Interaction between X-ray and Matter

Basics of diffraction

Hammond Chapter 8, 9, 10

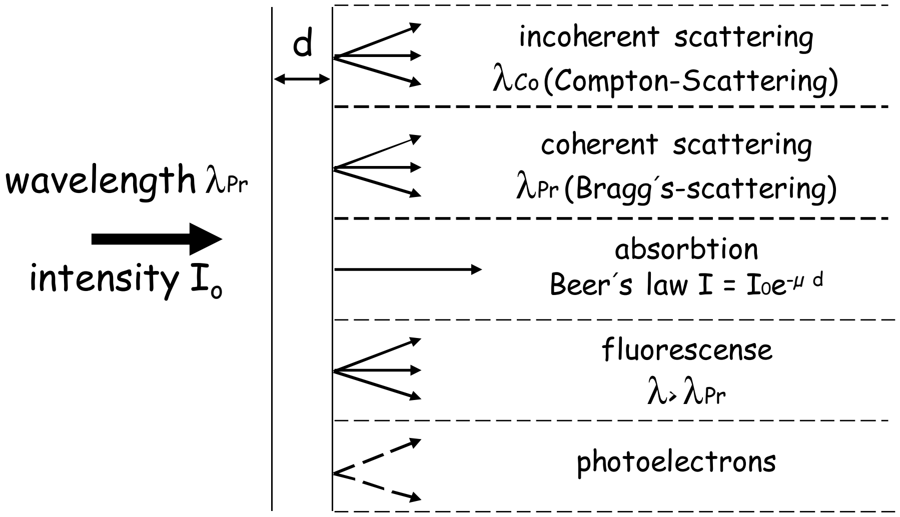
Pecharsky - Chapter 2

Sherwood Chapter 6

Krawitz - Chapter 5, 6

Birkholz – Chapter 1

Interaction between X-ray and Matter



wavelength λ_{Pr}

intensity I_o

d

incoherent scattering

λ_{Co} (Compton-Scattering)

coherent scattering

λ_{Pr} (Bragg´s-scattering)

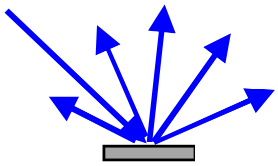
absorbtion

Beer´s law $I = I_0 e^{-\mu d}$

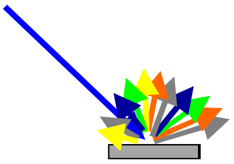
fluorescense

$\lambda > \lambda_{Pr}$

photoelectrons



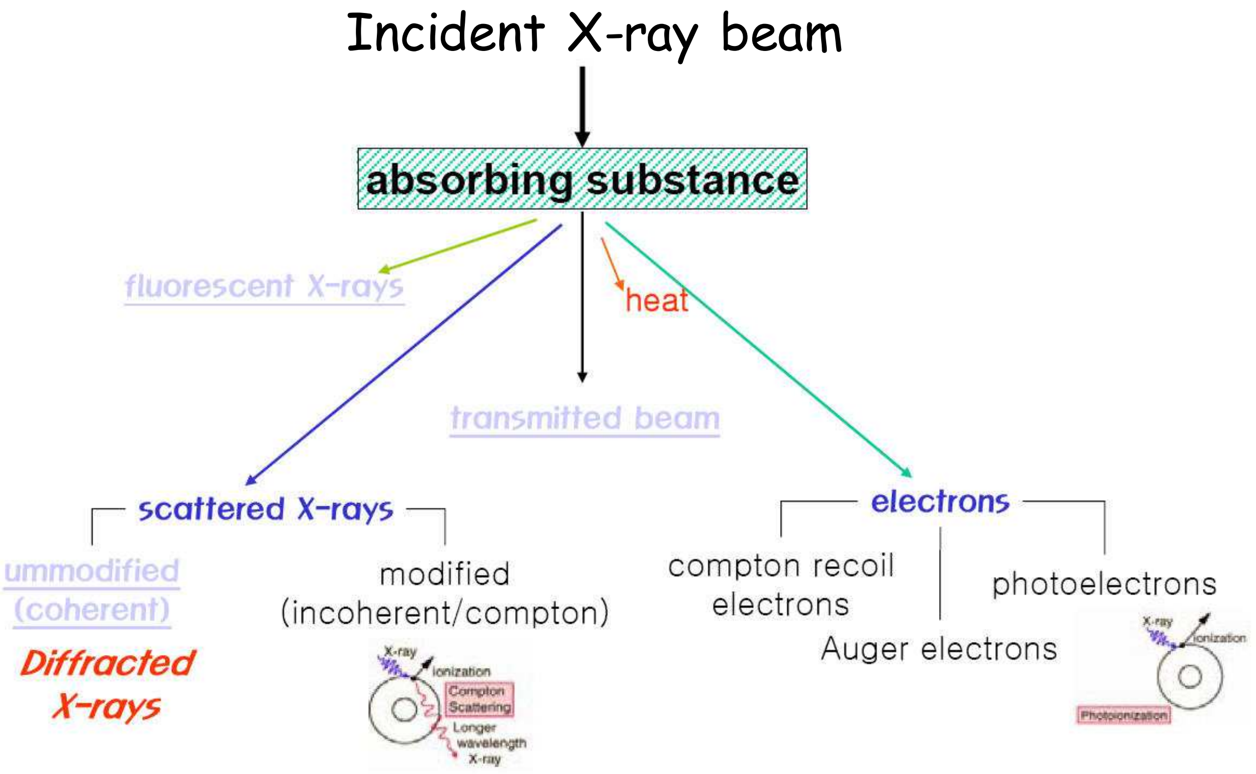
Elastic scattering (XRD)



Inelastic scattering (XRF)

- Incoherent (Compton) scattering – λ of scattered beam increases due to partial loss of photon energy in collision with the core electrons (Compton effect)
- Coherent scattering – scattered beam has the same λ as the primary beam

X-ray - matter interaction



Incident X-ray beam

absorbing substance

fluorescent X-rays

heat

transmitted beam

scattered X-rays

ummodified (coherent)

Diffracted X-rays

modified (incoherent/compton)

electrons

compton recoil electrons

Auger electrons

photoelectrons

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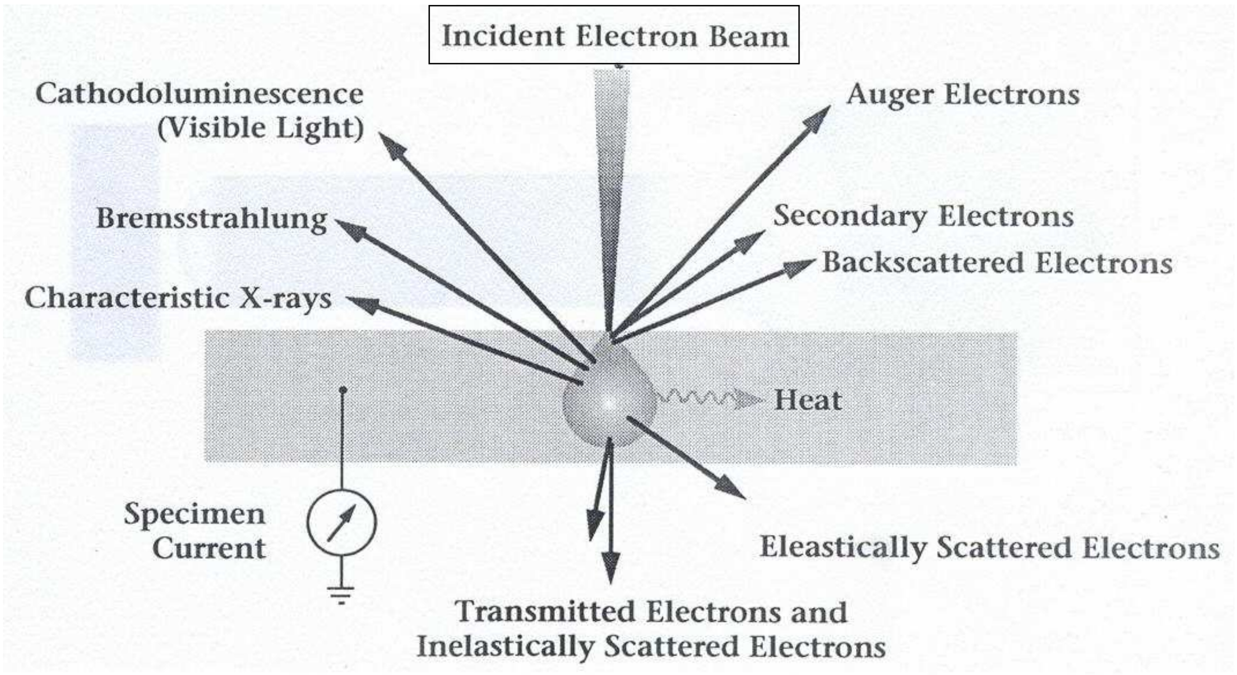
e' beam - matter interaction

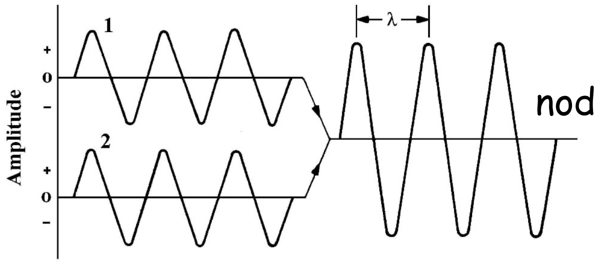
When an electron beam strikes a sample . . .



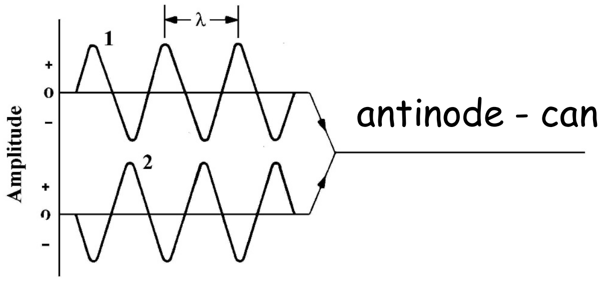
Interference

Interaction between two or more trains of waves of the same frequency emitted from coherent sources.

A series of stationary nodes and antinodes is established, known as interference.



node - reinforcement



antinode - cancellation

Diffraction

- Read
  - ✓ Pecharsky Chap 2, Hammond Chap 7, 8; Cullity Chap 2, Appendix 1; Krawitz Chap 3, 5

- Diffraction: coherent and elastic scattering of radiation by **periodic arrays of objects** resulting in **concerted constructive interference at specific angles**

- Diffraction occurs whenever wave motion encounters a set of **regularly spaced scattering objects**, provided the wavelength λ of the wave motion is the **same order of magnitude** as the repeat distance between the scattering centers

X-ray diffraction

- Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles
- The **electrons** in an atom **coherently** scatter light
  - ✓ The electrons interact with oscillating electric field of light wave
- Atoms in a crystal form a **periodic array** of coherent scatterers
  - ✓ The wavelength of X rays are similar to the distance between atoms
  - ✓ Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal
- X rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter

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X-ray Diffraction

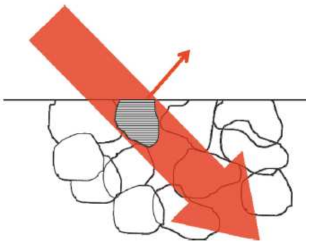
- X-rays are an ideal probe of electromagnetic radiation for the study of crystals as the **wavelength λ is of the same order as the distances between the atoms** in crystals

- Elastic scattering → no energy transfer & no wavelength change

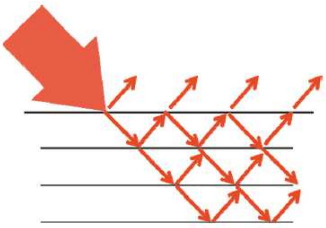
- When the **periodic array** consists of crystalline matter of 3-D arrangement of atoms, monochromatic X-ray radiation diffracts in a number of different directions in 3-D space

Kinematical vs. Dynamical theories of diffraction

- **Kinematical**
  - ✓ A beam scattered once is not scattered again
  - ✓ Interaction of diffracted beam with crystal is negligibly small
    - ▪Crystal consists of individual mosaic blocks
    - ▪Size of the crystallites is small
    - ▪Misalignment of crystallites is large enough, so that interaction of X-ray with matter at length scale larger than the size of the mosaics is negligible



- **Dynamical**
  - ✓ Accounts for scattering of diffracted beam & other interactions of waves inside the crystal
  - ✓ Needed when crystals are nearly perfect or when there is a strong interaction of the radiation with the material (electron diffraction



- Many dynamical effects (primary & 2ndary extinction, simultaneous diffraction, thermal diffuse scattering, etc.) are accounted for as corrections to the kinematical diffraction model

Rigaku Journal, 25(2), 2009, X-ray thin film measurement techniques

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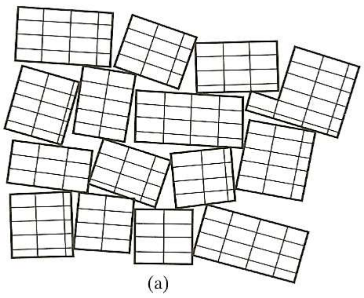
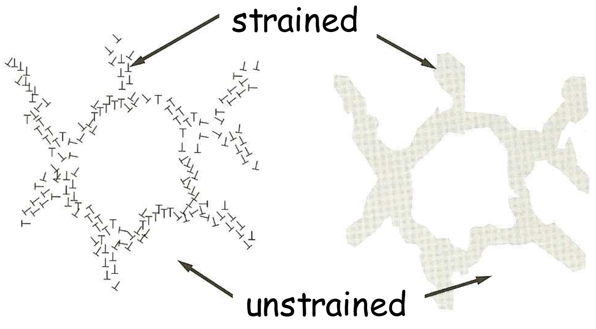
Mosaic structure

- Not perfectly regular lattice → collection of tiny blocks each slightly disoriented one from the other
- Angle of disorientation between the blocks is ε (< 1 degree)→ diffraction occurs at all angles between θ_B and $\theta_B + \varepsilon$
- Increases the integrated intensity relative to that obtained (or calculated) for an ideally perfect crystal ← strains & strain gradients associated with the groups of dislocations





Cullity page 174~176

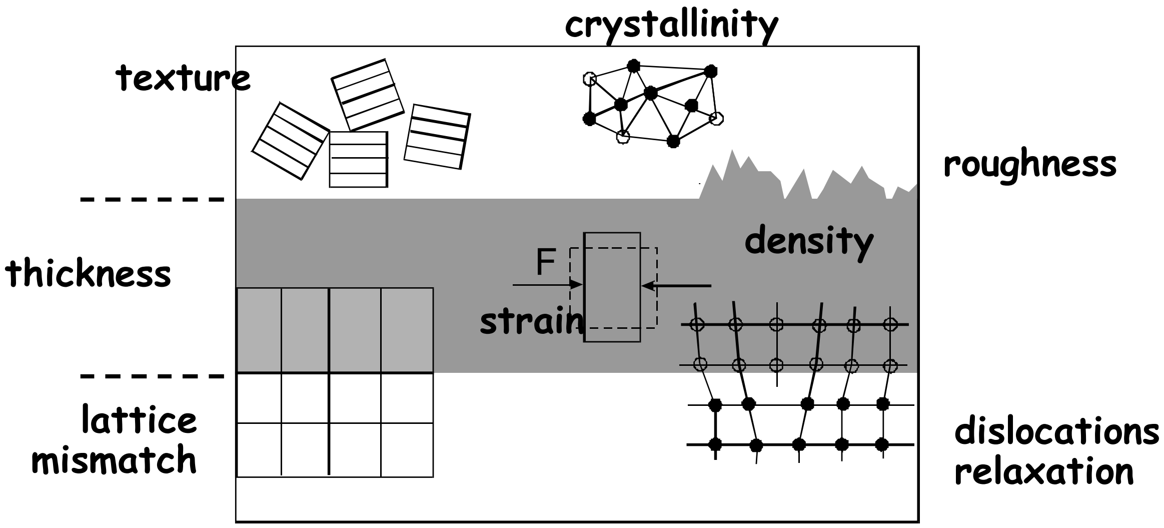
Range of Applications of X-Ray Analytical Methods

- Qualitative and quantitative element analysis (XRF)
- Qualitative and quantitative phase analysis (XRD)
- % crystallinity
- Micro-strain and crystallite size determination
- Residual stress and texture analysis
- Grazing incidence diffraction (GID) and reflectometry (XRR)
- High Resolution X-ray Diffraction (HRXRD)
- Structure solution and refinement
- Micro-diffraction (phase identification, texture, stress…)
- Nano-structure investigations by small angle X-ray scattering (SAXS)

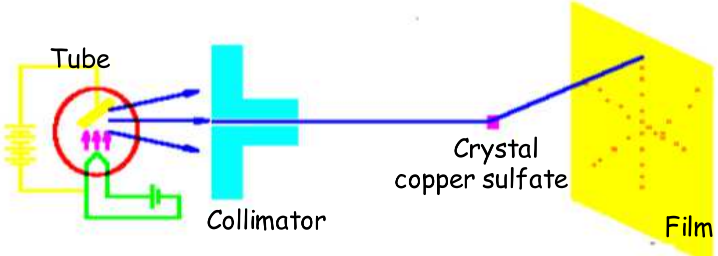
What can we do with XRPD?

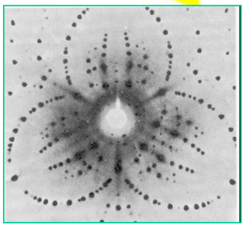
- **Qualitative phase analysis (Identification of unknown phases)**
- **Quantitative phase analysis**
- Accurate lattice parameter measurement
- % crystallinity
- Measurement of crystal size
- Measurement of internal elastic strains
- Preferred orientation measurement
- Cation site disorder
- Micro-diffraction (phase identification, texture, stress…)
- Structure refinement (vs. single crystal)

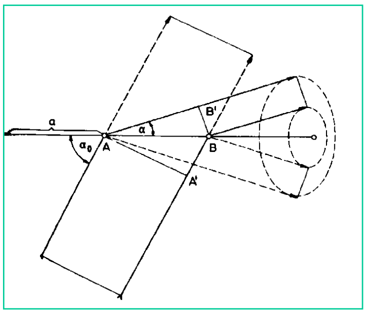
What can be measured by X-ray analysis of Thin Film ???



Max von Laue's Experiment in 1912, Univ. of Munich
Single Crystal X-ray Diffraction



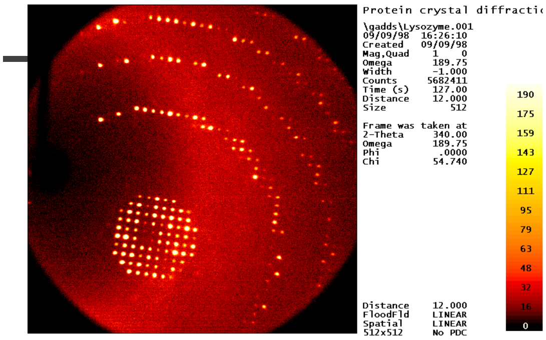




Max von Laue put forward the conditions for scattering maxima → the Laue equations:

$$a(\cos\alpha-\cos\alpha_0)=h\lambda$$
$$b(\cos\beta-\cos\beta_0)=k\lambda$$
$$c(\cos\gamma-\cos\gamma_0)=l\lambda$$

Proved
(1) Wave nature of X-ray
(2) Periodicity of the arrangement of atoms within a crystal



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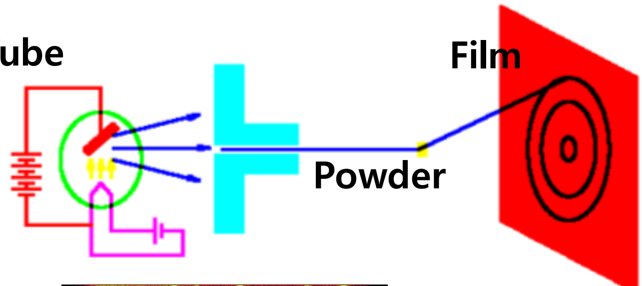
Protein crystal diffracti

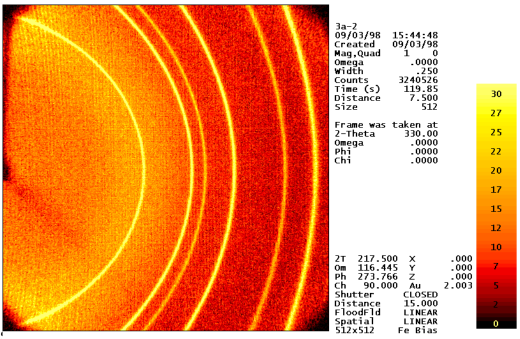
\gadds\Lysozyme.001
09/09/98  16:26:10
Created   09/09/98
Mag,Quad     1    0
Omega       189.75
Width       -1.000
Counts     5682411
Time (s)    127.00
Distance    12.000
Size           512

Frame was taken at
2-Theta     340.00
Omega       189.75
Phi          .0000
Chi         54.740

Distance    12.000
FloodFld    LINEAR
Spatial     LINEAR
512x512     No PDC
```

Single crystal Diffraction





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3a-2
09/03/98  15:44:48
Created   09/03/98
Mag,Quad     1    0
Omega        .0000
Width         .250
Counts     3240526
Time (s)    119.85
Distance     7.500
Size           512

Frame was taken at
2-Theta     330.00
Omega        .0000
Phi          .0000
Chi          .0000

2T  217.500  X       .000
Om  116.445  Y       .000
Ph  273.766  Z       .000
Ch   90.000  Au     2.003
Shutter     CLOSED
Distance    15.000
FloodFld    LINEAR
Spatial     LINEAR
512x512    Fe Bias
```
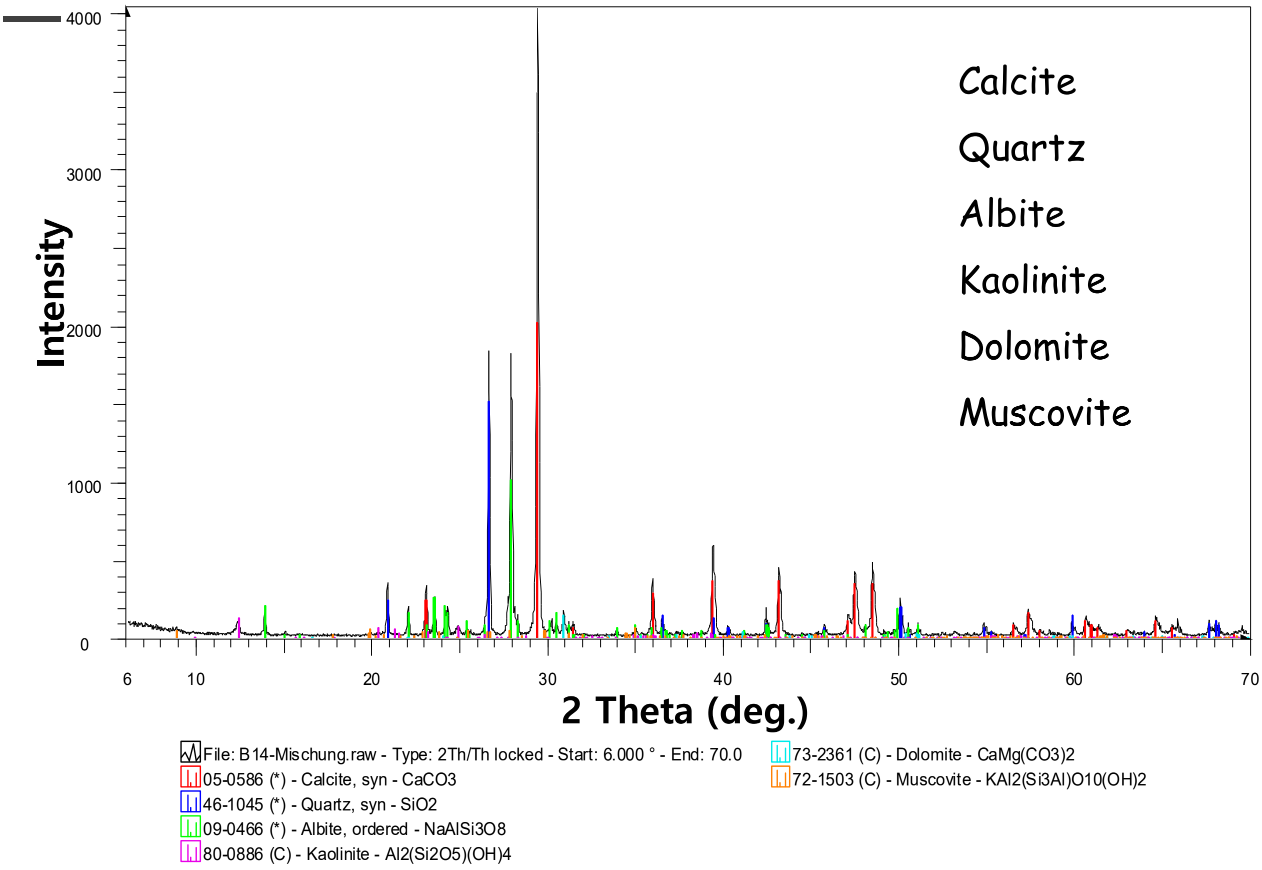

Powder X-ray Diffraction



Calcite

Quartz

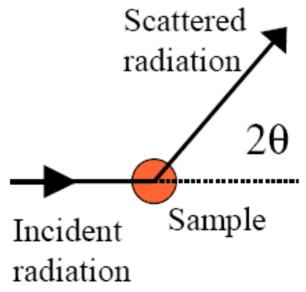
Albite

Kaolinite

Dolomite

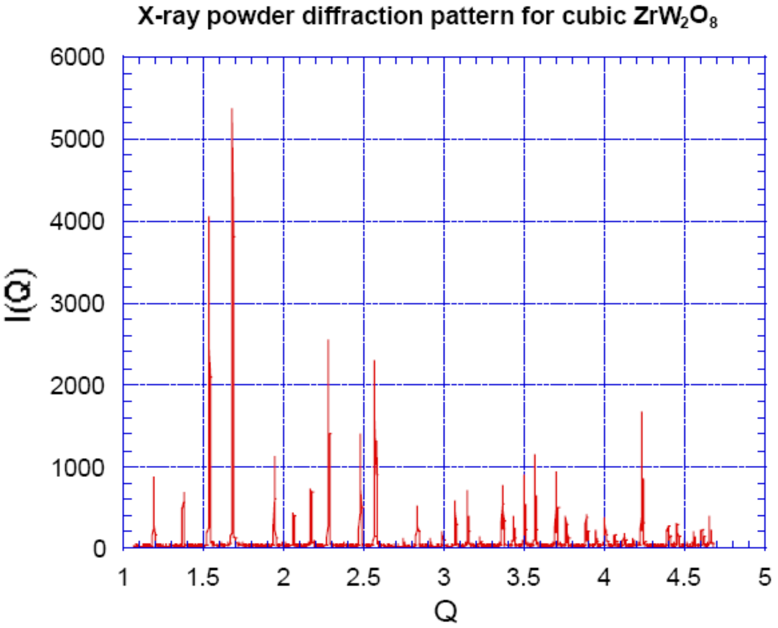
Muscovite

XRPD pattern



2θ is the Bragg angle

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$$

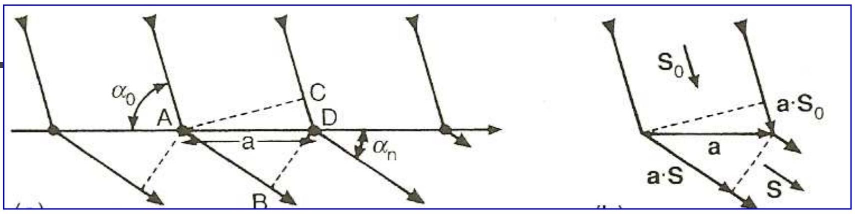


Camera vs. Diffractometer

- Diffraction camera
  - ✓ I is measured thru amount of blackening it produces on a film.
  - ✓ All diffraction lines recorded simultaneously. Variation in I of incident beam during exposure has no effect on the relative I.
  - ✓ Quantitative measurements of line position & intensity need at least two steps (recording pattern on the film + microphotometer record of the film).
- Diffractometer
  - ✓ I is measured directly by an electronic X-ray detector.
  - ✓ Diffraction lines recorded one after another → incident beam intensity must be kept constant → voltage & current needs to be stabilized.
  - ✓ Quantitative measurement of line position & intensity is made in one operation.

Laue vs. Bragg

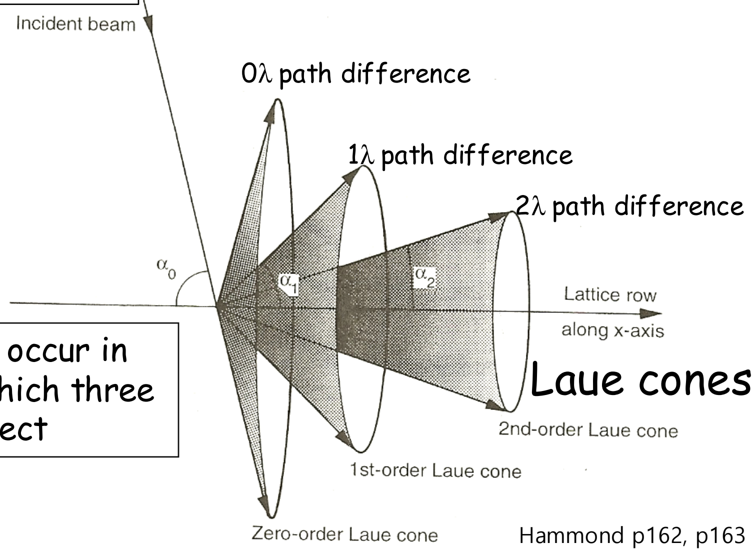
- **Laue**
  - ✓ Crystals consist of 3-D network of rows of atoms.
  - ✓ Crystal behaves as a 3D diffraction grating.
  - ✓ Laue equations
- **Bragg**
  - ✓ Crystals consist of planes of atoms which behaves as reflecting planes.
  - ✓ Strong reflected beam is produced when the path difference between reflections from successive planes in a family is equal to whole number of wavelengths.
  - ✓ Bragg's law



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

$$\boxed{\begin{aligned} a(\cos\alpha_n - \cos\alpha_0) &= \mathbf{a}\cdot(\mathbf{s}-\mathbf{s}_0) = n_x\lambda \\ b(\cos\beta_n - \cos\beta_0) &= \mathbf{b}\cdot(\mathbf{s}-\mathbf{s}_0) = n_y\lambda \\ c(\cos\gamma_n - \cos\gamma_0) &= \mathbf{c}\cdot(\mathbf{s}-\mathbf{s}_0) = n_z\lambda \end{aligned}}$$

Laue equation

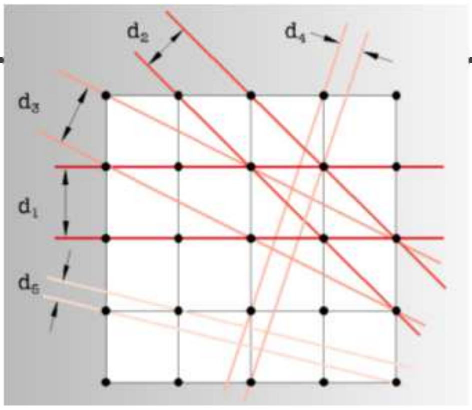


Laue cones

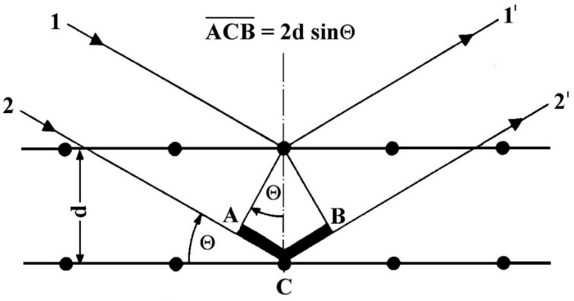
Diffracted beams only occur in those directions along which three Laue cones intersect

Hammond p162, p163

Bragg's Law



reflection ≠ diffraction
(see page 94 of Cullity)



$$\frac{'AC'}{d} = \sin\Theta$$

$$'AC' = d\sin\Theta$$

$$'ACB' = 2d\sin\Theta$$

$$'ACB' = n\lambda$$

↘ Constructive interference

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

n = 1, 2, 3, ... (Reflection order)

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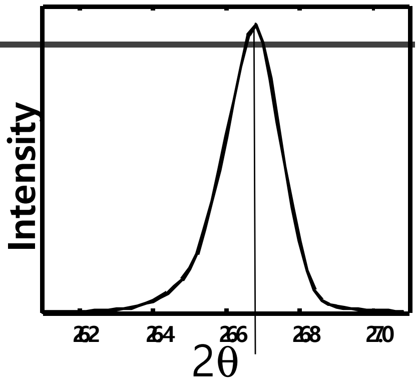
d-value vs. lattice constants



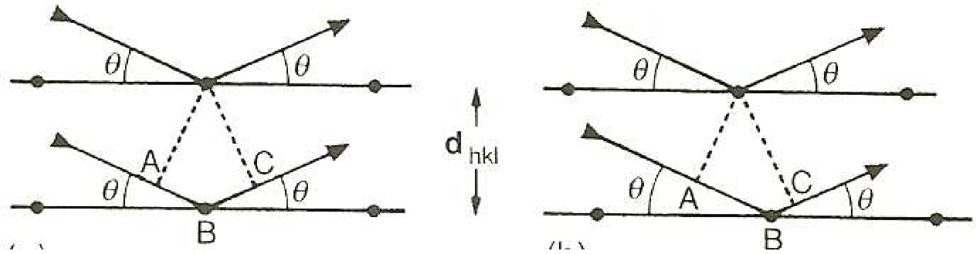
Bragg´s law $\lambda = 2\,d\,sin\,\theta$

- λ, θ known → d can be calculated

$$1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$$

d-value of a tetragonal elementary cell

- h, k, l --- Miller indices of the peaks
- a, c --- lattice parameter
- a, c known → can get θ, the peak position
- θ, peak position known → can get lattice parameters



The path difference between the waves scattered by atoms from adjacent (*hkl*) lattice planes of spacings d_{hkl} is given by

$$(\mathrm{AB}+\mathrm{BC}) = (d_{hkl}\sin\theta + d_{hkl}\sin\theta) = 2d_{hkl}\sin\theta.$$

Hence for constructive interference:

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

where n is an integer (the order of reflection or diffraction).

$$\lambda = 2\left(\frac{d_{hkl}}{n}\right)\sin\theta = 2d_{nh\,nk\,nl}\sin\theta$$ Bragg's law

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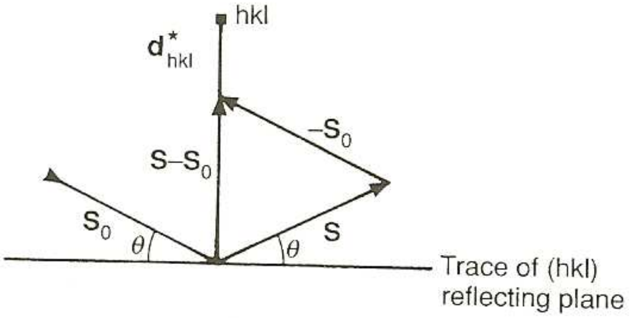
Bragg's law



$$|\mathbf{s}-\mathbf{s}_0| = 2\sin\theta$$

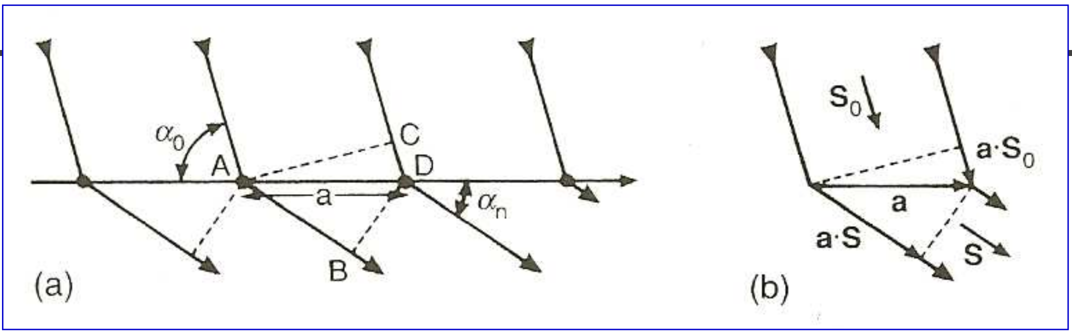
$$|\mathbf{d}^*_{hkl}| = 1/d_{hkl}$$

$$\lambda = 2\left(\frac{d_{hkl}}{n}\right)\sin\theta = 2d_{nh\,nk\,nl}\sin\theta$$

$$\frac{(\mathbf{s}-\mathbf{s}_0)}{\lambda} = \mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*.$$

$$\underbrace{\mathbf{a}\cdot(\mathbf{s}-\mathbf{s}_0) = n_x\lambda}_{\text{Laue equation}} = \mathbf{a}\cdot\mathbf{d}^*_{hkl}\cdot\lambda = \mathbf{a}\cdot(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)\lambda = h\lambda$$

$$n_x = h,\ n_y = k,\ n_z = l$$



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

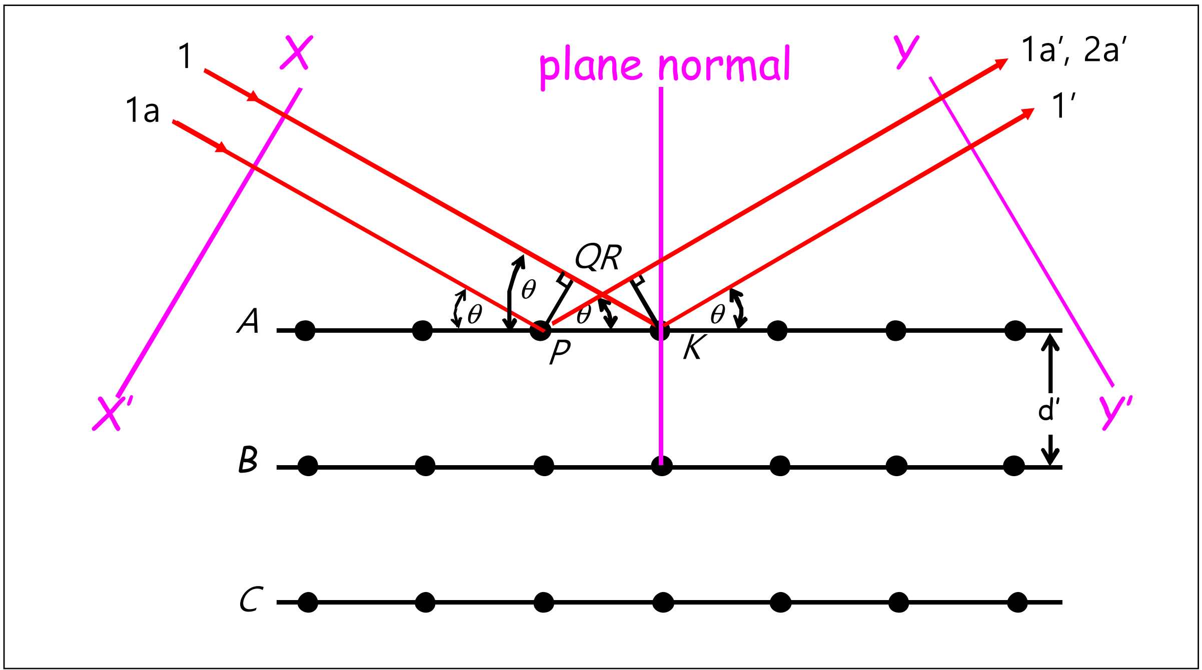
Laue equation　　　　Laue indicies

$$a(\cos\alpha_n - \cos\alpha_0) = \mathbf{a}\cdot(\mathbf{s}-\mathbf{s}_0) = n_x\lambda = \mathbf{h}\lambda$$
$$b(\cos\beta_n - \cos\beta_0) = \mathbf{b}\cdot(\mathbf{s}-\mathbf{s}_0) = n_y\lambda = \mathbf{k}\lambda$$
$$c(\cos\gamma_n - \cos\gamma_0) = \mathbf{c}\cdot(\mathbf{s}-\mathbf{s}_0) = n_z\lambda = \mathbf{l}\lambda$$

3rd order diffaction from (111) = 1st order diffraction from 333 (Laue index).
333 planes have 1/3 spacing of (111).

Hammond p162

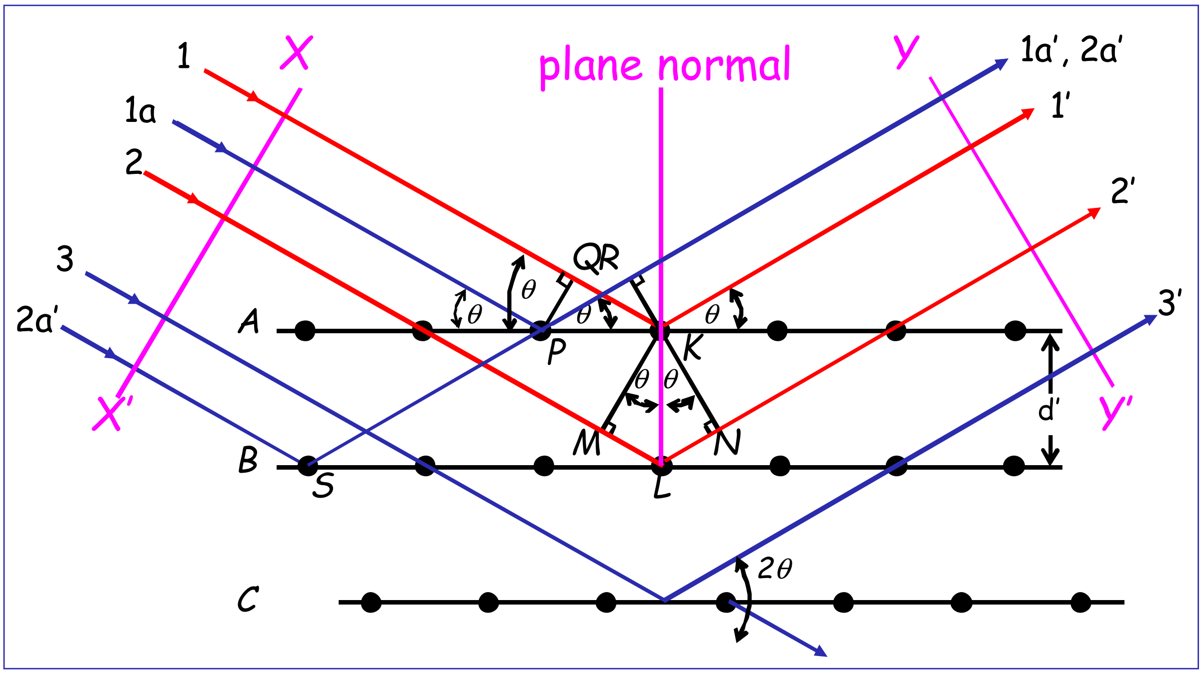
Bragg's law



Scattered by atoms P, K (1′, 1a′) : The beams are in phase

Prof. Jeong Hyo Tae, Kangnung National Univ.

Bragg's law



Scattered by atoms P, K (1', 1a') : The beams are in phase

Scattered by atoms K and L : ML + LN = 2d'sinΘ = nλ

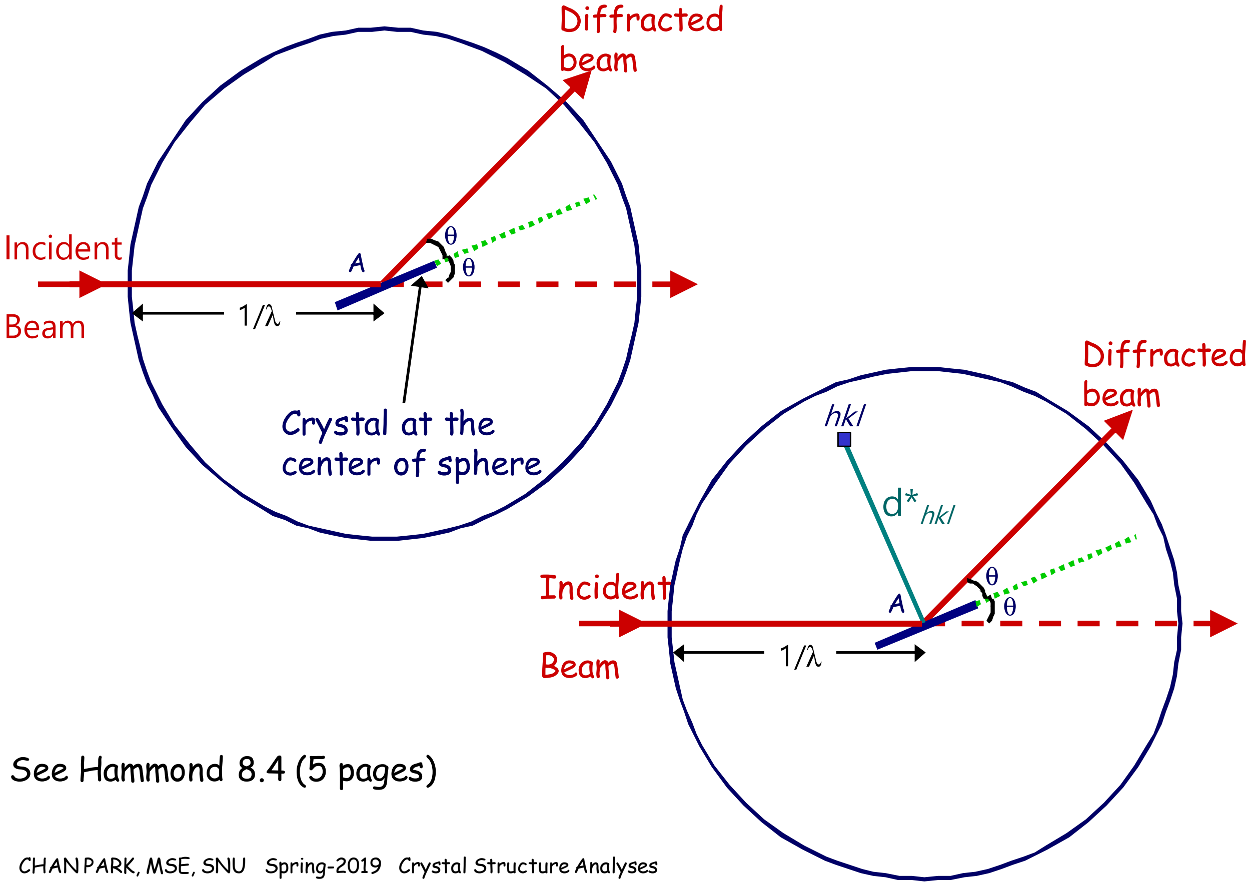
<u>For fixed value of λ there can be several angles of incidence;</u> Θ_1, Θ_2, Θ_3

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

- Condition for diffraction
  - ✓ Incident beam
  - ✓ Diffracted beam
  - ✓ Plane normal

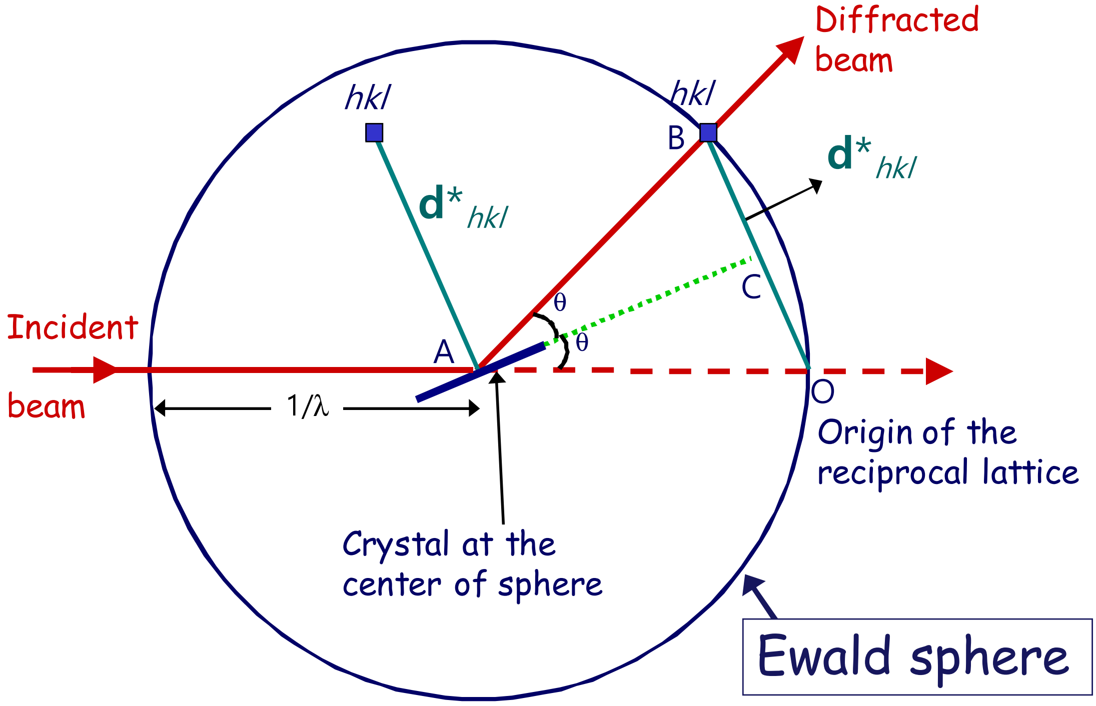
  } co-planar
- $\sin\Theta = n\lambda/2d \leq 1$
- If λ = 500 Å, the crystal could not possibly diffract
- If λ = 0.1 Å, diffraction angles too small to be measured
- n=1, $\lambda < 2d$ → (i.e.) $d = 3\text{Å}$, $\lambda < 6\text{Å}$

Ewald reflecting sphere



See Hammond 8.4 (5 pages)

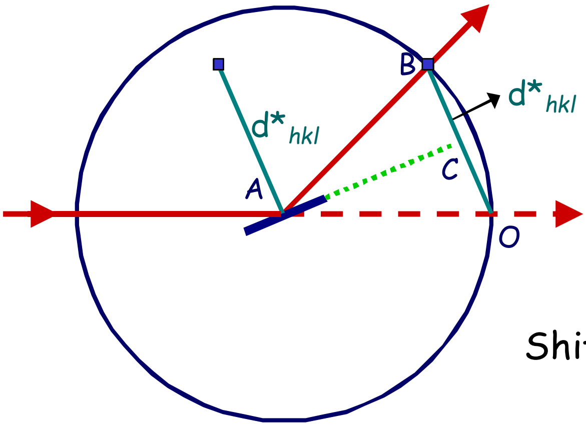
Ewald reflecting sphere

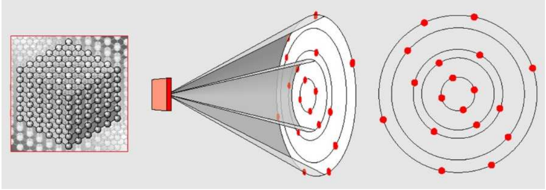


$$|\mathbf{OC}| = (1/\lambda)\sin\theta = \tfrac{1}{2}\,|\mathbf{d}^*_{hkl}| = \tfrac{1}{2}\,(1/d_{hkl}) \rightarrow \lambda = 2d_{hkl}\sin\theta$$

Hammond page 199

Ewald reflecting sphere





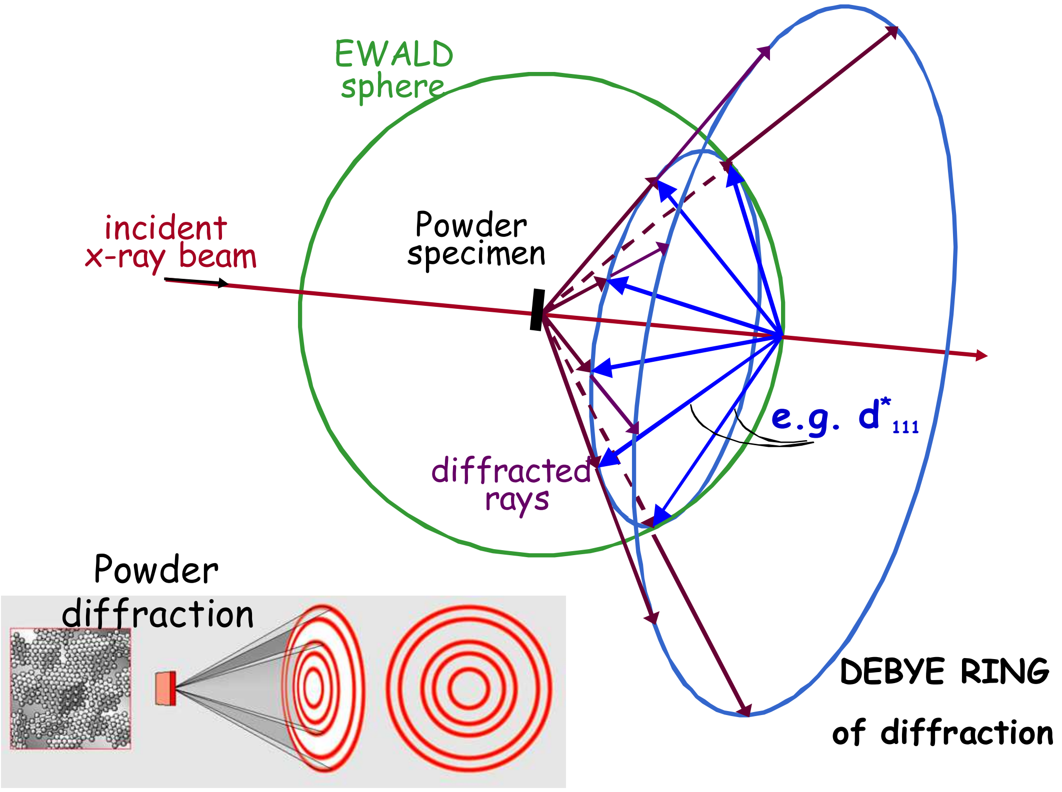
Single Crystal Diffraction

Shift origin from A to O → **OB** = **d***$_{hkl}$

- Bragg's law ≡ reciprocal lattice point for reflecting plane (hkl) should intersect the sphere
- If the reciprocal lattice point does not intersect the sphere, then the Bragg's law is not satisfied → no diffracted beam

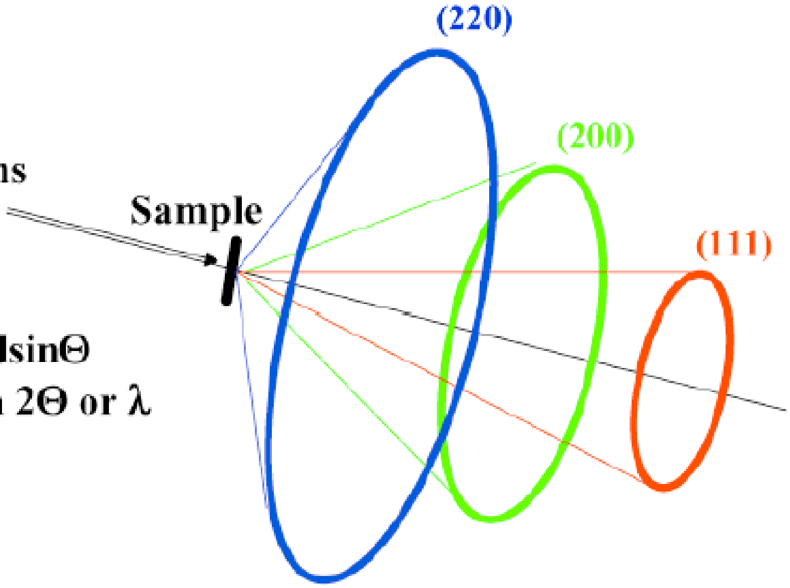
Hammond page 199

Origin of powder diffraction pattern



Powder Diffraction gives Scattering on Debye-Scherrer Cones

Incident beam
x-rays or neutrons

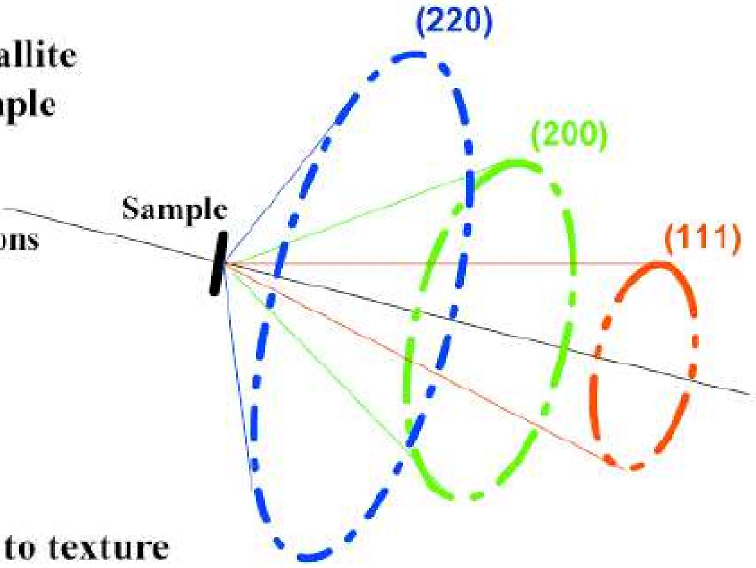


Bragg's Law $\lambda = 2d\sin\Theta$
Powder pattern – scan 2Θ or λ

Texture Measurement by Diffraction

Non-random crystallite orientations in sample

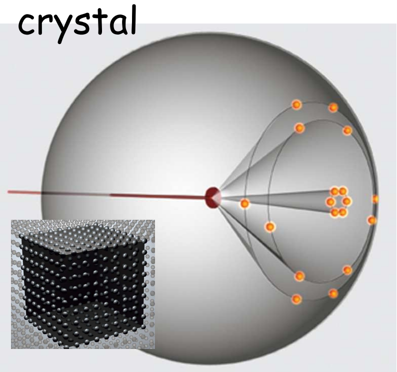
Incident beam
x-rays or neutrons



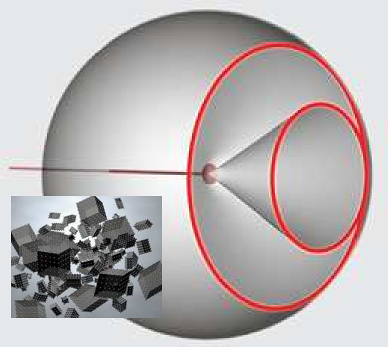
Debye-Scherrer cones
- **uneven intensity due to texture**
- **different pattern of unevenness for different hkl's**
- **intensity pattern changes as sample is turned**

Debye rings from ----

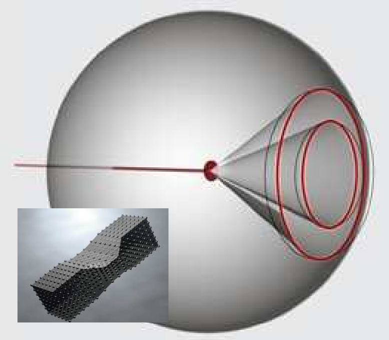
single crystal



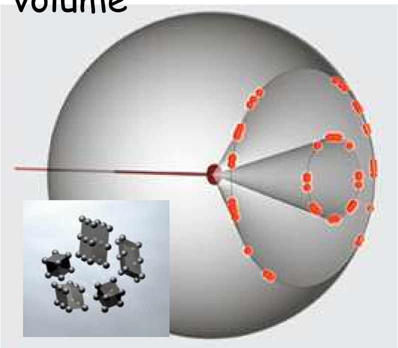
powder



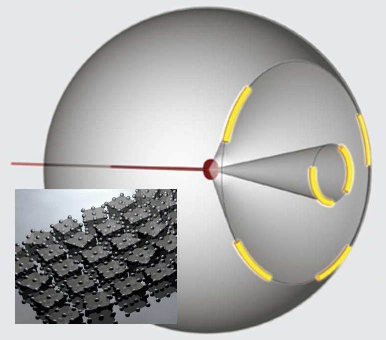
strained material



small volume



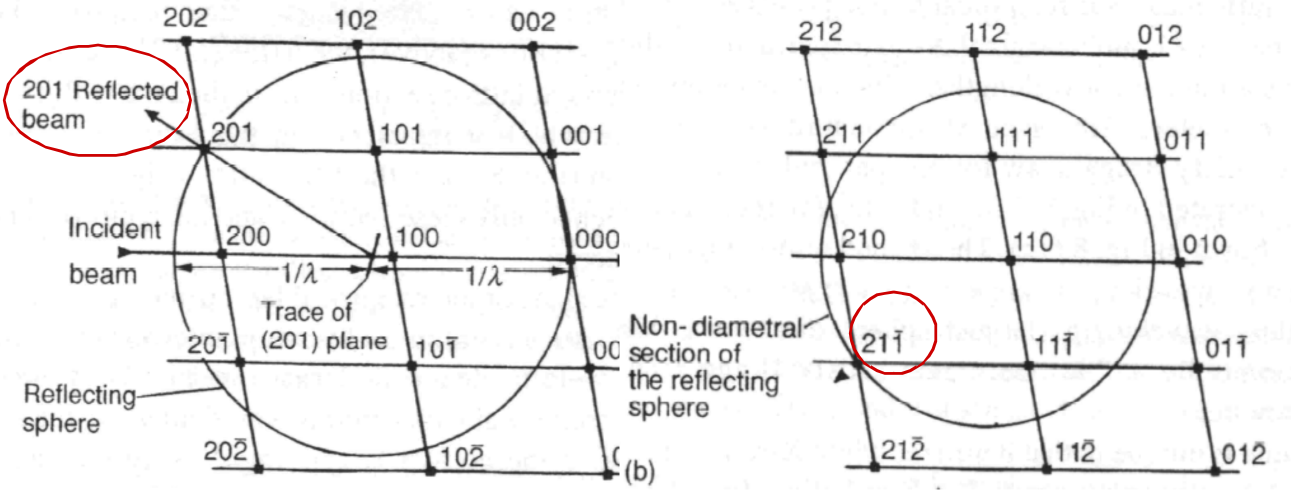
textured material



Jon Giencke

Ewald reflecting sphere

Section of reciprocal lattice of a monoclinic crystal ⊥ b*

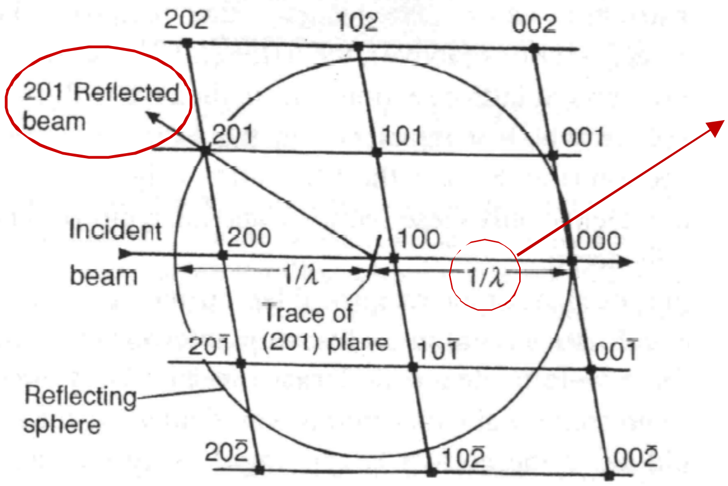


h0l reciprocal lattice section *h1l* reciprocal lattice section

<u>Origin of the reciprocal lattice</u> is not at the center of the sphere, but is <u>at the point where the direct beam exits the sphere</u>

Hammond page 200

Ewald reflecting sphere

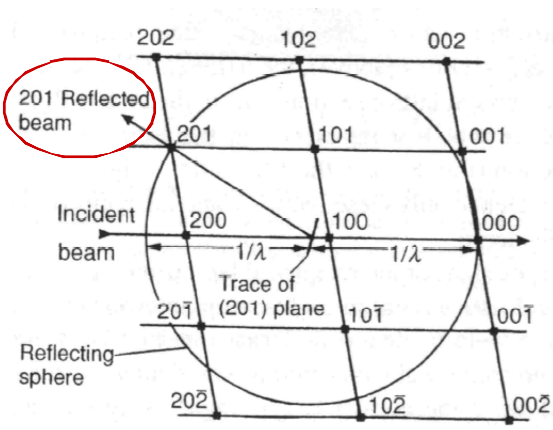


Change λ → radius of sphere changes → other points can intersect sphere

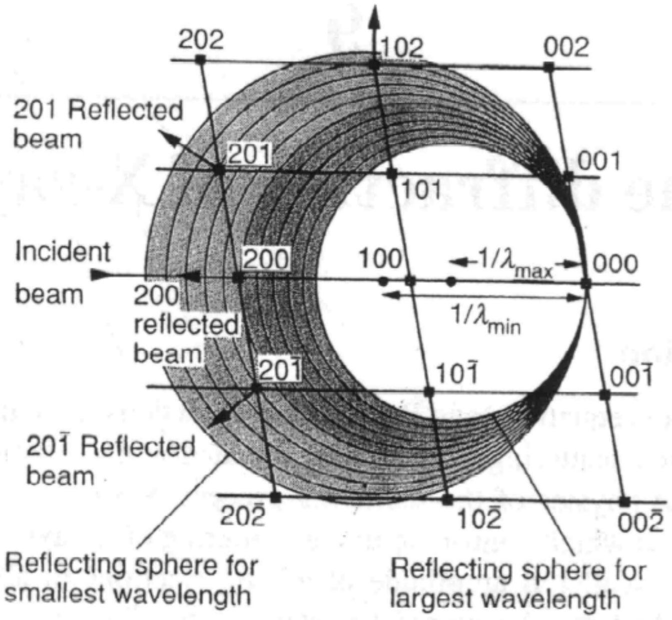
If λ can change continuously → other planes can reflect as their reciprocal lattice points successively intersect the sphere → Laue's original X-ray experiment using white radiation

Hammond page 200

Ewald reflecting sphere



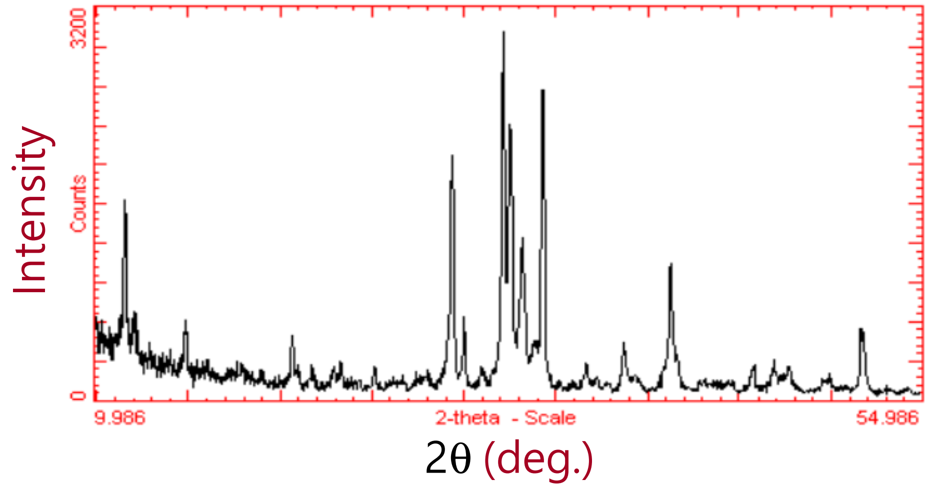
Hammond page 200

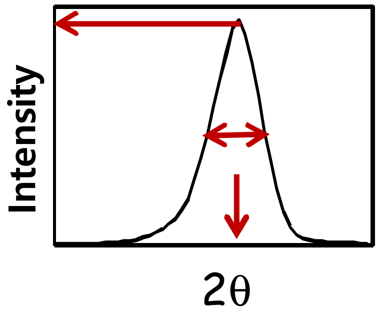


Hammond page 201

- All the planes in the shaded region satisfy Bragg's law for the particular sphere on which they lie (for that particular λ)
- Monochromatic radiation → crystal and the sphere should move to have more intersection (to have diffracted beams from more planes)

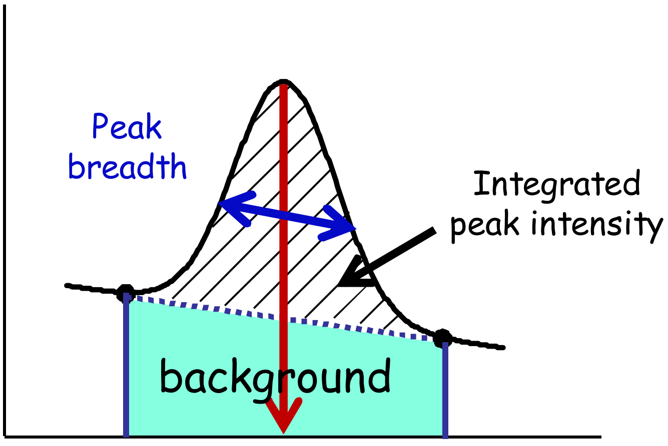
θ – 2θ X-ray diffraction pattern





- Positions, intensities, shapes → crystal structure, physical state, etc.

Peak position is determined by ---

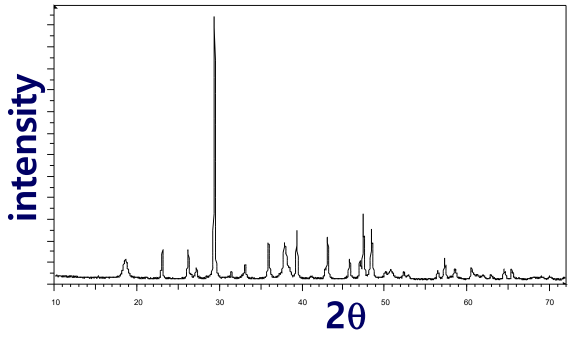


Peak position

Size & Shape of unit cell

2θ & intensity of XRD pattern

- 2θ
  - ✓ Size & shape of the unit cell (← λ = 2d sinθ)
- Intensity
  - ✓ Atomic scattering factor
  - ✓ Structure factor (atomic position, occupancy, etc.)
  - ✓ Polarization
  - ✓ Multiplicity
  - ✓ Temperature
  - ✓ Microabsorption
  - ✓ Crystallite size
  - ✓ Residual stress
  - ✓ Preferred orientation (texture)
  - ✓ Degree of crystallinity
  - ✓ Anomalous scattering
  - ✓ Source intensity, voltage drift, take-off angle, slit width, axial divergence, detector dead time, etc.



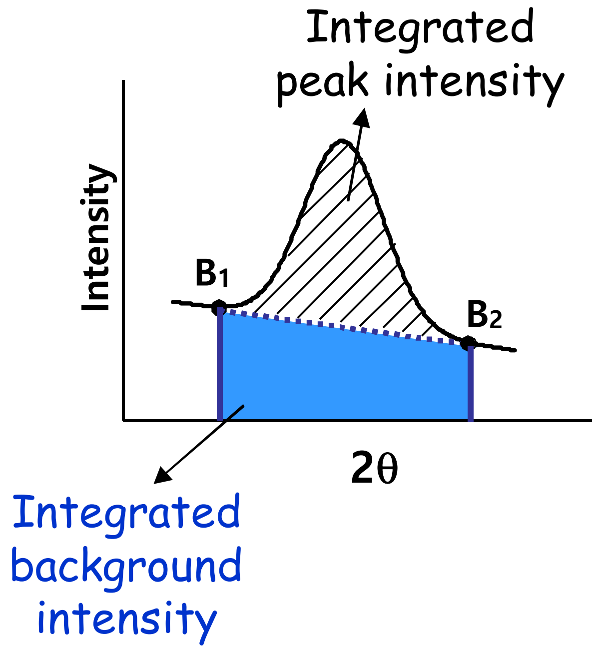
- 2theta
  - ✓ Geometry (crystal system, lattice parameter) (shape & size)
  - ✓ Contents of unit cell
- Intensity
  - ✓ Atom type
  - ✓ Arrangement
  - ✓ Orientation
- Shape of diffraction lines
  - ✓ Instrument broadening
  - ✓ Particle dimension
  - ✓ Strain

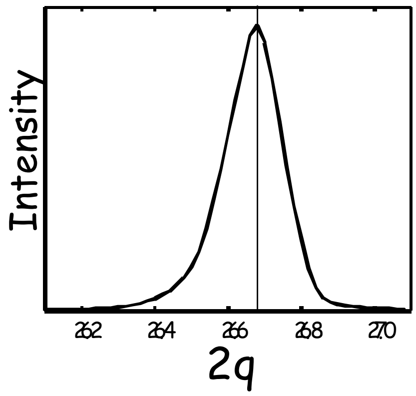
D-spacing accuracy

- Diffractometer misalignment
- Specimen displacement error
- Problems in establishing true peak position
- Background
- Kα2
- ---

Bish & Post Chap 3

Integrated intensity





Asymmetric profile due to axial divergence

Intensity

- Structure sensitive
  - ✓ Atomic scattering factor
  - ✓ Structure factor
  - ✓ Polarization
  - ✓ Multiplicity
  - ✓ Temperature
- Sample sensitive
  - ✓ Absorption
  - ✓ Crystallite size
  - ✓ Degree of crystallinity
  - ✓ Particle orientation
- Instrument sensitive
  - ✓ Absolute intensities
    - Source intensity
    - Diffractometer efficiency
    - Take-off angle of tube
    - Receiving slit width
    - Axial divergence allowed
  - ✓ Relative intensities
    - Divergence slit aperture
    - Detector dead-time
- Measurement sensitive
  - ✓ Method of peak area measurement
  - ✓ Method of background subtraction
  - ✓ $\alpha 2$ stripping or not
  - ✓ Degree of data smoothing employed

Bish & Post Chap 3

Crystal structure determination

- Two step process

(1) Determination of the size & shape of the unit cell ← peak position

(2) Determination of lattice type & distribution of the atoms in the structure ← intensities of the diffraction spots

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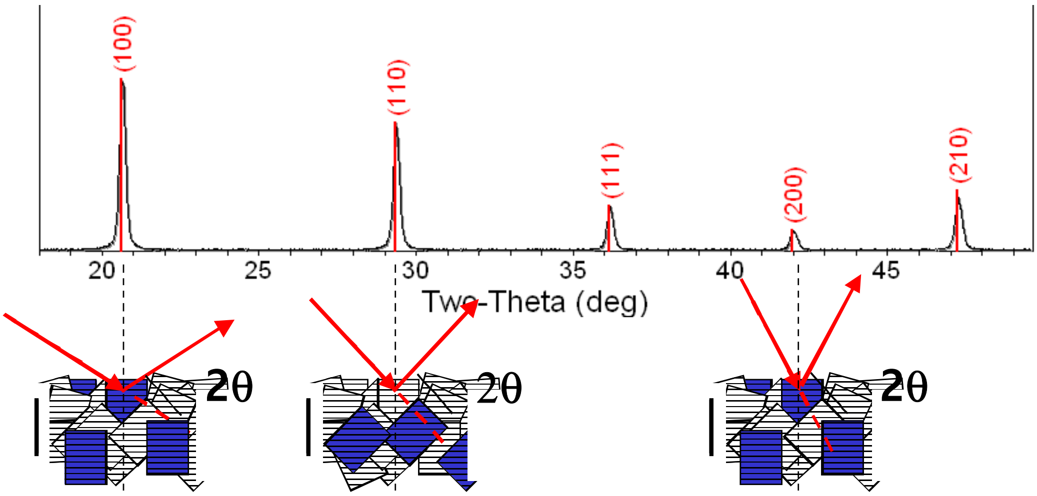
A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.



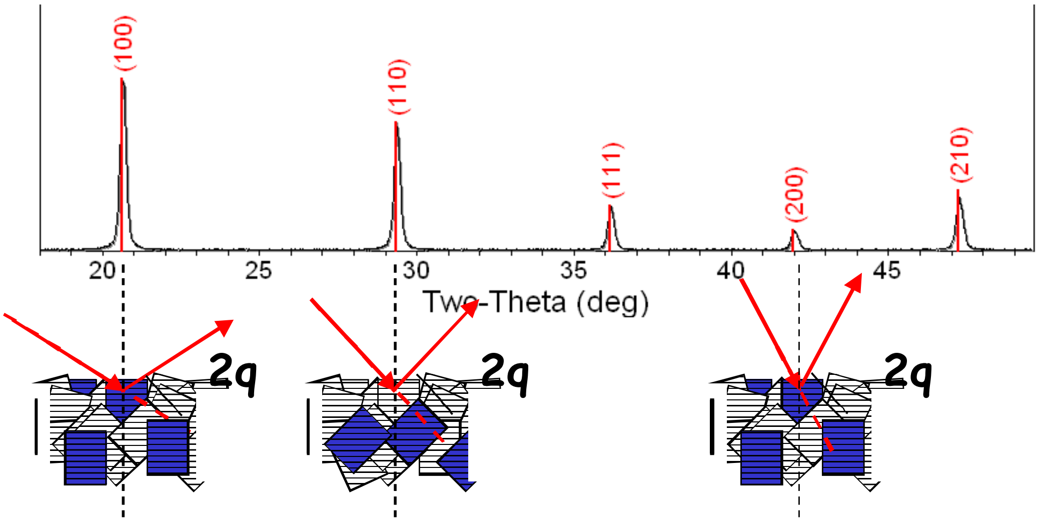
At 20.6°2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (200) planes are // to the (100) planes. → they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 41°2θ.

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

Scott A Speakman

A polycrystalline sample can contain thousands of crystallites.
→ all possible diffraction peaks can be observed.



- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane which perpendicularly 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.

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