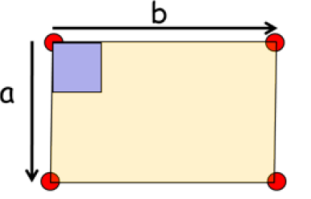# *2D lattices*
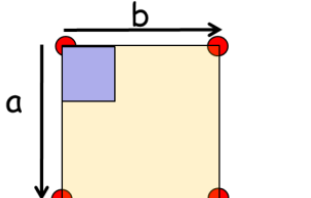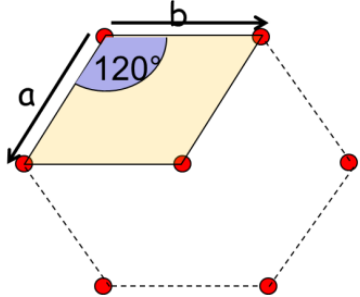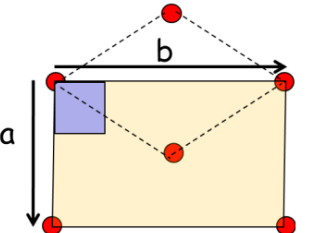
Lattice: (P=primitive; C=centered)		Max symmetry	Symmetry operation
	Oblique P a ≠ b γ ≠ 90°, 120°	2-fold axis (180°)	2
	Rectangular P a ≠ b γ = 90°	2-fold axis (180°) 2 reflection lines	2mm
	Square P a = b γ = 90°	4-fold axis (90°) 2 reflection lines 2 mirror planes	4mm
	Hexagonal P a = b γ = 120°	6-fold axis (30°) 3 reflection lines 3 mirror planes	3m = 3mmm 6
	Rhombic P (dashed) a = b γ ≠ 90°, 120°	2-fold axis (180°) 2 reflection lines	2mm
	Rectangular C a ≠ b γ = 90°		c2mm

Hermann–Mauguin:
1,2,3,4,6 for the rotation axis
m for the reflection line
Combining:
3m: a 3-fold rotation axis lying on a reflection line
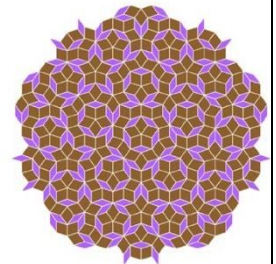6mm: a 6 fold axis lying on two symmetry lines

Penrose tilling
Quasicrystal: repeated
pattern but no lattice
→ no translational
symmetry
(Al-Pd-Mn)

2D symmetry figures

Point symmetry operation: leaves (at least) one point of the crystal fixed

Symmetry operations: symbols		
⸲	1-fold: no symmetry	
◖	2-fold: 180° symmetry	diad
▲	3-fold: 120° symmetry	triad
■	4-fold: 90° symmetry	tetrad
⬡	6-fold: 60° symmetry	hexad

Symmetry operations: symbols		
●	Atom at lattice point	
╱	Mirror line	m
╌╌╴	Glide line	g
	Primitive	p
	Centred	c

Examples:

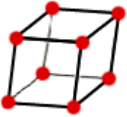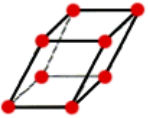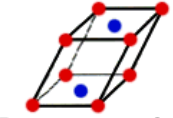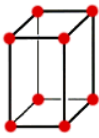|		Oblique lattice: 180° symmetry p2
	→	
	→	
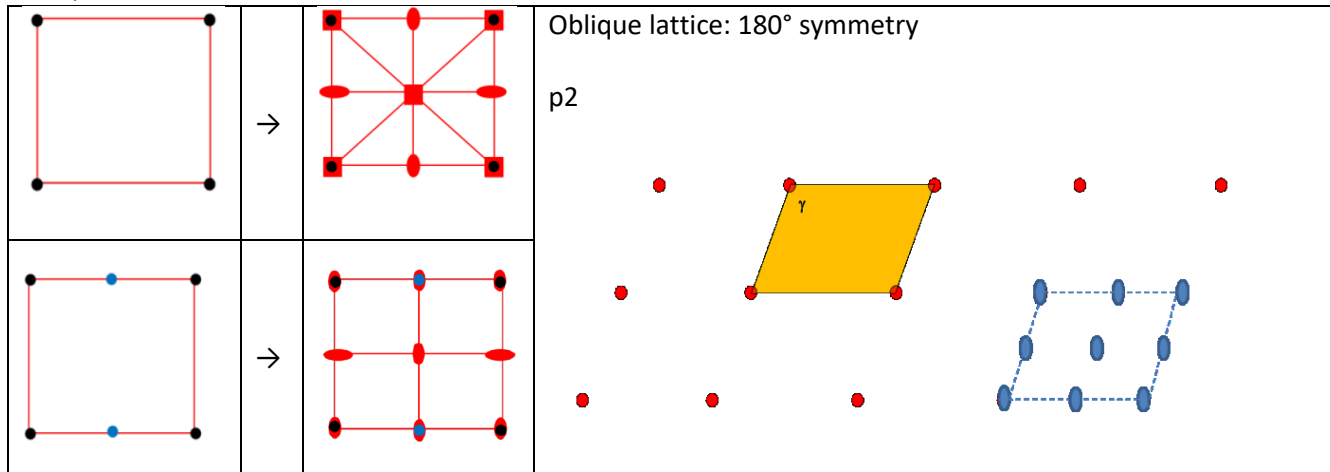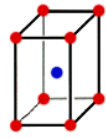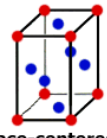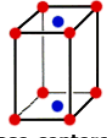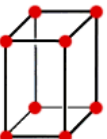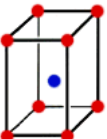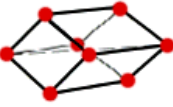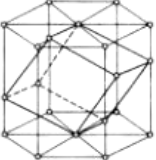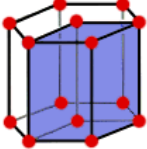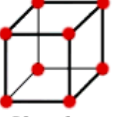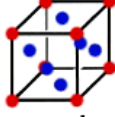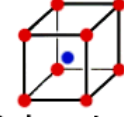
The 17 2D plane groups:

Lattice type	Symmetry operations	Plane group
Oblique		p1
Oblique		p2
Rectangular		Pm
Rectangular		Pg
Rectangular C (rhombus)		Cm
Rectangular		Pmm (p2mm)
Rectangular		Pmg (p2mg)
Rectangular		Pgg (p2gg)

Lattice type	Symmetry operations	Plane group
Rectangular C (rhombus)		Cmm (c2mm)
Square		P4
Square		P4m (p4mm)
Square		P4g (p4gm)
Hexagonal		P3
Hexagonal		P3m
Hexagonal		P31m
Hexagonal		P6
Hexagonal		P6m (p6mm)

3D Bravais lattices & 32 point groups

System	Bravais lattices	Symmetry point groups		
		No c.o.sym.	Center o.s.	min. sym.
Triclinic a≠ b ≠ c α≠β≠γ≠90°	1-fold axis	1	$\bar{1}$	None
Monoclinic a ≠ b ≠ c ; α = γ = 90°; β ≠ 90	2-fold axis Simple Base-centered	2 m	$\dfrac{2}{m}$	1 diad or inversion diad
Orthorhombic a≠ b ≠ c α=β=γ=90°	3*2-fold axis Simple Body-centered Face-centered Base-centered	222 2mm	mmm	3 diads at 90°
Tetragonal a= b ≠ c α=β=γ=90° 4-fold axis	4-fold axis Simple Body-centered	4 $\bar{4}$ 422 4mm $\bar{4}2m$	$\dfrac{4}{m}$ $\dfrac{4}{mmm}$	1 tetrad or inversion tetrad
Rhombohedral (=trigonal) a= b = c α=β=γ≠90°	3-fold axis =	3 32 3m	$\bar{3}$ $\bar{3}m$	1 triad or inversion triad
Hexagonal a= b ≠ c α=β=90, γ=120°	6-fold axis	6 $\bar{6}$ 622 6mm $\bar{6}m2$	$\dfrac{6}{m}$ $\dfrac{6}{mmm}$	1 hexad or inversion hexad
Cubic a= b = c α=β=γ=90°	4*3-fold axis Simple Face-centered Body-centered	23 423 $\bar{4}3m$	m3 m3m	4 triads at 109,47°
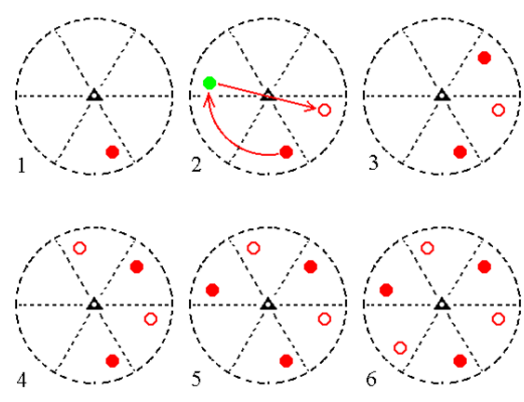
3D symmetry operators

Symmetry operations: symbols	
$\bar{2}$ = m	Roto-inversion; 180°
$\bar{3}$	Roto-inversion; 120°
$\bar{4}$	Roto-inversion; 90°
$\bar{6}$	Roto-inversion; 60°
$\dfrac{3}{m}$	Mirror plane is in-plane: *diad* (m⊥3 is equal to $\bar{6}$)
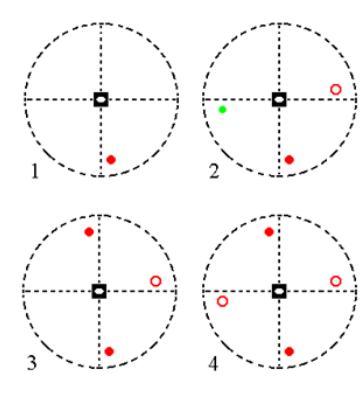
Symmetry operations: symbols	
◖	◗ + inversion ($\bar{2}$ = m)
△	▲ + inversion
▫	■ + inversion
⬡	⬢ + inversion
●	Point above plane
○	Point below plane

Examples: (Exercise 4.6)

$\bar{3}$:   Rotate 120° + invert 180°
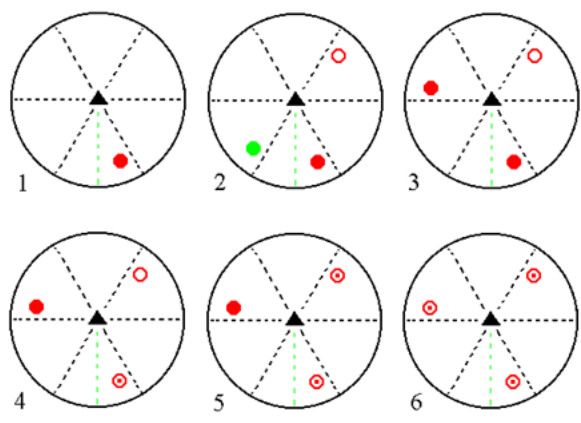
$\bar{4}$:   Rotate 90° + invert 180°

3m:
Rotate 60° + mirror

▲	3-fold
Full ring	flat mirror plane
⋰	guiding lines

Identical to $\bar{6}$
(rotate 60° + invert 180°)

Glide plane
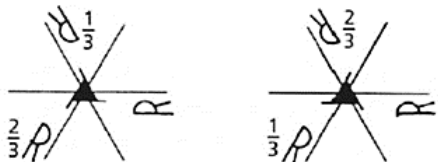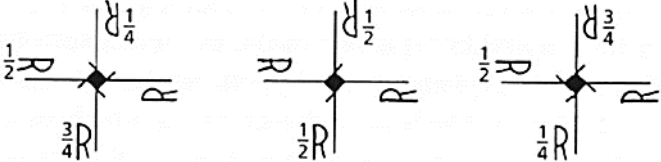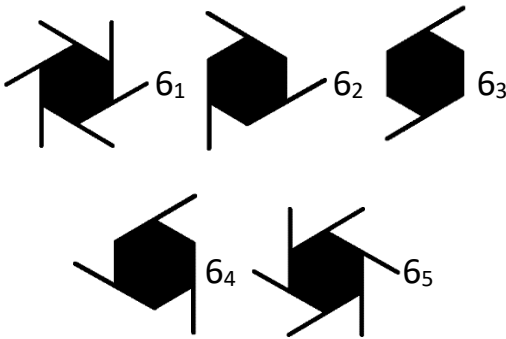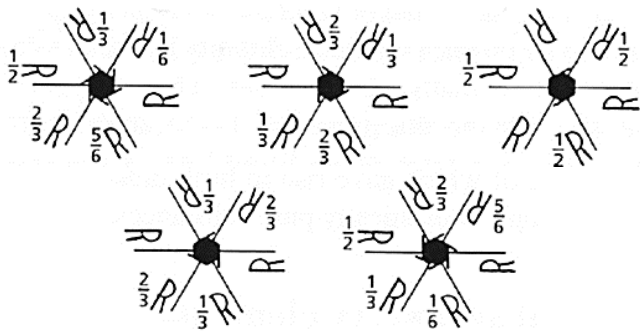
- usually symbolized by a,b,c according to which plane of the unit cell they are parallel to
- the n glide = glide along the half of a diagonal of a face
- the d glide = a fourth of the way along either a face or space diagonal of the unit cell

3D screw axis

Rotation: counter-clockwise & up

Enantiomorphs are NOT each other's mirror images!
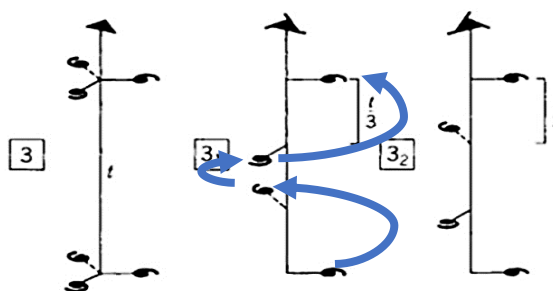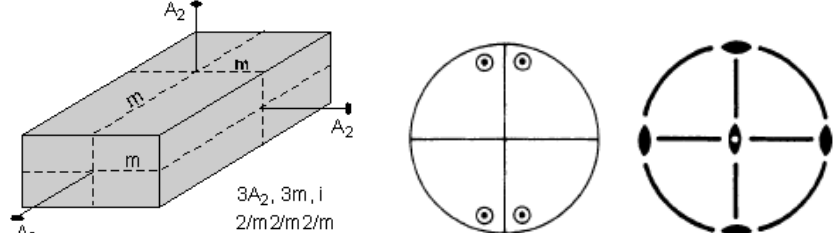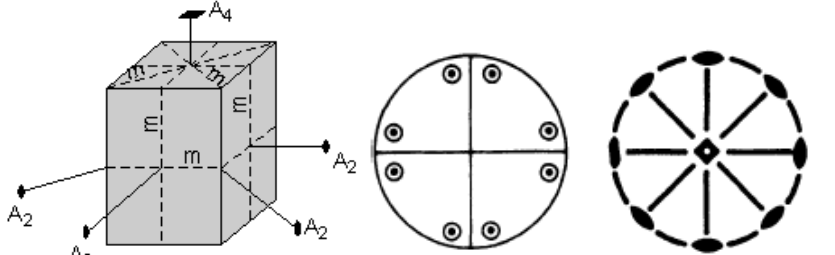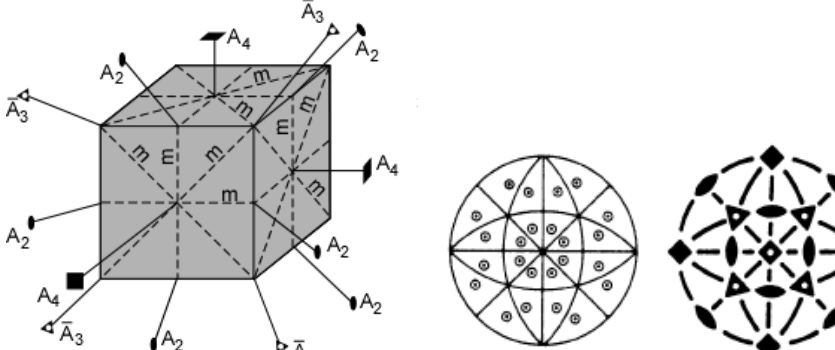
Enantiomorph symbol	Figures
2_1	
3_1 3_2	
4_1 4_2 4_3	
6_1 6_2 6_3 6_4 6_5	

230 space groups in 3D

Construction and stereographic projection

Space groups: symbols		
$\bigcirc^{+}$	Point above plane	
$\bigcirc^{\frac{1}{2}+}$	Point ½ above plane	
$\bigcirc^{-}$	Point mirrored & below plane	
$\bigcirc^{\frac{1}{4}-}$	Point mirrored & ¼ below plane	
$\bigcirc^{+}$	All possibilities present	

Stereographic projections for all space groups:

http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

Examples: (Exercise 4.10)

Orthorhombic: 3 two-fold axes 3 mirror planes Inversion symmetry:	
Tetragonal One 4-fold axis 4 twofold axes (2 unique) 5 mirror planes (3 unique) Inversion symmetry:	
Cubic Three 4-fold axis Four 3-fold axis Six 2-fold axis 9 mirror planes Inversion symmetry	
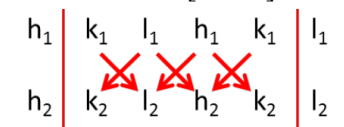
Hexagonal One 6-fold axis 2 two-fold axis 7 mirror planes (3 unique) Inversion symmetry	

Example: Exercise 4.12

The 7 point symmetry groups of the hexagonal system			
6		$\bar{6}$	
622		6mm	
$\bar{6}$m2		$\dfrac{6}{m}$	
$\dfrac{6}{mmm}$			

Miller indices

Point	
Fraction coordinates are multiplied into integers in the vector notation	
Point coordinates	*Point vector*
½, 0, 1	[1 0 2]
⅔, 1, ½	[4 6 3]

Family of vectors	
The family of vectors who, due to crystal symmetry, are identical: *multiplicity*	
⟨1 0 0⟩ *cubic*	[1 0 0], [0 1 0], [0 0 1] [$\bar{1}$ 0 0], [0 $\bar{1}$ 0], [0 0 $\bar{1}$]

Angle between directions is given by **scalar product**. For directions $[u_1\ v_1\ w_1]$ and $[u_2\ v_2\ w_2]$ at an angle φ:

$$\cos\varphi = \frac{u_1\,u_2 + v_1\,v_2 + w_1\,w_2}{\sqrt{u_1{}^2 + v_1{}^2 + w_1{}^2}\cdot\sqrt{u_2{}^2 + v_2{}^2 + w_2{}^2}}$$

Planes	
Parallel planes make up families of planes. Intersects are inversed and integers used	
Axis intersects	*Plane index*
½, 0, 1	(2 0 1)
¼, ½, ⅔	(8 4 3)

Multiplicity of planes	
Again, dependent on crystal symmetry	
{1 1 0} *cubic*	(1 1 0), (1 0 1), (0 1 1), ($\bar{1}$ 1 0), (1 $\bar{1}$ 0), ($\bar{1}$ 0 1), (1 0 $\bar{1}$), (0 $\bar{1}$ 1), (0 1 $\bar{1}$), …

Zone axis: set of planes in a crystal whose intersections are parallel. The intersection of two planes $(h_1\ k_1\ l_1)$ and $(h_2\ k_2\ l_2)$ passing origo:

Zone axis $[u\ v\ w]$:

$$u = (k_1 l_2 - k_2 l_1),$$
$$v = (l_1 h_2 - l_2 h_1),$$
$$w = (h_1 k_2 - h_2 k_1)$$

Weiss zone law:
Check whether an axis is parallel to a family of planes:
If $uh + vk + wl = 0$ → axis lies in the family.

Plane made of by two vectors:
Find the plane (*h k l*) that gives the Weiss zone law:
$hu_1 + kv_1 + lw_1 = 0$ and $hu_2 + kv_2 + lw_2 = 0$

Hexagonal: Miller-Bravais indices

Introduce index i=-(h+k) → (h k i l)
The planes of the zone belonging to the z-axis can be obtained by permutation!
Zone axis: [U V T W] → do it with Miller planes
Weiss law: $hU + kW + iT + lW = 0$

Miller – Miller-Bravais transformations

Miller-Bravais to Miller	Miller to Miller-Bravais
u=(U-T) v=(V-T) w=W	U = (2u-v)/3 V = (2v-u)/3 T = -(u+v)/3 = -(U+V) W=w

Crystal diffraction: structure factor

When an electromagnetic wave falls in on an electron (charged particle) the electron will start oscillating with the same wavelength as the incoming wave and there will be a defined phase relationship, i.e. the radiation is coherent.

Scattering intensity I is proportional to charge and scattering angle 2ϑ, and inversely proportional to mass.

$$I \propto \left(\frac{e^2}{c^2 m_e}\right)^2 (1 + \cos^2 2\theta)$$

Atomic scattering factor:

$$f = \frac{amplitude\ scattered\ by\ one\ atom}{amplitude\ scattered\ by\ a\ single\ electron}$$

Maximum scattering intensity is forward → intensity ∝ to Z. In all other directions intensity is lowered.
An atom with Z electrons can be expected to scatter Z times → lighter elements become 'invisible'.
The atom is the size scale of X-rays → destructive interferences can occur among the scattered waves.
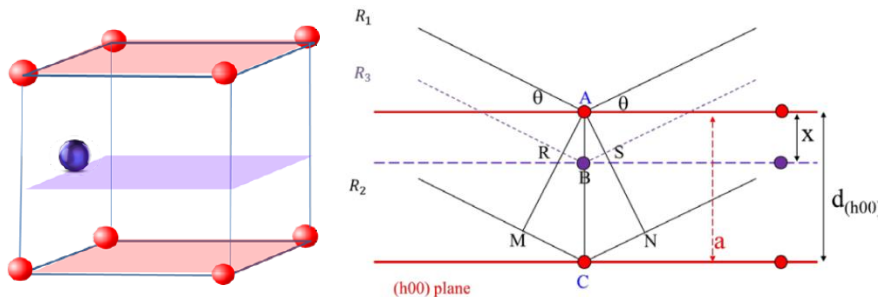
Detectable:

$$\boldsymbol{I}_{hkl} \propto \left|F(\vec{h})\right|^2$$

Red planes are at lattice points, and fulfil the Bragg equation; d=(h00).
If the atom B is situated halfway between A&C, it will destructively interfere with their intensity.
The more similar its form factor is to A&C, the more significant the extinction.

For more than one atom / unit cell → *phase difference* of the waves scattered by different atoms

Structure factor expression:	$F(hkl) = \sum_0^N f_n\, e^{i2\pi\,(hx_n+ky_n+lz_n)}$	$e^{i\pi n} = \begin{cases} 1 & when\ n\ is\ even \\ -1 & when\ n\ is\ odd \end{cases}$

Summation over all atoms at all lattice sites!

Example: (Exercise 6.4)

	FCC: 4 atoms Equivalent atoms are at: (0 0 0), (½ ½ 0), (½ 0 ½), (0 ½ ½) $F = f\left[e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}\right]$	**Interference enhancement**: (h k l) all even or odd: $F=4f$ (111), (200), (220), (333), (420), … **Extinctions**: (h k l) mixed oddity: $F=0$ (100), (211); (210), (032), (033), …
	BBC: 2 atoms Equivalents: (0 0 0), (½ ½ ½)	h+k+l even: $F=2f$ h+k+l odd: $F=0$

Reciprocal lattice

The **direct lattice** describes mathematically the arrangement of the motif (atoms or molecules) in the crystal. There are 14 Bravais lattices.

The **reciprocal lattice** is an array of points where each lattice point is associated with a particular set of planes of the direct lattice.

- The reciprocal mathematically connects the direct lattice planes, the Bragg law and the directions of the diffracted beam (**Reciprocal: '**multiplicatory inverse')

Reciprocal lattice vector d₁*
- Defines the normal of a crystal plane
- Length is inversely proportional to interplanary distance
  - |d₁*|=1/|d₁|
- The reciprocal vectors draw up the reciprocal lattice points

Addition rule is valid:
$$\mathbf{d}^*_{hkl} \cdot \mathbf{d}^*_{mno} = \mathbf{d}^*_{h+m\ k+n\ l+o}$$

Reciprocal unit cell
- Defined by a*, b*, and *c

Unit cell volume:
- $V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$ and $V^* = 1/V$

$$\mathbf{a}^* = \mathbf{d}^*_{100} \perp \mathbf{b}^*, \mathbf{c}^* \text{ and } |\mathbf{a}^*| = a^* = 1/\mathbf{d}^*_{100}$$
$$\mathbf{b}^* = \mathbf{d}^*_{010} \perp \mathbf{a}^*, \mathbf{c}^* \text{ and } |\mathbf{b}^*| = b^* = 1/\mathbf{d}^*_{010}$$
$$\mathbf{c}^* = \mathbf{d}^*_{100} \perp \mathbf{a}^*, \mathbf{b}^* \text{ and } |\mathbf{c}^*| = c^* = 1/\mathbf{d}^*_{001}$$

Rule: $\mathbf{a} \cdot \mathbf{a}^* = 1$

Connection to Miller indices and plane families

Plane axial interceptions	Plane Miller index	Reciprocal vector
1/h, 1/k, 1/l	(h k l)	d_hkl* = ha* + kb* + lc*

Angles and distances

Interplanary angle	d-spacing between planes (h k l)
Scalar product $\mathbf{a}^* \cdot \mathbf{b}^* = |\mathbf{a}^*||\mathbf{b}^*|\cos\theta$	$(1/\mathbf{d}_{hkl})^2 = \mathbf{d}^*_{hkl} \cdot \mathbf{d}^*_{hkl}$ $= (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$

Orthorhombic d-spacing	Tetragonal d-spacing	Cubic d-spacing
$\dfrac{1}{\mathbf{d}^2} = \dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}$	$\dfrac{1}{\mathbf{d}^2} = \dfrac{h^2 + k^2}{a^2} + \dfrac{l^2}{c^2}$	$\dfrac{1}{\mathbf{d}^2} = \dfrac{h^2 + k^2 + l^2}{a^2}$

Weiss-zone law

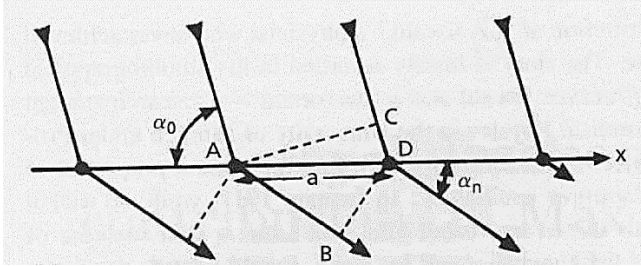A plane (h k l) lies in a zone [u v w] when $\mathbf{d}^*_{hkl} \perp \mathbf{r}_{uvw}$

$$\mathbf{d}^*_{hkl} \cdot \mathbf{r}_{uvw} = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (u\mathbf{a} + v\mathbf{b} + w\mathbf{c}) = 0$$

Relationships to direct space:	*Bravais lattice*	Simple cubic	FCC	BCC
	Reciprocal lattice	Simple cubic	BCC	FCC

Laue equations: conditions for diffraction

Constructive interference from 3 atoms:

Bragg law:

$$|\mathbf{s} - \mathbf{s_0}| = 2\sin\theta = \lambda|\mathbf{d}^*_{hkl}|$$

$$2\sin\theta = \lambda|h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*|$$

Conditions for constructive interference:

$$(AB - CD) = a(\cos\alpha_n - \cos\alpha_0) = n_x\lambda$$

Laue equations:

$$a(\cos\alpha_n - \cos\alpha_0) = \mathbf{a}\cdot(\mathbf{s} - \mathbf{s_0}) = n_x\lambda = h\lambda$$
$$b(\cos\beta_n - \cos\beta_0) = \mathbf{b}\cdot(\mathbf{s} - \mathbf{s_0}) = n_y\lambda = k\lambda$$
$$c(\cos\gamma_n - \cos\gamma_0) = \mathbf{c}\cdot(\mathbf{s} - \mathbf{s_0}) = n_z\lambda = l\lambda$$

$$\frac{(\mathbf{s} - \mathbf{s_0})}{\lambda} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

Ewald sphere

- Representation of diffraction on crystal; crystal is in centre
- Peaks in a spectrum = norms of the reciprocal vectors
- Radius = 1/λ (reciprocal wavelength)

- Draw reciprocal lattice in same scale
- → intersections of reciprocal sphere points with sphere surface = *diffracted beam maximi*

- Find all possible diffraction points by rotating the reciprocal lattice
- Equal to rotating the Ewald sphere
- → *Resolution sphere* of R=2/λ
- Maximum n.o. peaks = n.o. reciprocal lattice points circumscribed by the resolution sphere
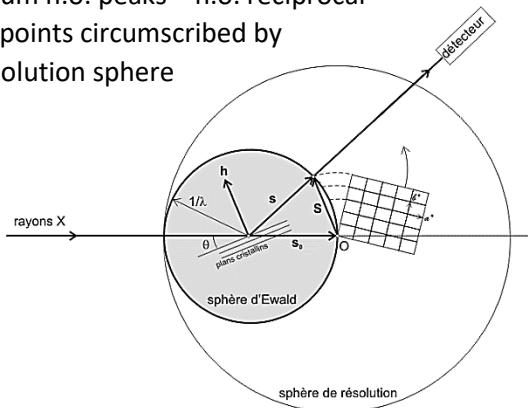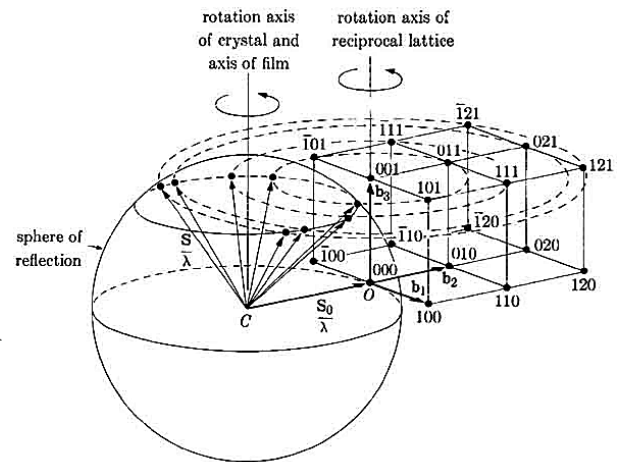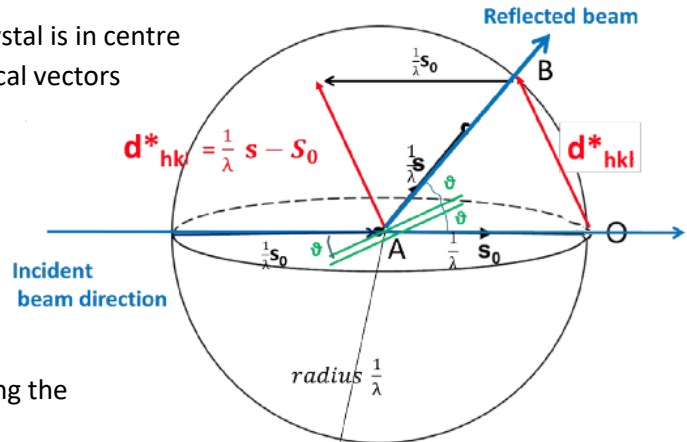
Laue technique
- Varies the size of the Ewald sphere by varying λ
  → Min/max spheres, peaks in between
- Used for thin single crystals, fixed in place
- Transmission or reflection mode measurement
  o Film placed behind (T) or before (R) sample
- Cannot measure lattice constants or peak intensity
  o Crystal orientation analysis & quality evaluation
  o Phase distribution and grain orientation mapping
  o Strain/stress mapping
- The curves of points represent zone groups of planes
  o T-mode gives circles; R-mode gives hyperbolae
- Laue pattern can be converted to a *stereographic projection*
  o Done by software
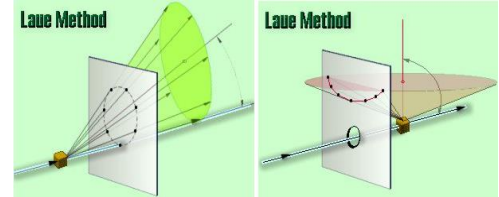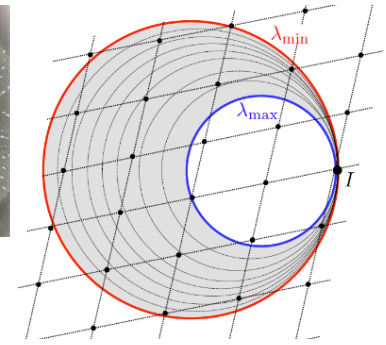
Stereographic projection
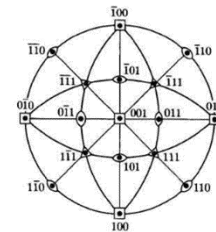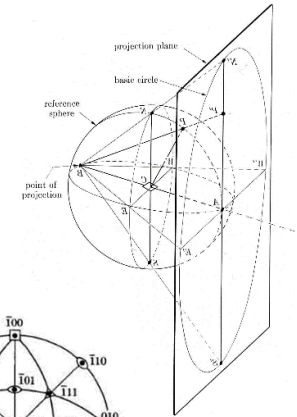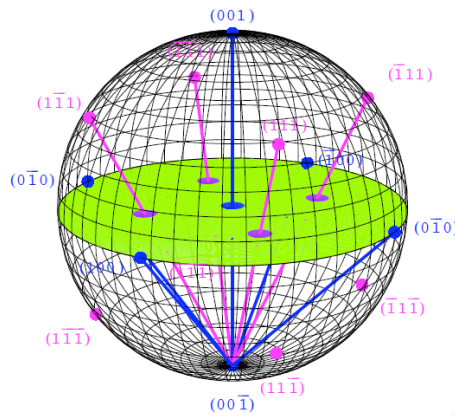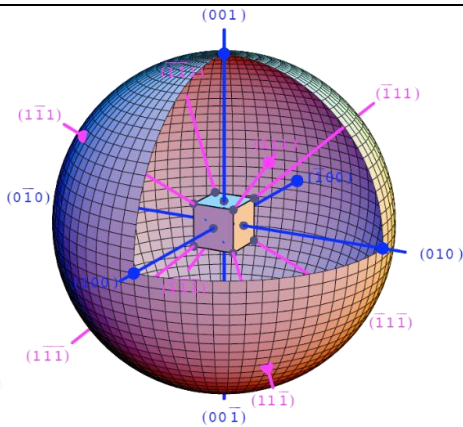
- Crystal is imagined in the middle of the sphere
- Crystal plane normal (poles) are projected onto the sphere
- Projected points are transferred to the equatorial plane
  o Projecting towards the sphere's south pole
  o *Alternatively:* extend from south pole to the north tangential surface
- The resulting *stereographic projection* represents the 3D crystal in 2D
- Angles between axes/poles can be measured with the Wulff net
  o Rotate net until the points to compared are on the same circle
  o Count the difference in latitude (1 line = 10°)
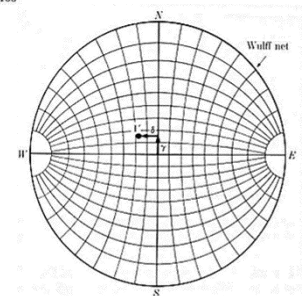
Diffraction & interference

Narrow gap diffraction:

Interference occurs when the width is of the order of the wavelength

Destructive:
$BC = (n+\frac{1}{2})\,\lambda$

Destructive:
$BC = n\,\lambda$
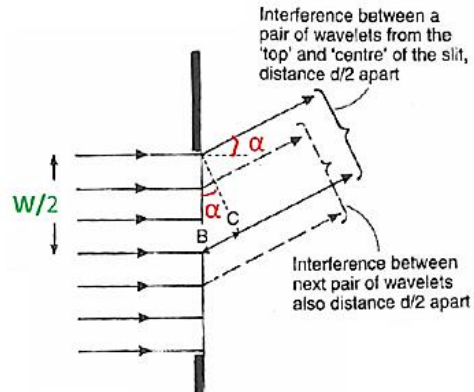
Diffraction from grating:

Distance between slits on the order of magnitude of the wavelength, slits very narrow → Huygen's wavelet approximation

Destructive:
$A \sin(\alpha) = (n+\frac{1}{2})\,\lambda$

Constructive:
$A \sin(\alpha) = n\,\lambda$
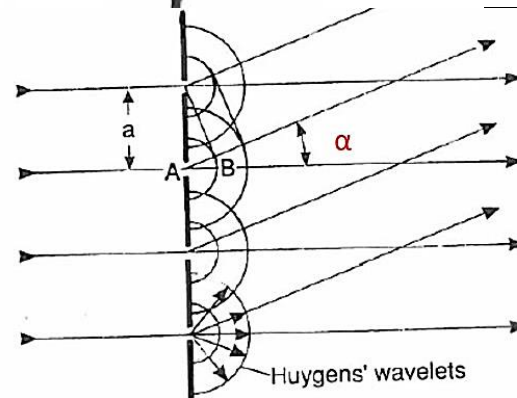
If the wavelength is too small (scale of diffraction gap/grating is too big), the interference fringes will be too close together do discern → continuous irradiation

Bragg law:

$2\,d \sin(\theta) = n\lambda$
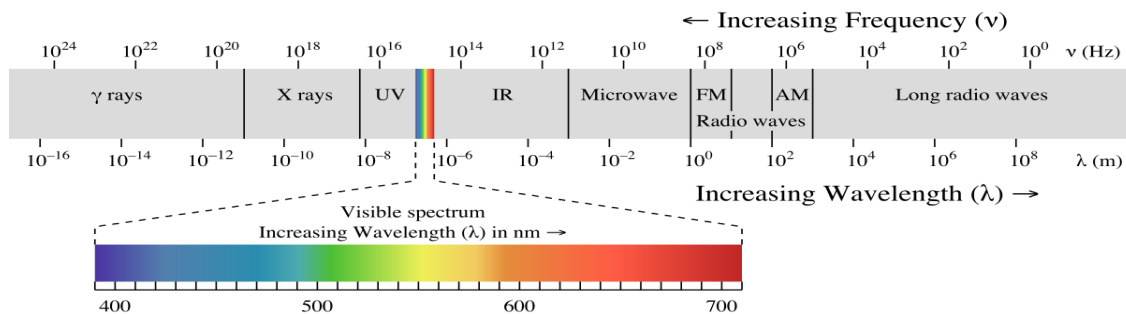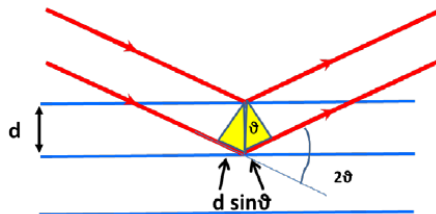
Diffraction methods

- **X-ray diffraction (XRD):** interference of multiple (layered) reflections
  - A *collective* phenomenon, only occurring at specific angles
- Bragg diffraction: diffraction via imaginary diffraction planes (geometrical construction)
  - **Laue indices**: planes with common factors
- Diffractometer → diffracted spectrum (diffractogram): intensity vs. angle 2ϑ
  - Lattice type and parameters, atomic structure, strain, crystallites; texture & size & quality, …
  - Small sources (tube, lab diffractometer) and big ones (synchrotrons)

methods	λ	θ
Laue method	Variable	fixed
Rotation techniques	fixed	Variable
Powder diffraction	fixed	Variable

Electron diffraction
Wavelength by de Broglie $\lambda = h/p$ (h: Planck)
Electrons accelerated by voltage U
→ $E_{pot} = eU$ and $p = (2m_e eU)^{\frac{1}{2}}$
TEM: Tunnelling Electron Microscopy

Another possibility: Neutron diffraction

Powder diffraction

- Randomly oriented microcrystals, often in a powder
- All planes of d_{hkl} spacing diffract at the same 2θ angle
  - Intensity cone of semi-angle 2θ about the direct beam: *Debye-Scherrer rings*
- Disadvantage: conversion of 3D to 2D data array
  - → inevitable loss of information
- Assumptions: perfect statistical distribution
  - Ignore possibility of preferential break planes
- Find out: lattice (type, parameters → phase), strain & deformation, size of microcrystals, quality
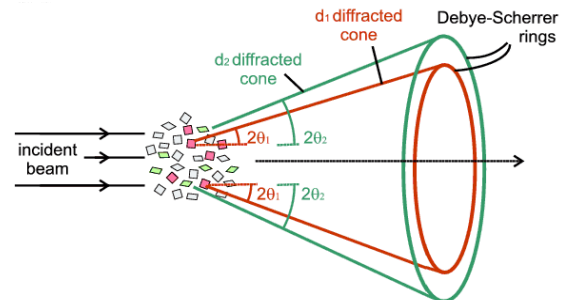
The Debye-Scherrer method (1930)

- Classic method: sample in cylindrical camera
  - Debye-Scherrer rings captured on photographic film
- Sample is a rod shape or powder in a capillary tube
  - Added feature: sample rotation
- Chambers typically 57,3 mm (1mm = 2°) or 114,6 mm (1mm = 1°)
  - Can control ambience (inert gas/vacuum)
- Very small samples can give very good resolution (0,001 Å)
- Beam leftovers collected and absorbed by lead
  - 'parasitic beam'

- Modern equivalent: film replaced with detector array
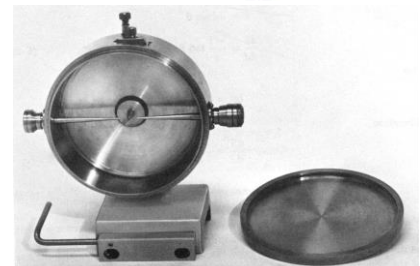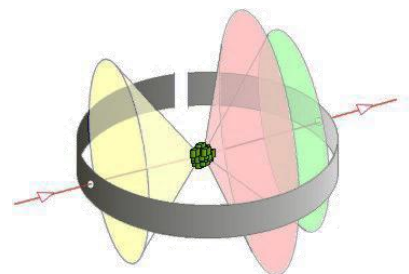
Resolving power

Increases with increasing R and θ

$$\lambda = 2d\sin\theta$$
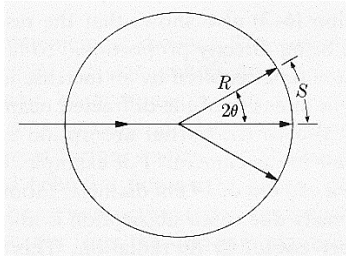
$$0 = 2dCos\theta\delta\theta + 2\sin\theta\delta d$$

$$\frac{\delta\theta}{\delta d} = \frac{-1}{d}\tan\theta$$

Resolution increases with θ

$$S = 2\theta R; \quad \delta\theta = \frac{\delta S}{2R}$$

$$\frac{\delta S}{\delta d} = \frac{-2R}{d}\tan\theta$$

$$\frac{d}{\delta d} = \frac{-2R}{\delta S}\tan\theta, \text{ or} \quad \delta S = -2R\frac{\delta d}{d}\tan\theta$$

δS is the distance between 2 close peaks measured on the detector (film) surface

Seemann-Bohlin chamber

Euclides:
"*the angles in the same segment of a circle are equal*"

- Polycrystalline sample fixed between A & B
- Photographic film mounted between N & M
- All beams diffracted by a select plane will focus at F
  - Regardless of where they refracted
- Much higher intensity than Debye-Scherrer: larger sample
- Higher resolution then Debye-Scherrer (factor 2)
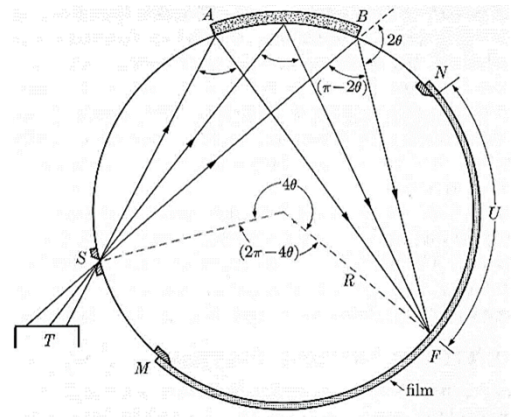
Bragg-Brentano geometry

- Most common in modern diffractometers
- Approximates parallel beam at large radius
  - As *2ϑ* is varied, the focusing circle shrinks
- With a flat sample, focusing is never perfect
- Focus improves by smaller sample areas and larger machines
- Detector is electronic: scintillation counter or similar
  - Digitized signal, step scattered intensity
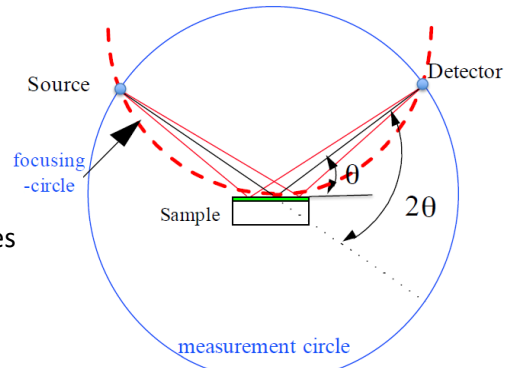
Grazing incidence geometry

- Measuring ultra-thin layers (<10-20 nm)
- Thin film epitaxy, film quality, …
- **Parabolic mirror:** parallel beams
  - Can be replaced by **Soller slit**

Parallel beam geometry

- Same geometry as above
- Measure irregular shapes without distortion

Parabolic Göbel mirrors

- Multilayer crystal mirror: works by Bragg diffraction
  - *d*-spacing varies in a controlled manner
- Picks up a slice (ca 1°) of the divergent primary beam
  - High-energy parallel beam produced
- Extremely expensive to manufacture
  - Specific to wavelength and machine geometry

Other parallelization methods

Soller slits	**Channel-cut crystal monochromator**	**Beam compressor**

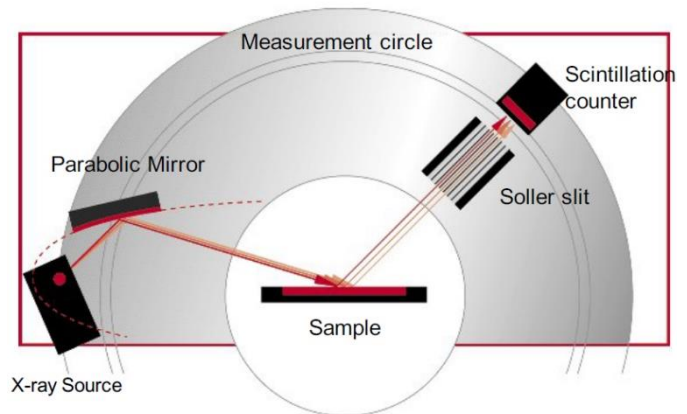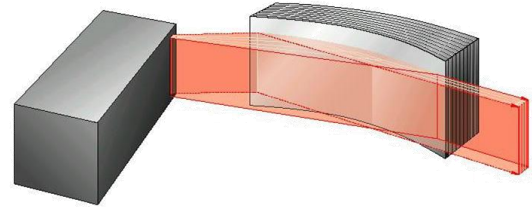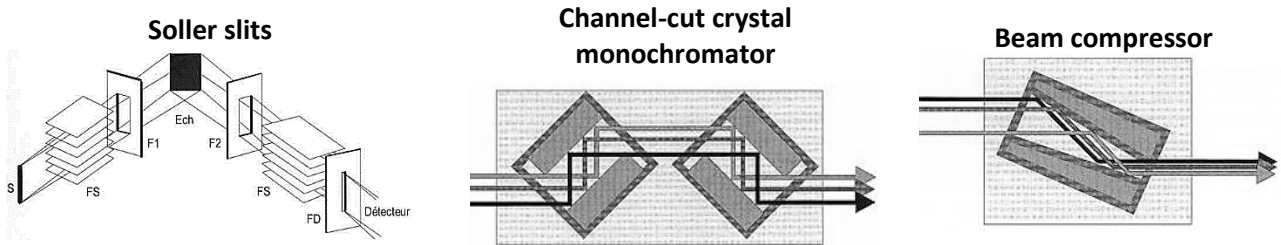- Channel-cut crystal monochromators are used for high-resolution measurements.
- They provide highly monochromatic beam (better than curved crystals or parabolic mirror)
- The disadvantage is a significant loss of intensity and rather complicated and delicate alignment

Monochromators

Flat crystal monochromator
Simplest and cheapest: rather low efficiency.
Only the selected wavelength is diffracted and redirected; all others pass.
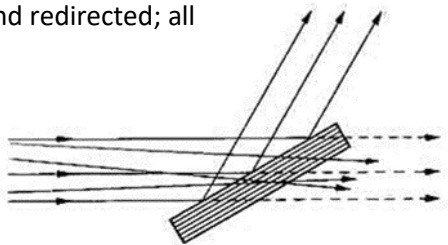
Curved crystal monochromator (Johansson)
Improvement of the flat crystal.
The crystal's curvature radius is twice that of the focusing circle; then cut to fit the focusing circle.

Beam absorption

Symbol	Description		
I	Intensity (E/s)		$-\dfrac{dI}{I} = \mu dx$
μ	Linear absorption coefficient		
μ^*	Mass absorption coefficient (cm^2/g)		$I_x = I_0 e^{-\mu x}$
w_i	Substance i weight fraction		
θ	Angle of incidence		$\mu^* = \dfrac{\mu}{\rho}$
ρ	Density		
x	Depth		
G_x	Energy fraction absorbed at depth x	$G_x(x) = 1 - e^{\frac{-2\mu x}{\sin\theta}}$	$\mu^* = \displaystyle\sum_{i=1}^{N} w_i \mu_i^*$

Powder diffraction

- Identification of d_{hkl} values and corresponding intensities
    - Intensity generally drop with increasing 2ϑ
- Compare spectrum with the reference or search in the database;
    - Phase identification software, Hanawalt tables
- For a known structure, peaks can normally be identified by logic – extinctions make it harder
- **Problems**:
    - Peaks missing (weak, hidden, extinct), extra peaks
    - Mismatch of relative intensities, peaks shifted (sample misalignment)
    - Distorted / too wide peaks (crystal size)
    - High background (amorphous phase, fluorescence)
- **ICDD**: International Centre for Diffraction Data
    - **PDF**: Powder Diffraction File (L3, s.20-22)

Rietveld method

- Fit the whole spectrum, not the individual peaks
- Include background and peak shapes in the algorithm
    - → minimize intensity difference
- Possible even when peaks overlap completely

$$R = \sum_i w_i (Y_{io} - Y_{ic})^2$$
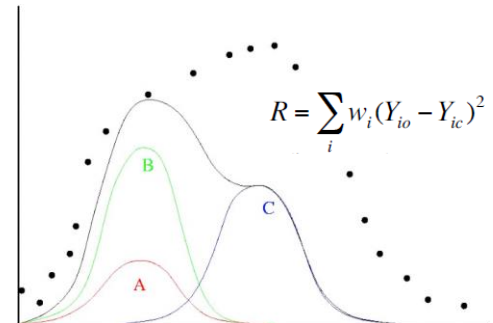
Graphic technique

1. Know the basic lattice structure (cubic, orthorhombic, …)
2. Combine Bragg's law with the expression for interplanary distance
3. Plot $sin^2(\vartheta)$ as a function of $(h^2+k^2+l^2)$ and find k as an expression of a
4. Solve for a by substituting the other parameters with experimental data
5. Requirement: All abscissa values (y-values) of the plotted line must be integers

Errors in Bragg-Brentano geometry

Sample displacement

- Greatest source of errors in PXRD: beam is refracted too low/high
- → no convergence at detector → observed peak is shifted
- Use the right sample holders & correct sample preparation
- Internal calibrations and correction algorithms
- Error is avoided using parallel-beam optics
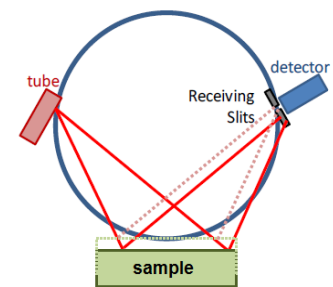
Flat specimen

- Sample is flat; focusing circle is not → surface misalignment
    - Asymmetric broadening at low angles 2θ
- Use narrow divergence slits, smaller sample
- Error is avoided using parallel-beam optics

Other:

- Poor counting statistics, scan speed, grain size problem, …

$$\Delta 2\theta = -\frac{2l\cos\theta}{R}$$

|	
l	Displacement distance
R	Goniometer radius
$\Delta 2\theta$	Peak displacement (rad)
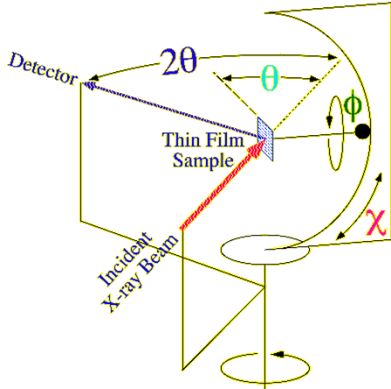
Pole figures

- Diffractometer equipped with Eulerian cradle needed
- Measuring preferred orientation of crystals (powder/film)
- XRD already known, suitable 2ϑ peak selected
  - Fix 2ϑ and χ, and rotate around φ; φ-scan
- Obtain the stereographic projection (contour maps) of the distribution of poles for a chosen set of planes
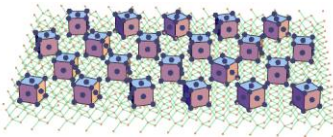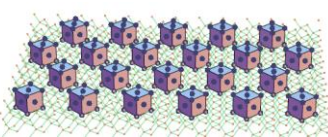 - Width of distribution indicates strength of preference
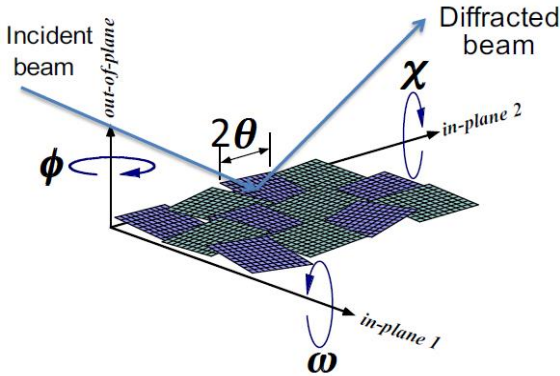
Rocking curve scan: Ω-scan

- Fix 2ϑ and scan a range of ω while rotating φ
- Grain surface alignment (textured thin films)
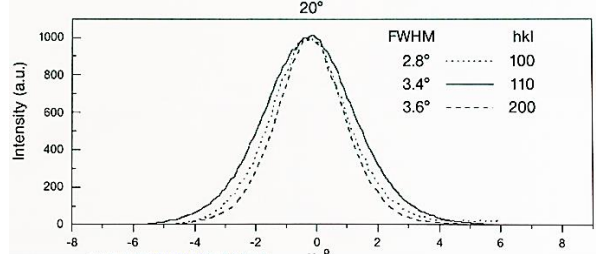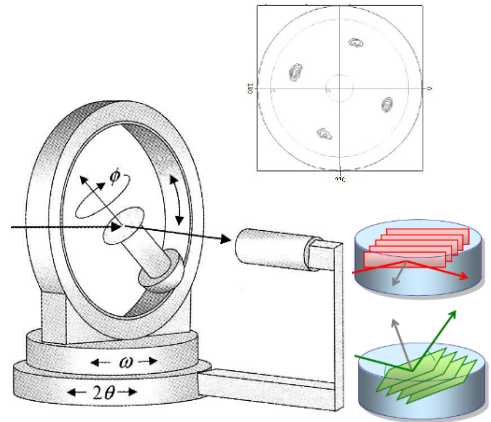
Fiber texture   *Epitaxial film*

Azimuthal scan: φ-scans

- Distinguish between textured and epitaxial films
- Must use planes NOT parallel to the sample surface
- If the scan shows peaks, crystallites are aligned
- X is found as the angle between the film normal and the normal of the chosen plane (angle between d_1^* and d_2^*)

Fixed 2ϑ and χ, vary φ

Beam broadening: sources of peak shape distortions

- Distribution of d-spacings for every plane family
  - Surface tensions of nanoparticles
  - Impurities, shape, surface treatment
  - Instrument effects
- Measured as peak half-height width distortion β
- Peak width can indicate nanocrystallite size!
- Instrument calibration is important!
  - Gauss: $\beta_{meas}^2 = \beta_{peak}^2 + \beta_{instr}^2$
  - Cauchy: $\beta_{meas} = \beta_{peak} + \beta_{instr}$
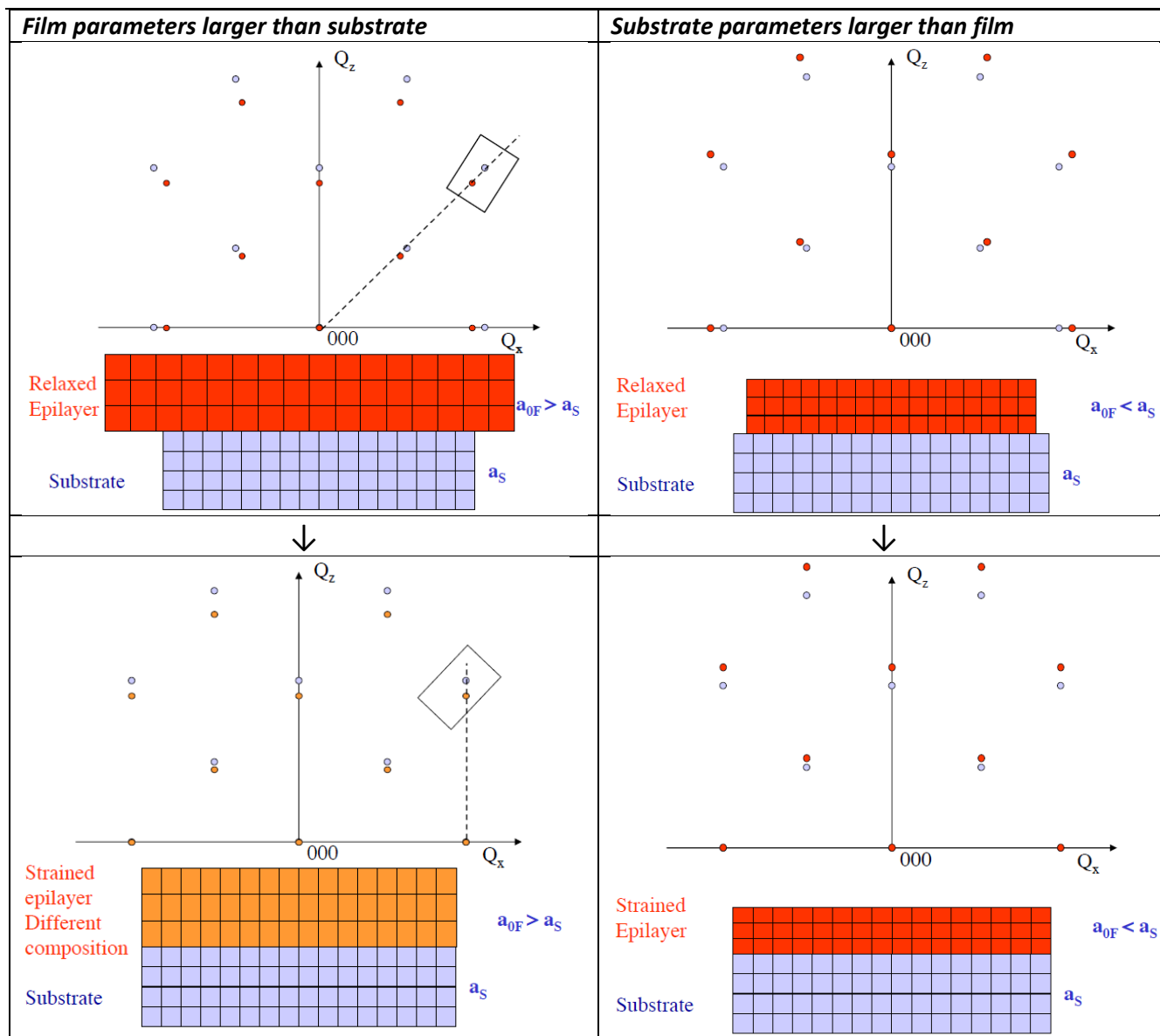
Distortion by deformation:

$$\beta_{def} = \delta(2\theta) = 2\frac{\delta d}{d}\tan\theta$$

$$\varepsilon = \frac{\delta d}{d} \qquad \sigma = \varepsilon E = \tfrac{1}{2}\beta E \cot\theta$$
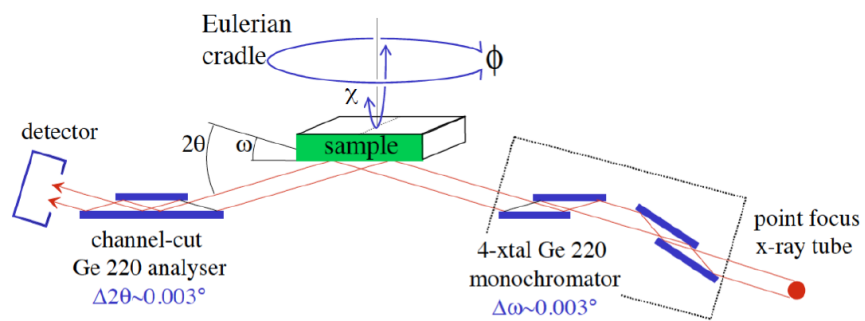
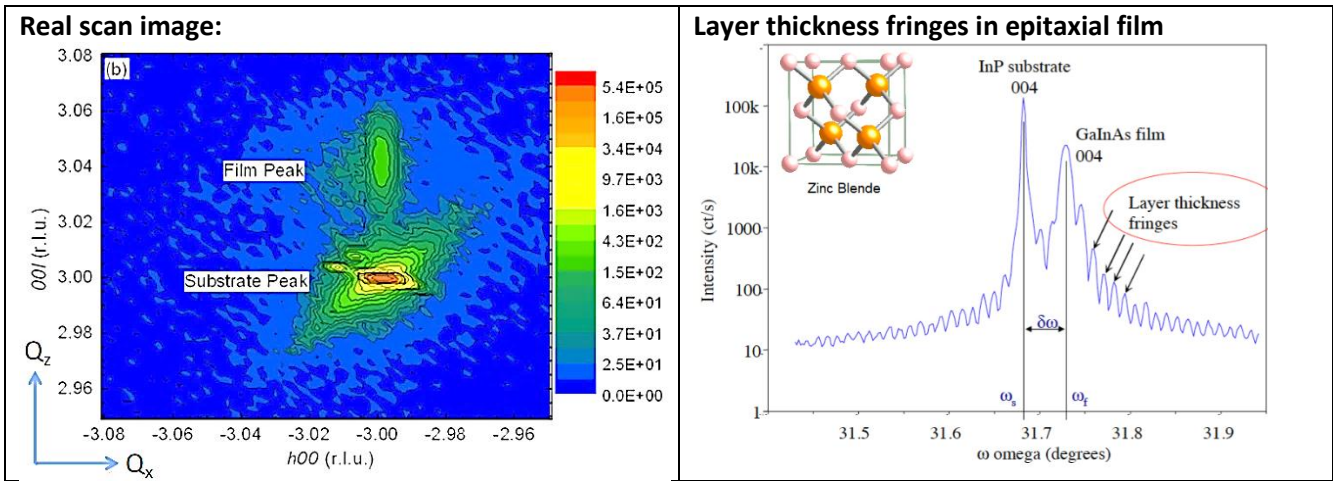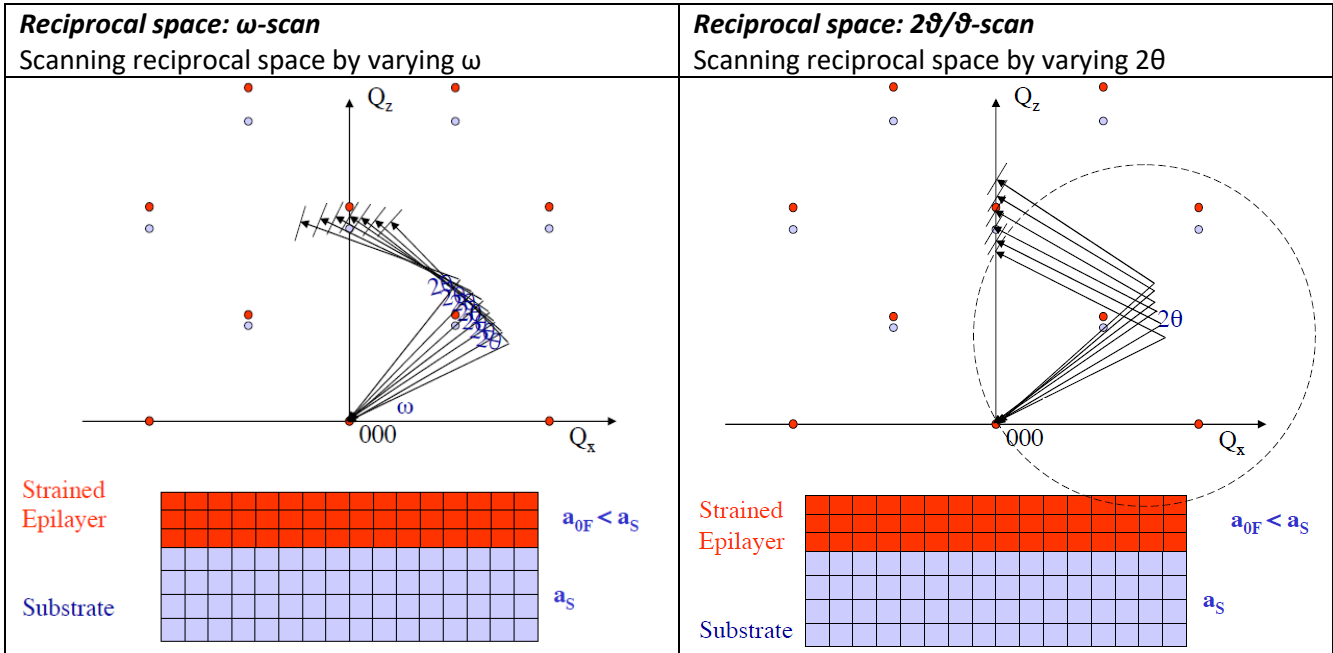Nanocrystallite size D: (P. Scherrer formula)

$$\beta_{ncr} = \frac{K\lambda}{D\cos\theta} \qquad K = \frac{2}{\sqrt{\pi}}\sqrt{\ln 2} \approx 0{,}9$$

Reciprocal space mapping of epitaxial films

Film parameters larger than substrate	**Substrate parameters larger than film**

High-resolution diffraction optics

Reciprocal space: ω-scan Scanning reciprocal space by varying ω	*Reciprocal space: 2ϑ/ϑ-scan* Scanning reciprocal space by varying 2θ
  Strained Epilayer $a_{0F} < a_S$ Substrate a_S	 Strained Epilayer $a_{0F} < a_S$ Substrate a_S

Real scan image:	**Layer thickness fringes in epitaxial film**

Rocking curves for epitaxial layers

- Normal is perpendicular to the substrate surface
  - ω is also the diffraction angle ($\omega = \vartheta$)
- Double-axis measurement: total intensity refracted over a range of 2ϑ is mapped as a function of ω

In a double-axis measurement, the wide-open detector can see several different angles of 2Theta- so both the Si and Si(Ge) peaks are observed