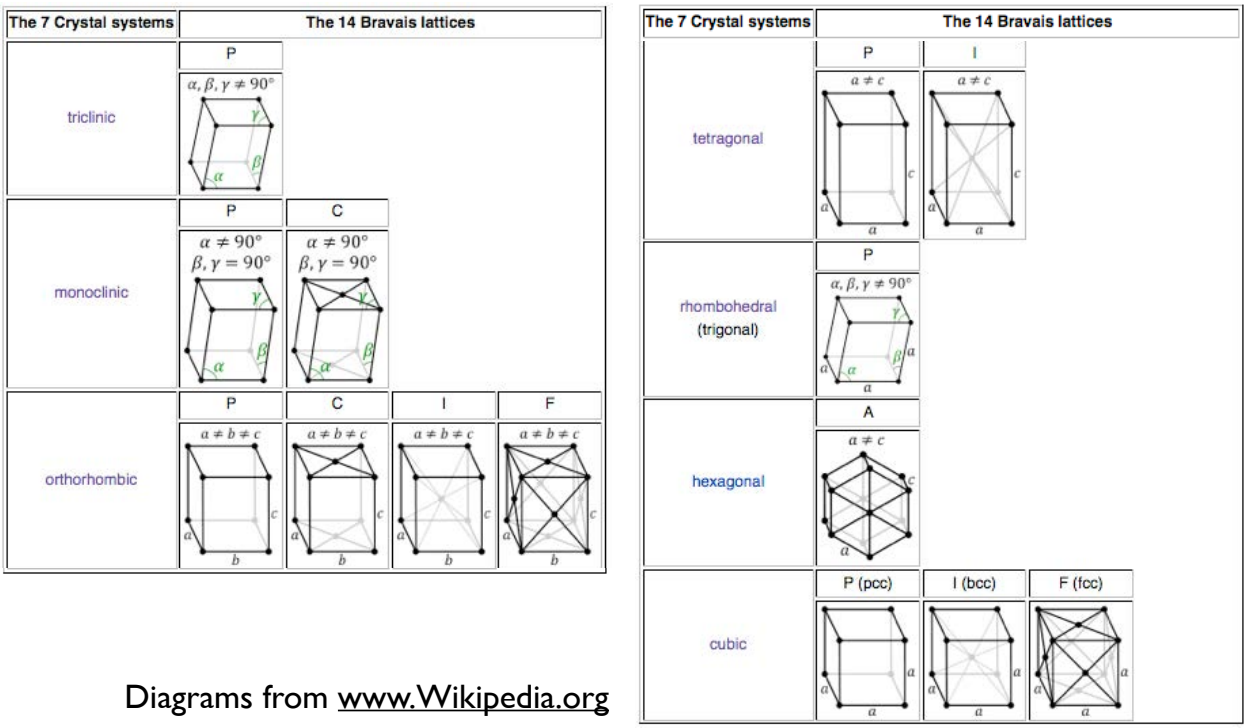
A/B/C: Centred on a single face - one additional lattice point centred on A, B or C face



Diagrams from www.Wikipedia.org

14 Bravais lattices

Combinations of crystal systems and lattice point centring that describe all possible crystals
- Equivalent system/centring combinations eliminated => 14 (not 7 x 4 = 28) possibilities



Diagrams from www.Wikipedia.org

14 Bravais lattices

Crystal System	Defining Symmetry (rotation or inversion)	Conventional Unit Cell	Conventional Lattice Types
Cubic	4 triads	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	P, I, F
Hexagonal	1 hexad	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	P
Trigonal	1 triad	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	P, R
Tetragonal	1 tetrad	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P, I
Orthorhombic	3 diads	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P, C, I, F
Monoclinic	1 diad	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ, \beta \geq 90^\circ$	P, C
Triclinic	-	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	P

Crystallography - lattice vectors

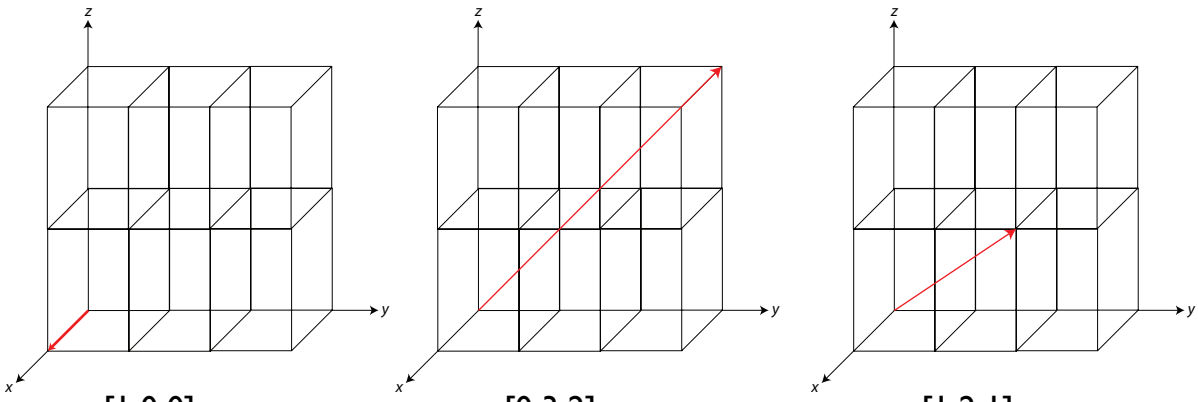
A lattice vector is a vector joining any two lattice points

Written as linear combination of unit cell vectors ***a***, ***b***, ***c***:

$$\boldsymbol{t} = U\boldsymbol{a} + V\boldsymbol{b} + W\boldsymbol{c}$$

Also written as: $\boldsymbol{t}$ = [U V W]

Examples:



[1 0 0] [0 3 2] [1 2 1]

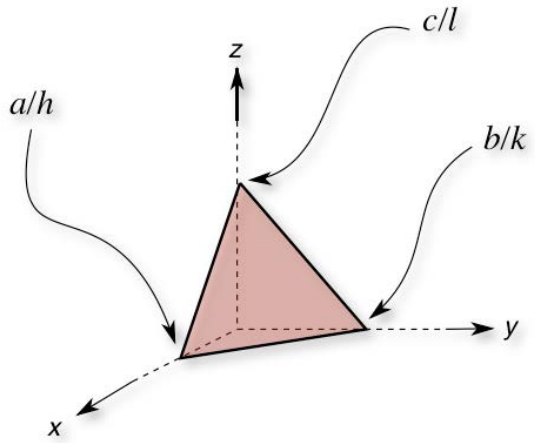
Important in diffraction because we "look" down the lattice vectors ("zone axes")

Crystallography - lattice planes

Lattice plane is a plane which passes through any 3 lattice points which are not in a straight line

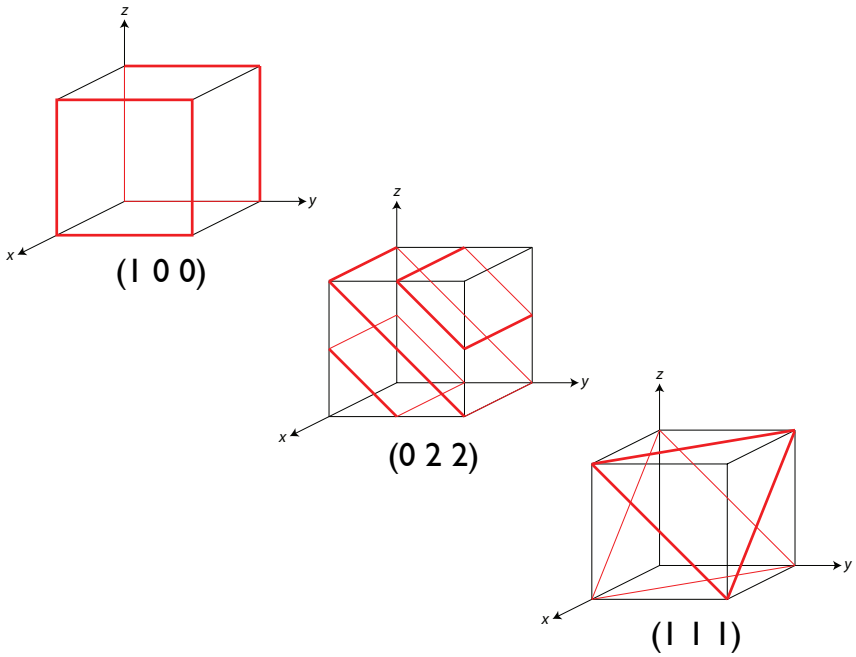
Lattice planes are described using Miller indices (*h k l*) where the *first* plane away from the origin intersects the *x*, *y*, *z* axes at distances:

a/*h* on the *x* axis
b/*k* on the *y* axis
c/*l* on the *z* axis



Crystallography - lattice planes

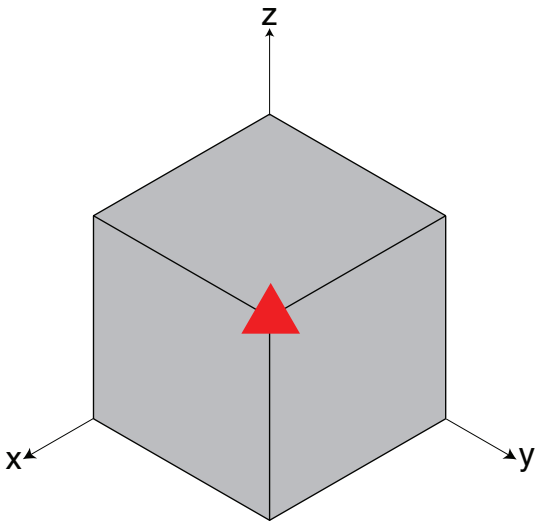
Sets of planes intersecting the unit cell - examples:



Lattice planes and symmetry

Lattice planes in a crystal related by the crystal symmetry

For example, in cubic lattices the 3-fold rotation axis on the [1 1 1] body diagonal relates the planes (1 0 0), (0 1 0), (0 0 1):



Set of planes {1 0 0} = (1 0 0), (0 1 0), (0 0 1), (-1 0 0), (0 -1 0), (0 0 -1)

Weiss Zone Law

If the lattice vector [*U V W*] lies in the plane (*h k l*) then:

$$hU + kV + lW = 0$$

Electron diffraction:

Electron beam oriented parallel to lattice vector called the "*zone axis*"

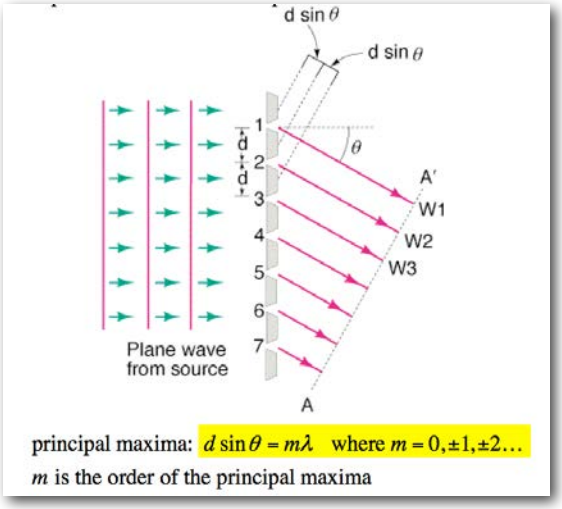
Diffracting planes must be parallel to electron beam
- *therefore they obey the Weiss Zone law**

(*at least for zero-order Laue zone)

Electron diffraction theory

Optics: scattering from slits

In zone-axis condition our TEM optics and sample are similar to grating in Fraunhofer far-field diffraction geometry



Incident plane wave (far-field) on diffraction grating =>
Periodic array of spots in diffraction plane

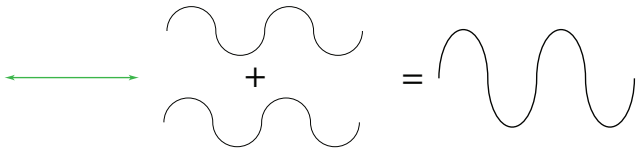
Optics: scattering from slits – video

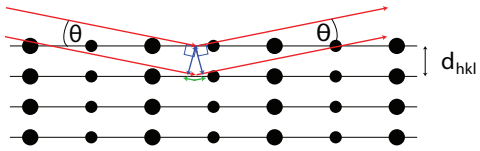
Video: From one to many slits

Diffraction theory – Bragg law

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

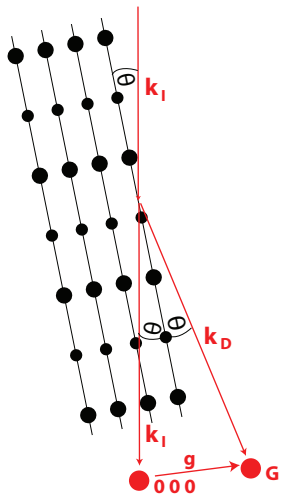
=> Bragg law:
$n\lambda = 2d_{hkl}\sin\theta$





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

Diffraction theory - 2-beam condition



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

Multi-beam scattering condition

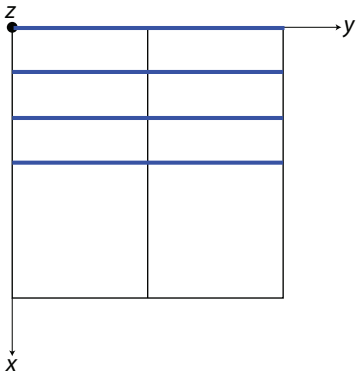
Electron beam parallel to low-index crystal orientation [U V W] = zone axis

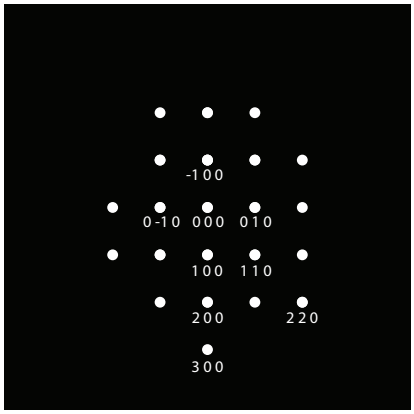
Crystal "viewed down" zone axis is like diffraction grating with planes parallel to e-beam

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





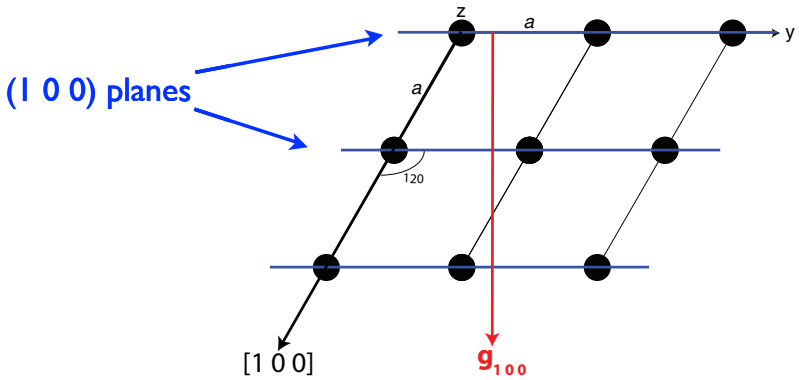
Note reciprocal relationship: smaller plane spacing => larger indices (*h k l*)
& greater scattering angle on diffraction pattern from (0 0 0) direct beam

Also note Weiss Zone Law obeyed in indexing ($hU + kV + lW = 0$)

Scattering from non-orthogonal crystals

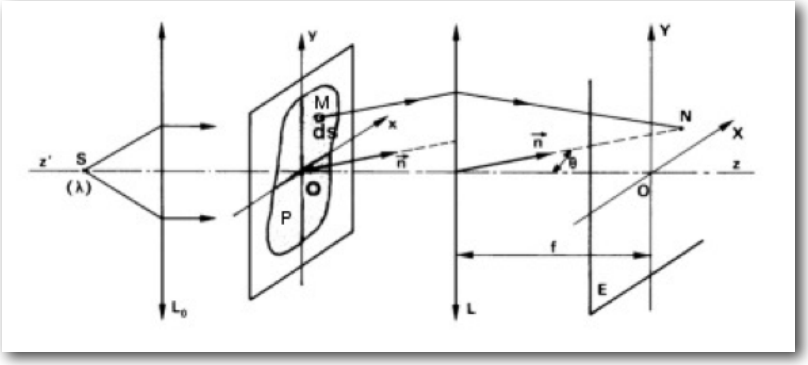
With scattering from the cubic crystal we can note that the diffracted beam for plane (1 0 0) is parallel to the lattice vector [1 0 0]; makes life easy

However, not true in non-orthogonal systems - e.g. hexagonal:



=> care must be taken in reciprocal space!

Diffraction as Fourier Transform



For transmitting object $t(x,y)$ can be proved that diffraction pattern in X, Y plane has amplitude:

$$A(u,v) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} t(x,y)e^{-i2\pi(ux+vy)}dxdy$$

This is the Fourier transform of the object
=> TEM diffraction pattern is Fourier transform of the sample

Each diffraction spot contains frequency information on the plane that creates it

Basic properties of Fourier transform

- Linearity:
$$\begin{aligned} \boldsymbol{FT}\{\alpha g(x)\} &= \alpha \boldsymbol{FT}\{g(x)\} = \alpha G(u) \\ \boldsymbol{FT}\{\alpha g(x) + \beta h(x)\} &= \alpha \boldsymbol{FT}\{g(x)\} + \beta \boldsymbol{FT}\{h(x)\} = \alpha G(u) + \beta H(u) \end{aligned}$$

- Shift:
$$\boldsymbol{FT}\{g(x-a)\} = e^{-2i\pi ua}\boldsymbol{FT}\{g(x)\}$$
$$I(u) = (e^{2i\pi ua}\boldsymbol{FT}\{g(x)\}) \cdot (e^{-2i\pi ua}\boldsymbol{FT}\{g(x)\}) = G^*(u) \cdot G(u)$$

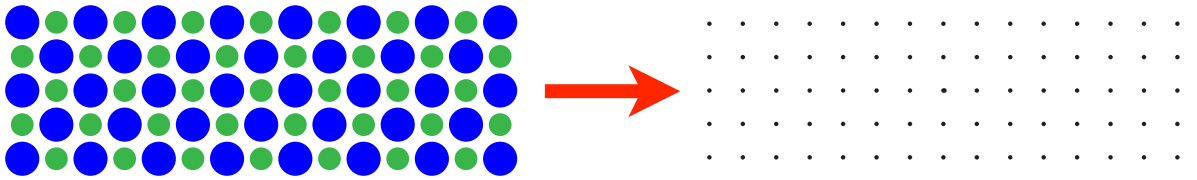
- Reciprocity:
$$\boldsymbol{FT}\{g(ax)\} = \frac{1}{|a|}G(\frac{u}{a})$$

- Convolution:
$$\boldsymbol{FT}\{g(x)*h(x)\} = \boldsymbol{FT}\{g(x)\} \otimes \boldsymbol{FT}\{h(x)\} = G(u) \otimes H(u)$$

- Conservation of angle

The reciprocal lattice

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

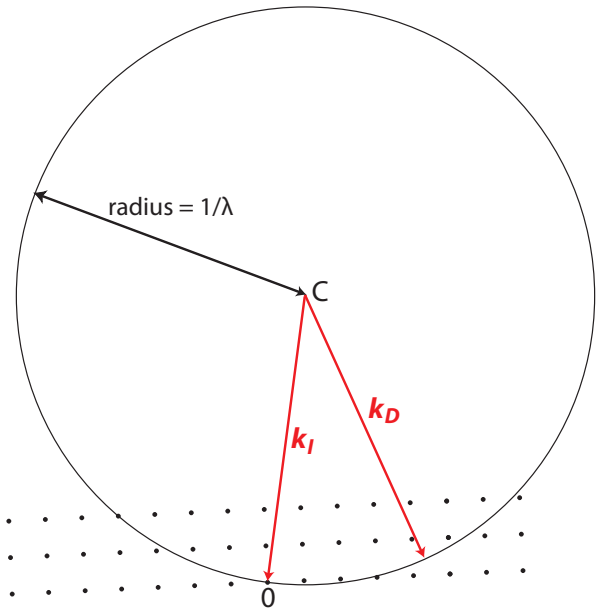
$\mathbf{g}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

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

The Ewald sphere

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

Ewald sphere for Bragg scattering (X-ray)

Schematic for X-ray: large λ => small radius $1/\lambda$

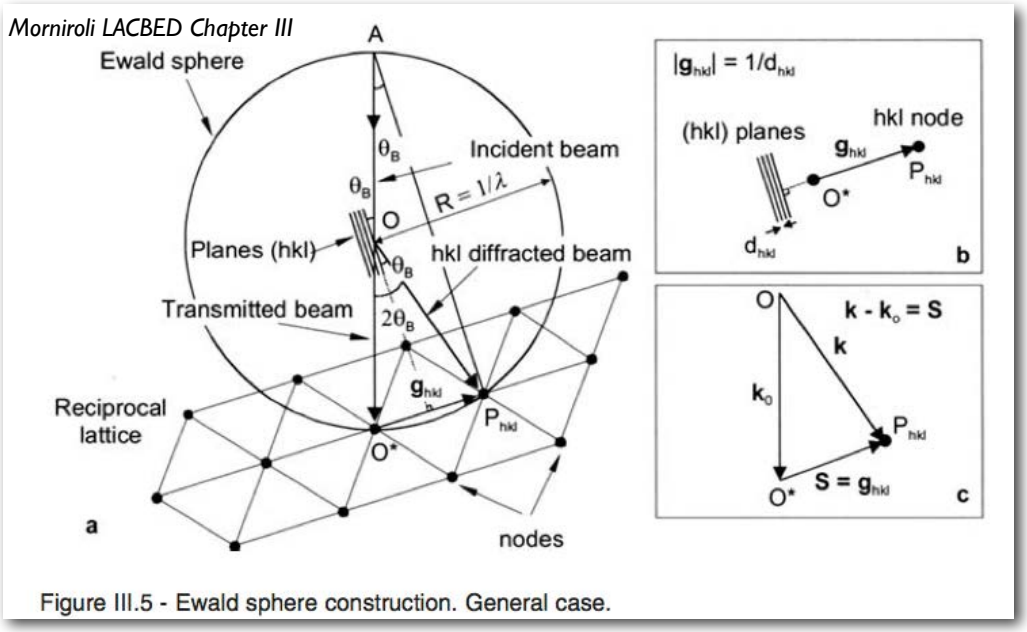
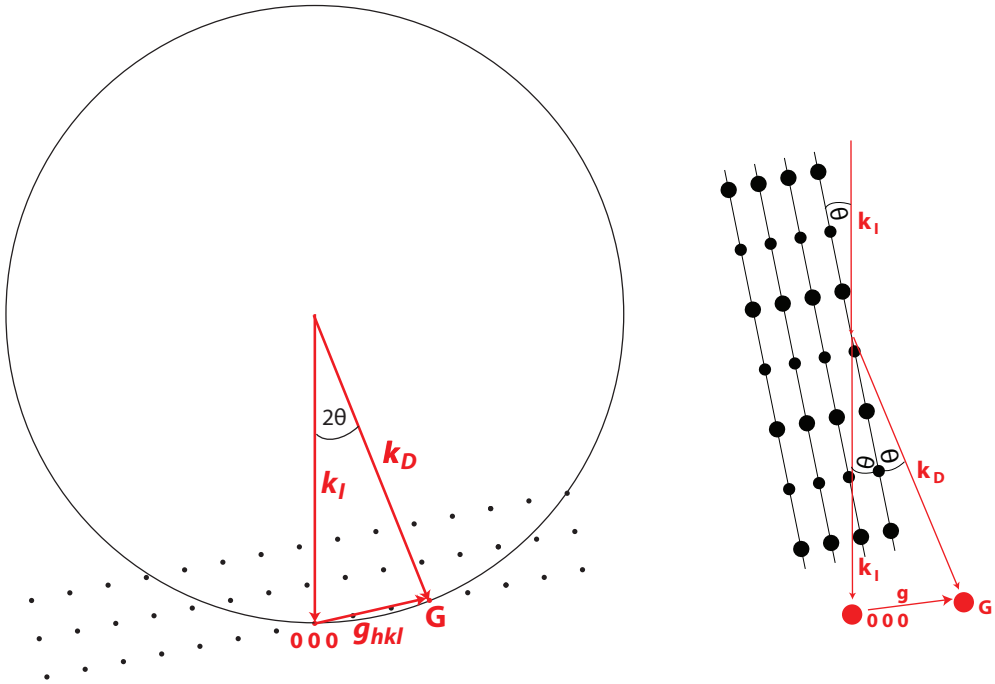


Figure III.5 - Ewald sphere construction. General case.

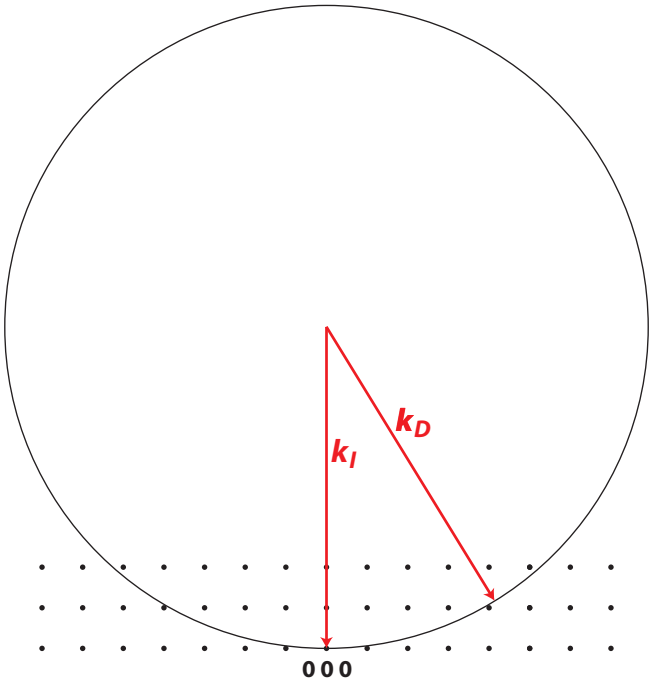
Exercise: prove that Bragg's law is met when sphere intersects reciprocal lattice node

Ewald sphere in 2-beam condition



2-beam condition with one strong Bragg reflection corresponds to Ewald sphere intersecting one reciprocal lattice point

Ewald sphere and multi-beam scattering



Assume reciprocal lattice points are infinitely small

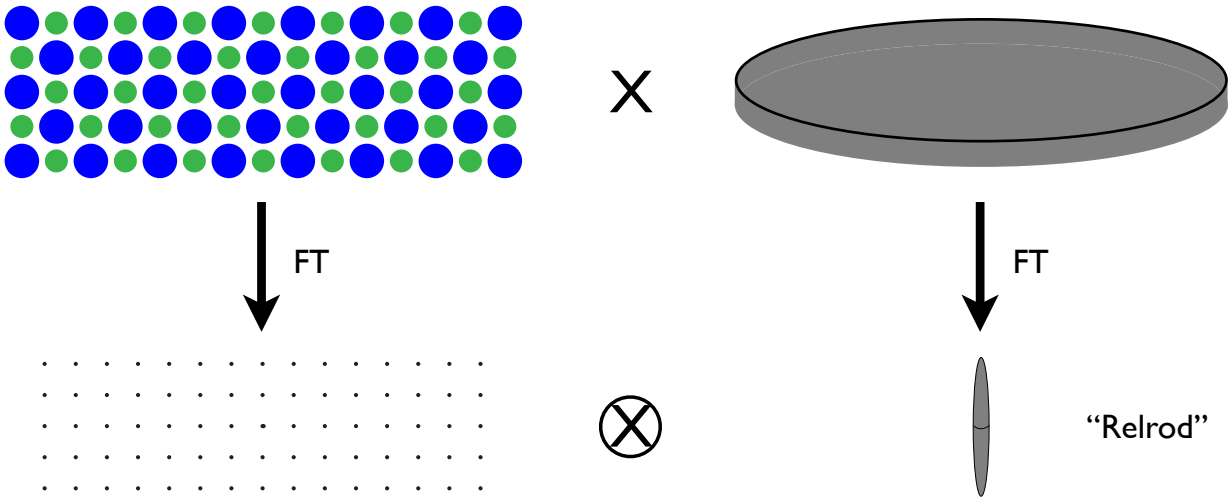
With crystal oriented on zone axis, Ewald sphere may not intersect reciprocal lattice points

However, we see strong diffraction from many planes in this condition

Because reciprocal lattice points have size and shape!

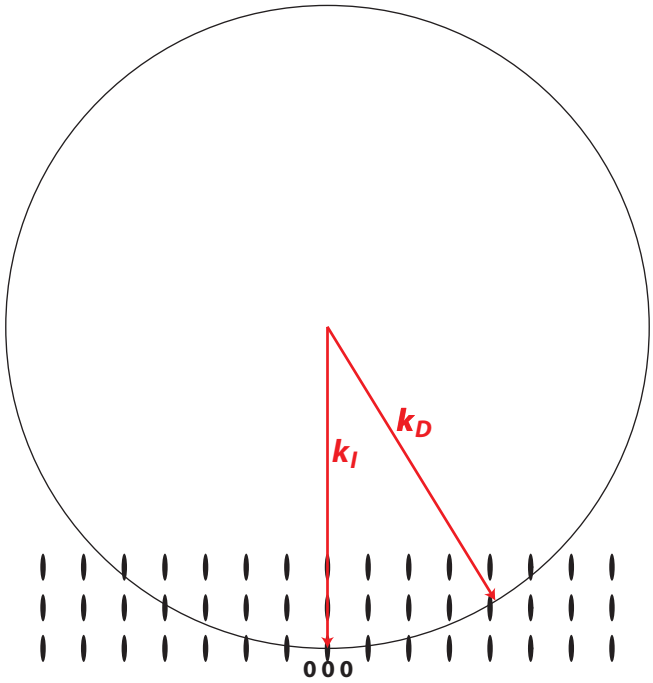
Fourier transforms and reciprocal lattice

Real lattice is not infinite, but is bound disc of material with diameter of selected area aperture and thickness of specimen - i.e. thin disc of material



2 lengths scales in reciprocal space!

Ewald sphere intersects Relrods

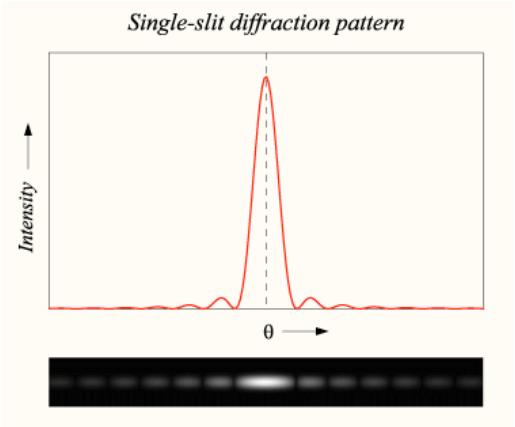


Relrod shape

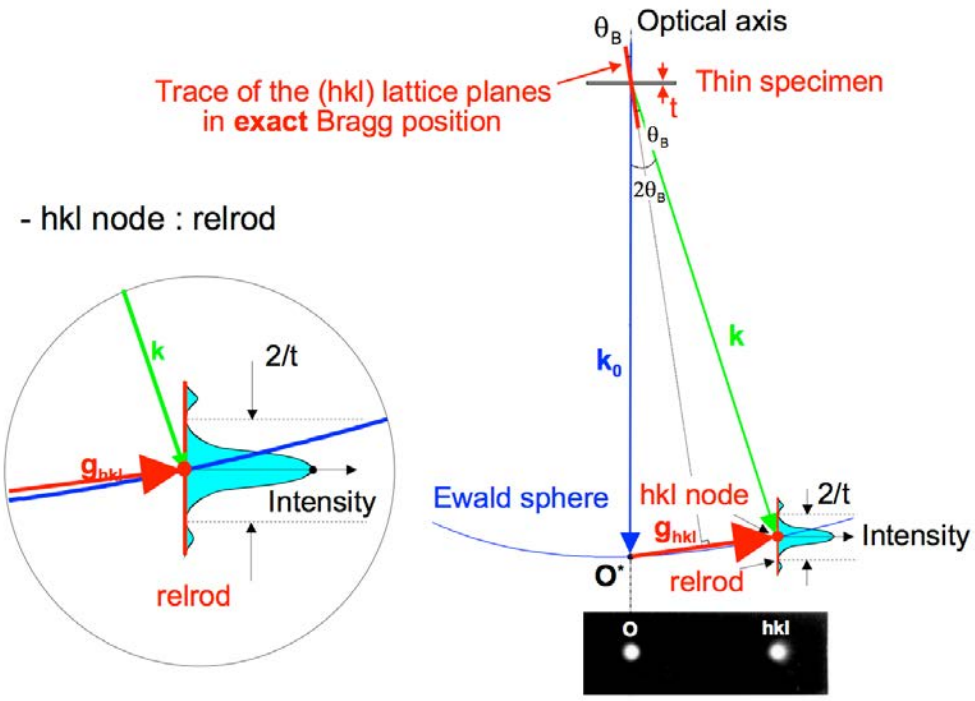
Shape (e.g. thickness) of sample is like a "top-hat" function

Therefore shape of Relrod is: $(\sin(x)/x)^2$

Can compare to single-slit diffraction pattern with intensity: $I \propto \left(\frac{\sin x}{x}\right)^2$

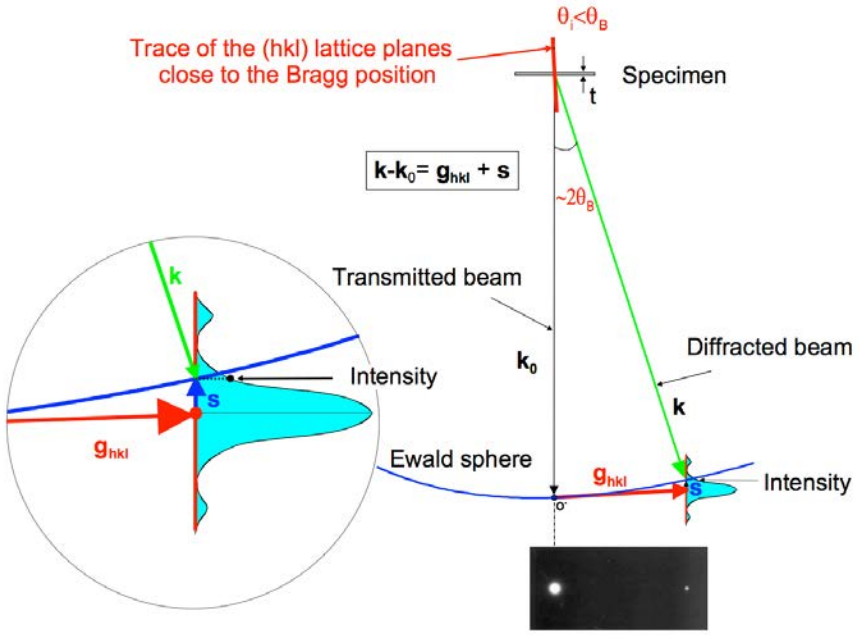


Relrod shape



Intensity in the electron diffraction pattern

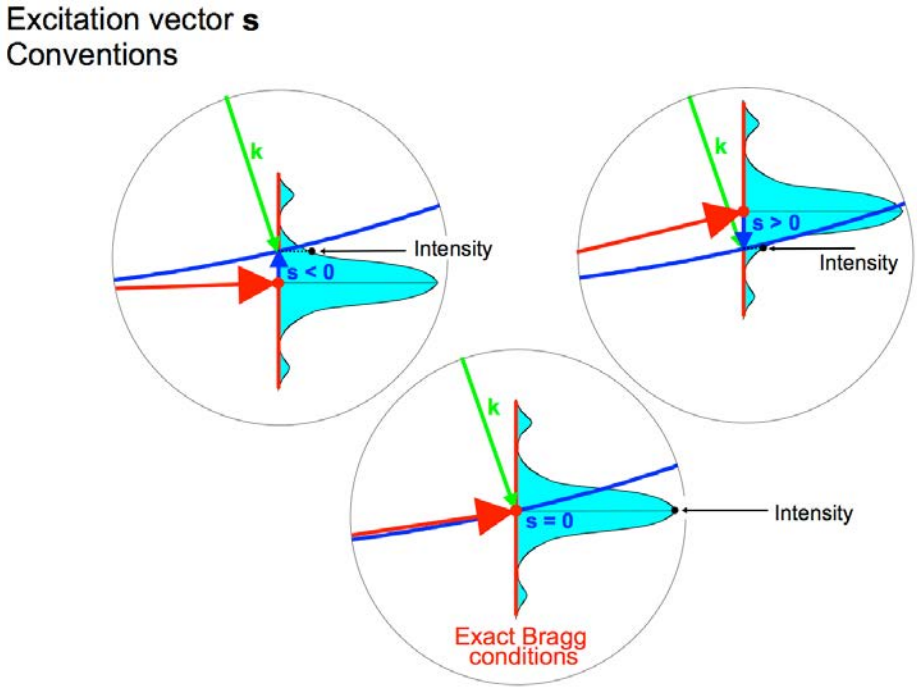
Excitation error



Tilted slightly off Bragg condition, intensity of diffraction spot much lower

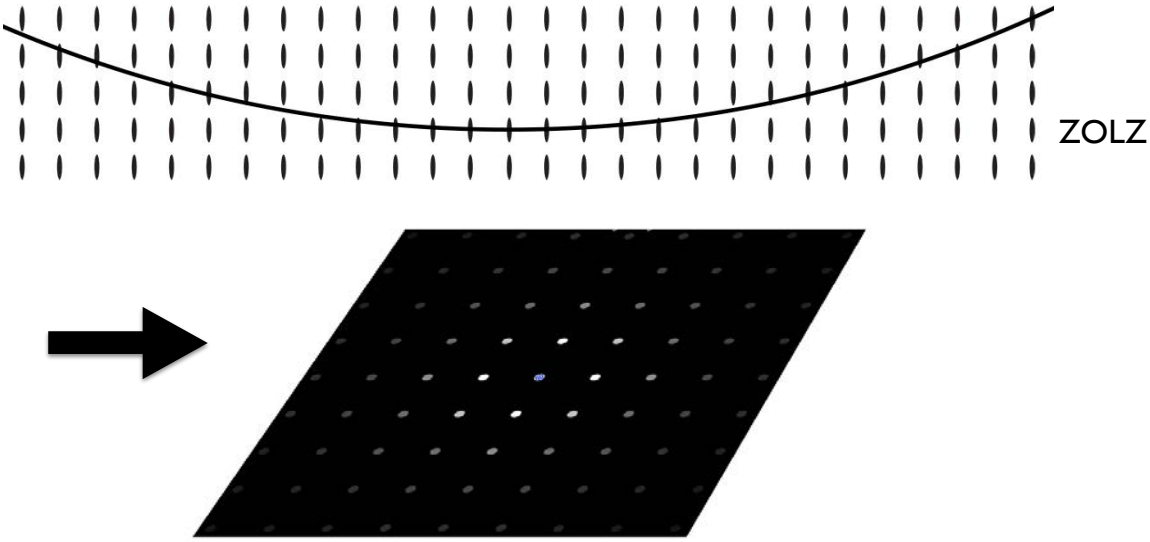
Introduce new vector **s** - "*the excitation error*" that measures deviation from exact Bragg condition

Excitation error



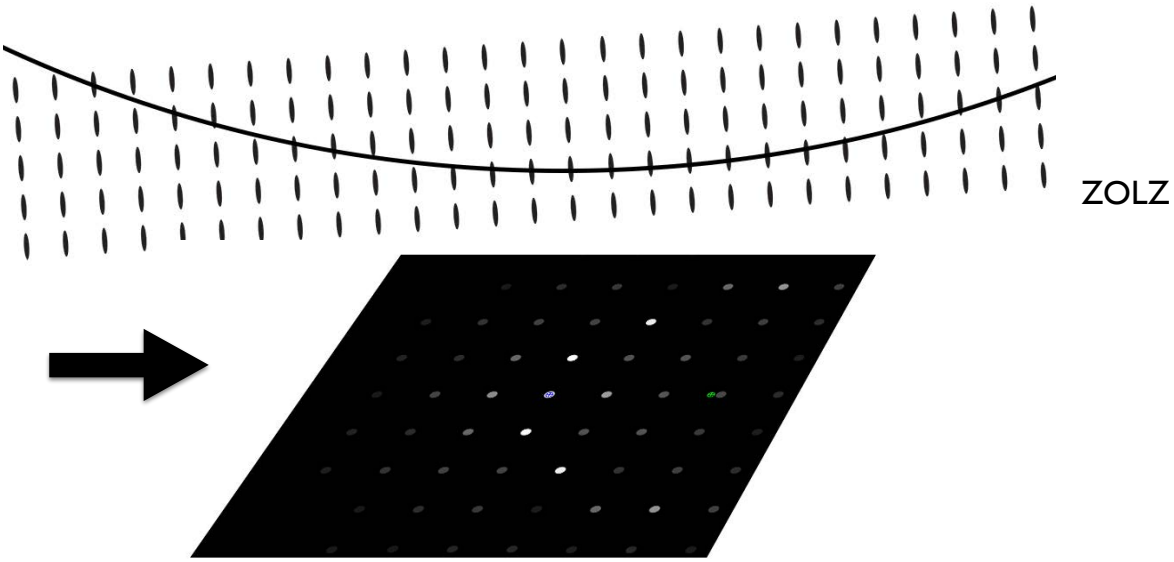
Tilting effect on SADP

- Zone axis diffraction pattern: Ewald sphere is tangential to zero-order Laue zone of reciprocal lattice



Quiz: what changes occur in SADP when tilt the crystal a little (e.g 1–3°)?

Tilting effect on SADP

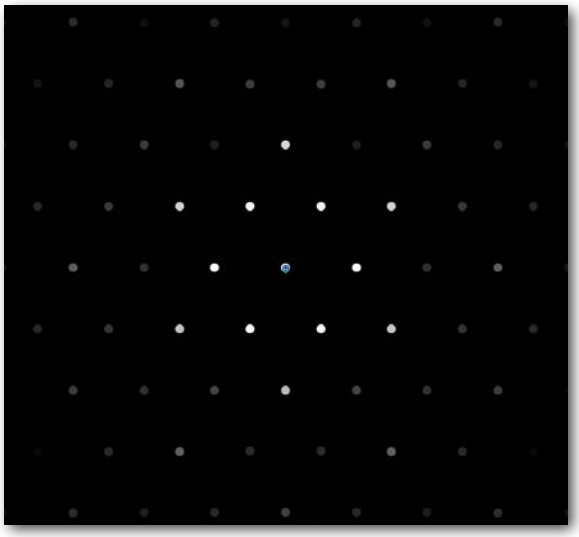


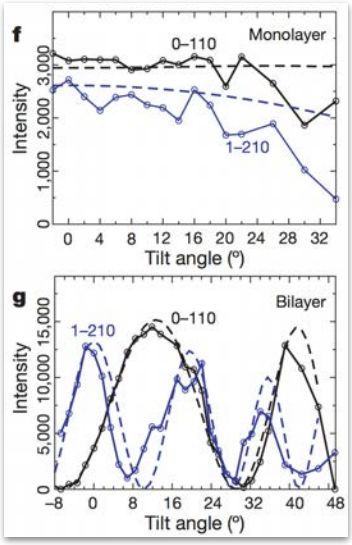
- Loci of intersections of Ewald sphere with relrods hardly changes, therefore the projected positions of reflections in the SADP do not move.
- However, the excitation errors for the relrods change a lot, so reflection intensities also change significantly.

Quiz: graphite → graphene

Diffraction pattern of graphite on [0 0 1] zone axis:

What happens to relrod shape as graphite thinned → graphene?
How will this affect diffraction spot intensity for tilted sample?





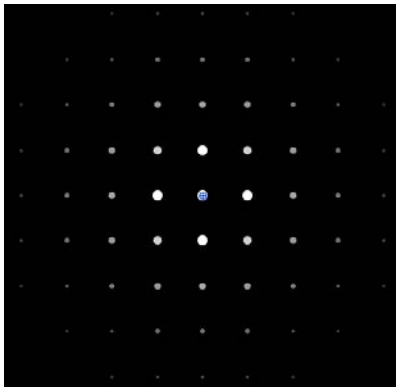
References – Graphene: Meyer *et al.* Nature **446** (2007) 60-63;
Monolayer MoS_2: Brivio *et al.* Nano Lett. **11** (2011) 5148-5153

Zone axis diffraction and symmetry

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

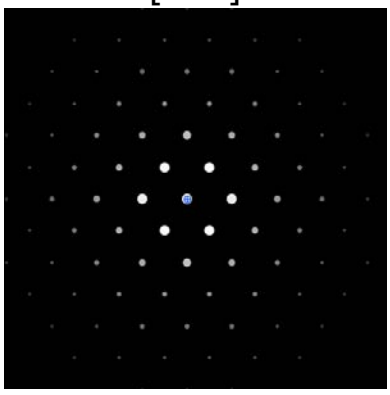
Example: FCC aluminium

[0 0 1]



4-fold rotation axis

[1 1 0]



2-fold rotation axis

Symmetry quiz

- Defining symmetry of cubic material are four 3-fold rotation axes (triads) on the <1 1 1> body diagonals.
- Inversion symmetry element is combination of rotation axis with centre of symmetry (e.g. $\bar{2}$, $\bar{3}$, $\bar{6}$).
- FCC Al has space group Fm$\bar{3}$m. If we take SADP on [1 1 1] zone axis what symmetry does ZOLZ pattern have?
- In ZOLZ lose 3rd dimension of information (i.e. have 2D projection). Therefore $\bar{3}$ symmetry "flattened" to give 6-fold symmetry in [1 1 1] SADP ⇒ loss of higher symmetry

➡ Friedel's Law: $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$

Elastic scattering theory

Electron diffraction: Elastic scattering

Assumptions $\Longrightarrow$ elastic scattering

$\vec{k}_i$: incident wavevector

$\vec{k}_g$: scattered wavevector

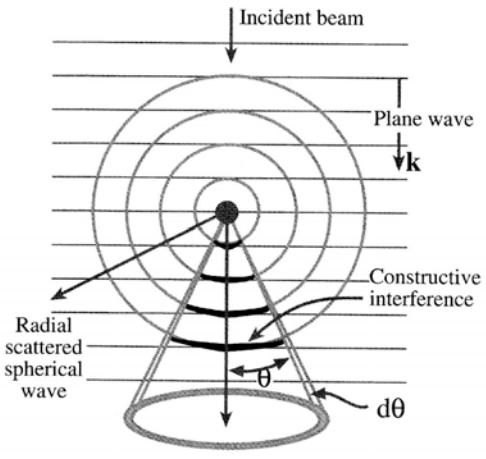
$\vec{g}$: reciprocal lattice vector

$\vec{s}_g$: deviation from exact Bragg condition

1. Energy conservation : $|\vec{k}_g| = |\vec{k}_i|$.
2. Momentum transfer : $\vec{k}_i + \vec{g} + \vec{s}_g = \vec{k}_g$.

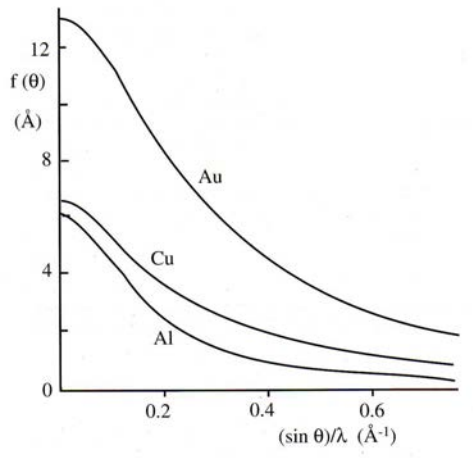
Scattering theory - Atomic scattering factor

Consider coherent elastic scattering of electrons from isolated atom



Differential elastic scattering cross section:

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



Atomic scattering factor

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

Structure factor

Amplitude of a diffracted beam from a unit cell:

$$A_{\text{cell}} = \frac{e^{2\pi i \mathbf{k}\mathbf{r}}}{r} \sum_i f_i(\theta) e^{2\pi i \mathbf{K}\mathbf{r}_i}$$

$\mathbf{r}_i$: position of each atom => $\mathbf{r}_i = x_i\,\mathbf{a} + y_i\,\mathbf{b} + z_i\,\mathbf{c}$

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

Define structure factor: $F_{hkl} = \sum_i f_i\, e^{[2\pi i(hx_i + ky_i + lz_i)]}$

Intensity of reflection: $I_{hkl} \propto |A_{\text{cell}}|^2 \propto F_{hkl}.F_{hkl}^*$

Note f_i is a function of $\mathbf{s}$ and (h k l)

Forbidden reflections

Consider FCC lattice with lattice point coordinates:
0,0,0; ½,½,0; ½,0,½; 0,½,½

Calculate structure factor for plane (h k l) (assume single atom motif):

$$F_{hkl} = \sum_i f_i\, e^{[2\pi i(hx_i + ky_i + lz_i)]}$$

where: $e^{i\theta} = \cos\theta + i\sin\theta$

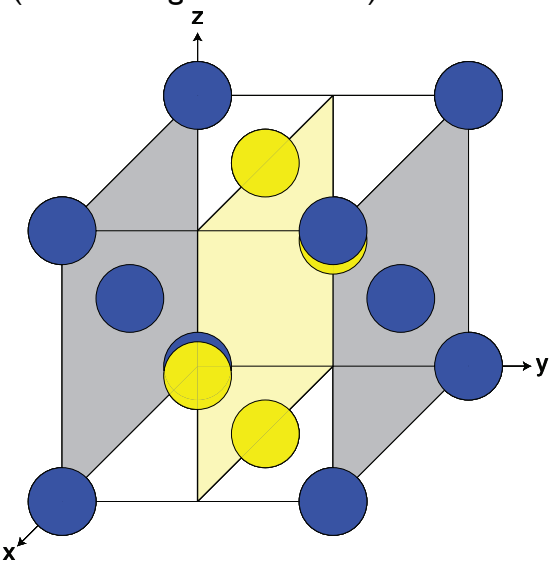
For atomic structure factor f find:

$$F_{hkl} = f\left[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right]$$

Since: $e^{n\pi i} = (-1)^n$

For h k l all even or all odd: $F_{h\,k\,l} = 4f$

For h k l mixed even and odd: $F_{h\,k\,l} = 0$



Extinction rules

Face-centred cubic: reflections with mixed odd, even *h*, *k*, *l* absent:

$$F_{hkl} = f_i\left[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right]$$

Body-centred cubic: reflections with *h* + *k* + *l* = odd absent:

$$F_{hkl} = f_i\left[1 + e^{\pi i(h+k+l)}\right]$$

Reciprocal lattice of FCC is BCC and vice-versa

Theory of electron diffraction in TEM – Resources

- "Transmission Electron Microscopy" by Williams and Carter Chapters 3, 11, 12: Derivation of Bragg and Laue equations, introduction of diffraction vector ***g***, excitation error ***s***
- "Large Angle Convervent Beam Electron Diffraction", Morniroli (electronic on-line from EPFL library), Chapters 2 and 3: Elegant pictorial way to understand electron diffraction with parallel incident beam
- JEMS – Pierre Stadelmann's electron microscopy simulation software: contact Prof. Stadelmann (CIME) to use