CHEM-E5140
Materials Characterization

XRD Lecture

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X-Ray Diffraction

- X-Ray Radiation
  - Nature of X-rays
  - Production of X-rays
  - Absorption of X-rays
- Theoretical Background of Diffraction
  - Bragg's law
  - Reciprocal space
  - Ewald sphere
  - Intensity of diffraction beam – structure factor
- X-Ray Diffractometry
  - Diffractometer and x-ray optics
  - Applications

What are X-Rays?

- Discovered by Wilhelm Röntgen (1845-1923) at 1895 .
- X-rays are **short-wavelength** and **high energy** electromagnetic radiation.
- Wavelength 0.1Å to 100Å, (3×10^{16} Hz to 3×10^{19} Hz) (**0.5 – 2.5Å used in diffraction**).
- Production of X-rays: X-ray tube and synchrotron.

Properties of X-Rays

Wavelength 1 µm 100 nm 10 nm 1 nm 100 pm 10 pm 1 pm 100 fm

visible light

soft X−rays

gamma rays

ultraviolet light

hard X−rays

Photon energy 1 eV 10 eV 100 eV 1 keV 10 keV 100 keV 1 MeV 10 MeV

X-ray crystallography

Mammography

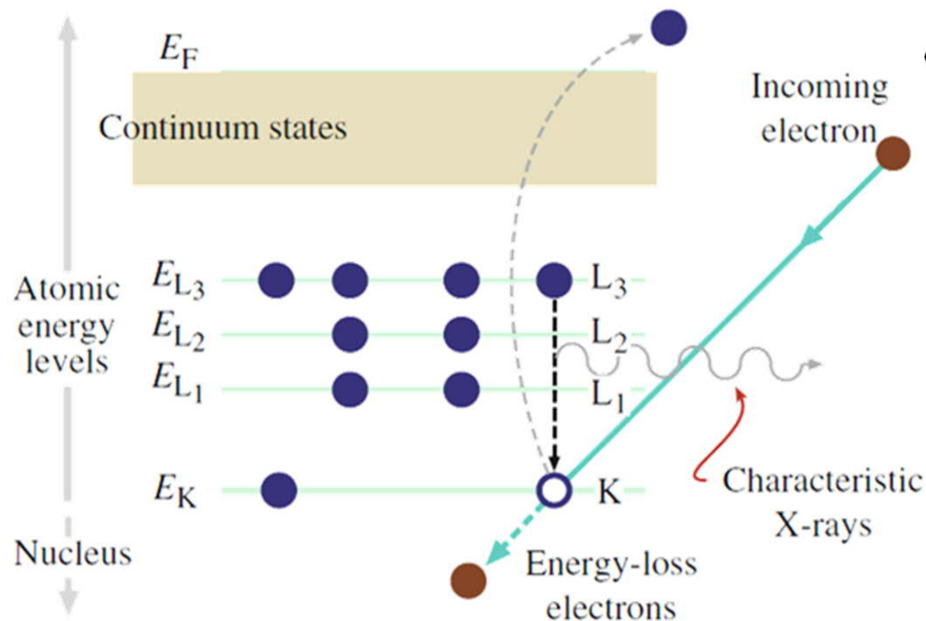
Medical CT

Airport security

http://en.wikipedia.org/wiki/File:X-ray_applications.svg

- Applications for X-Rays. Radiography; **X-ray crystallography (XRD)**; X-ray fluorescence spectrometry (XRF); X-ray photoelectron spectroscopy (XPS); X-ray microscopy.

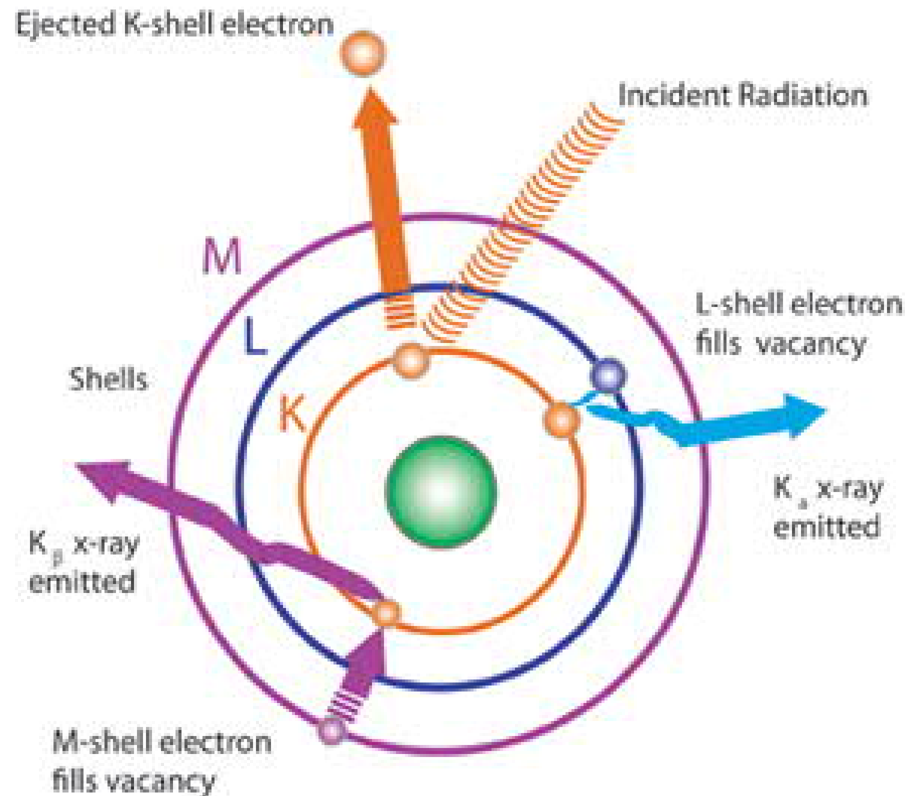
Generating Characteristic Radiation



L_3->K α_1
L_2->K α_2

- **The photoelectric effect is responsible for generation of characteristic x-rays. Qualitatively here's what is happening:**
  - An incoming high-energy photoelectron kick off a k-shell electron in the target, leaving a vacancy in the shell
  - An outer shell electron then "jumps" to fill the vacancy
  - A characteristic x-ray (equivalent to the energy change in the "jump") is generated

Generating Characteristic Radiation



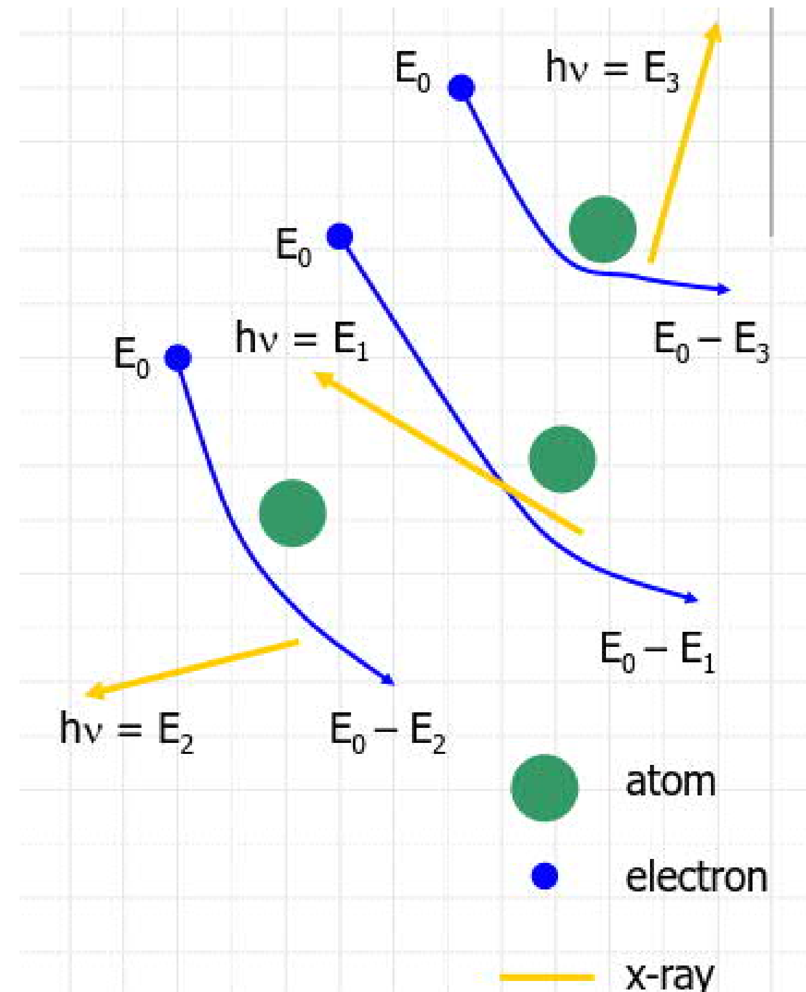
L-shell to K-shell jump produces a Kα x-ray

M-shell to K-shell jump produces a Kβ x-ray

- **The photoelectric effect is responsible for generation of characteristic x-rays. Qualitatively here's what is happening:**
  - An incoming high-energy photoelectron kick off a k-shell electron in the target, leaving a vacancy in the shell
  - An outer shell electron then "jumps" to fill the vacancy
  - A characteristic x-ray (equivalent to the energy change in the "jump") is generated

Continuous X-Ray Spectrum

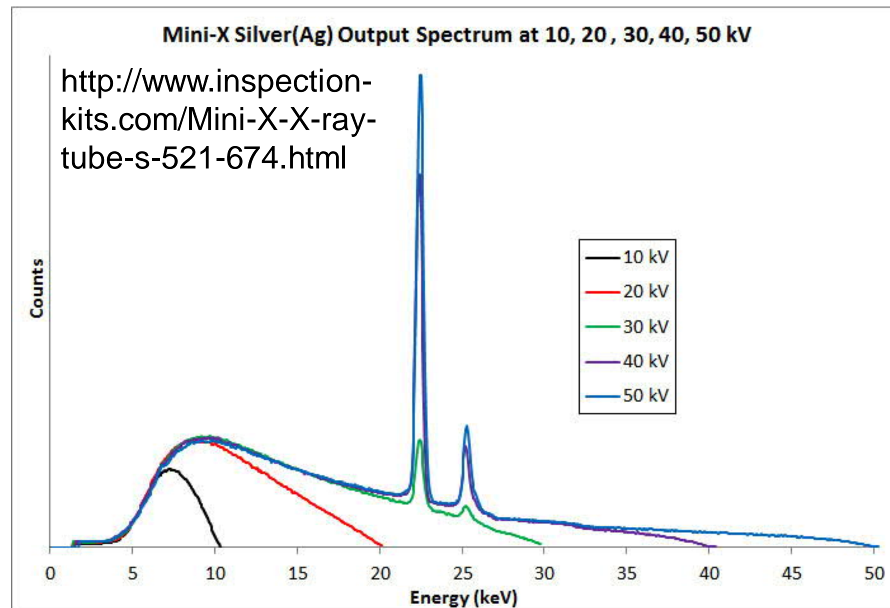
- Continuous spectrum arises due to the deceleration of the electrons hitting the target.
- This type of radiation is know as bremsstrahlung, German for “braking radiation”
- Some electrons lose all the energy in a single collision with a target atoms (which set limit of short wavelength).

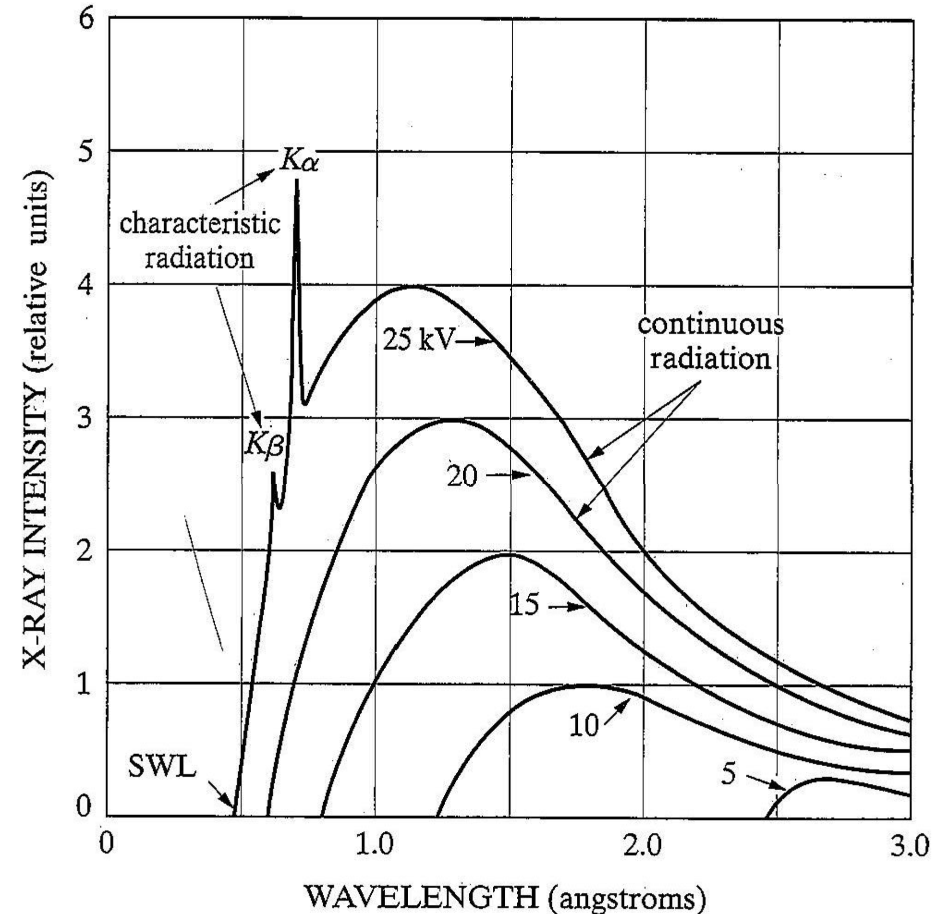


Continuous Spectrum

- The short wavelength wavelength (SWL) (λ in angstroms) is a function of the applied voltage V.
- The continuum reaches a maximum intensity at a wavelength of about 1.5 to 2 times the λ_{SWL} as indicated by the shape of the curve

$$\lambda_{SWL} = \frac{hc}{V} = \frac{12.398}{V}$$





X-Ray Source: X-Ray Tube

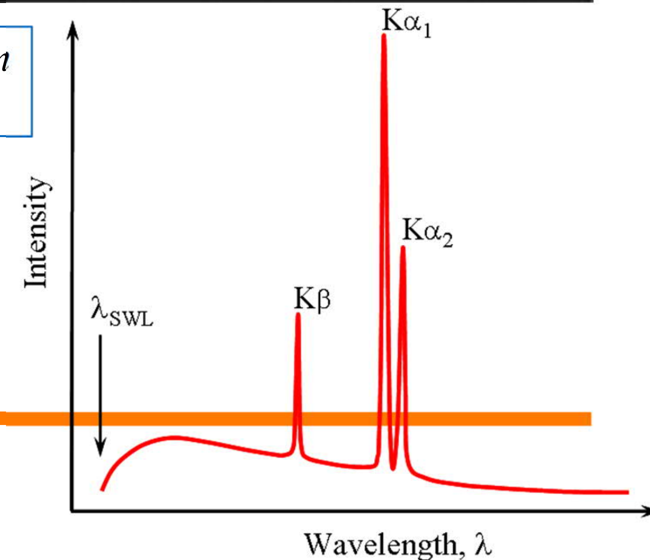
BERYLLIUM WINDOW
TUNGSTEN FILAMENT
GLASS
COOLING WATER
ELECTRONS
TO TRANSFORMER
TARGET
X-RAYS
FOCUSING CUP
VACUUM

SCHEMATIC CROSS SECTION OF AN X-RAY TUBE

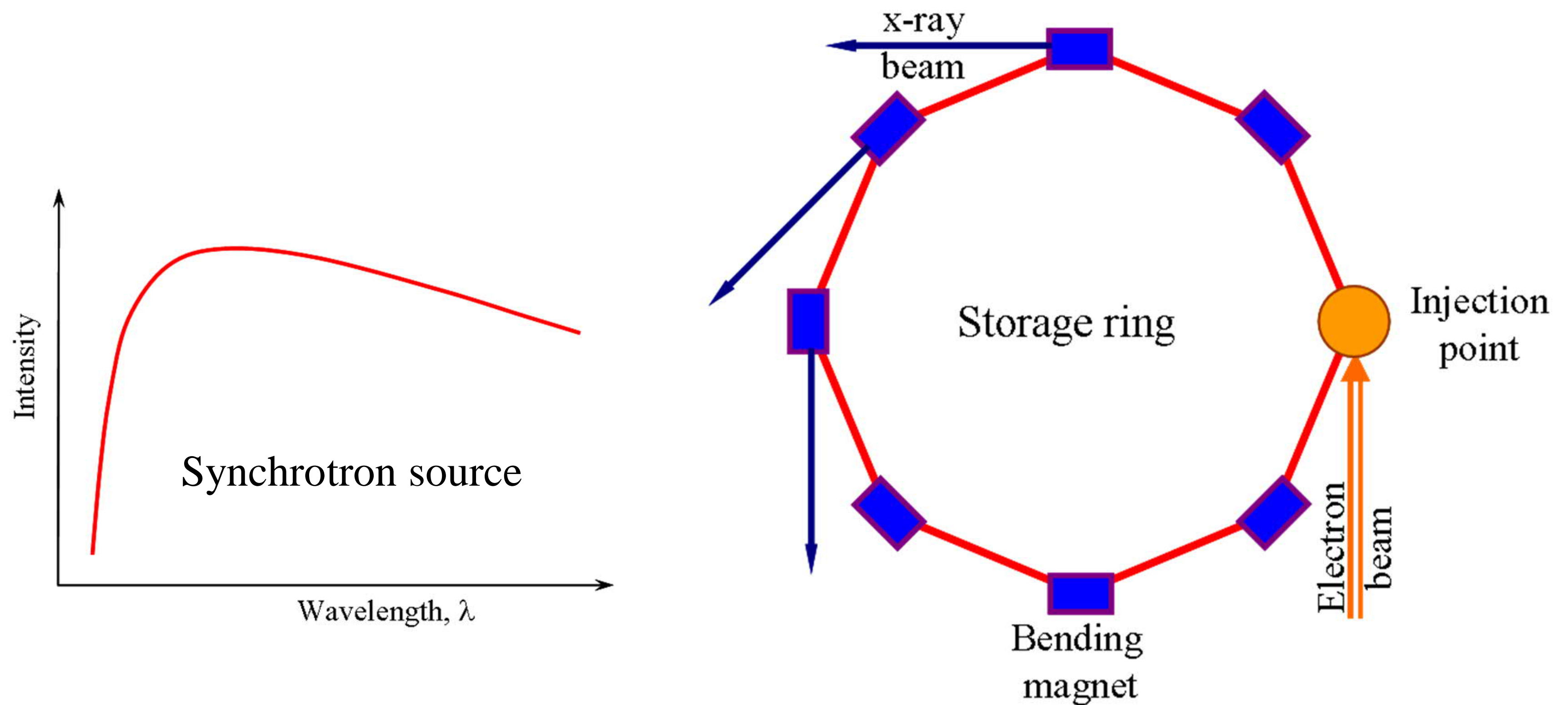
- A source of electrons
- A high accelerating voltage
- A metal target
- The efficiency is 1% or less.

$$I_{Kline} = Bi(V - V_K)^n$$

B: constant; V_K: the K excitation voltage; n: 1 ~ 2, mostly 1.5.



X-Ray Source: Synchrotron



Intensity is 4 to 12 orders of magnitude higher than from a conventional X-Ray source.

The divergence of beam is really small, almost can be considered as parallel.

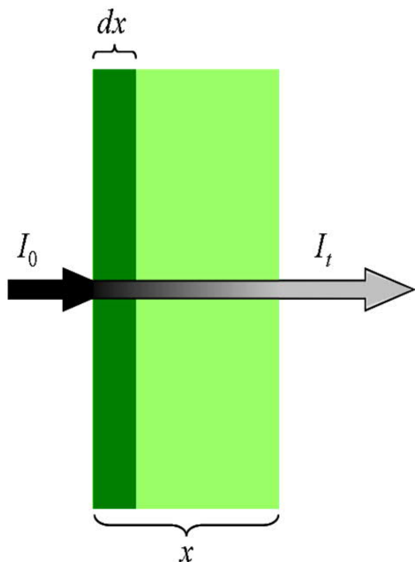
The high intensity is distributed in a wide range of wavelength.

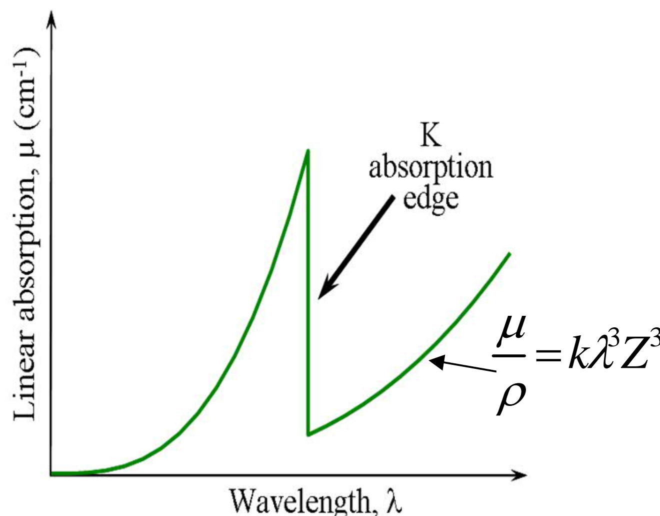
Characteristics of Common Anode Materials

Anode	At. #	$K\alpha_1$ (Å)	$K\alpha_2$ (Å)	Char Min (keV)	Opt kV	Advantages (Disadvantages)
Cr	24	2.290	2.294	5.98	40	High resolution for large d-spacings, particularly organics (High attenuation in air)
Fe	26	1.936	1.940	7.10	40	Most useful for Fe-rich materials where Fe fluorescence is a problem (Strongly fluoresces Cr in specimens)
Co	27	1.789	1.793	7.71	40	Useful for Fe-rich materials where Fe fluorescence is a problem
Cu	29	1.541	1.544	8.86	45	Best overall for most inorganic materials (Fluoresces Fe and Co $K\alpha$ and these elements in specimens can be problematic)
Mo	42	0.709	0.714	20.00	80	Short wavelength good for small unit cells, particularly metal alloys (Poor resolution of large d-spacings; optimal kV exceeds capabilities of most HV power supplies.)

Absorption of X-Rays

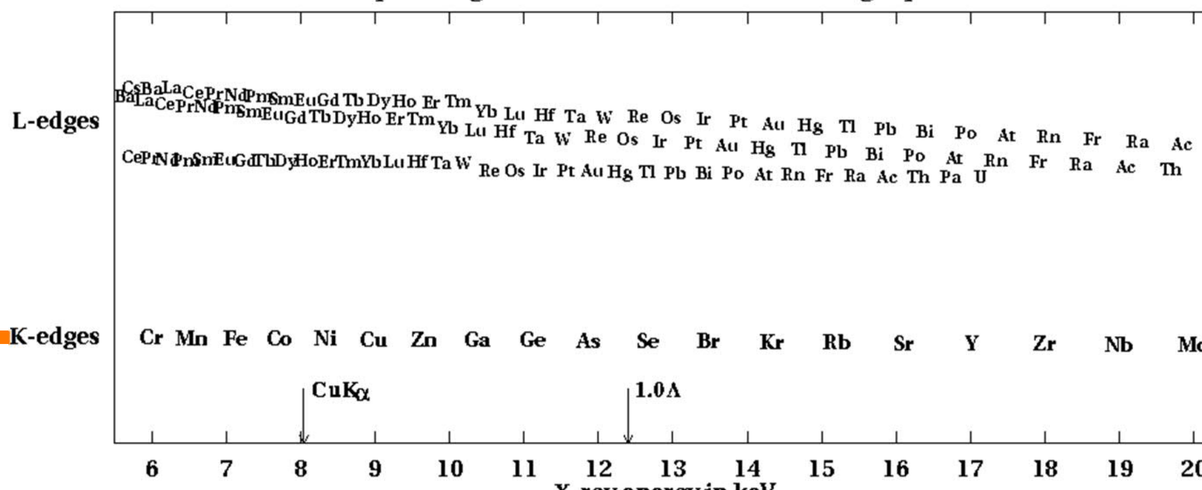
by scattering and true absorption



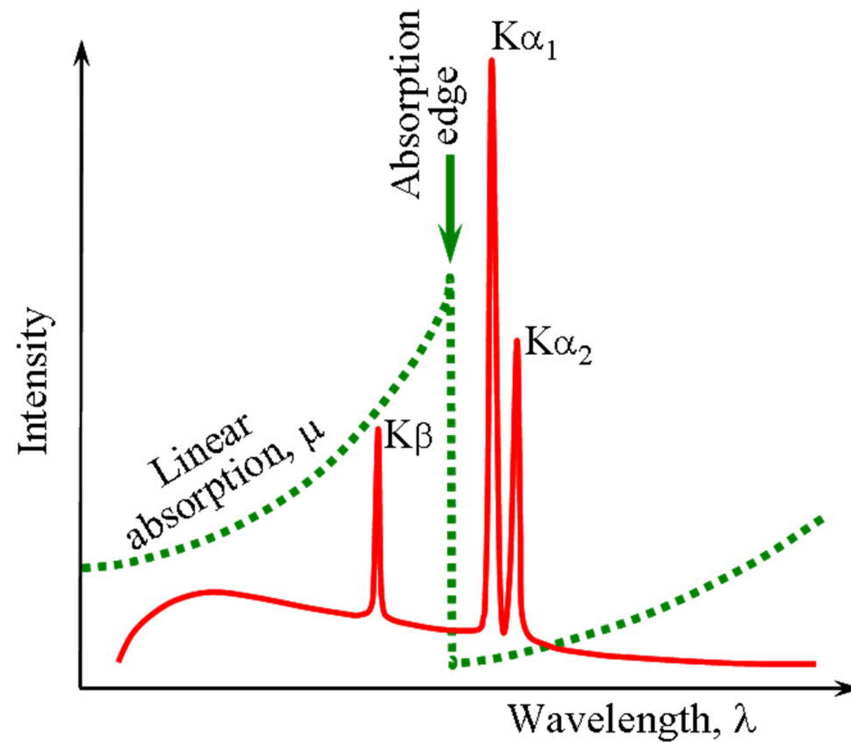


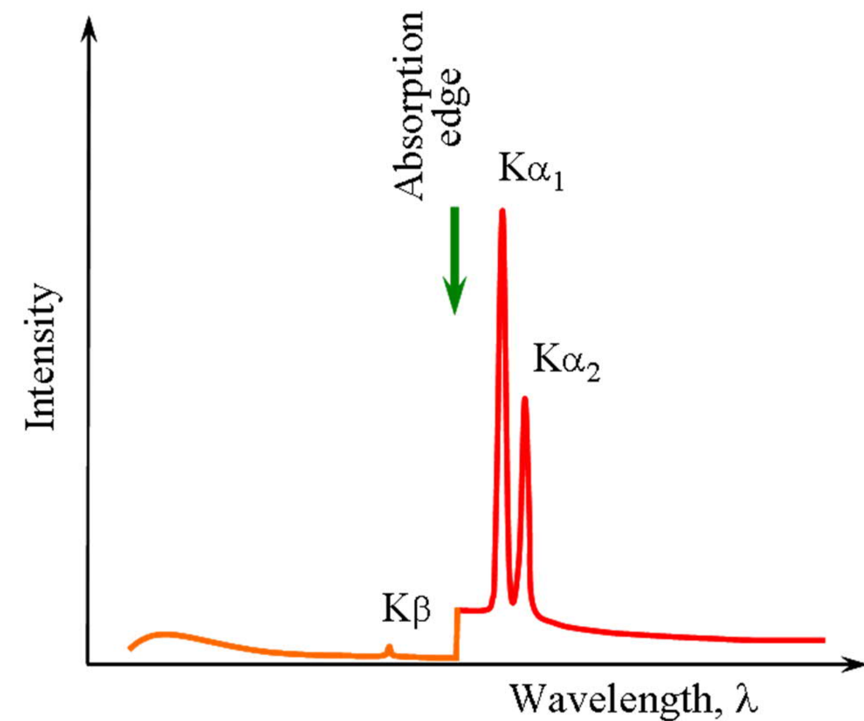
μ/ ρ : mass absorption coefficient, is a constant of material. The full table in "Vol. C of the international tables for crystallography "

$$I_t = I_0 exp(-\mu x)$$



β-Filters





Kα1/Kα2/Kβ is 10/5/2

β-filters will have an atomic number one less that of the target metal, for metals with Z near 30.

β Filters for Common Anodes

Target	Kα (Å)	β-filter	Thickness (μm)	Density (g/cc)	% Kα	% Kβ
Cr	2.291	V	11	6.00	58	3
Fe	1.937	Mn	11	7.43	59	3
Co	1.791	Fe	12	7.87	57	3
Cu	1.542	Ni	15	8.90	52	2
Mo	0.710	Zr	81	6.50	44	1

Note: Thickness is selected for max/min attenuation/transmission Standard practice is to choose a filter thickness where the α : β is between 25:1 and 50:1

Theoretical Background of Diffraction

X-ray wavefront and phase

- **Plane polarized** wave: electric field vector lies in the plane of the drawing.
- **Constructive** interference: wave front are in phase reinforcing each other.
- **Destructive** interference: fronts are out of phase cancelling each other.
- A **diffracted beam** is composed of a large number of scattered rays mutually reinforcing each other.

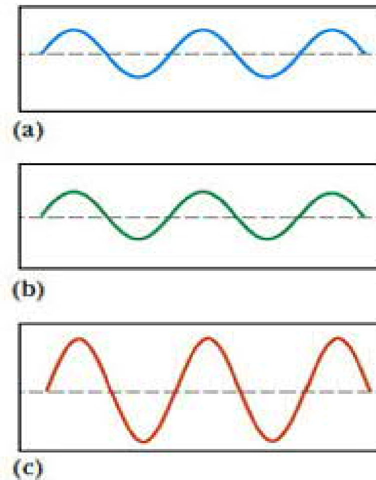


Figure 1 Constructive interference. If two waves having the same frequency and amplitude are in phase, as in (a) and (b), the resultant wave when they combine (c) has the same frequency as the individual waves, but twice their amplitude.

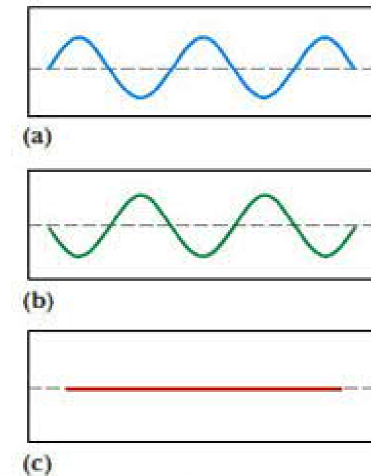


Figure 2 Destructive interference. When two waves with the same frequency and amplitude are 180° out of phase, as in (a) and (b), the result when they combine (c) is complete cancellation.

•Difference in the length of the path traveled leads to differences in phase.
•Phase differences produce a change in amplitude.

Diffraction: Braggs' Law

θ, 2θ – Bragg angles
$2\Delta = 2d_{hkl}\sin\theta$ – path difference
$2\Delta = n\lambda$ – constructive interference

Braggs' law: $n\lambda = 2d_{hkl}\sin\theta_{hkl}$

n: the order of reflection

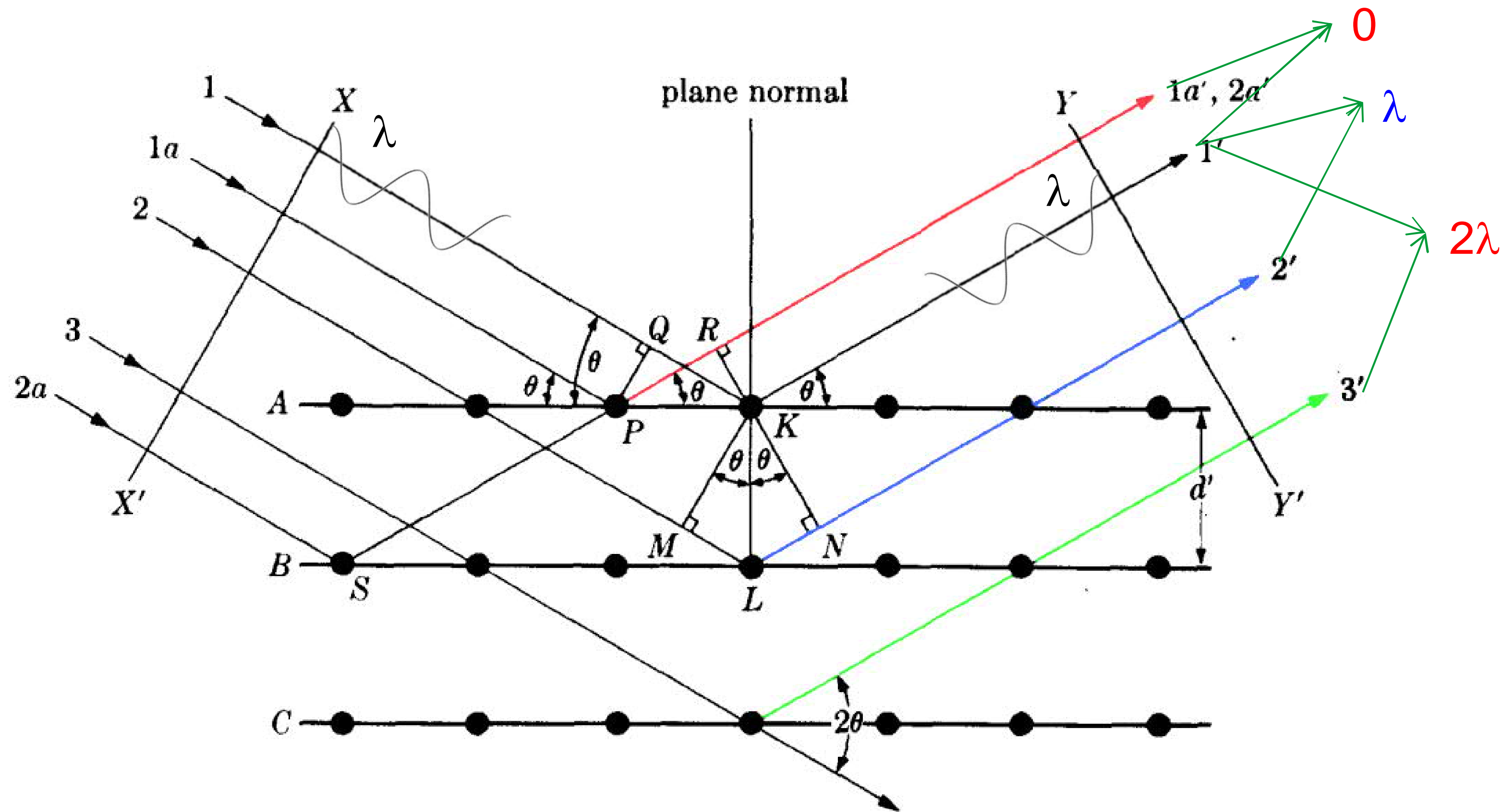


Fig. 3–2 Diffraction of x-rays by a crystal.

Diffraction is essentially a scattering phenomenon in which a large number of atoms cooperate.

n in Braggs' Law

The integer *n* is known as the order of reflection and its value is taken as 1 in all calculations.

$$\lambda = 2d \sin \theta$$

For any n>1 : $d_{hkl} = n d_{nh,nk,nl}$

$$2d_{hkl} \sin \theta_{hkl} = n\lambda \Rightarrow 2d_{nh,nk,nl} \sin \theta_{nh,nk,nl} = \lambda$$

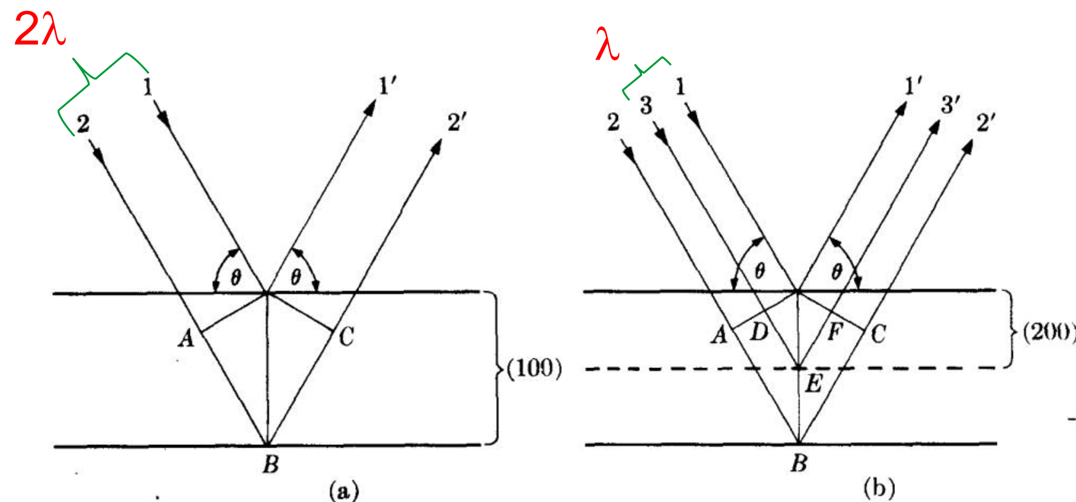
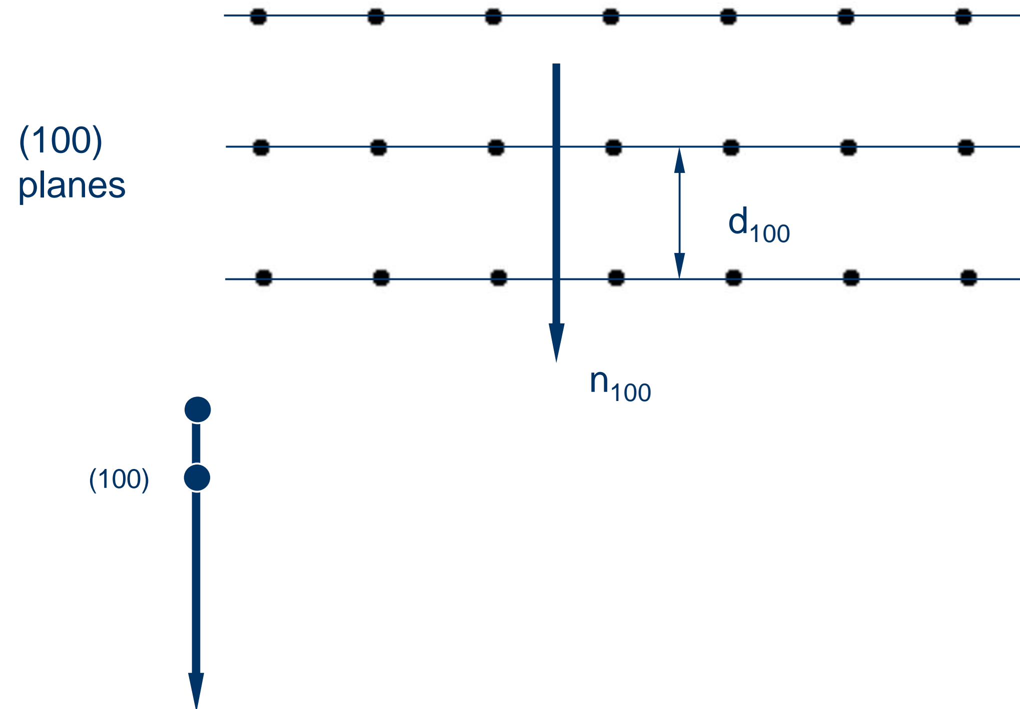


Fig. 3–3 Equivalence of (a) a second-order 100 reflection and (b) a first-order 200 reflection.

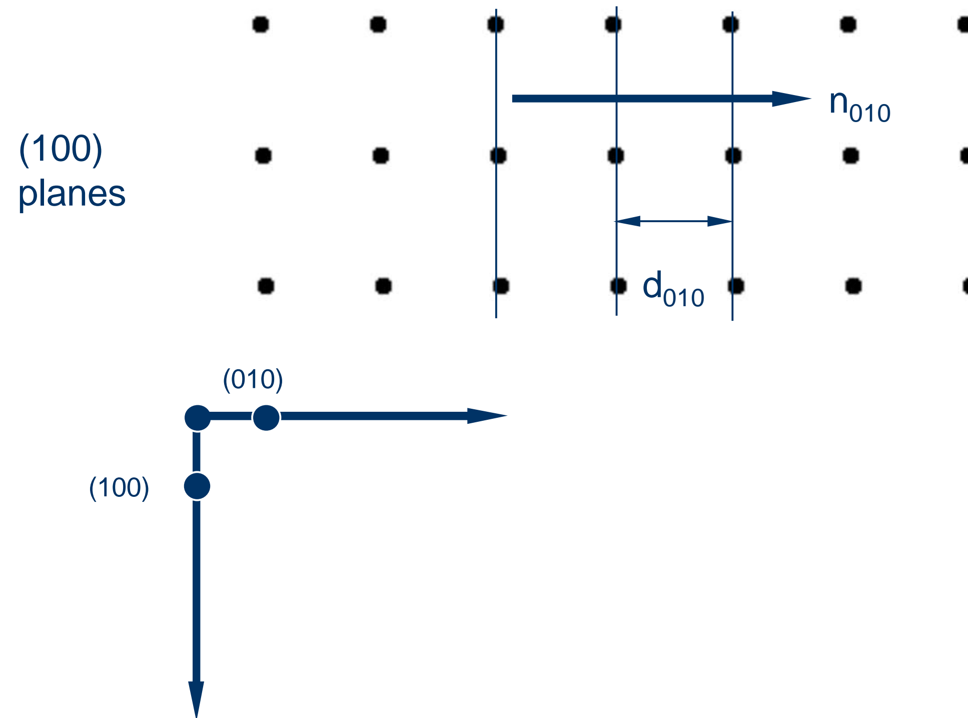
Reciprocal Lattice

Real space lattice → the (100) reciprocal lattice points



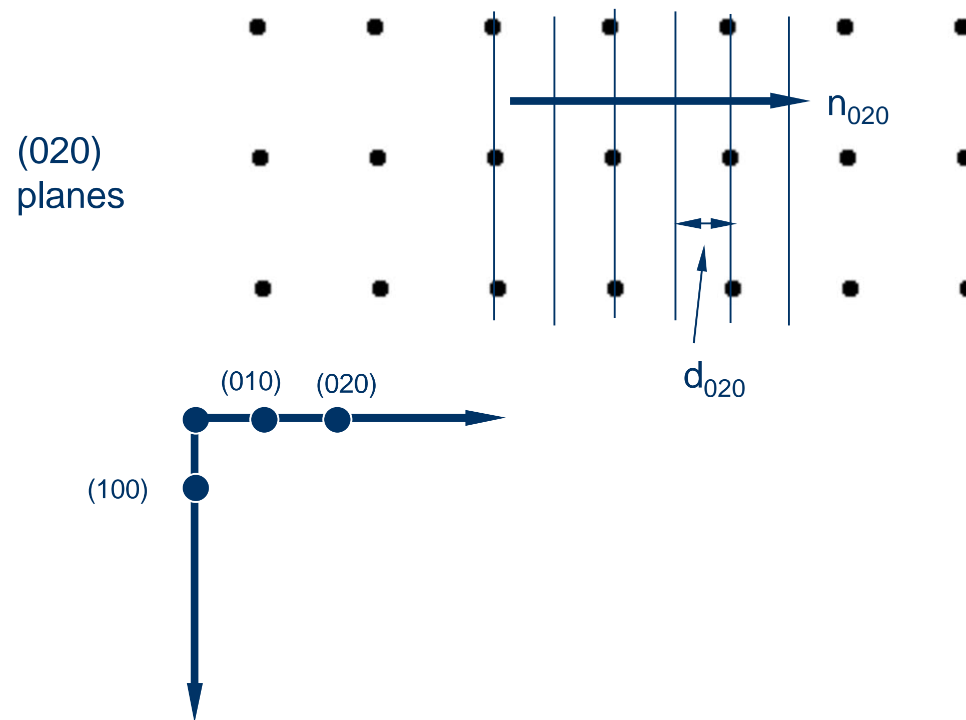
Reciprocal Lattice

Real space lattice → the (010) reciprocal lattice points



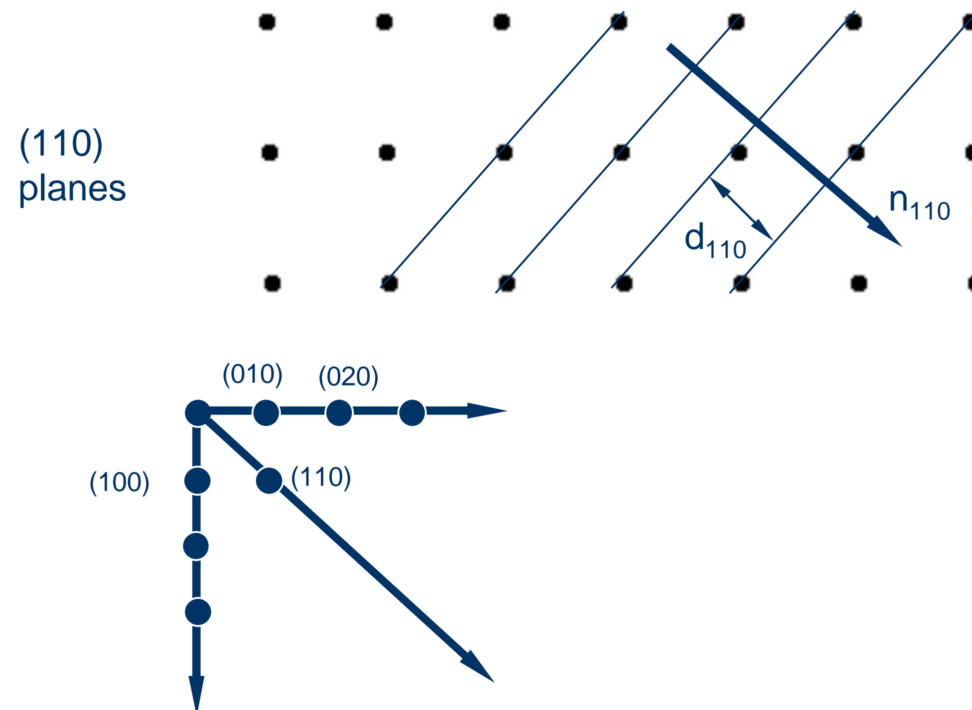
Reciprocal Lattice

Real space lattice → the (020) reciprocal lattice points



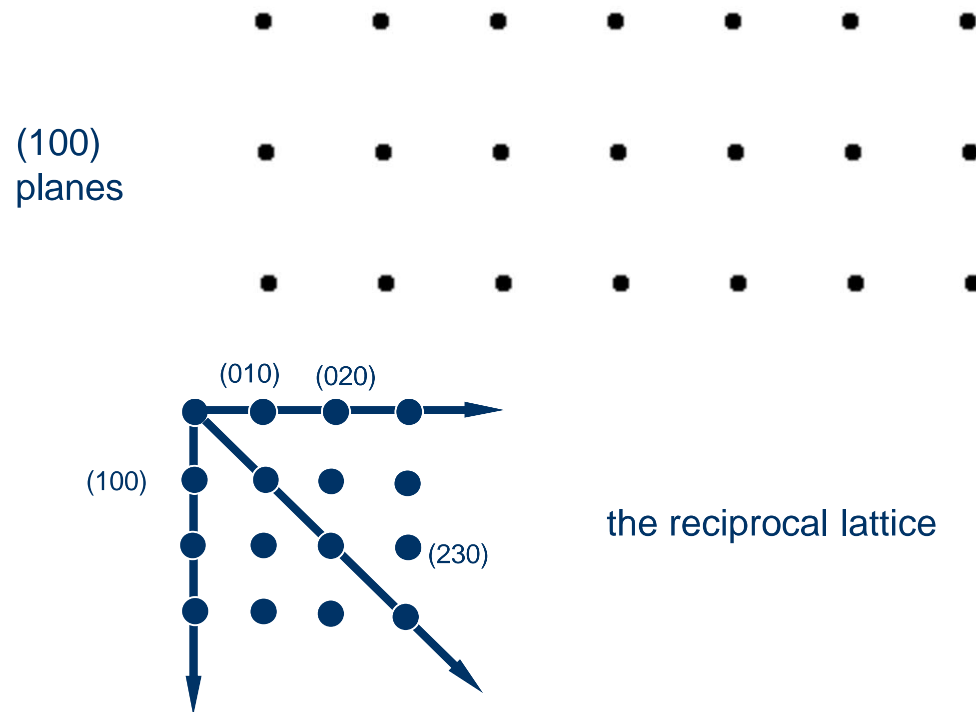
Reciprocal Lattice

Real space lattice → the (110) reciprocal lattice points



Reciprocal Lattice

Real space lattice → reciprocal lattice points



the reciprocal lattice

Reciprocal Lattice Notation

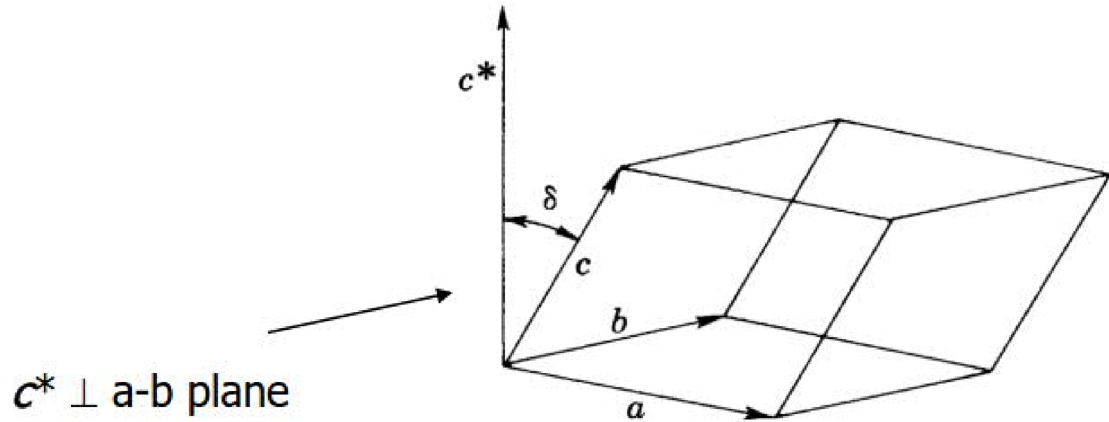
- Consider a real space unit cell with real lattice basis vectors a, b and c.
- We define a set of reciprocal lattice basis vectors by:

$$\mathbf{a}^* = \frac{1}{V}(\mathbf{b}\times\mathbf{c}) = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

volume of real space unit cell

$$\mathbf{b}^* = \frac{1}{V}(\mathbf{c}\times\mathbf{a})$$

$$\mathbf{c}^* = \frac{1}{V}(\mathbf{a}\times\mathbf{b})$$



$$|d^*_{hkl}| = \left|\frac{1}{d_{hkl}}\right|$$

Properties of Reciprocal Lattice

- The reciprocal space vectors in a reciprocal space lattice:

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

- The real and reciprocal space lattice vectors form an orthonormal set:

$$\mathbf{a}^* \perp \mathbf{b} \text{ and } \mathbf{c} \qquad \left.\begin{aligned} \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = 0 \\ \mathbf{a}^* \cdot \mathbf{a} = 1 \end{aligned}\right\}$$

similar for b^* and c^*

- The volume of a reciprocal unit cell:

$$V^* = \mathbf{a}^* \cdot (\mathbf{b}^* \times \mathbf{c}^*) \qquad V^* \cdot V = 1$$

- The vector $\mathbf{d}^*_{hkl}$ is perpendicular (*hkl*) plane in real space and its magnitude in a reciprocal lattice equals the reciprocal of plane spacing ($\mathbf{d}_{hkl}$) in real space:

$$|\boldsymbol{d}^*_{hkl}| = \left|\frac{1}{\boldsymbol{d}_{hkl}}\right|$$

Relationship of reciprocal lattice plane and real space directions

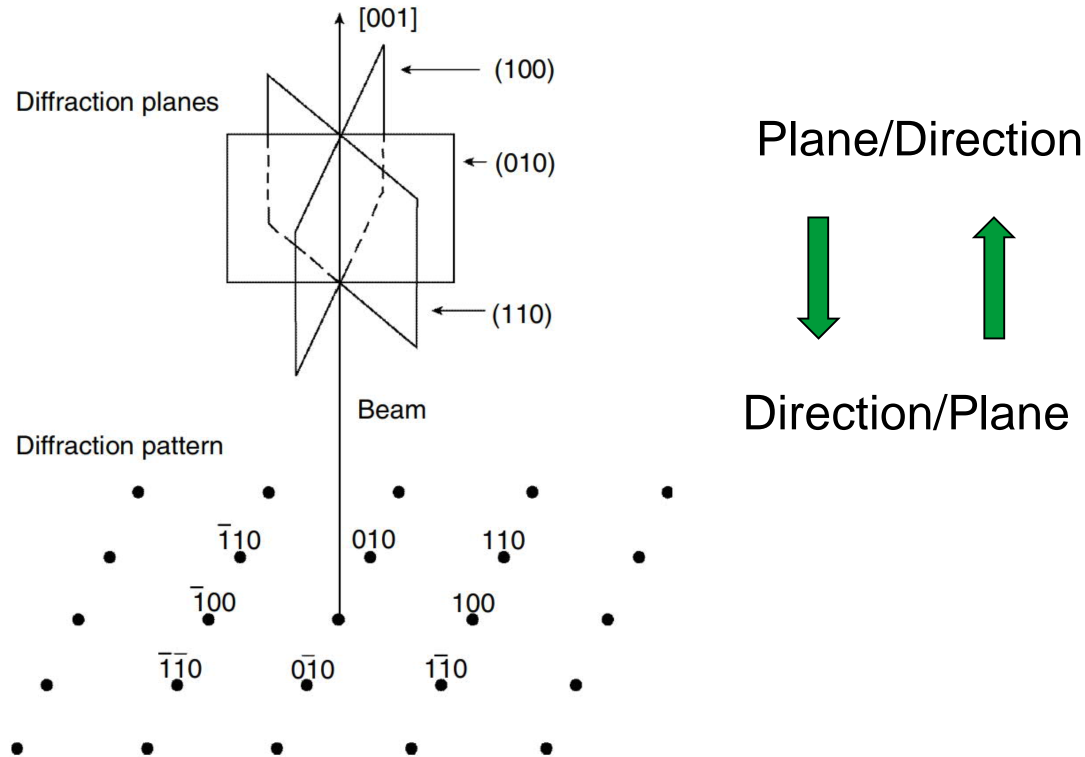


Figure 2.9 Relationship between a reciprocal lattice plane and real space directions. The reciprocal lattice plane is composed of diffraction spots from crystal planes (*hk*0). The zone axis [001] is perpendicular to the reciprocal lattice plane.

Reciprocal Lattice and Braggs' Law

Incident wave considered as a propagation vector k_0,

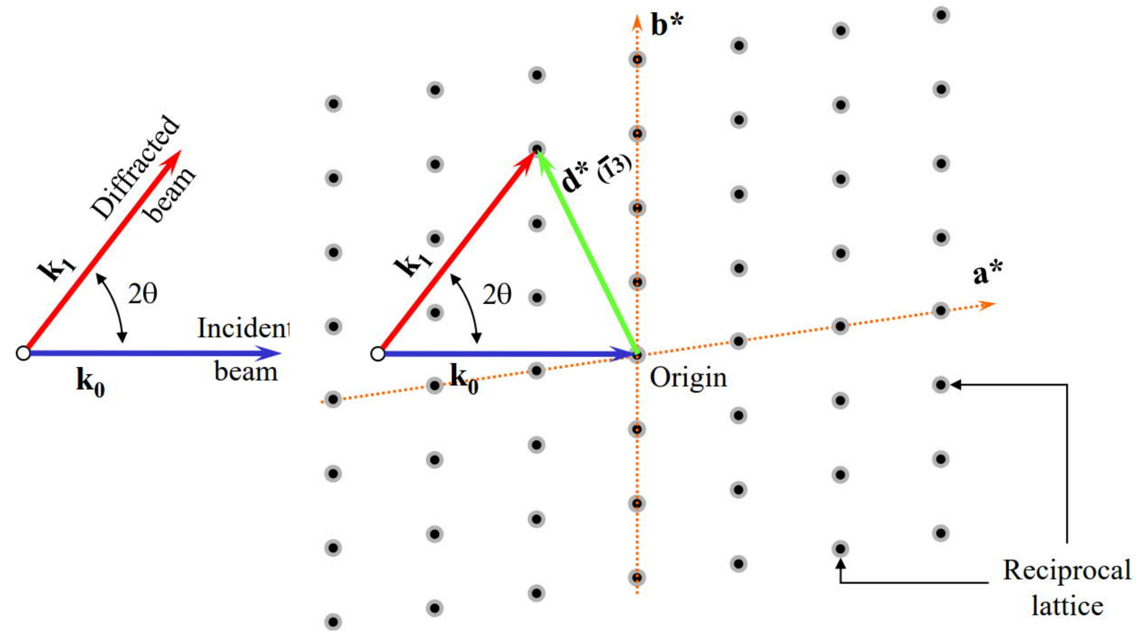
If the length of k_0 is:

$$|k_0| = 1/\lambda$$

The scattered wave is characterized by a different wavevector, k_1, with same length as k_0.

Braggs' law become:

$$k_1 - k_0 = d_{hkl}^*$$



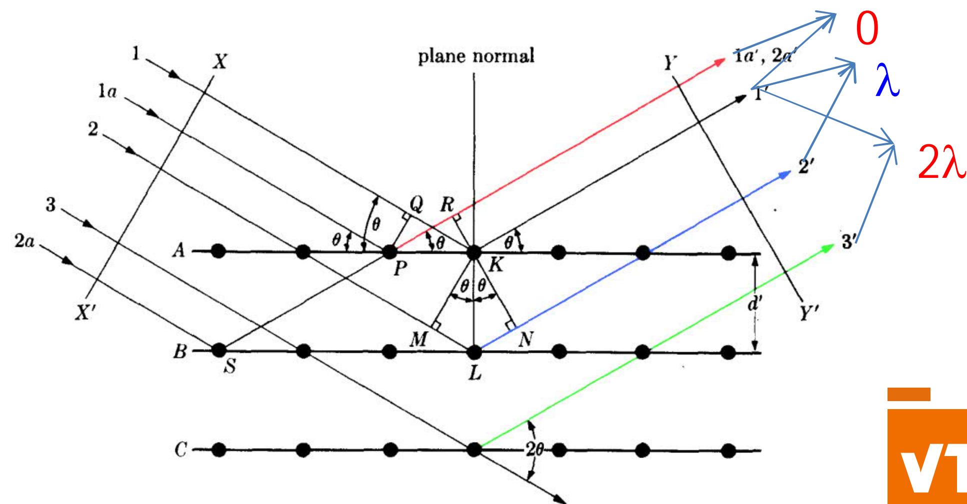
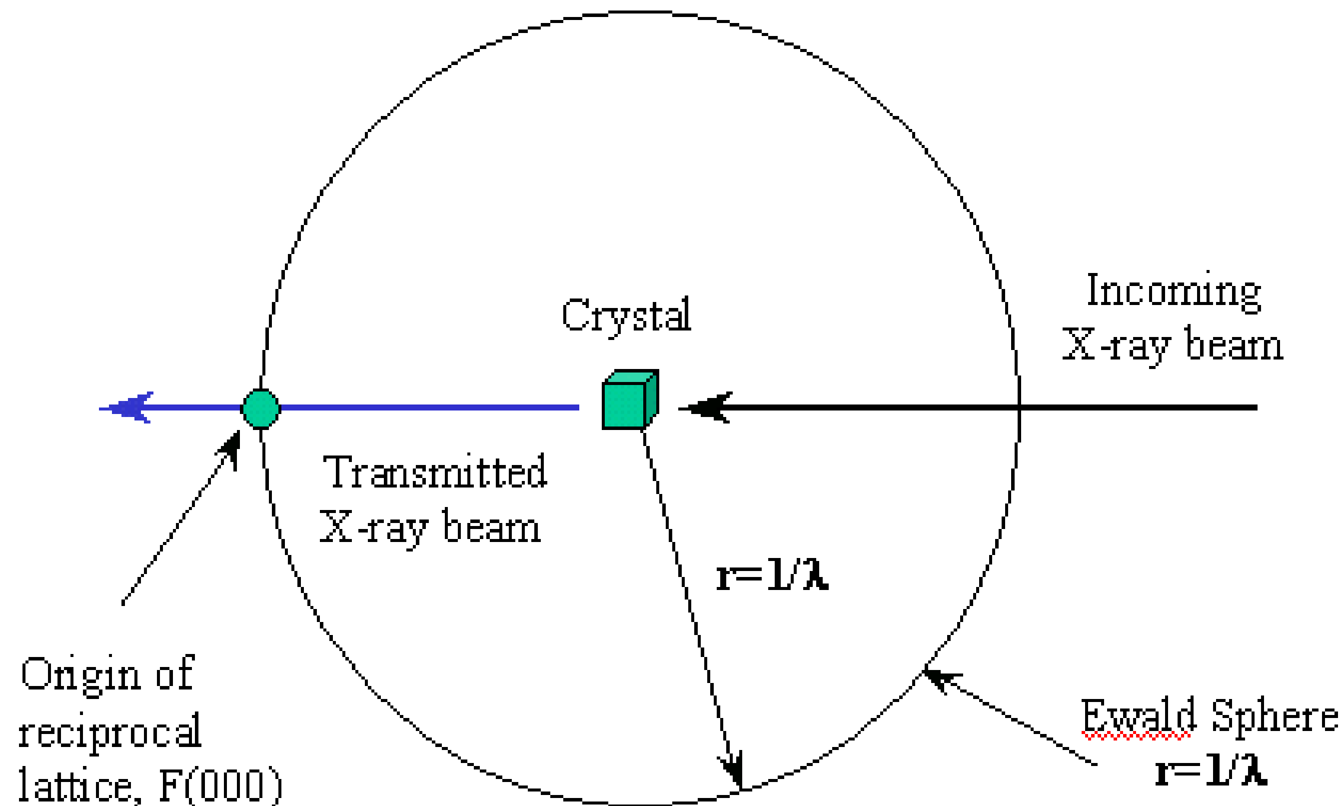


Fig. 3–2 Diffraction of x-rays by a crystal.

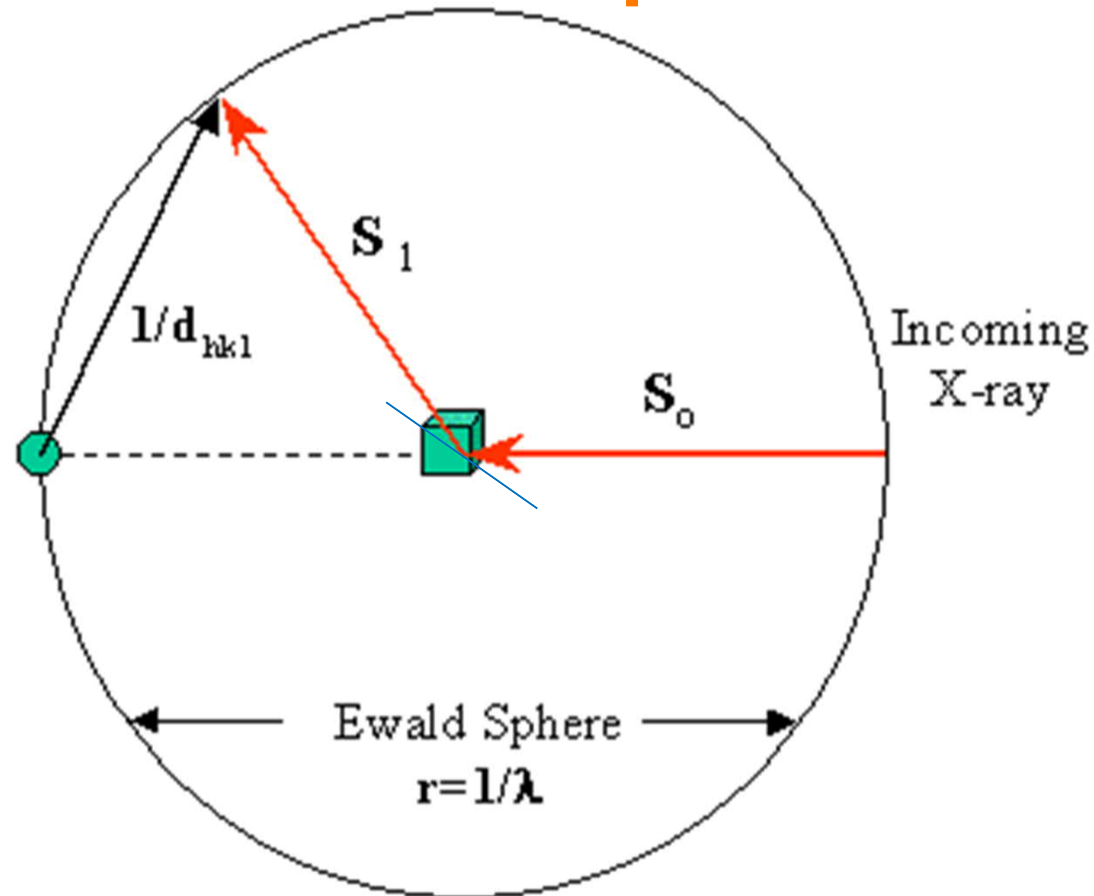
Construction of Ewald Sphere



Draw a sphere of radius 1/lambda, image a real crystal in the center.

http://www.ruppweb.org/Xray/tutorial/ewald.htm

Construction of Ewald Sphere



Braggs' law condition: whenever a reciprocal lattice point lies exactly on the Ewald sphere.

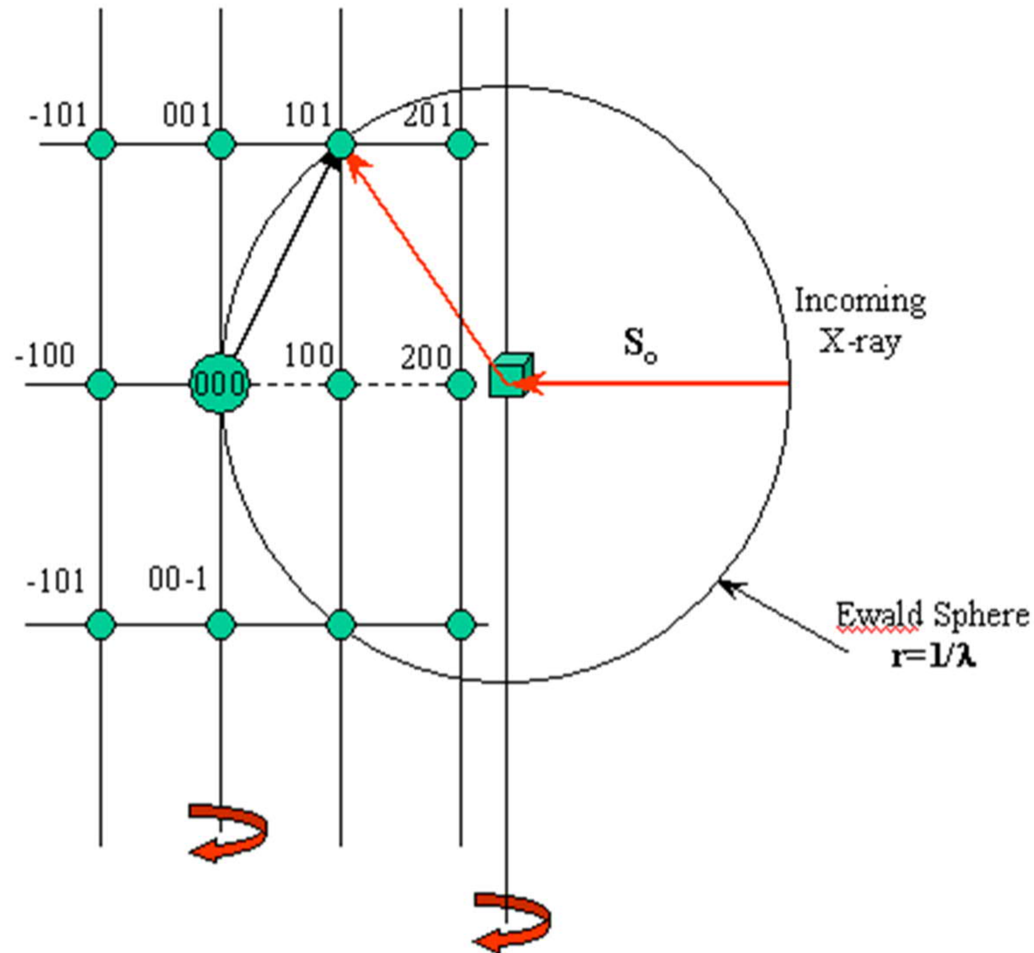
http://www.ruppweb.org/Xray/tutorial/ewald.htm

Reciprocal Space & Ewald Sphere

The chance for fulfill Braggs' law is modest:

To observe the reflections, then, we must:

1. Move the sphere
2. Move the crystal (rotate)
3. Change the size of the sphere (change wavelength of X-Ray)



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Reciprocal Lattice,Ewald sphere and Braggs' Law

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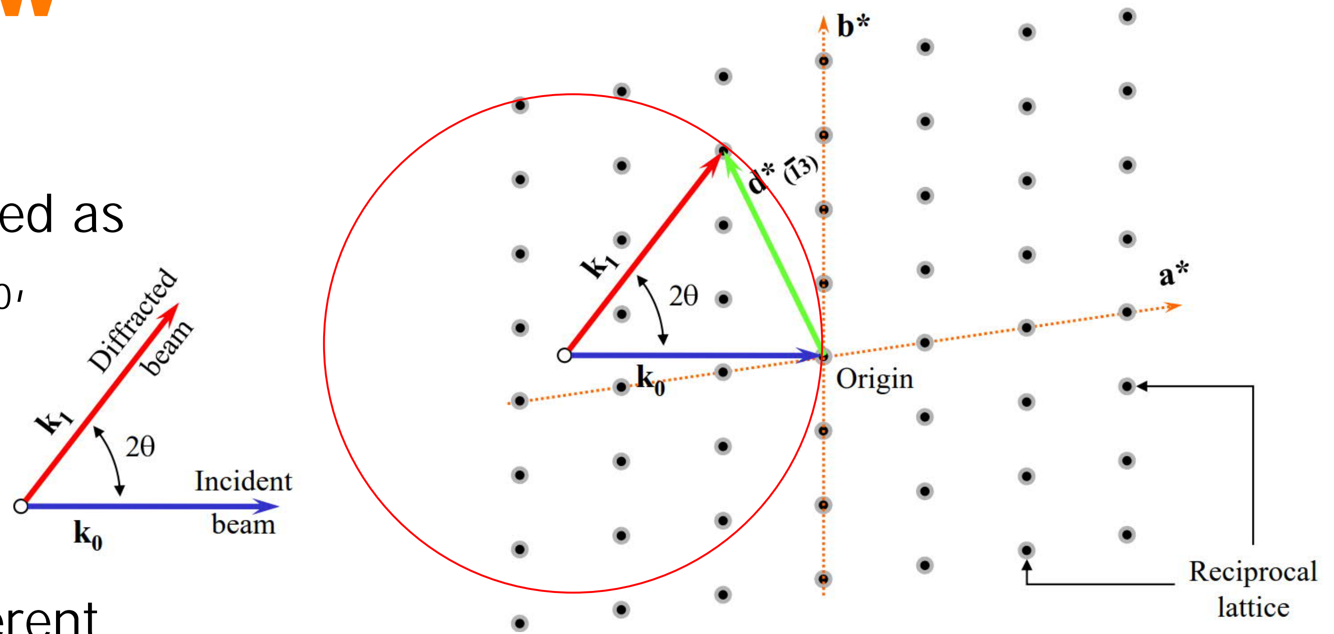


The scattered wave is characterized by a different wavevector, k_1, with same length as k_0.

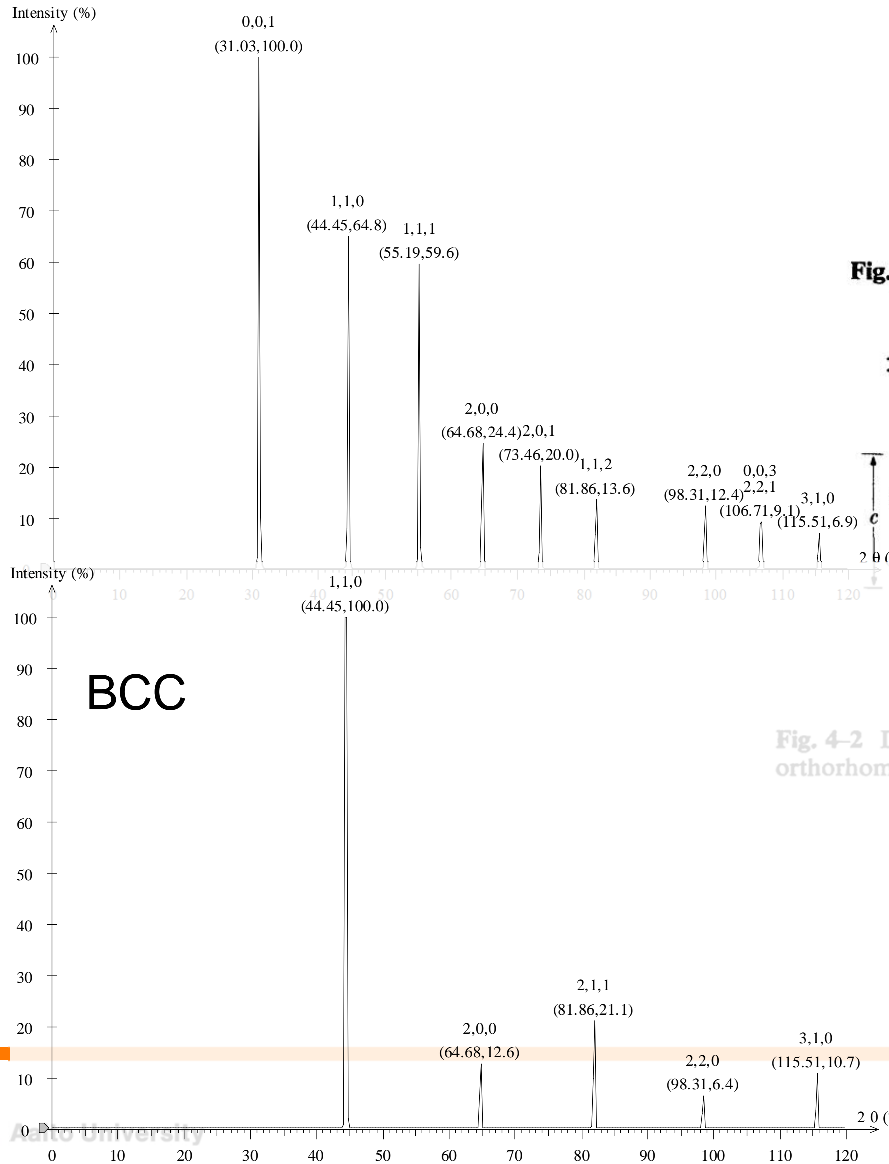
$|k1 - k0| = 2/\lambda \sin\theta$ $\quad \lambda = 2d \sin\theta$

Braggs' law become:

$$|k_1 - k_0| = d_{hkl}^* = 1/d_{hkl}$$

Intensity of Diffraction

Direction Vs Intensity



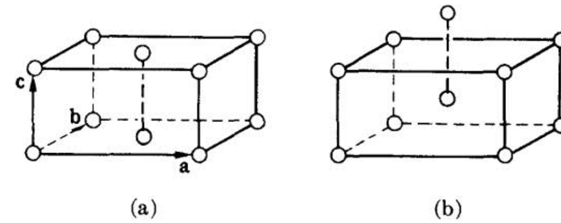


Fig. 4–1 (a) Base-centered and (b) body-centered orthorhombic unit cells.

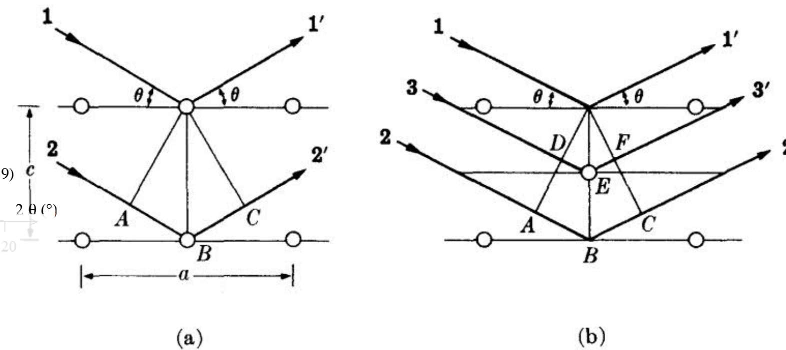


Fig. 4–2 Diffraction from the (001) planes of (a) base-centered and (b) body-centered orthorhombic lattices.

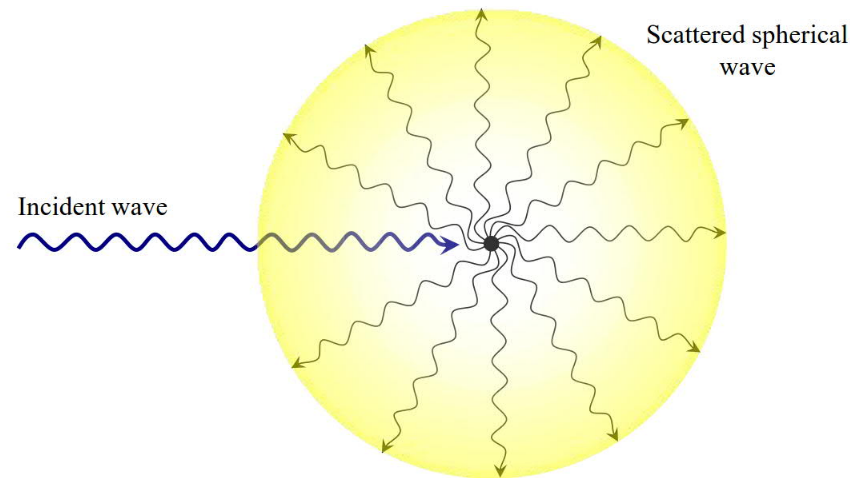
The unit cell and symmetry determine direction
The atoms in plane determine the intensity

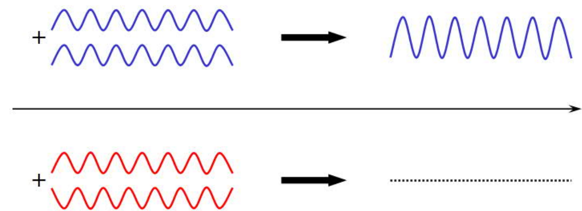
Scattering by one Electron

Thomson equation:

$$I = I_0 \frac{K}{r^2} \left(\frac{1 + \cos^2 2\theta}{2} \right)$$

I_0: the absolute intensity of the incident beam;
K: constant (K = 7.94 X10-30m^2);
r: distance from the electron to the detector in m
θ: the angle between the propagation vector of the incident wave and the direction of the scattered wave.

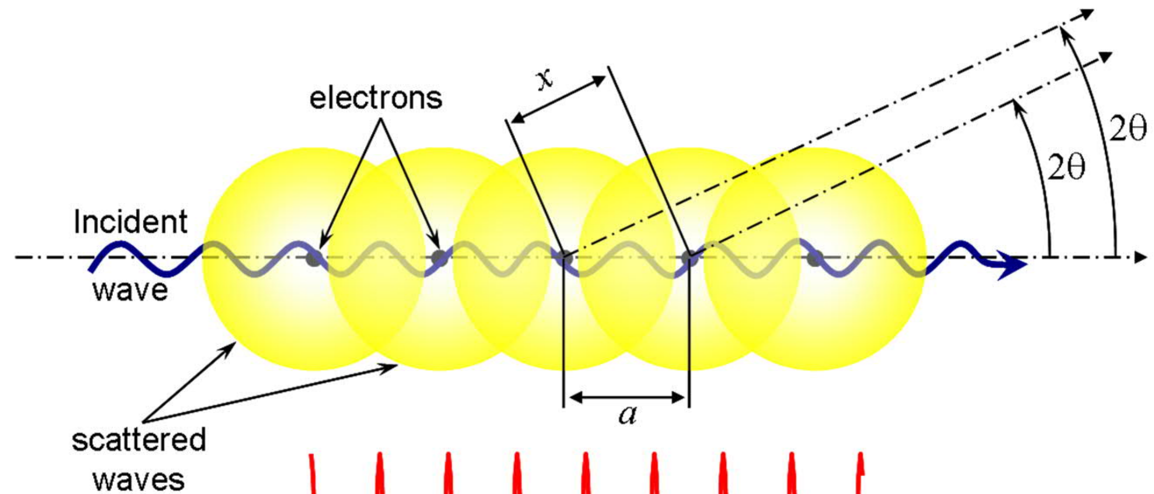




Coherent scattering

Scattering by Electrons

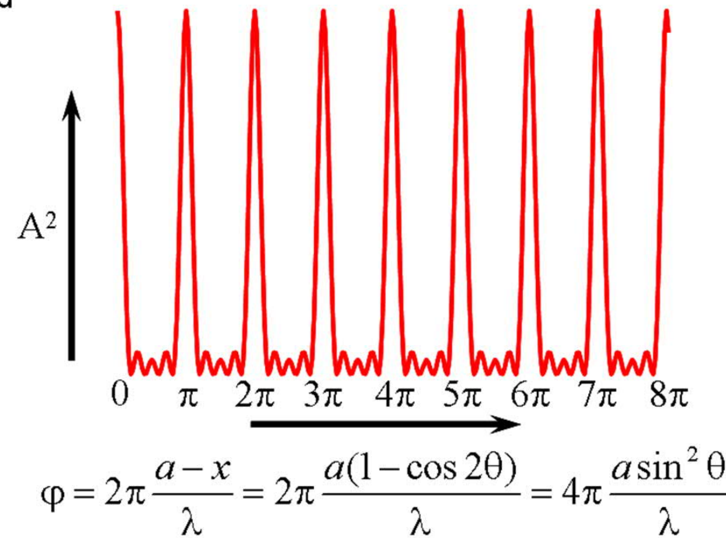
A one-dimensional periodic structure, the intensity diffracted by the row of N equally spaced points is proportional to the so-called **interference function:**



$$I(\varphi) \propto \frac{\sin^2 N\varphi}{\sin^2 \varphi}$$

φ: phase angle

$$I(\varphi) \propto N^2, \text{ when } \varphi = h\pi,$$
$$h = \ldots, -2, -1, 0, 1, 2 \ldots$$

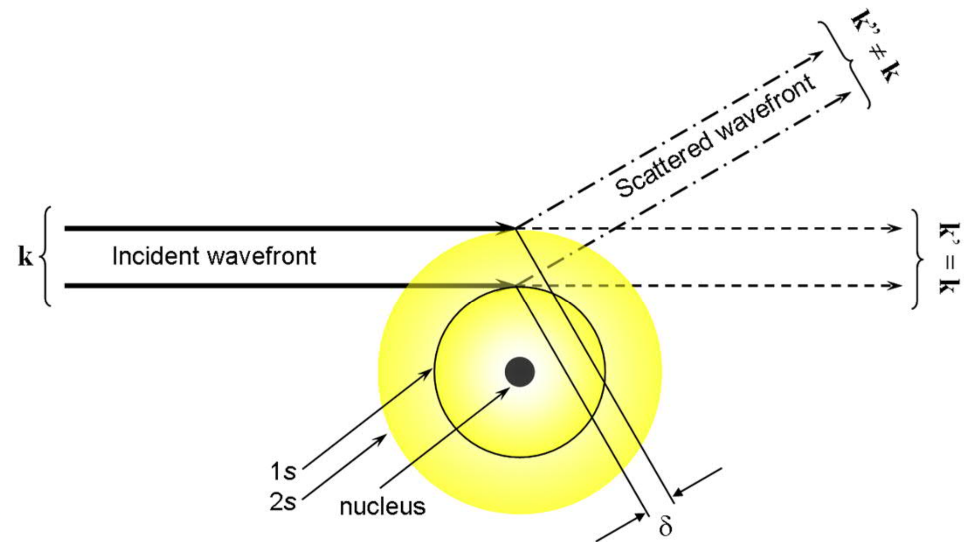


$$\varphi = 2\pi \frac{a - x}{\lambda} = 2\pi \frac{a(1 - \cos 2\theta)}{\lambda} = 4\pi \frac{a \sin^2 \theta}{\lambda}$$

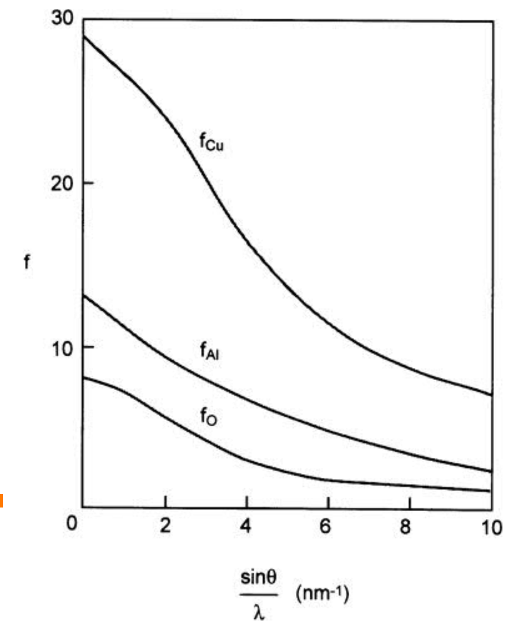
Scattering by Atom and Atomic Scattering Factor

- Atomic scattering factor, *f* also called form factor (because it depends on the way in which electrons are distributed around a nucleus), is descripting the efficiency of scattering of given atom in a given **direction**:

$$f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$$

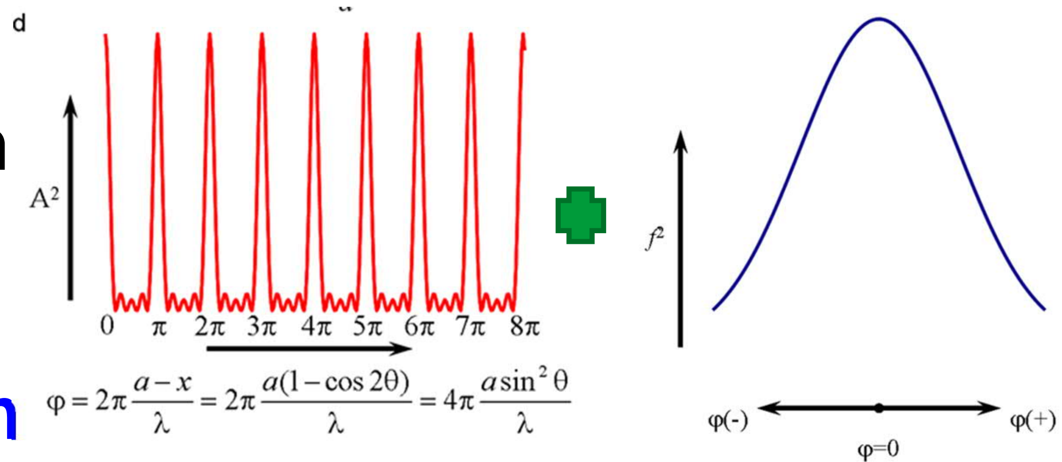


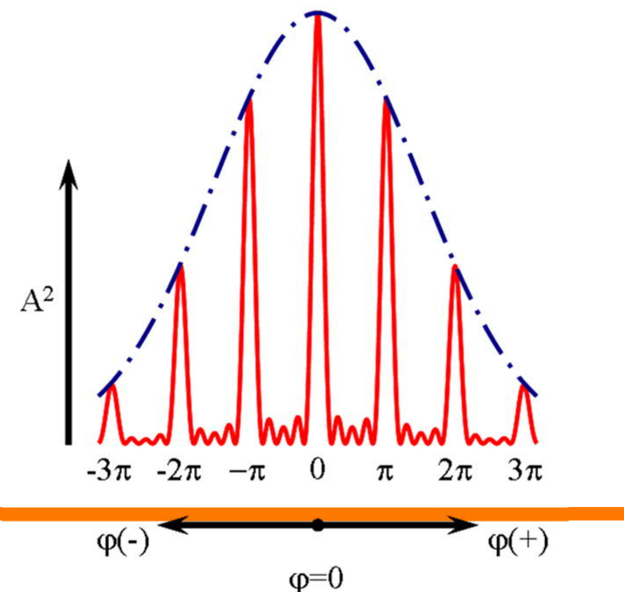
- $f = Z$ for scattering angle $2\theta = 0$.
- When $\theta \neq 0$, the waves scattered by individual electrons are more out of phase results in decreasing of *f* value.
- *f* also depends on the wavelength of the incident beam.



Scattering by Atoms

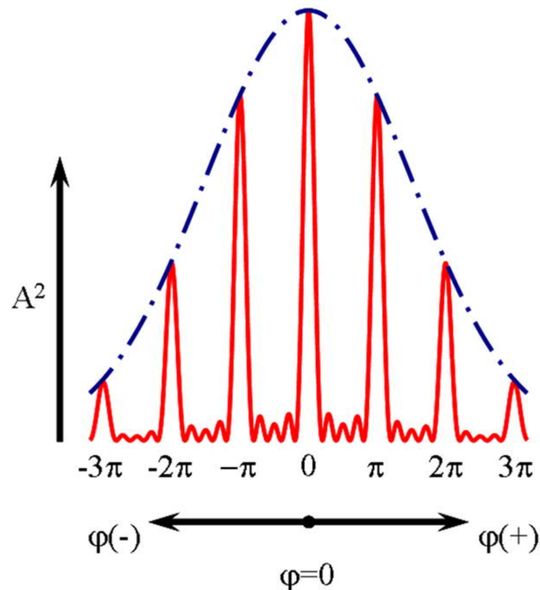
- The amplitude of the diffracted pattern from a row of N atoms is a product of the **interference function** and the corresponding atomic scattering function squared, $f^2(\varphi)$:



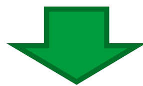


$$I(\varphi) \propto f^2(\varphi)\frac{\sin^2 N\varphi}{\sin^2 \varphi}$$

Scattering by Lattice



$$I(\varphi) \propto f^2(\varphi)\frac{\sin^2 N\varphi}{\sin^2 \varphi} = f^2(\varphi)\frac{\sin^2 Nh\pi}{\sin^2 h\pi}$$



$$I(\varphi) \propto f^2(\varphi)\frac{\sin^2 N_1 h\pi}{\sin^2 h\pi\varphi}\frac{\sin^2 N_2 k\pi}{\sin^2 k\pi}\frac{\sin^2 N_3 l\pi}{\sin^2 l\pi}$$

$f(\phi) \rightarrow F(\phi)$

F: the scattering function of one unit cell, is called structure factor or the structure amplitude. It counts for scattering factors of all atoms in the unit cell, together with other relevant atomic parameters. A diffraction pattern produced by a crystal lattice may be defined as:

$$I(hkl) \propto F^2(hkl)\frac{\sin^2 U_1 h\pi}{\sin^2 h\pi}\frac{\sin^2 U_2 k\pi}{\sin^2 k\pi}\frac{\sin^2 U_3 l\pi}{\sin^2 l\pi}$$

Where U1, U2 and U3 are the numbers of the unit cells in the corresponding directions.

$$I(hkl) = K \times G(\theta) \times F^2(hkl)$$

K is scale factor, $K=CU_1^2U_2^2U_3^2$, G is geometry factor, F is structure factor

Structure Factor

- F in general is a complex number (express both amplitude and phase at resultant wave).

- It absolute value |F| gives:

$$|F| = \frac{\text{amplitude of the wave scattered by all the atoms of a unit cell}}{\text{amplitude of the wave scattered by an electron}}$$

- It is related to the observed diffracted intensity:

$$I \propto |F|^2$$

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$

Scattering from a Unit Cell

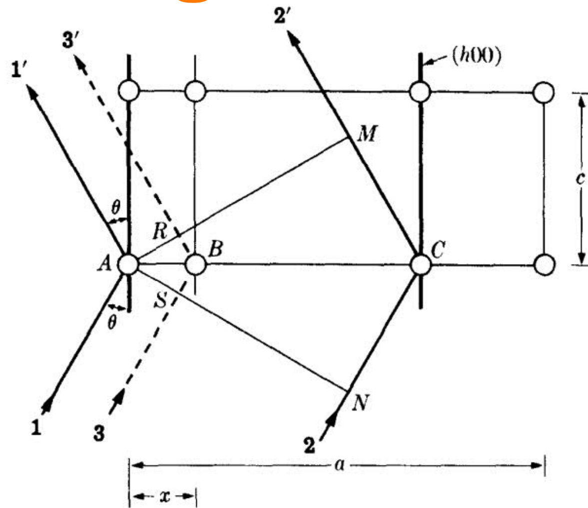


Fig. 4-8 The effect of atom position on the phase difference between diffracted rays.

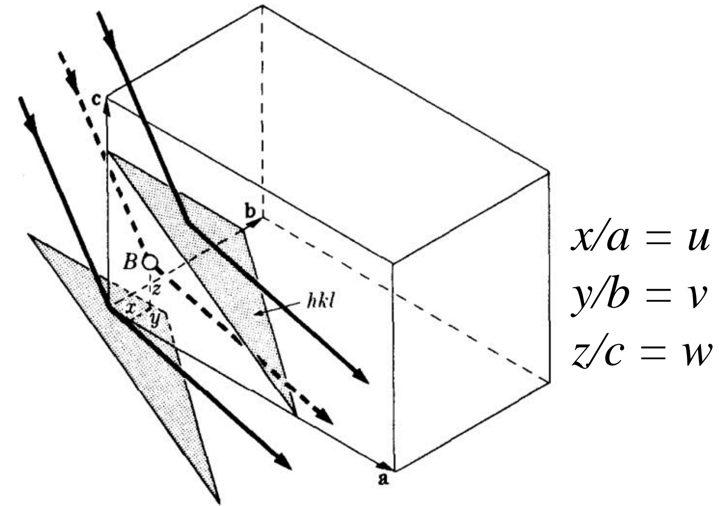


Fig. 4-9 The three-dimensional analogue of Fig. 4-8.

Phase difference between 1´and 3´:

$\phi_{3'1'} = 2\pi hu$

Phase difference between the wave scattered by atom B and scattered by atom A at the origin, for hkl reflection:

$\phi = 2\pi(hu+kv+lw)$

Scattering from An Unit Cell

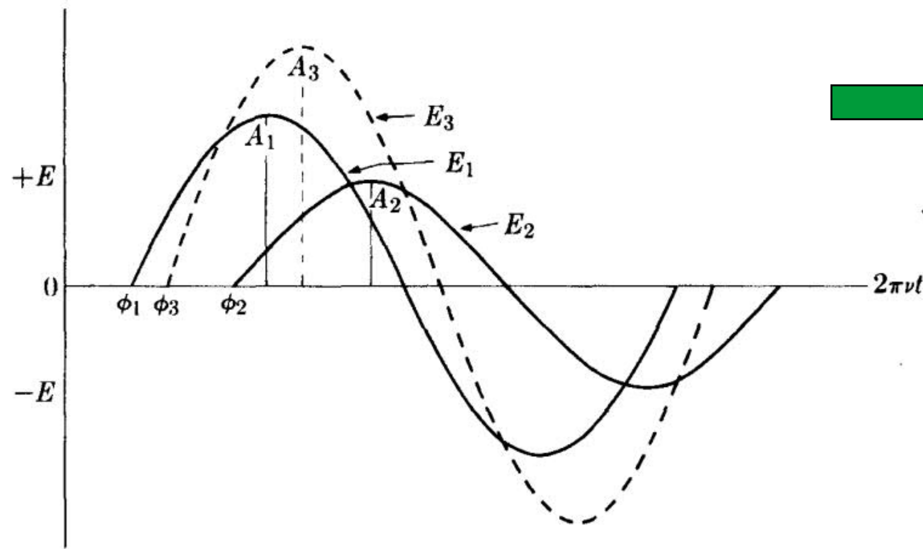


Fig. 4–10 The addition of sine waves of different phase and amplitude.

$$\mathbf{E}_1 = A_1 \sin(2\pi\nu t - \phi_1),$$
$$\mathbf{E}_2 = A_2 \sin(2\pi\nu t - \phi_2).$$

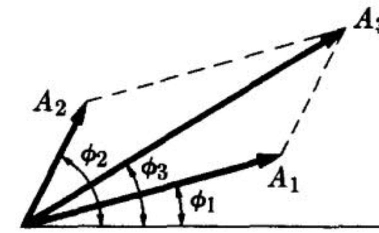


Fig. 4–11 Vector addition of waves.

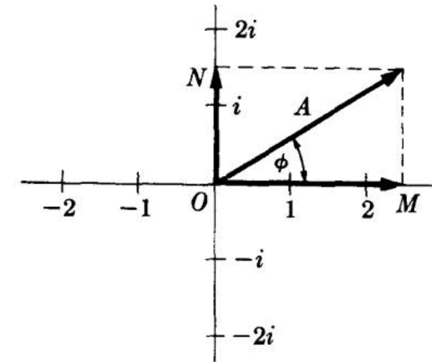


Fig. 4–12 A wave vector in the complex plane.

$$Ae^{i\phi} = A\cos\phi + Ai\sin\phi.$$

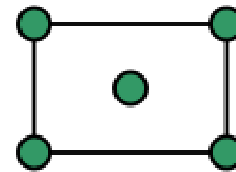
$$\phi = 2\pi(hu + kv + lw)$$

$$Ae^{i\phi} = fe^{2\pi i(hu+kv+lw)}$$

Structure Factor Calculations

- Simple case: Consider a unit cell containing two atoms located 000 and ½ ½ 0.

$$F = fe^{2\pi i(0)} + fe^{2\pi i(h/2+k/2)}$$
$$= f[1+e^{\pi i(h+k)}]$$



- Note that, if h+k is an odd number, F=0 otherwise F=2f. Alternatively, if h and k belong to the same parity class, F is non zero, otherwise it is zero.

- For all side centered unit cells, this kind of relationship exists. Certain reflection are systematically absent.

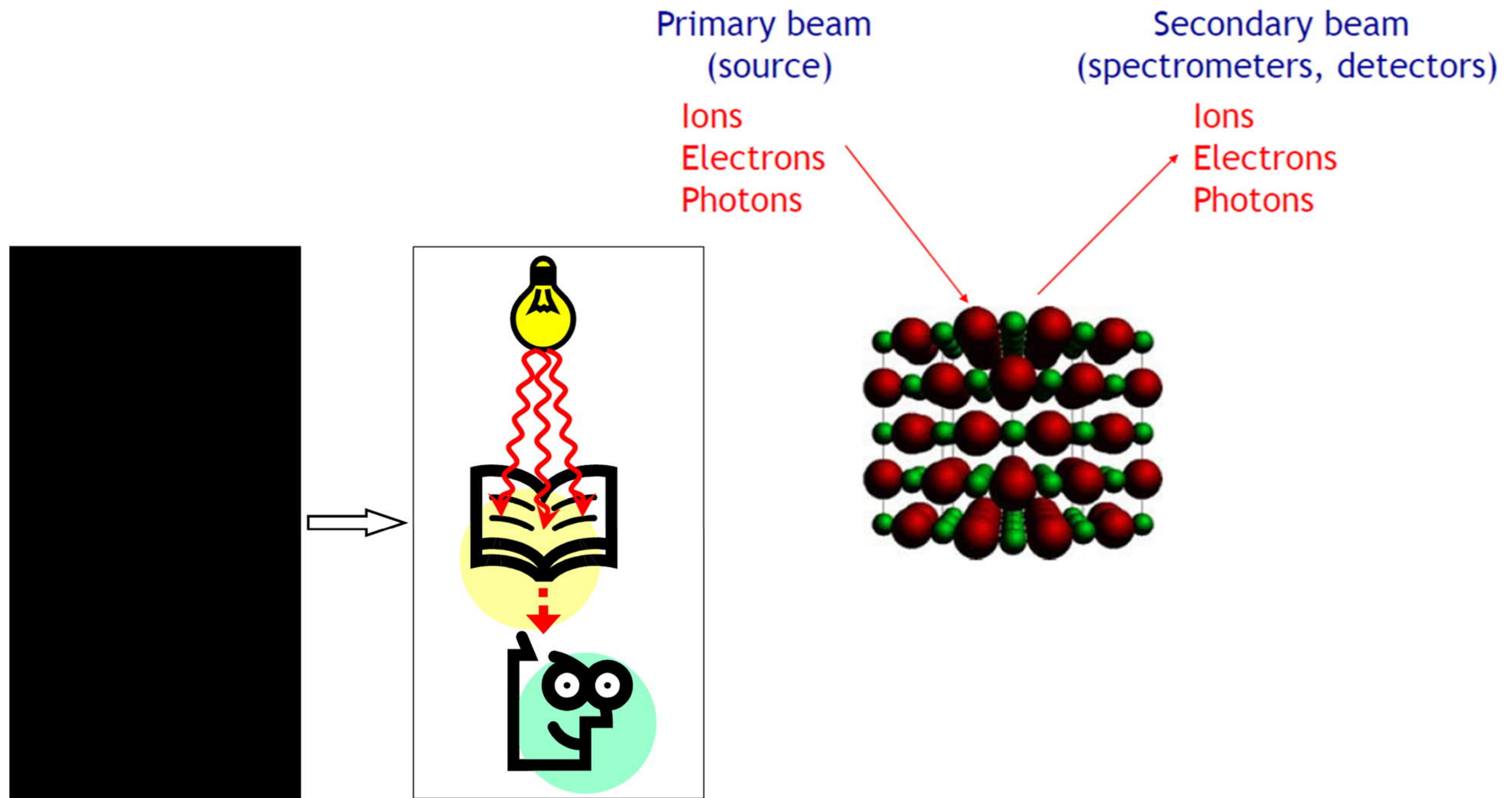
Intensities in Powder Diffraction

- The intensity of a line in powder pattern is determined by a combination of factor:
  - **Structure factor**
  - **Scale factor**
  - Multiplicity factor
  - Lorentz factor
  - Polarization factor
  - Absorption factor
  - Preferred orientation factor
  - Extinction factor
  - Temperature factor.

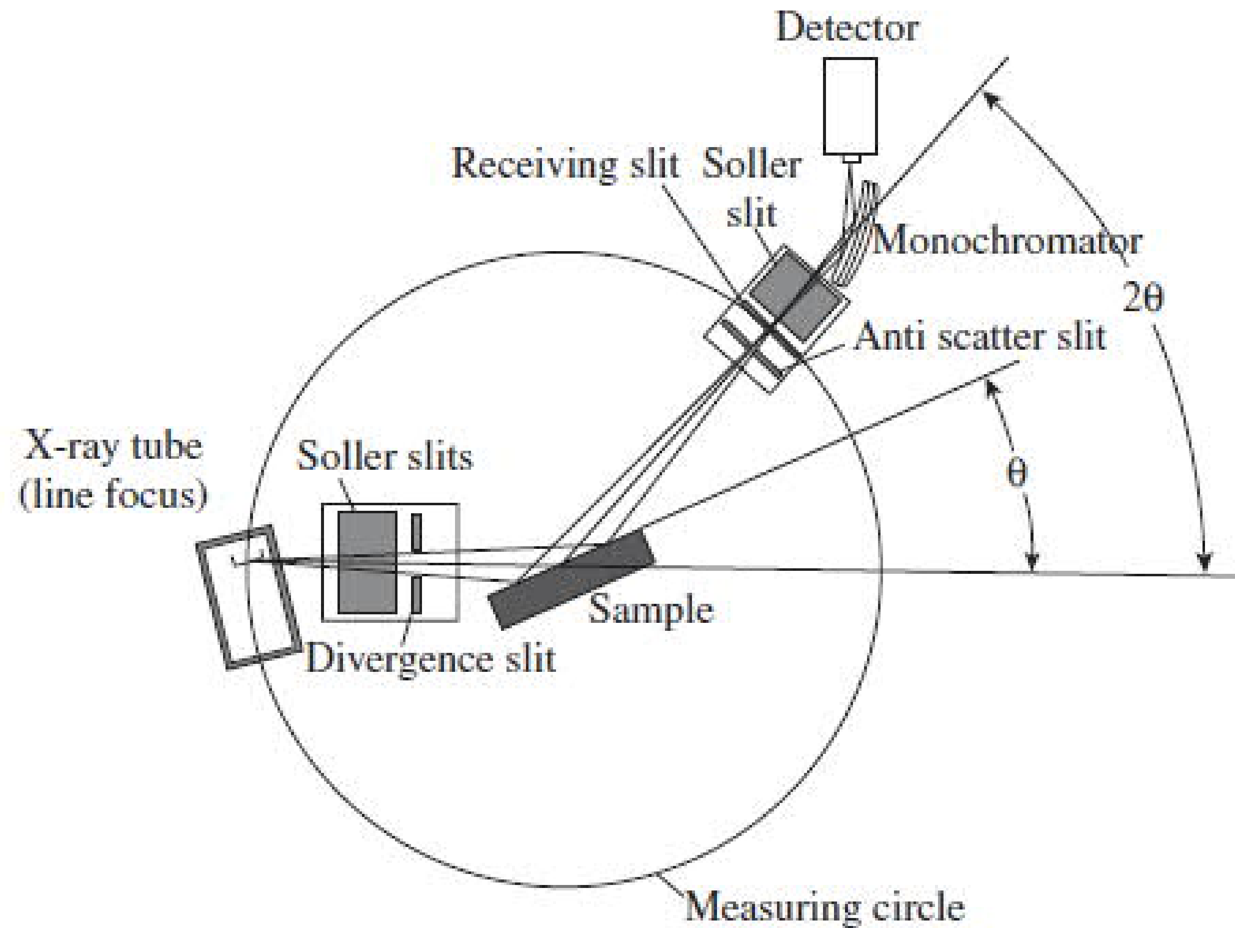
$$I_{hkl} = K \times p_{hkl} \times L_{\theta} \times P_{\theta} \times A_{\theta} \times T_{hkl} \times E_{hkl} \times |\mathbf{F}_{hkl}|^2$$

X-Ray Diffractometry

Applications in Materials Science

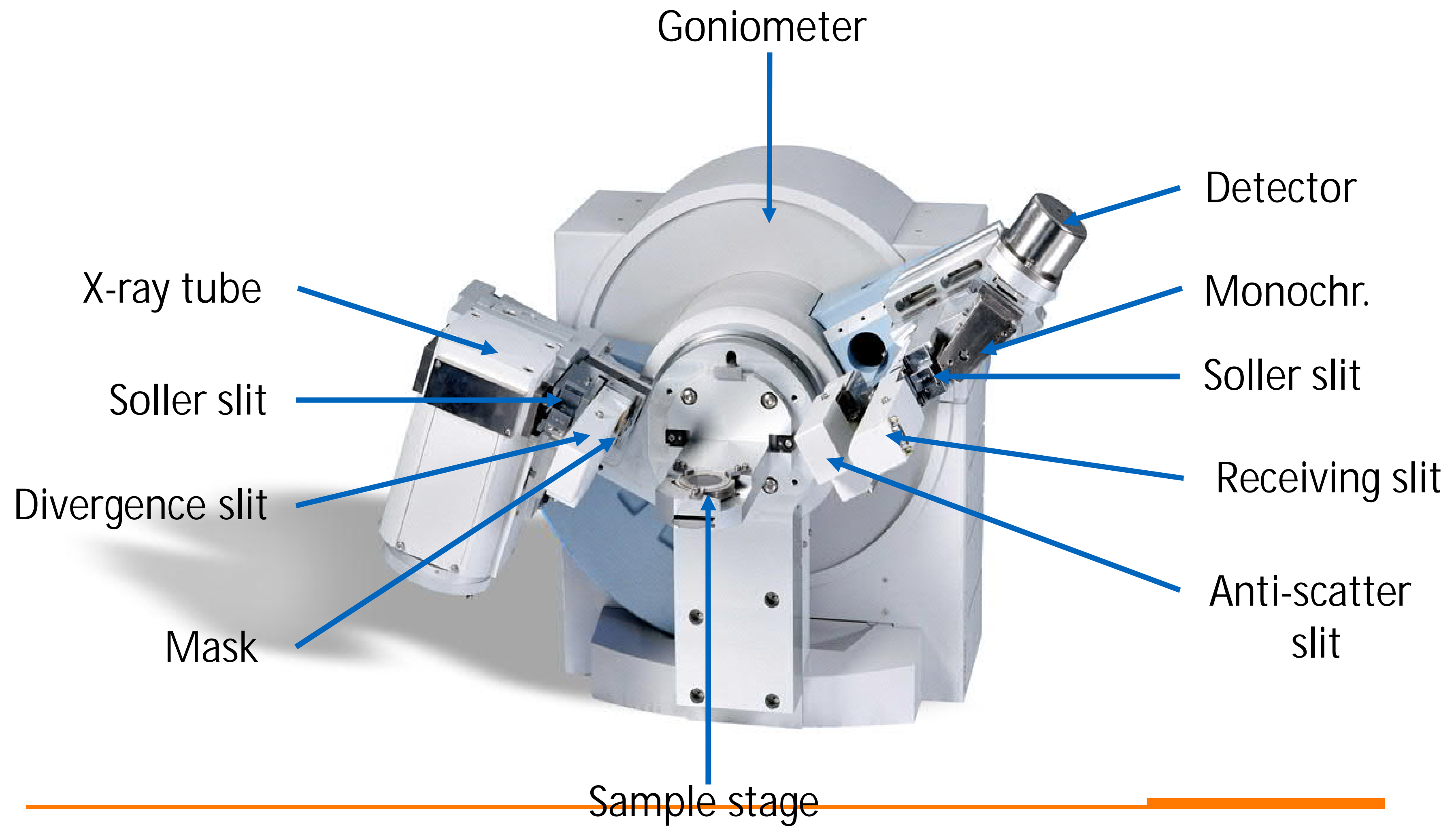


XRD Schematic Arrangement



Horizontal Bragg-Brentano geometric arrangement of x-ray diffractometer

Classical Powder Diffractometer

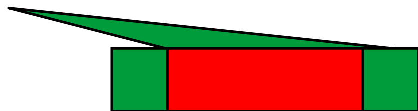


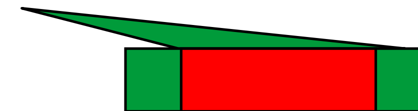
Divergence Slits

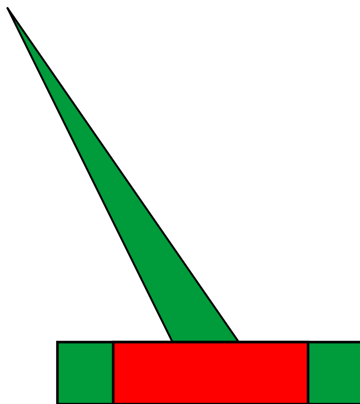
Fixed divergence slit

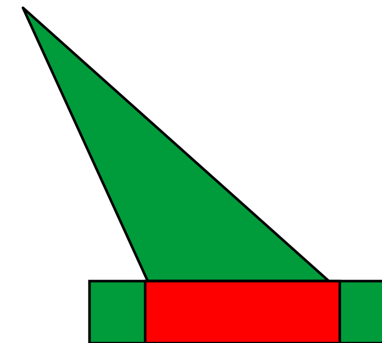
Programmable divergence slit

Fixed irradiated length

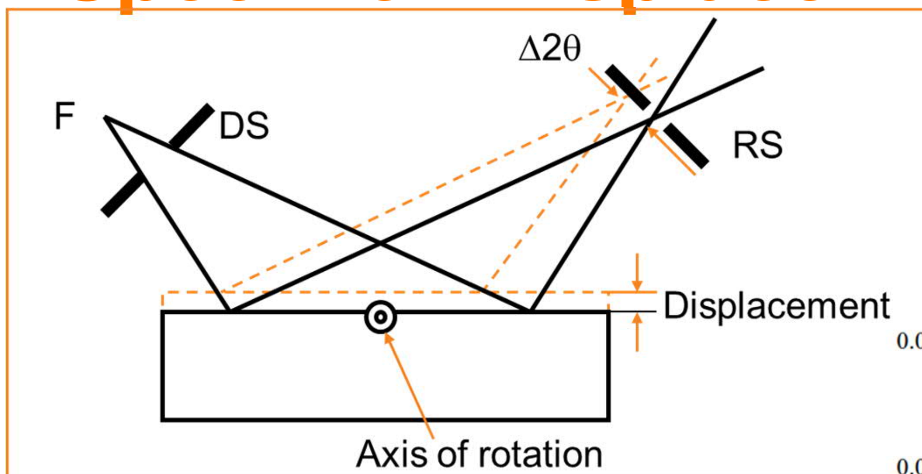




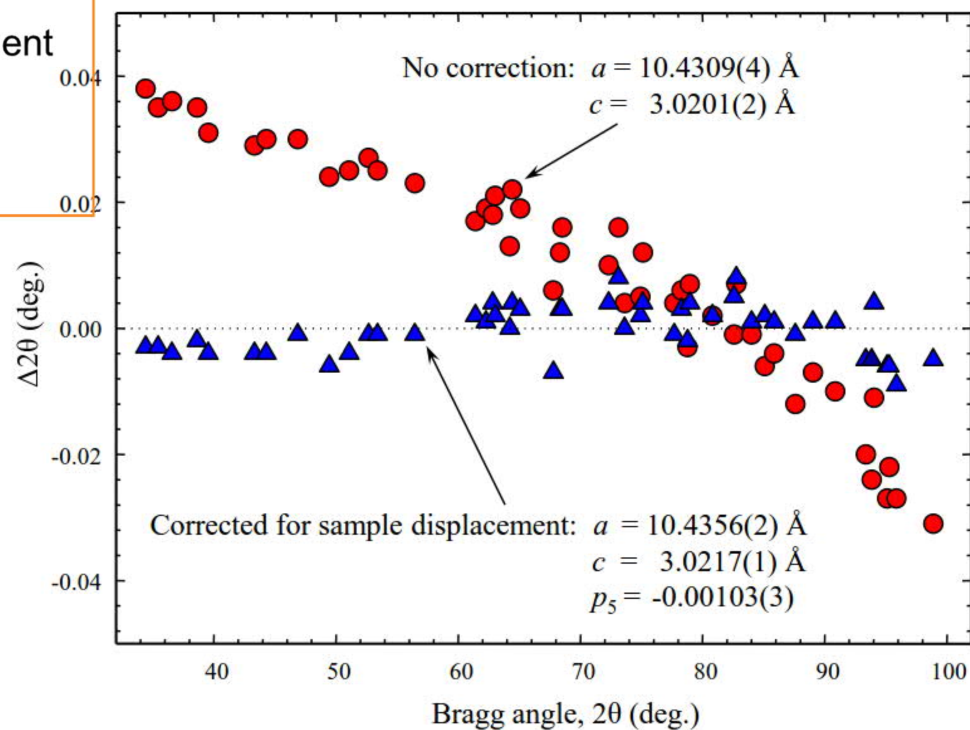




Specimen Displacement Correction



Reproducibly fix the sample in the center of the goniometer.
A height positioning accuracy of ±10 μm will be sufficient.



Diffraction methods

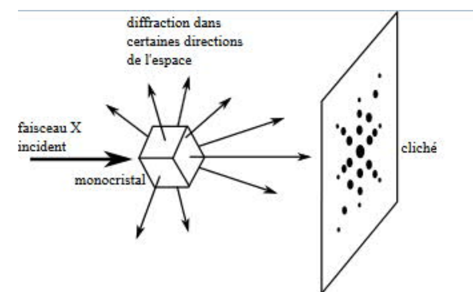
- Laue method
- Rotating crystal method
- Powder method

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

Method	λ	θ	
Laue	Variable	Fixed	Single crystal
Rotating crystal	Fixed	Variable (in part)	Single crystal
Powder	Fixed	Variable	Powder or polycrystal

Laue method

- Was developed first (1912 by Max Theodor Felix von Laue himself, [Nobel prize 1914]. Inspiration came from dr. Student Paul Ewald at LMU Münich.[1)])
- Beam of **white radiation** used.
- Sample is fixed (usually a single crystal).
- Transmission / back reflection Laue methods.
- Diffracted beams form spots on the film which lie on elliptical/hyperbola curves, originating from planes belonging to same zone (=pattern) .
- Is used mainly for determination of the crystal orientation or the assesement of the crystal quality.



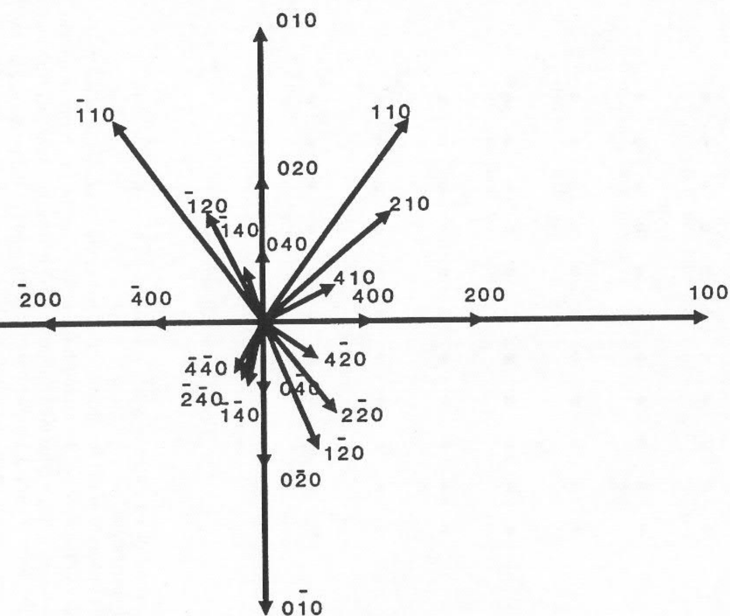


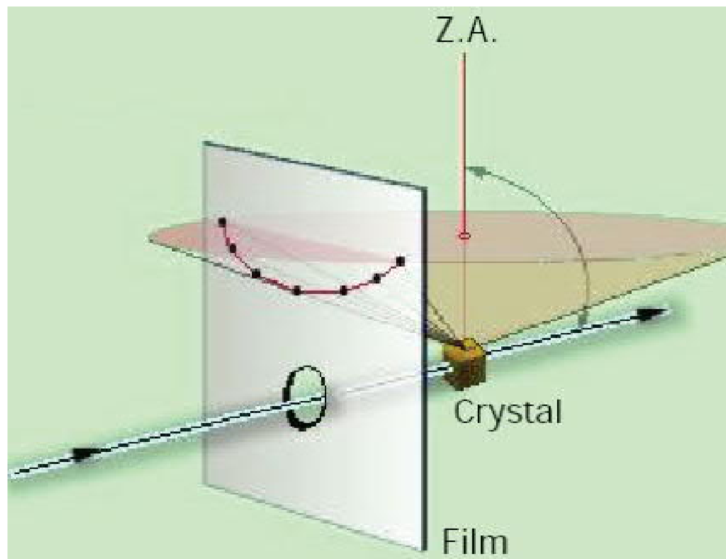
Figure 3.3. Representation of unit cell planes as d_{hkl} vectors.

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

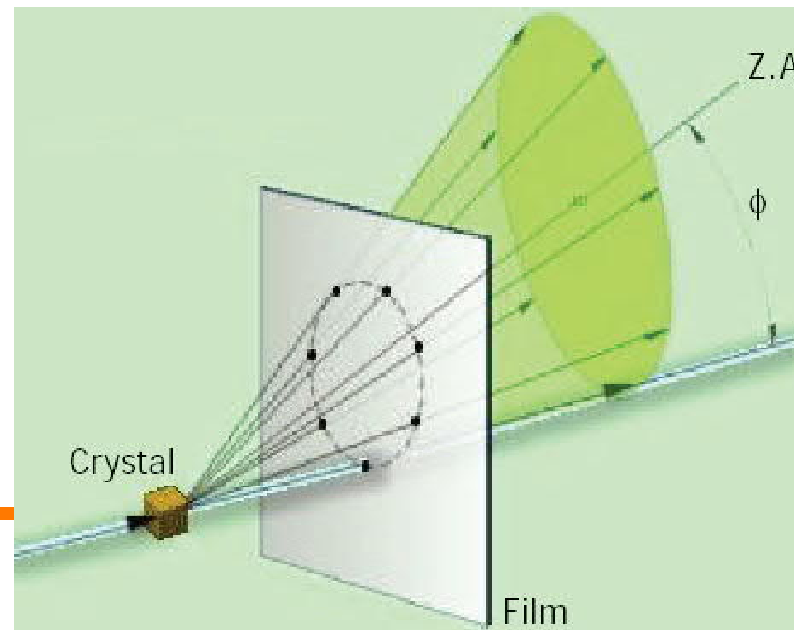
1) source/more information P.P. Ewald, 50Years of XRD, IUCR, 1962: http://www.iucr.org/publ/50yearsofxraydiffracti

Laue method, cont.

- Back-reflection laue



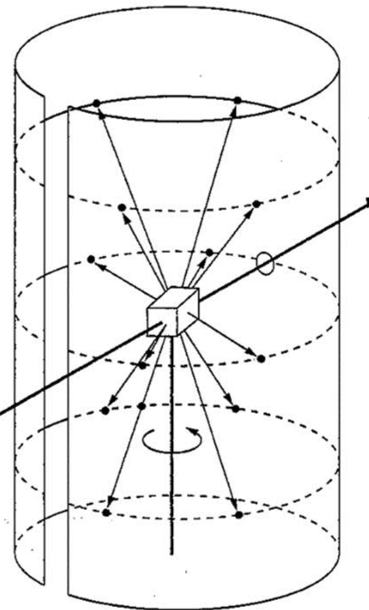
- Transmission laue



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

Rotating crystal method

- A monochromatic beam and a single crystal sample used.
- Sample is mounted with one of its axes (or other important direction) normal to the beam and rotated about the chosen direction.
- The diffracted beams are on imaginary cones which have cone axis coinciding with the rotation axis.
- Film is positioned cylindrically around the sample and the axis of rotation.
- Method is used in the determination of unknown crystal structures, i.e., polymers.



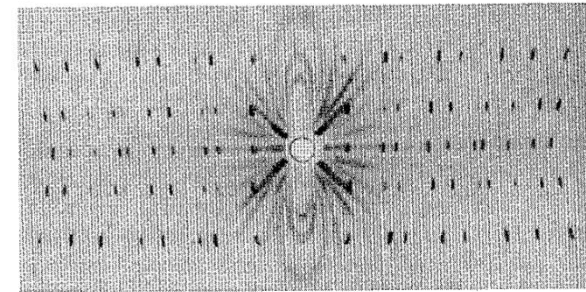


Figure 3-15 Rotating-crystal pattern of a quartz crystal (hexagonal) rotated about its c axis. Filtered copper radiation. (The streaks are due to the white radiation not removed by the filter.) (Courtesy of B. E. Warren.)

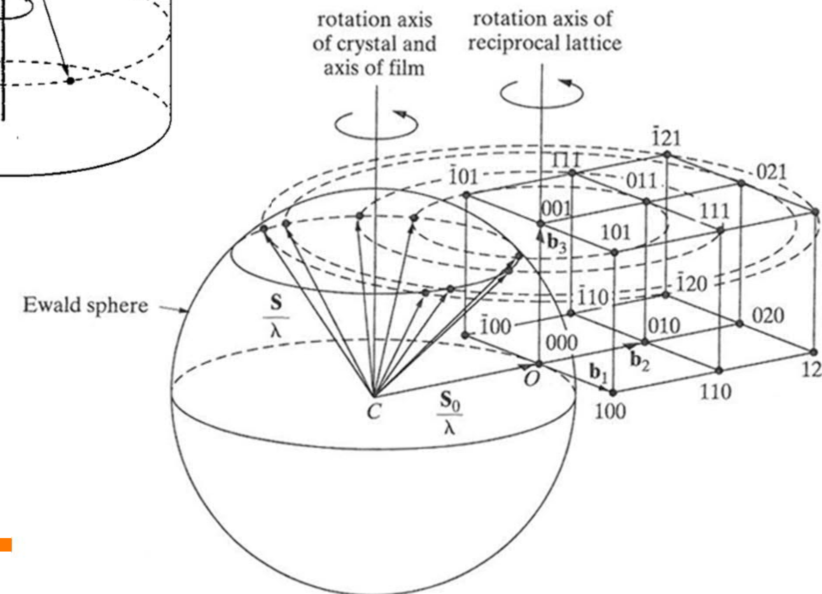


Figure 3-16 Reciprocal-lattice treatment of rotating-crystal method.

Origin of powder diffraction

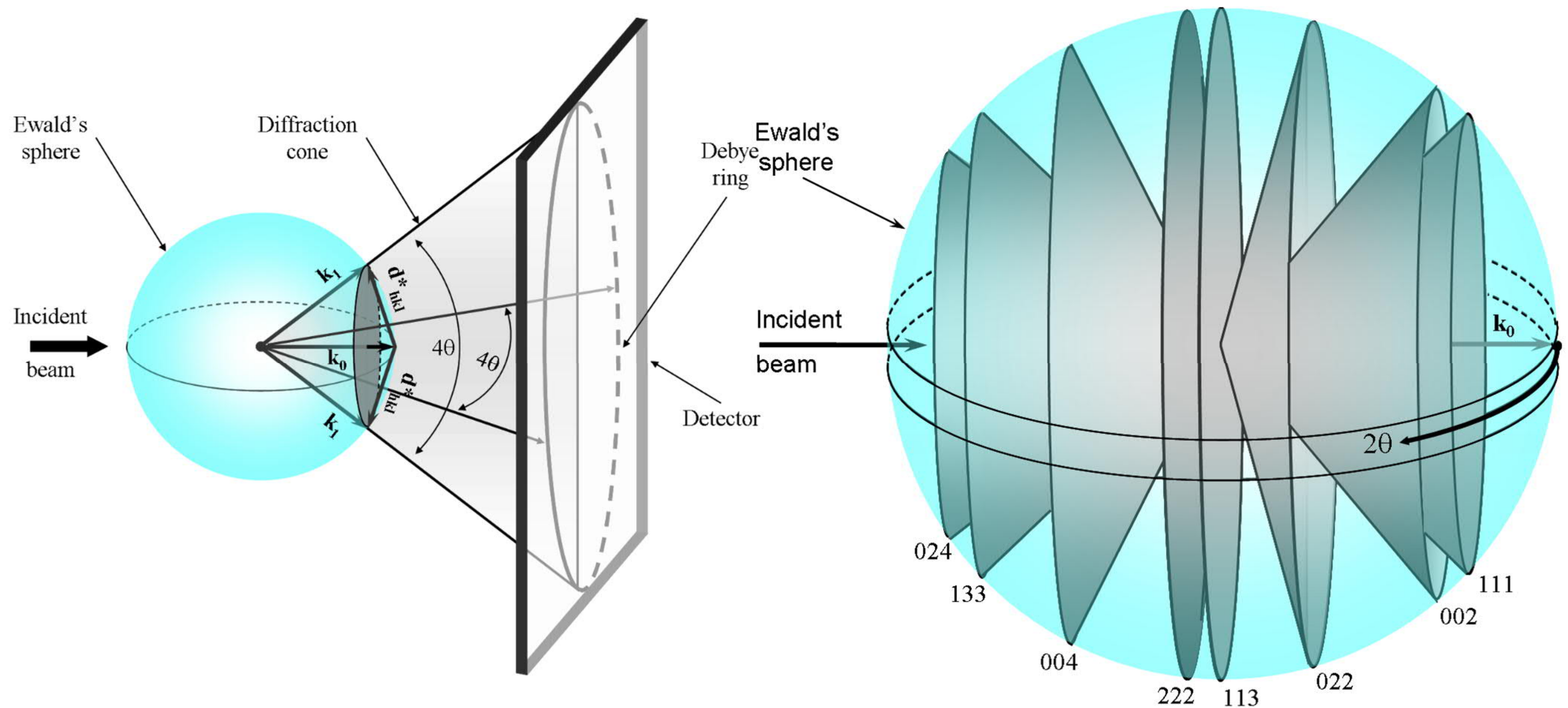
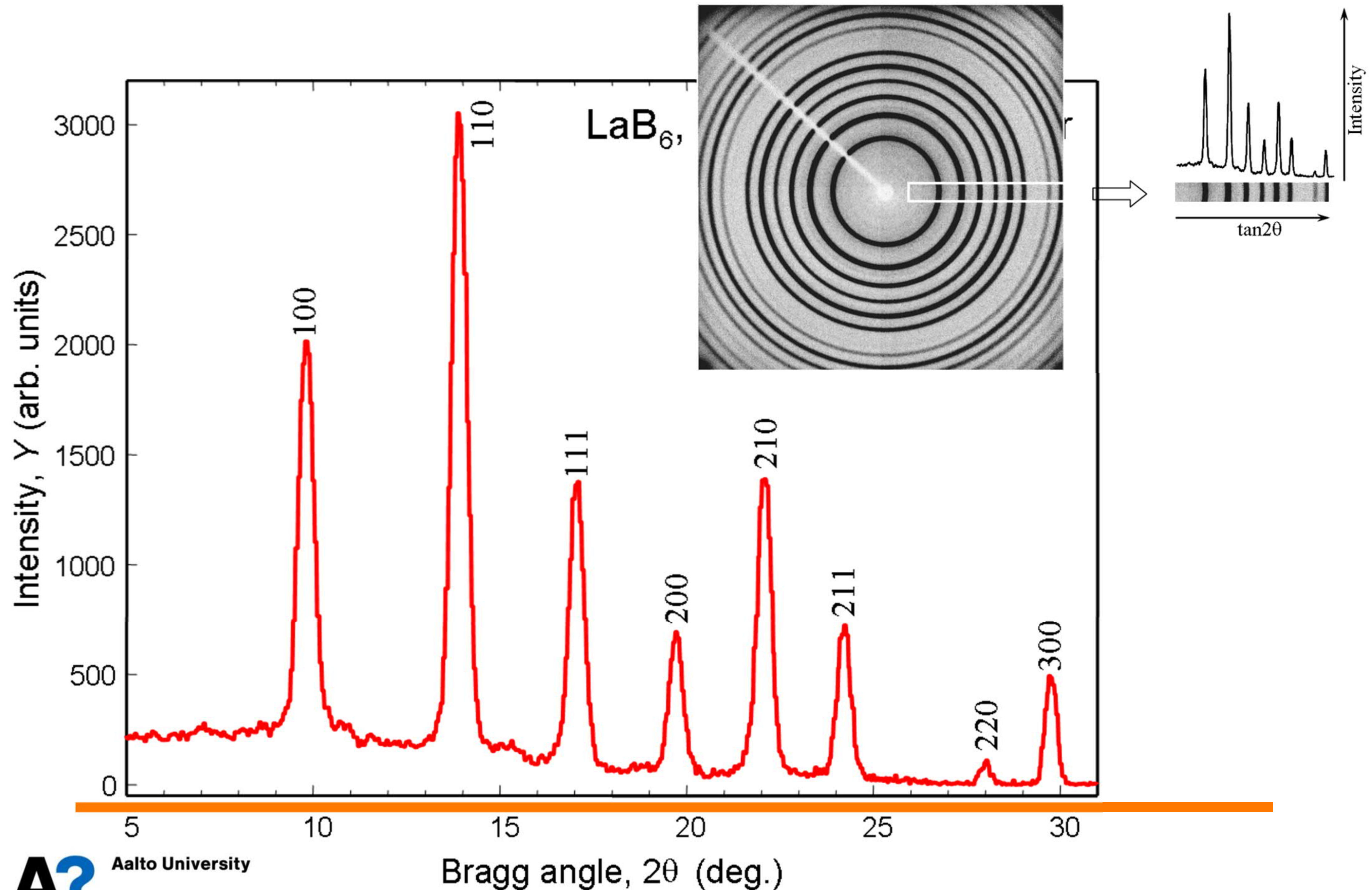


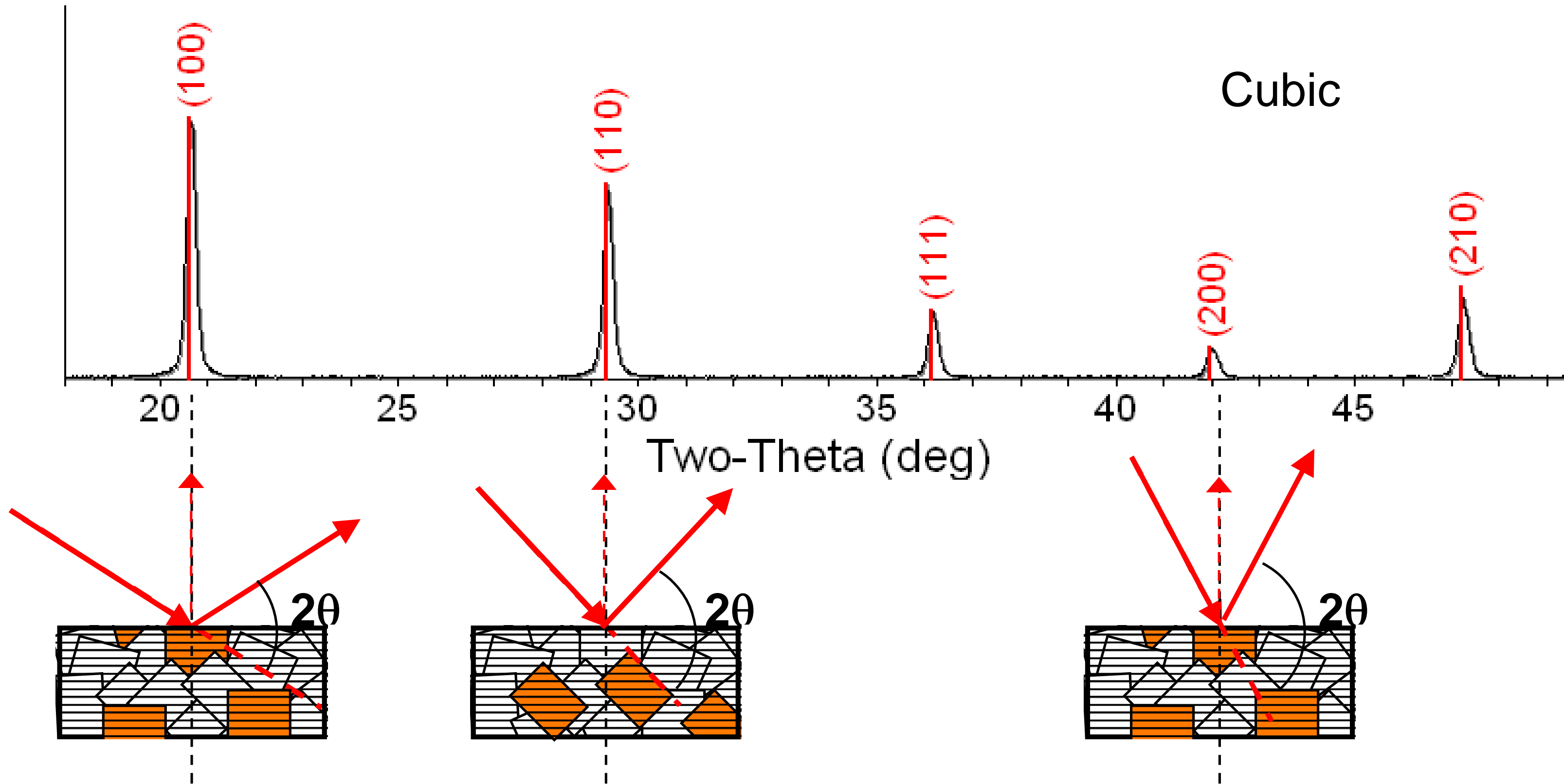
Fig. 8.1 The origin of the powder diffraction cone as the result of the infinite number of the completely randomly oriented identical reciprocal lattice vectors, $\mathbf{d}^*_{\mathbf{hkl}}$, forming a circle with their ends placed on the surface of the Ewald's sphere, thus producing the powder diffraction cone and the corresponding Debye ring on the flat screen (film or area detector).[3] The detector is perpendicular to both the direction of the incident beam and cone axis, and the radius of the Debye ring in this geometry is proportional to $\tan 2\theta$.

X-ray Powder diffraction Pattern



Powder diffraction

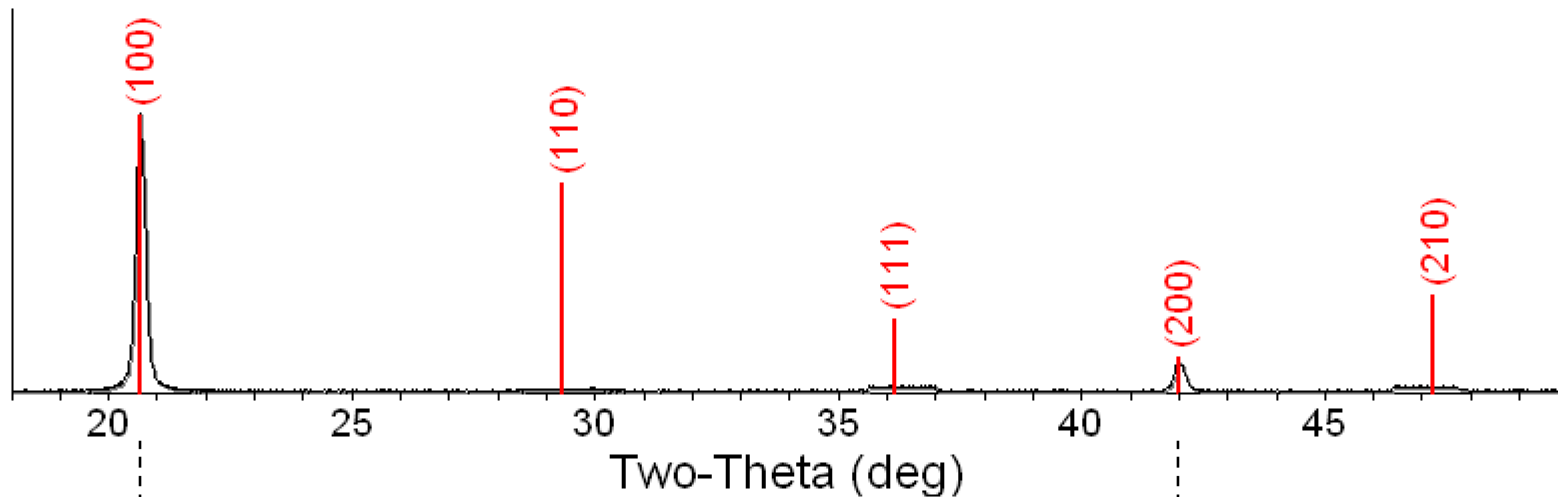
A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.

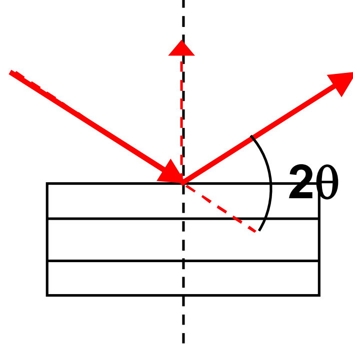


- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

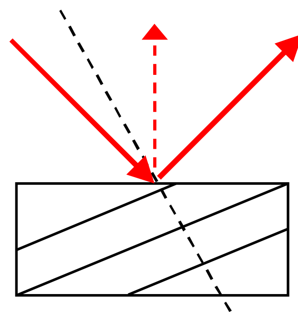
Single crystal diffraction

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

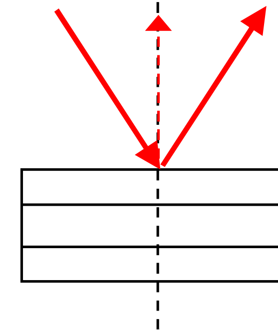




At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.



The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.



The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

Understanding powder diffraction pattern

Table 8.2 Powder diffraction pattern as a function of various crystal structure, specimen and instrumental parameters.[a]

Pattern component	Crystal structure	Specimen property	Instrumental parameter
Peak position	**Unit cell parameters:** $(a, b, c, \alpha, \beta, \gamma)$	*Absorption* Porosity	**Radiation (wavelength)** *Instrument/sample alignment* Axial divergence of the beam
Peak intensity	**Atomic parameters** $(x, y, z, B$, etc.)	*Preferred orientation* Absorption *Porosity*	Geometry and configuration **Radiation (Lorentz, polarization)**
Peak shape	*Crystallinity* Disorder Defects	*Grain size* *Strain* *Stress*	**Radiation (spectral purity)** **Geometry** **Beam conditioning**

[a] Key parameters are shown in **bold**. Parameters that may have a significant influence are shown in *italic*.

Quality of intensity measurements!

- The measured intensity is directly proportional to the number of counts and therefore, the accuracy of intensity measurement is governed by statistics.

$$\sigma = \sqrt{N}$$

$$\varepsilon = \frac{Q\sigma}{N} = \frac{Q}{\sqrt{N}}$$

where σ is standard deviation, ε is error at certain confidence level, Q = 0.67, 1.64, 2.59 and 3.09 for 50, 99, 99.9% confidence levels, respectively

Table 12.1 Effect of counting time on the statistical error during a single measurement.

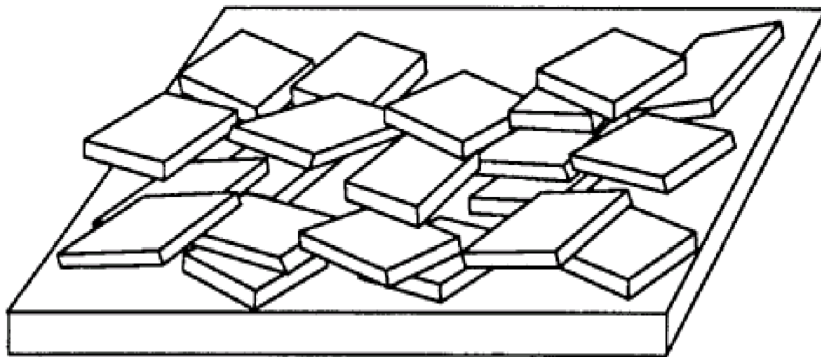
Photon flux (counts per second)	Counting time (s)	Number (N) of registered counts	Spread = $\sqrt{N}$ (counts)	Error at 90% confidence (%)
100	1	100	10	16.4
100	25	2,500	50	3.3

Collect at least 10000 counts for strongest peak!

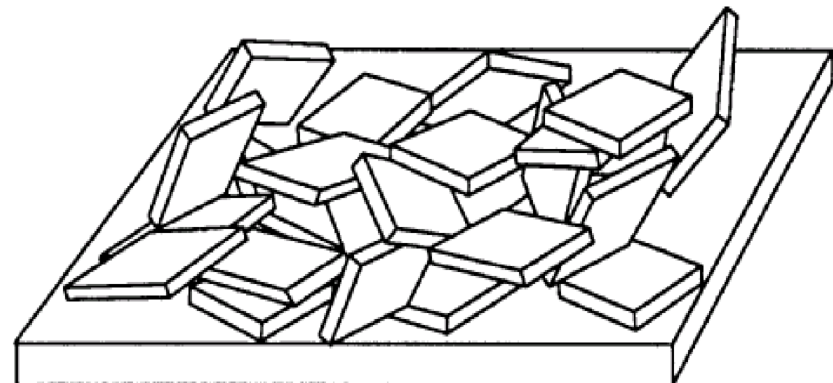
Preferred Orientation

- Extreme problem for samples with crystal related shape or non-spherical particles

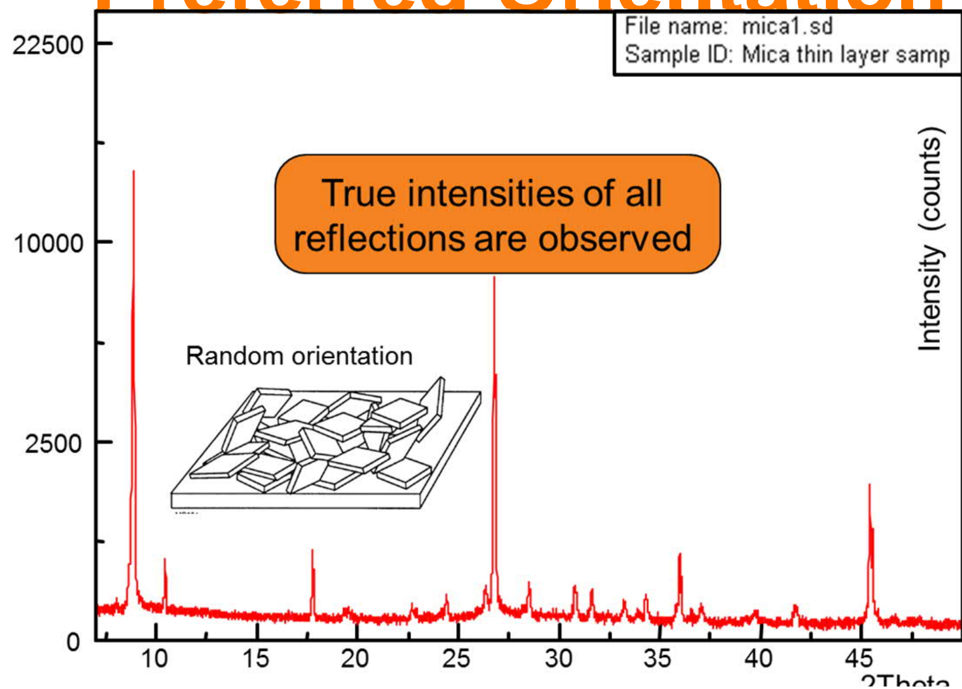
Preferred orientation

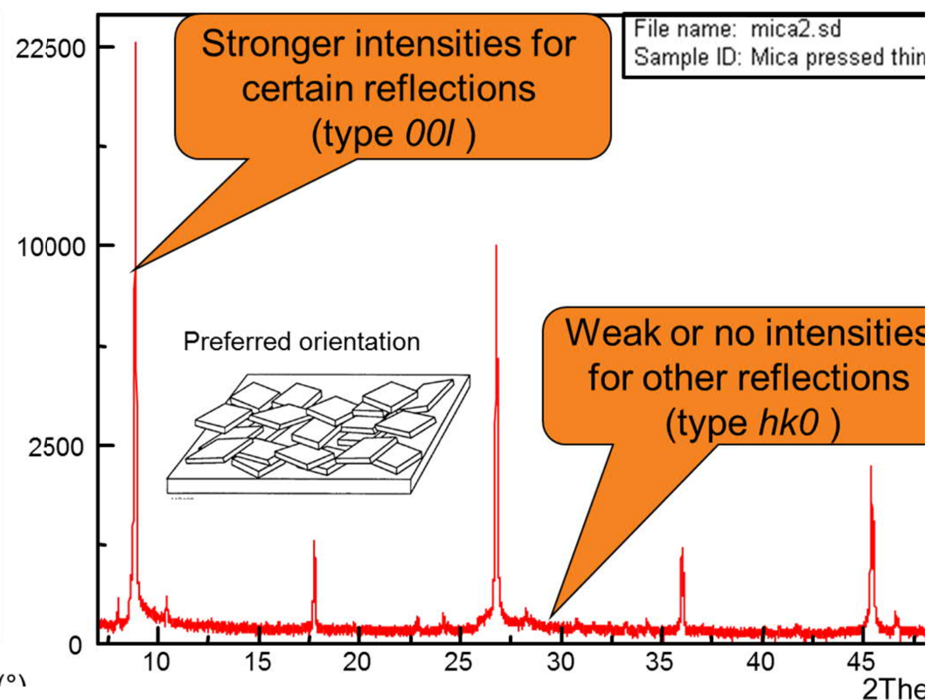


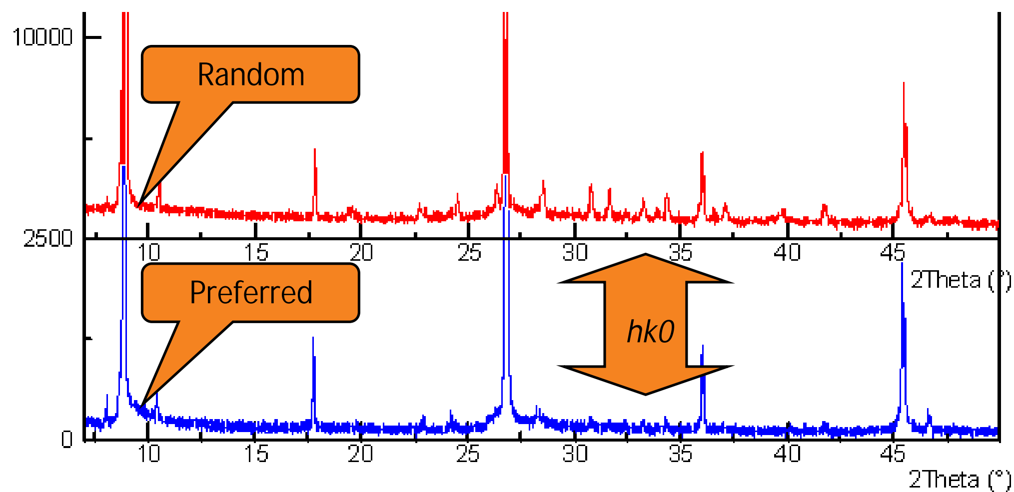
Random orientation



Preferred Orientation



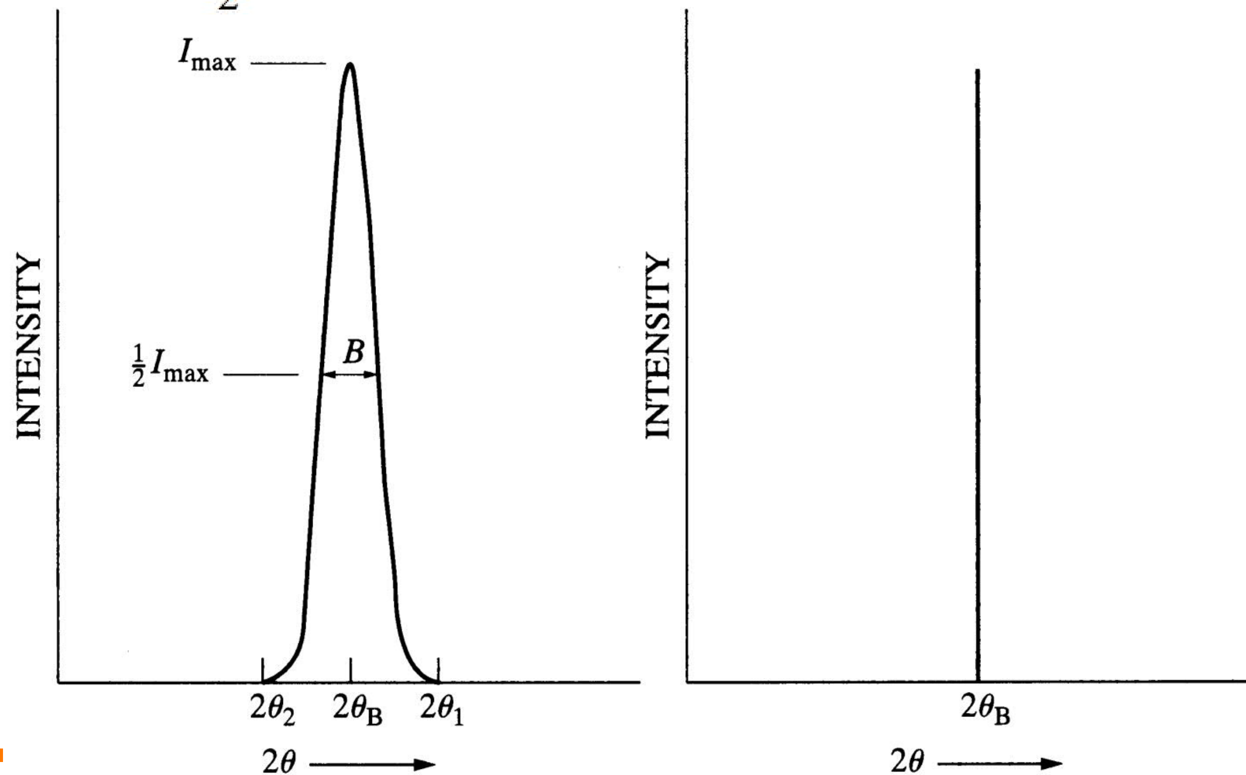




Crystal Size

For angle θ_B diffracted intensity is maximum
For θ_1 and θ_2 – intensity is 0.
For angles $\theta_1 > \theta > \theta_2$ – intensity is nonzero.

$$B \approx \frac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2$$



Crystal Size

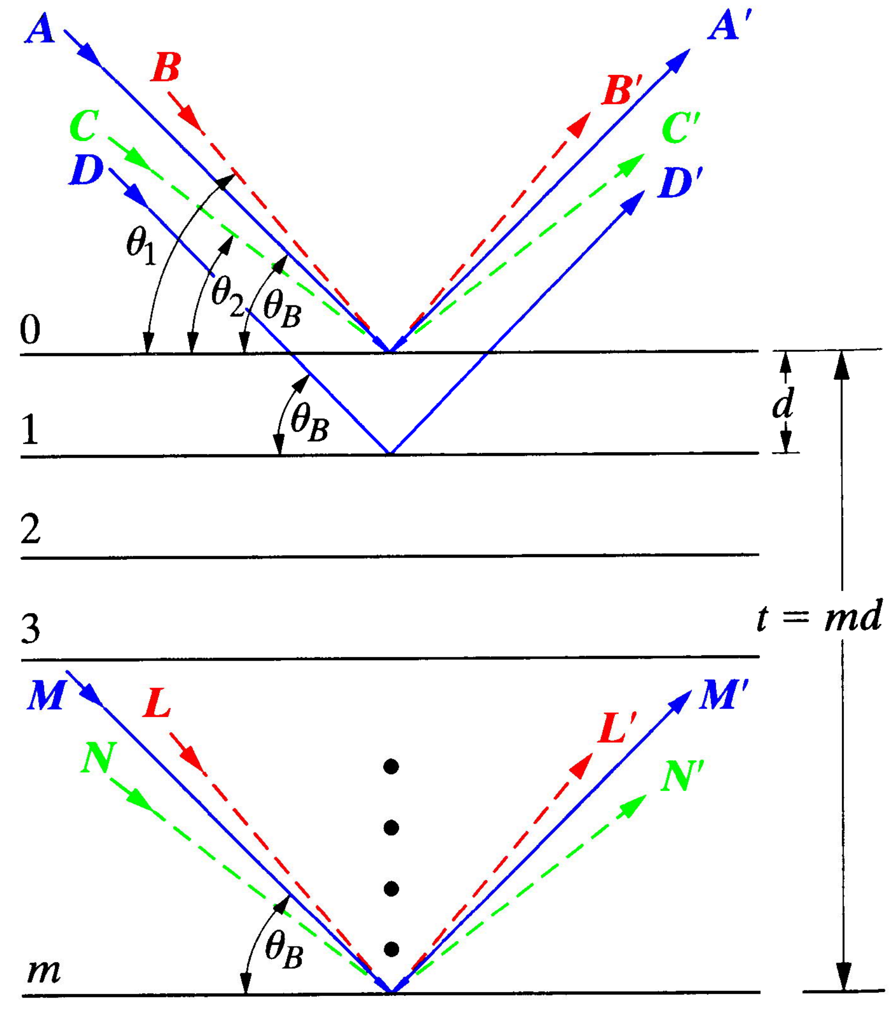
Suppose the crystal of thickness t has (m + 1) planes in the diffraction direction.
θ is variable with value θ_B that exactly satisfies Bragg's Law:

$$\lambda = 2d \sin \theta_B$$

Rays A, D, ..., M makes angle θ_B; path difference is λ, so A′, D′ ...M′ are all in phase.

Rays B, L makes angle θ_1; if path different of B′, L′ is (m+1)λ, in the midway there is a plane is out of phase with B′, therefore at θ_1 intensity is 0.

Rays C, N makes angle θ_2; if path different of C′, N′ is (m-1)λ, in the midway there is a plane is out of phase with C′, therefore at θ_1 intensity is 0.



Aalto University

Scherrer Equation

$$2t\sin\theta_1 = (m+1)\lambda,$$
$$2t\sin\theta_2 = (m-1)\lambda.$$

Subtracting:

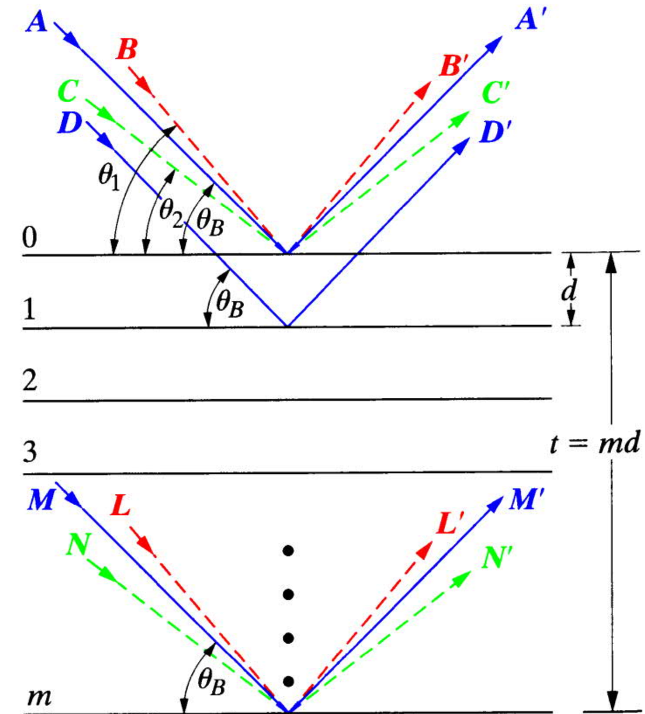
$$t(\sin\theta_1 - \sin\theta_2) = \lambda,$$
$$2t\cos\left(\frac{\theta_1+\theta_2}{2}\right)\sin\left(\frac{\theta_1-\theta_2}{2}\right) = \lambda.$$

θ_1 and θ_2 are close to θ_B, so:

$$\theta_1 + \theta_2 \approx 2\theta_B,$$
$$\sin\left(\frac{\theta_1-\theta_2}{2}\right) \approx \left(\frac{\theta_1-\theta_2}{2}\right).$$

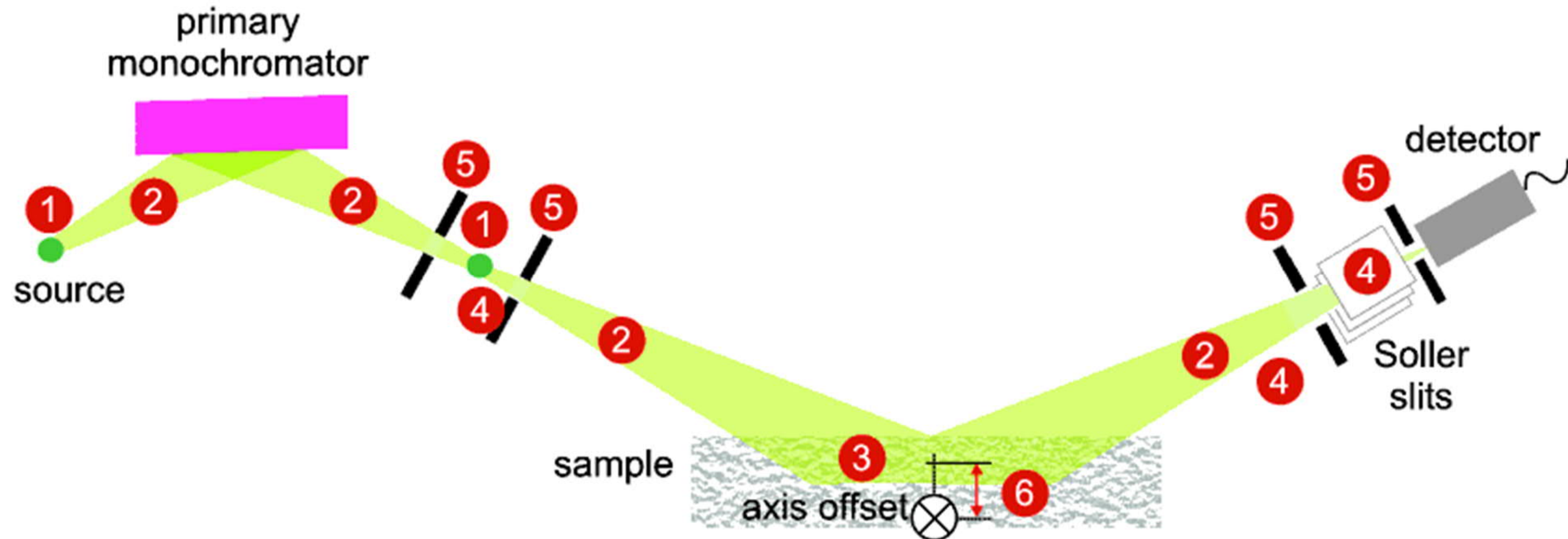
Thus:

$$2t\left(\frac{\theta_1-\theta_2}{2}\right)\cos\theta_B = \lambda,$$
$$t = \frac{\lambda}{B\cos\theta_B}$$



B is peak broaden due to crystal size,
Its value is measured peak width substrat peak width from instrumentation.

Instrument broadening



- the source of radiation (X-rays or neutrons) has a finite physical size (i.e. is not a perfectly sharp spot or line)
- the radiation is not perfectly monochromatic, but rather consists of a small range, δλ, of wavelengths around the mean, λ
- the active diffracting volume within the sample is finite and therefore diffraction occurs away from the true center of the diffractometer - this factor can be compounded by a low sample absorption to the radiation
- axial divergence of the incident/diffracted beams
- the configuration of defining slits used in the diffractometer
- any misalignment of the diffractometer

Crystal size measurement - Application Scherrer Equation

$$t = \frac{K\lambda}{B\cos\theta}$$

B = FWHM (in radians); t = diameter of the crystallites; λ is wavelength of anode material; θ: Bragg angle (in radians); K is shape factor.

$B = B_{ob} - B_{std}$

Particles:	Shape factor:
Spheres	0.89
Cubes	0.83 - 0.91
Tetrahedra	0.73 - 1.03
Octahedra	0.82 - 0.94

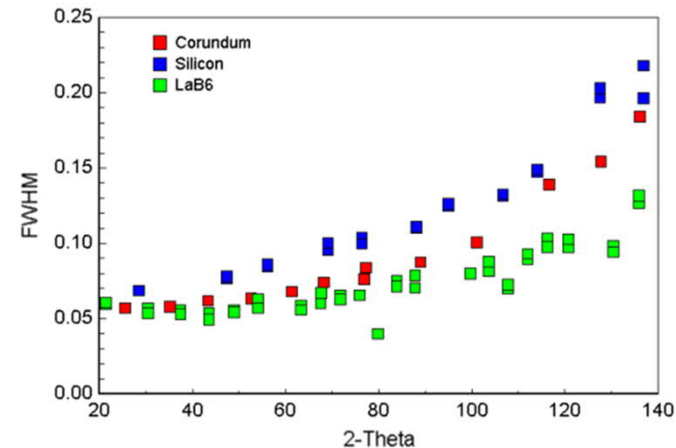


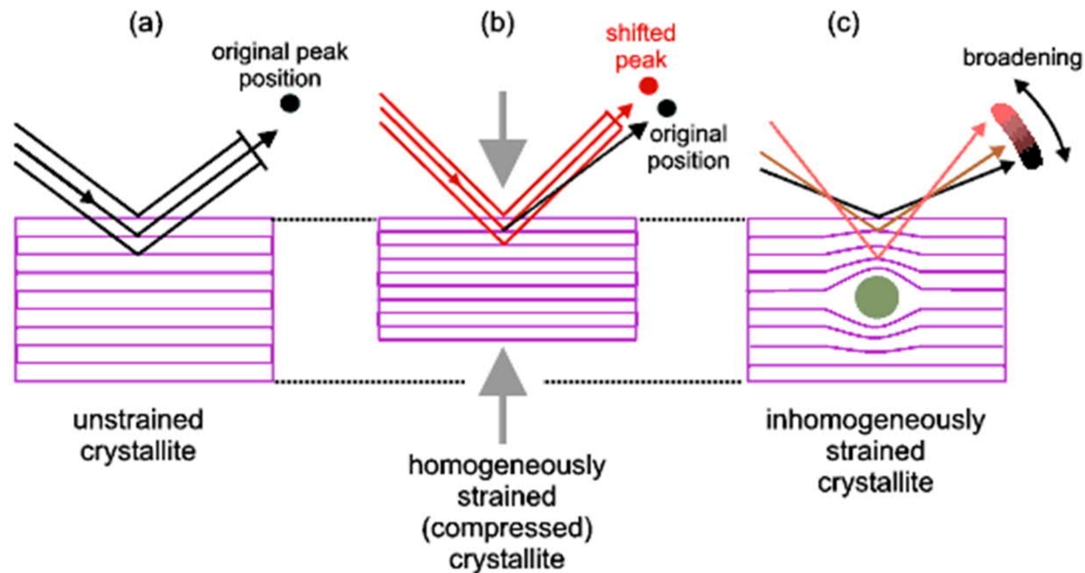
Figure 3 FWHM peak width as a function of diffraction angle for three different samples.

http://prism.mit.edu/xray/documents/5a%20Estimating%20Crystallite%20Size%20Using%20XRD.pptx

Condition: when strain caused broadening is zero.

B is essentially zero when the crystallite size exceeds about 1000Å, (or >1ηm to be in safe side).

The Effect of Strain



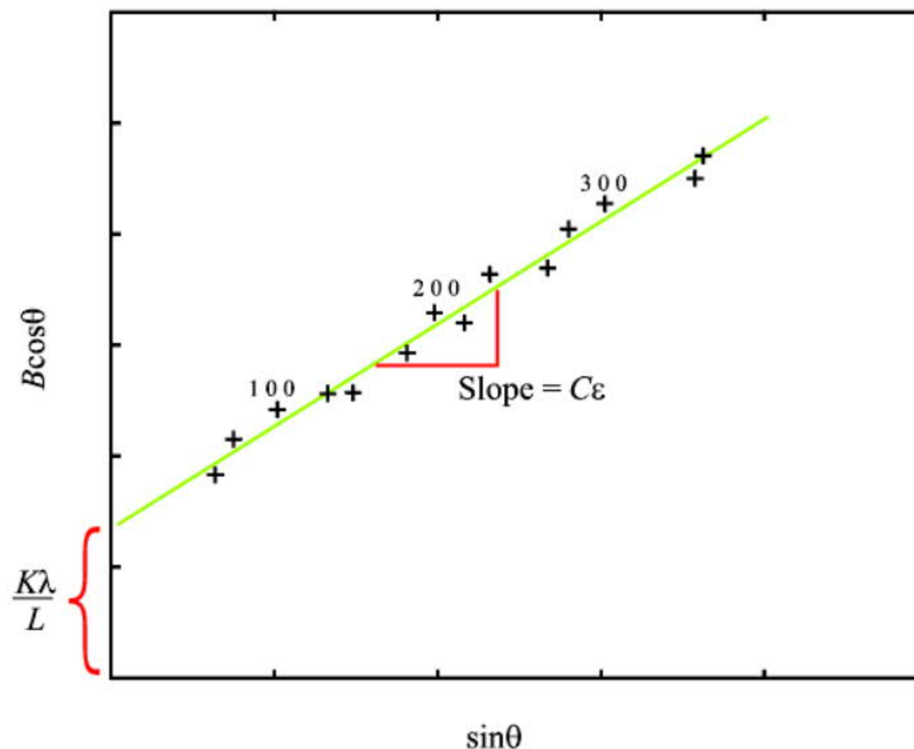
The uniform strain, macrostrain cause the peak shift, which is the basic for stress measurement. While the nonuninform strain, microstrain cause the peak broadening and also increase the integrated intensity.

$$B = 2\varepsilon \tan\theta$$

Peak Broadening

$$B_{size+strain} = \frac{K\lambda}{L\cos\theta} + C\varepsilon\tan\theta$$

$$B_{size+strain}\cos\theta = \frac{K\lambda}{L} + C\varepsilon\sin\theta$$



This is a y = b + mx function. Plot sin θ - $B_{size+strain}\cos\theta$, the crystal size and strain can be get from the curve.

http://pd.chem.ucl.ac.uk/pdnn/peaks/sizedet.htm

Books and Internet sources

- **Elements of X-ray Diffraction**, Second Edition, by B.D. Cullity.
- **Elements of X-ray Diffraction**, Third Edition, by B. D. Cullity & S. R. Stock
- **Fundamentals of Powder Diffraction and Stucturual Characterization of Materials**, Second Edition, by Vitalij K. Pecharsky & Peter Y. Zavalij
- **Materials Characterization**, introduction to Microscopic and Secptroscopic Methods, second edition, by Yang Leng
- **X-Ray Diffraction: A Practical Approach**. By Suryanarayana, C., Norton, M. Grant
- http://epswww.unm.edu/labs/x-ray-diffraction-lab/intro-course-info/
- **http://web.stanford.edu/group/glam/xlab/MatSci162_172/LectureNotes.html**
- http://www.ruppweb.org/Xray/tutorial/ewald.htm
- http://pd.chem.ucl.ac.uk/pdnn/peaks/sizedet.htm
- PANAlytical basic course