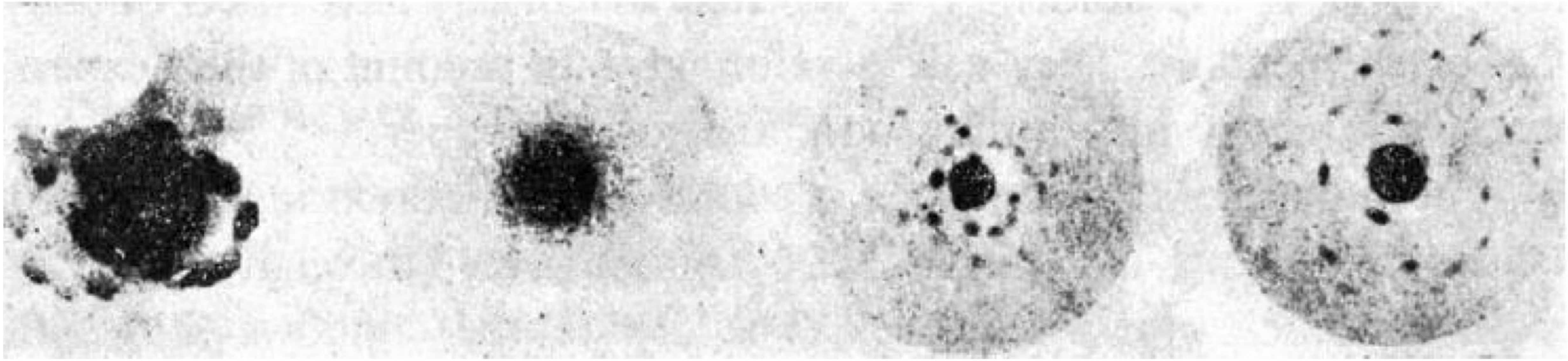
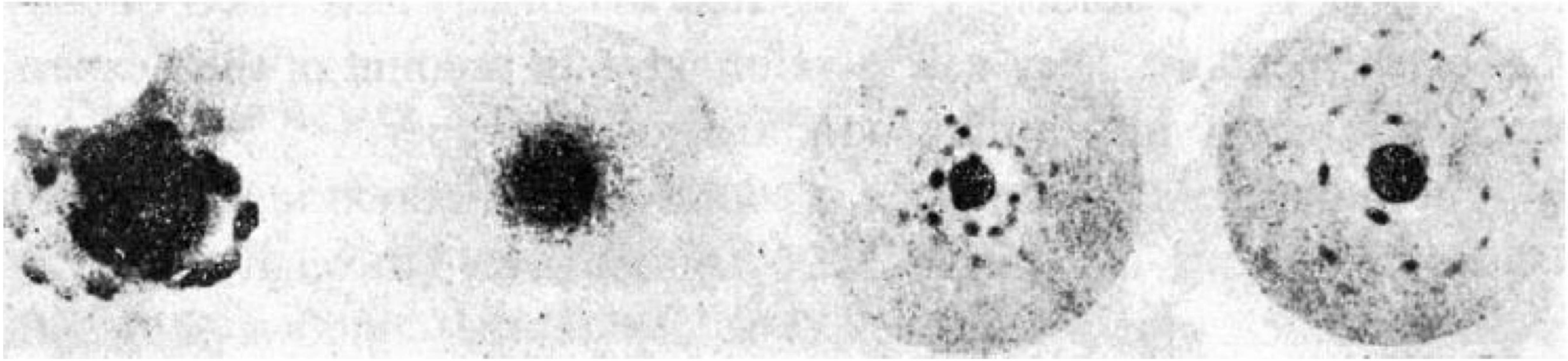
Von Laue - Theoretical physicist claiming X-Rays are waves

Elements of XRD Analysis



First X-Ray pattern by Walter Friedrich and Paul Knipping on ZnS, 1912



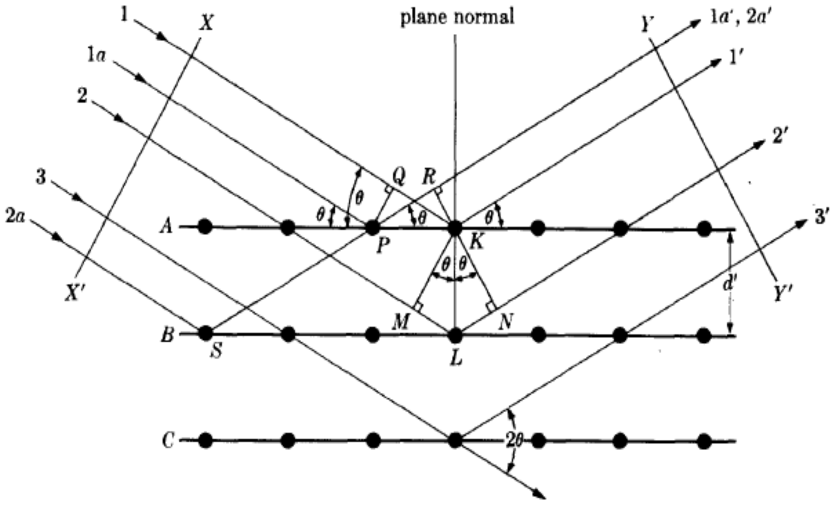
Laue: ZnS crystal is an infinite collection of cubes with Zn and S occupying alternate columns!

L. and W. Bragg: Look there are spots which are not so bright! – There should also be atoms on the walls of the cubes!

H. Armstrong: ‘This is repugnant to sense! - Absurd to nth degree. It seems you will say that the rock salt does not contain molecules of ‘NaCl’ but a simple extension of N-Cl atoms?

Xray study components:

$$\lambda = 2d_{nh,nk,nl}\sin\theta$$



Intensity $I = |F|^2 p\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)e^{-2M}$

$$F = \sum_{1}^{n} f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

Atomic scattering factor (f_n) and phase interference

Intensity along Bragg’s angle $I\ \alpha\ FF^*$

Other factors:

Polarization

Multiplicity

Lorentz

Absorption

Temperature

Somewhere around two-dozen nobel prizes for work on X-Rays. Venki Ramakrishnan the latest among them for structure of R

Crystals and Structure

Solids in our universe is almost a singularity. It is a region with extreme densities of atoms with sharp boundaries with almost no densities.

More surprising is the occurrence of ‘order’ in the packing of atoms in the solids.

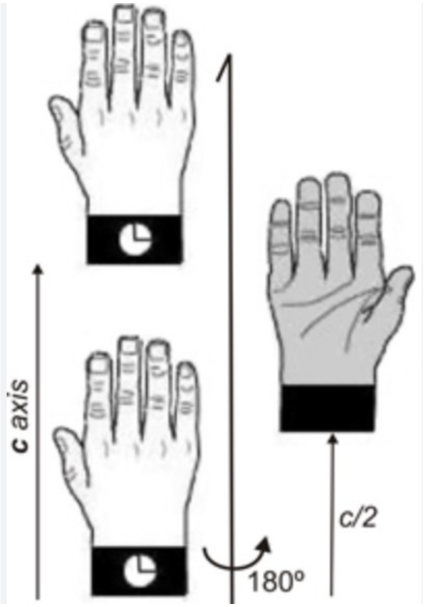
Therefore, a common analysis (characterization) of a solid material:

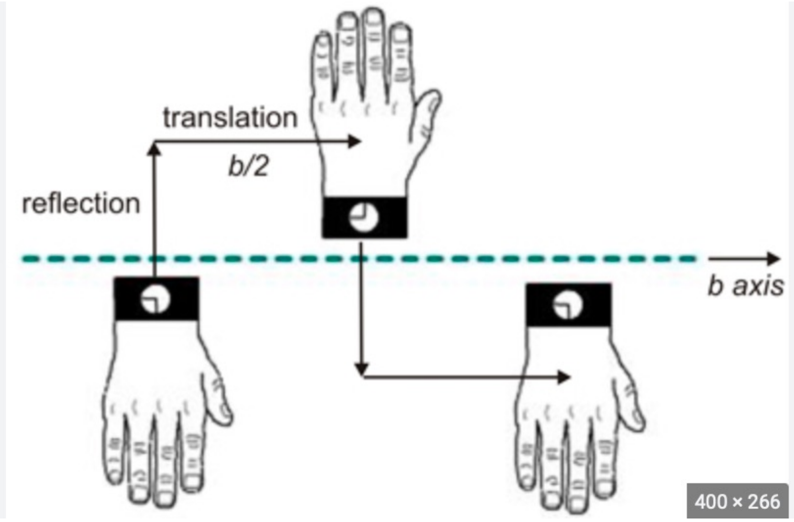
1. Investigation of the geometry of the repeating scheme
2. Investigation of the shape of the motif

Symmetry operations

Repetition upon

- Translation
- Rotation
- Screw motion – reflection + translation
- Reflection
- Glide-reflection – reflection + translation
- Roto-reflection

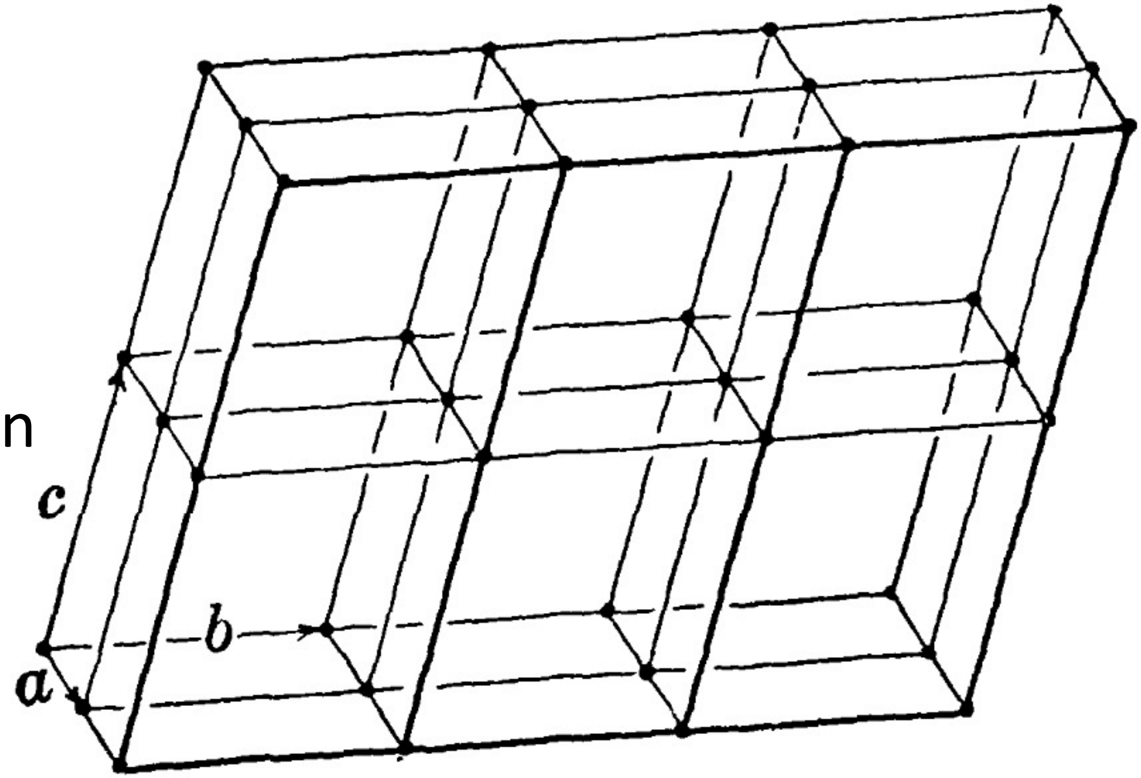




A complete set of combinations of these symmetry operations leads to 230 space groups.

A crystal system may or may not have many of these symmetry operations; but by definition should atleast have translation!

Translation is a vector: A magnitude with direction

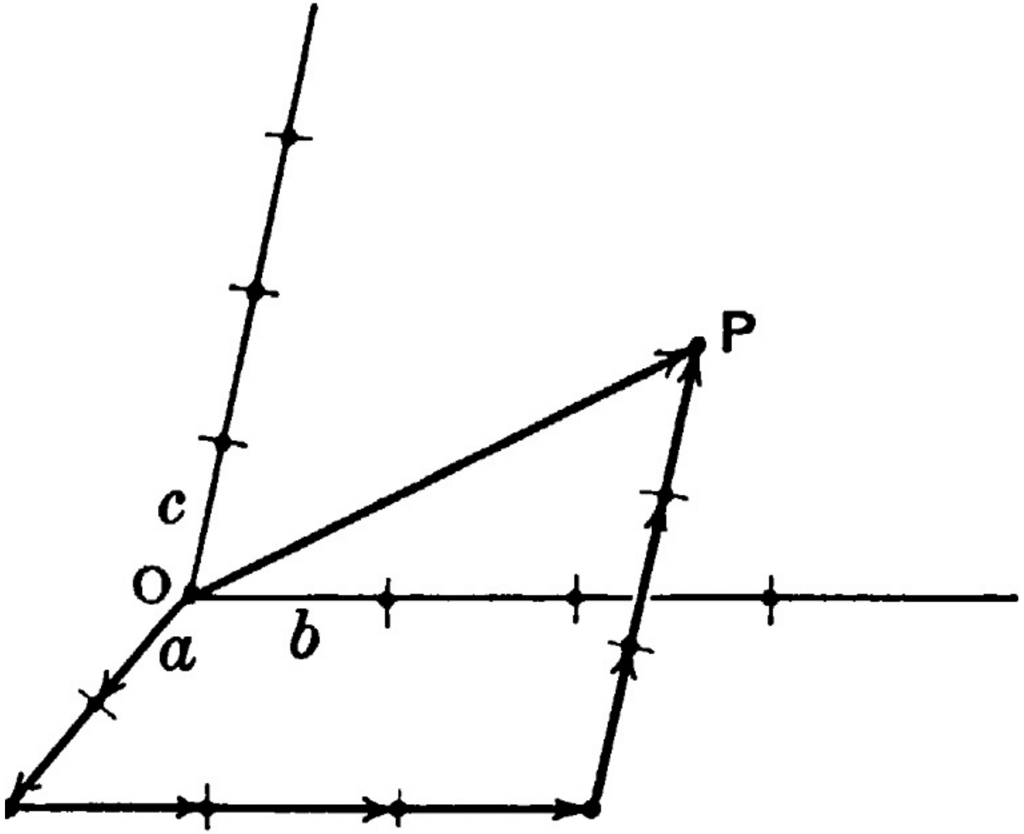


Any point in a crystal when translated with the vector will give an infinite set of points called as 'point space lattice'

An enclosed volume that spans the space in the crystal is called a cell; and a cell which encloses only one lattice point is called as primitive cell.

- Given a point lattice,

  with a translational vector $O\vec{P}$



We define three vectors and three integers

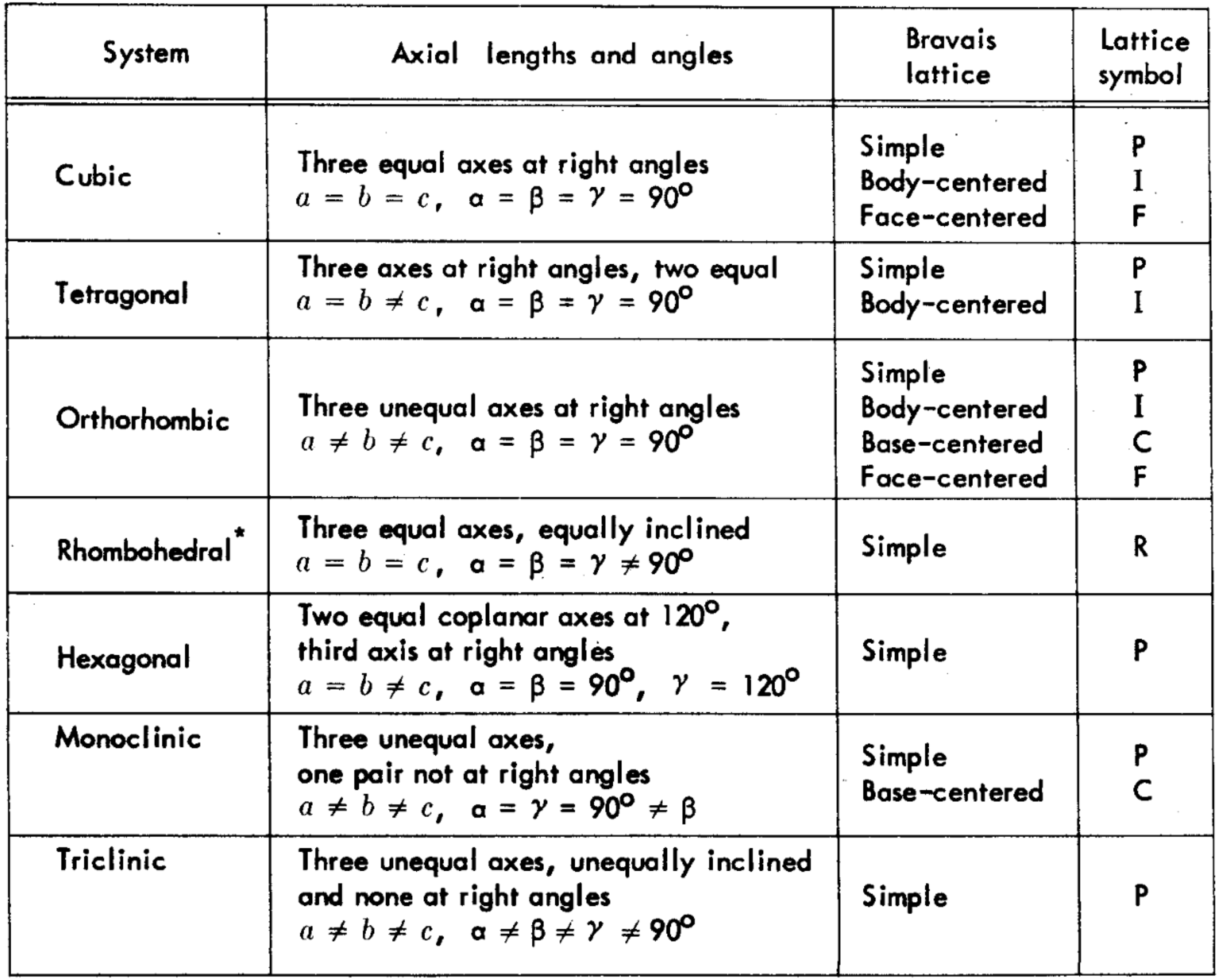
$$O\vec{P} = u\vec{a} + v\,\vec{b} + w\,\vec{c}$$

Represented by [u,v,w]

Crystal Systems

All translational vectors in 3D space is described by 3 unique non-collinear vectors:

$$\vec{a}\,,\vec{b}\ and\ \vec{c}$$



System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	P

Rational plane

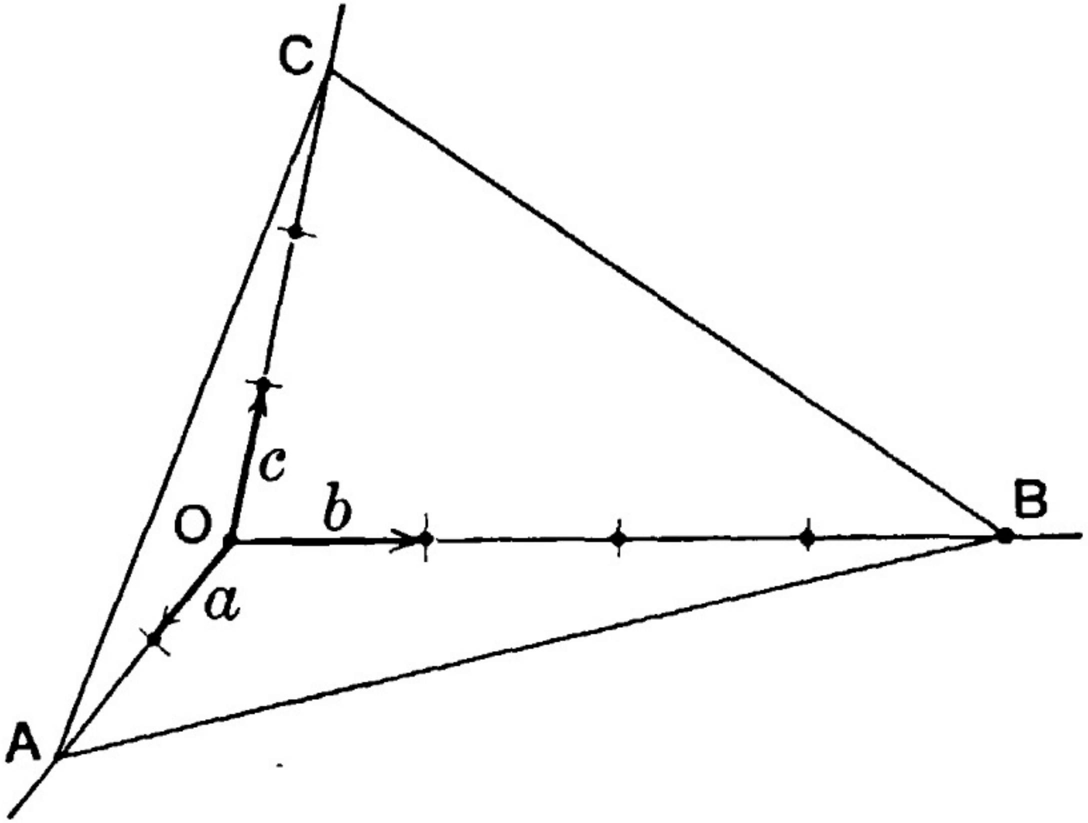
A plane containing lattice points not all collinear.

If the plane intercepts $\vec{a}$ axis at A units, $\vec{b}$ direction at B units

It can be written in the intercept form as

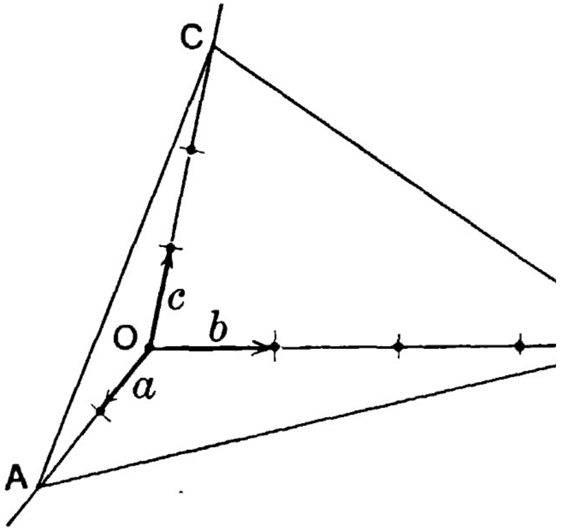
$$\frac{x}{A}+\frac{y}{B}+\frac{z}{C}=1$$

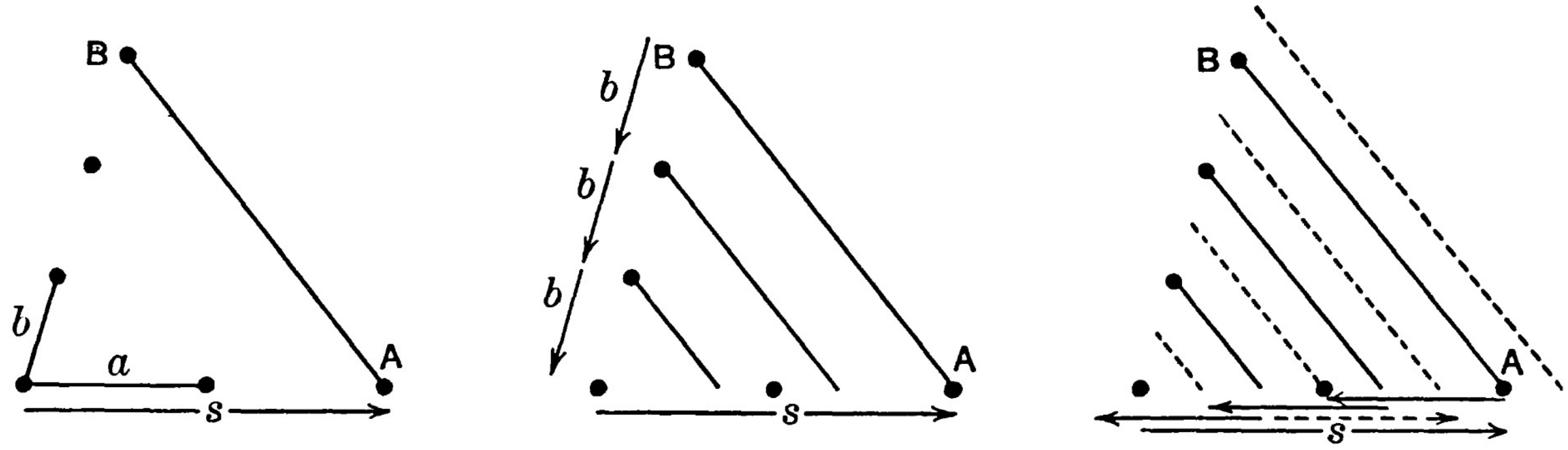
* x,y and z are along the $\vec{a}$, $\vec{b}$ and $\vec{c}$ directions.



Parallel planes

- How many (rational) planes parallel can we construct with the previous plane ?

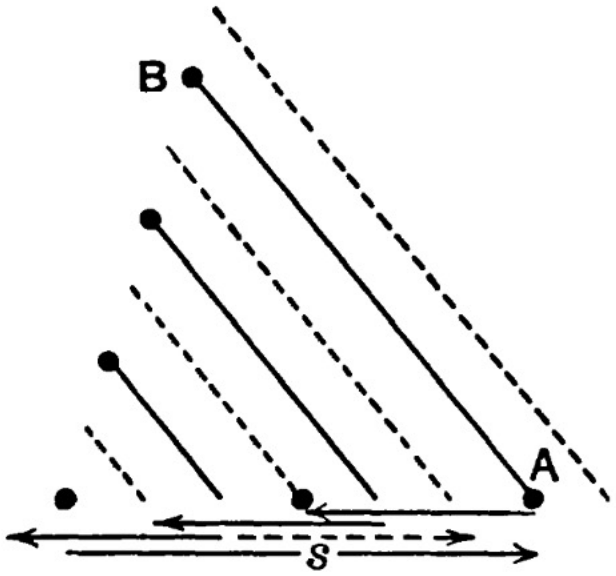




Lets look at this in 2 dimensions

So, if $A = 2\vec{a}$ and $B = 3\vec{b}$ and $C = 4\vec{c}$

- In 2D, there are 2 x 3 = 6 lines between origin and the said plane.
- In 3D, you will have A x B x C lines, if there are no common factors.



- Lastly,

  If A, and B has a common factor t

  Then the number of lines between AB and origin is A x B/t

Following this, If B and C has common factor r, and C and A has common factor s.

The total number of planes between ABC and origin is ABC/(rst)

Length of the intercept of the first plane from origin = L/(ABC/rst)

Equation of this plane is then:

$$\frac{x}{\frac{A}{\frac{ABC}{rst}}}+\frac{y}{\frac{B}{\frac{ABC}{rst}}}+\frac{z}{\frac{C}{\frac{ABC}{rst}}}=1$$

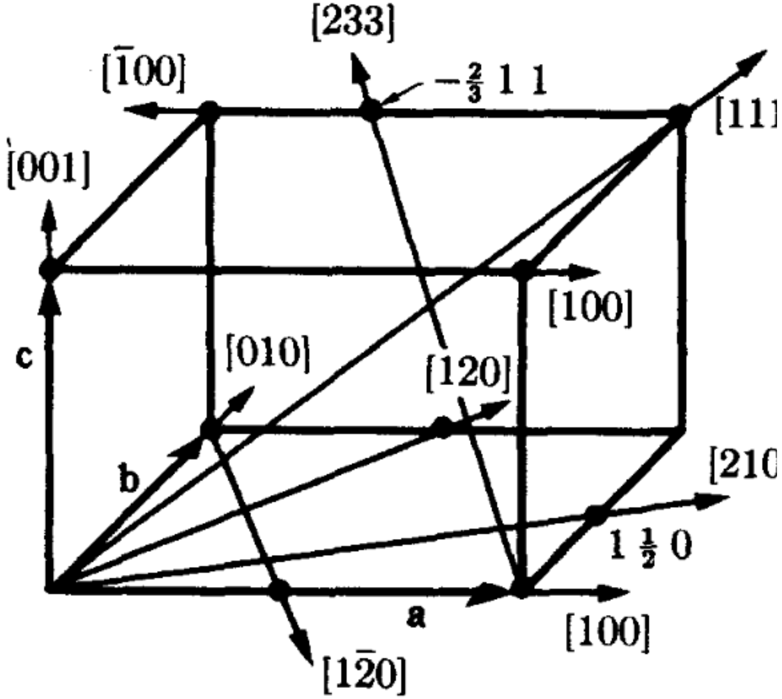
Recasting this:

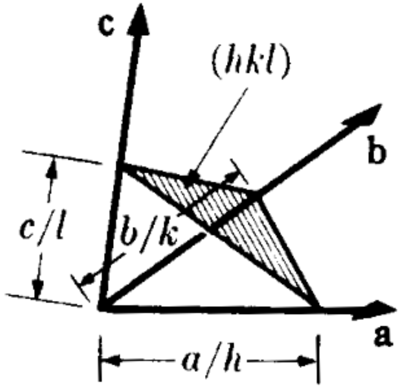
$hx+ky+lz=1$ is the equation of the first plane from the origin

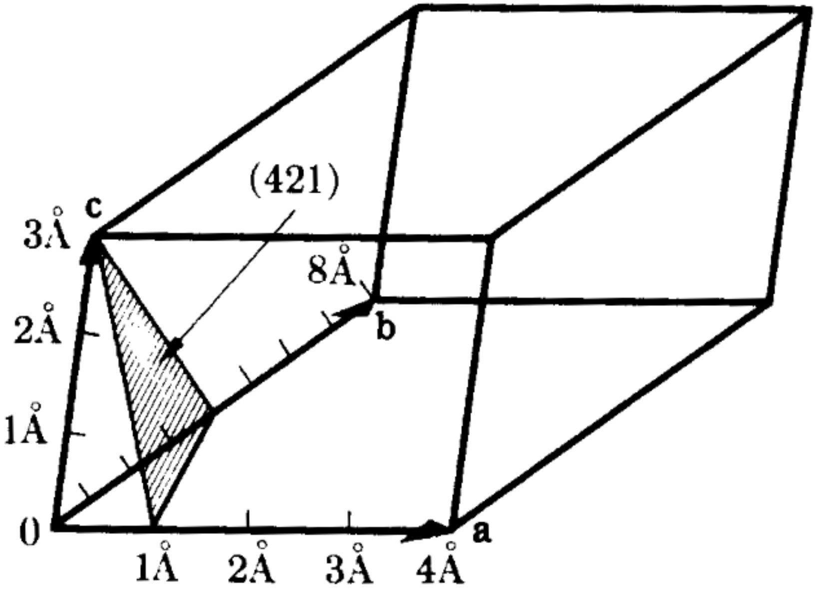
Where $h=\frac{BC}{rst}$ and $\mathrm{k}=\frac{AC}{rst}$ and $h=\frac{BA}{rst}$

So, we represent this set of planes with (h,k,l) whose intercepts are 1/h, 1/k and 1/l

Examples of indices

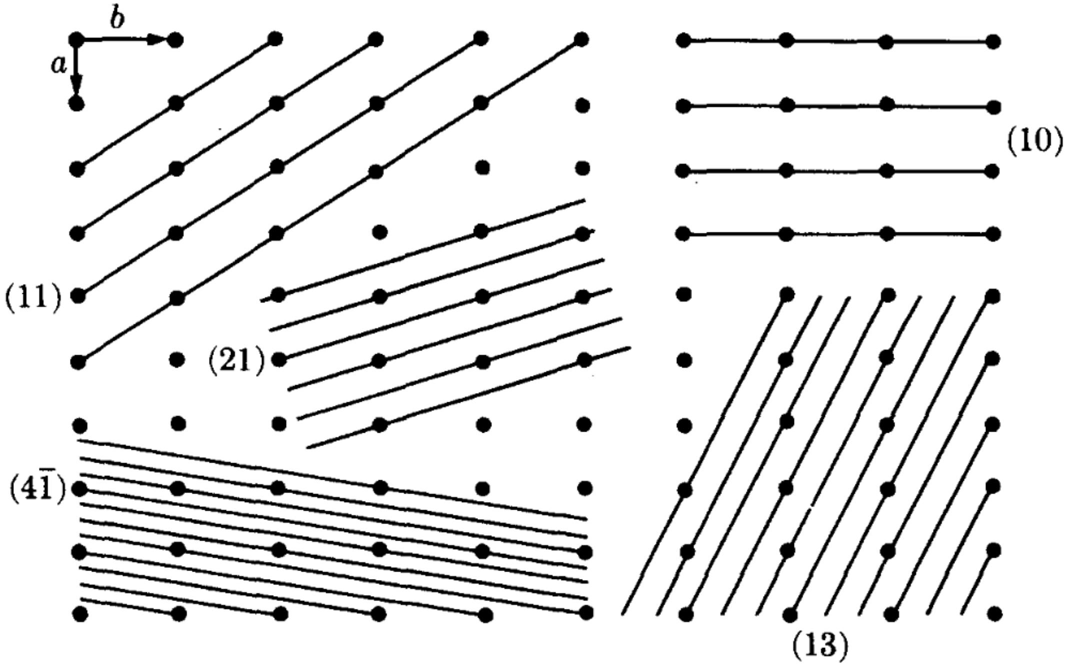






For a cubic system, the set of planes designated by (h,k,l) are separated by

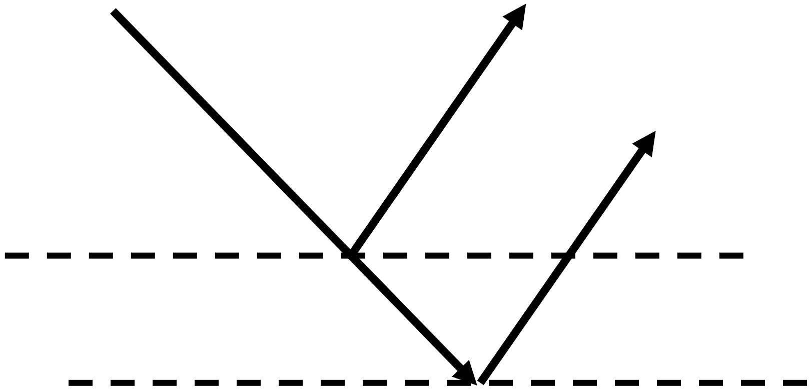
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



Larger h,k,l values, smaller interplanar spacing

Remember, [h,k,l] will always be normal to (h,k,l) in cubic systems

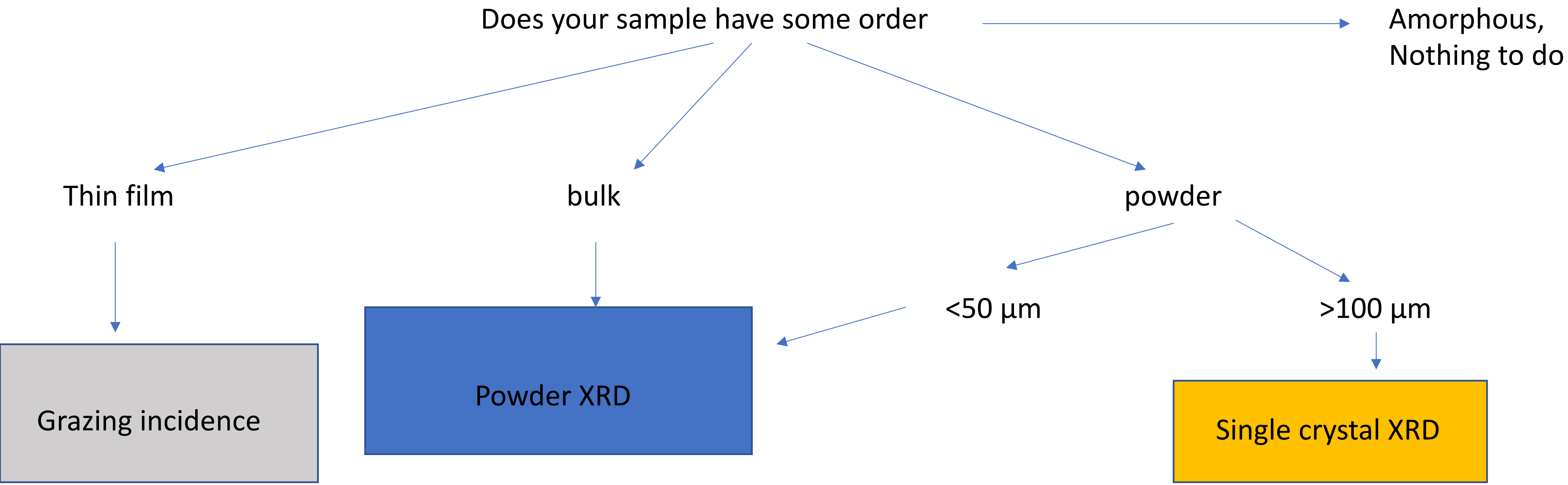
The Idea



- In crystals with atomic ordering,

Radiations reflected by independent planes have path differences proportional to the interplanar spacing!

If the path difference is integer multiple of wavelength, then ‘diffraction’ information can be used to inspect the interplanar spacing!



Does your sample have some order

Amorphous,
Nothing to do

Thin film

bulk

powder

<50 µm

>100 µm

Grazing incidence

Powder XRD

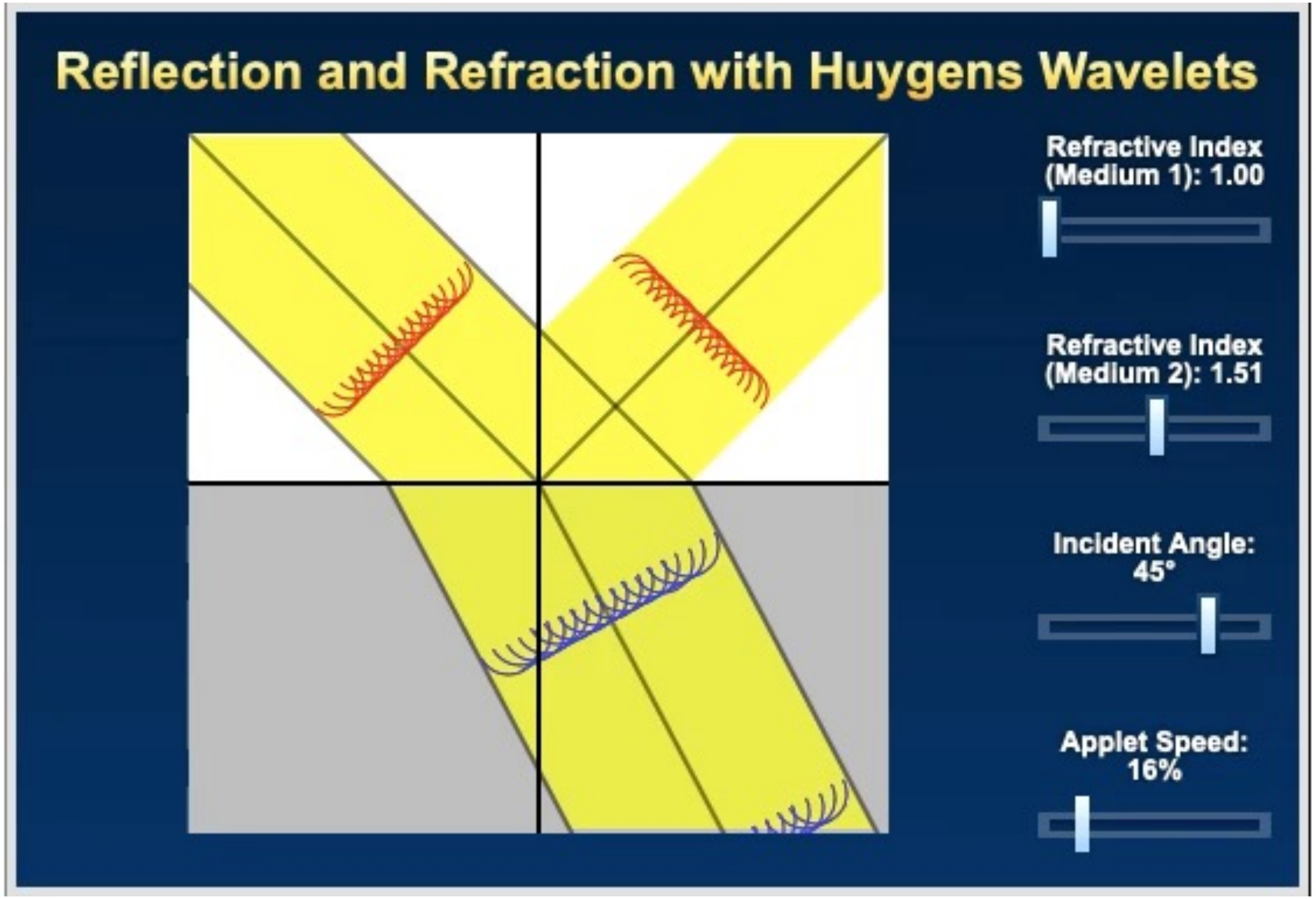
Single crystal XRD

In-plane and out of plane textures
Pole Figures
Residual Stress Analysis

Phase identification
Phase factor quantification
Out-of-plane crystal orientation
Crystallite size and Strain
Lattice parameter extraction

Crystal Structure
Lattice parameters
Atomic positions
Bond length and angles
Molecular packing density

Normal Reflection and refraction



Reflection and Refraction with Huygens Wavelets

Refractive Index (Medium 1): 1.00

Refractive Index (Medium 2): 1.51

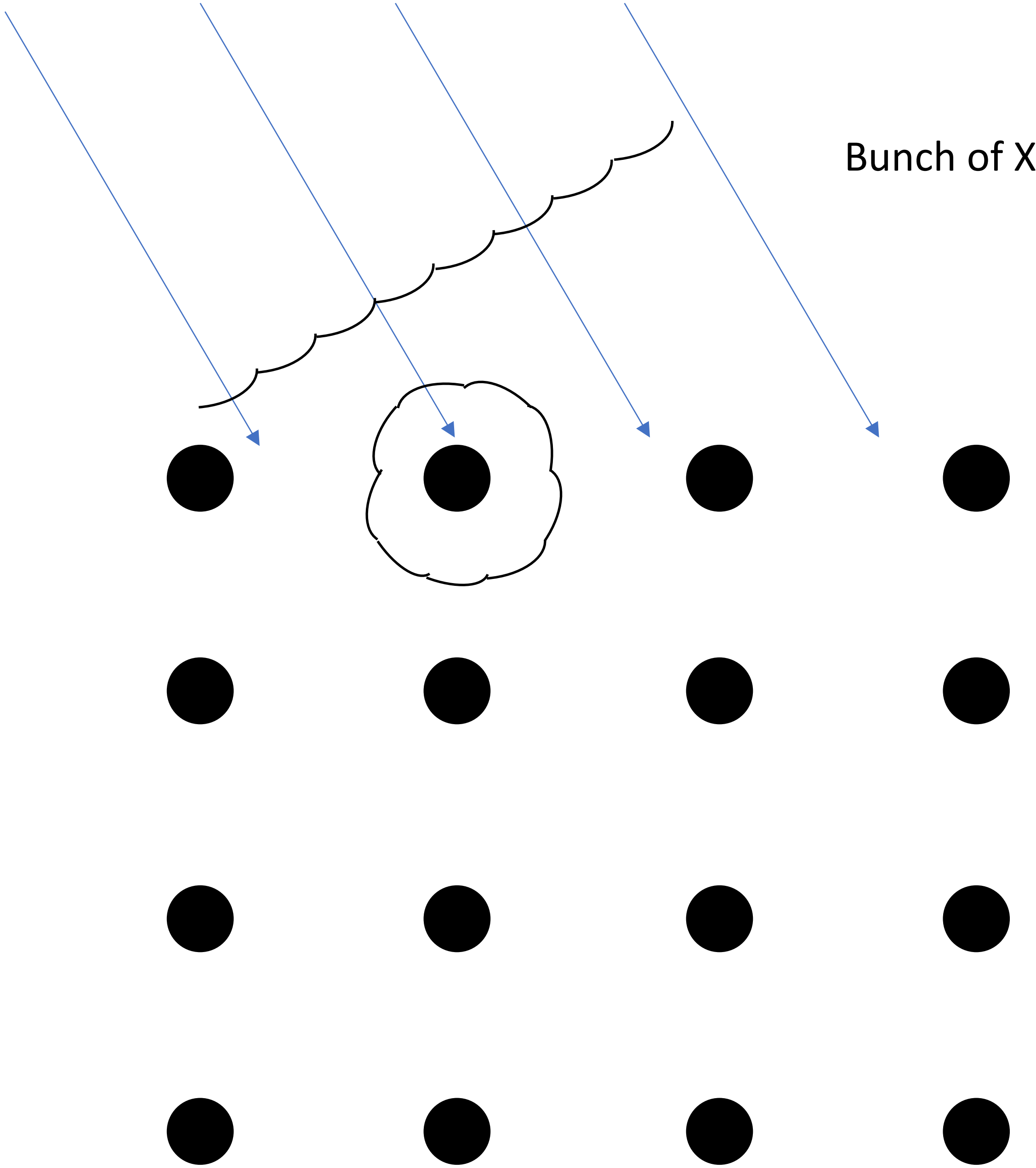
Incident Angle: 45°

Applet Speed: 16%

A normal reflection is observed when wavelets which are generated at the region of illumination destructively intersect in all direction except the one which has the name angle with the surface normal.

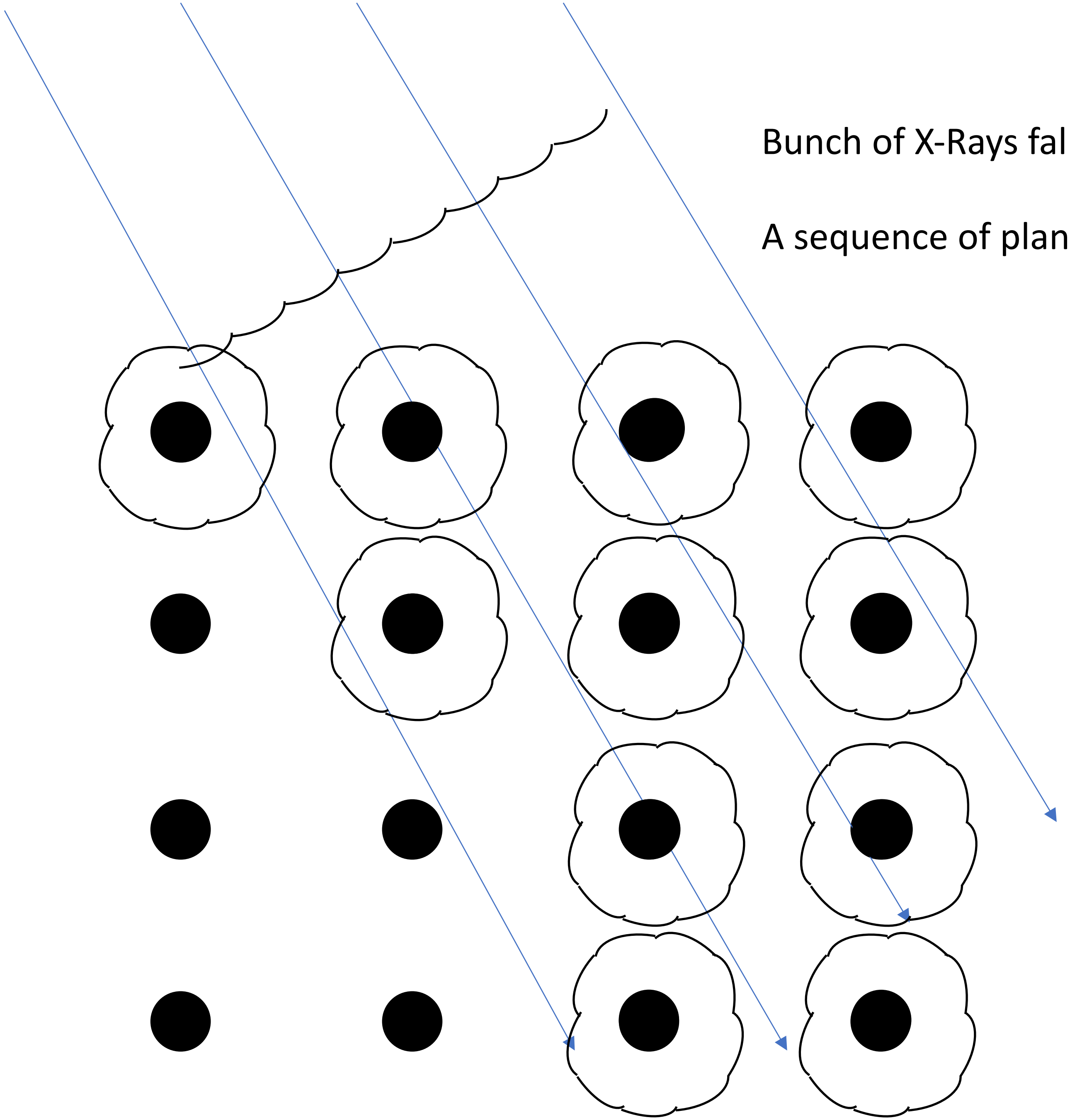
The surface atoms of the interface acts as secondary light sources.

Consider a periodic lattice



Bunch of X-Rays falling on sample

Consider a periodic lattice

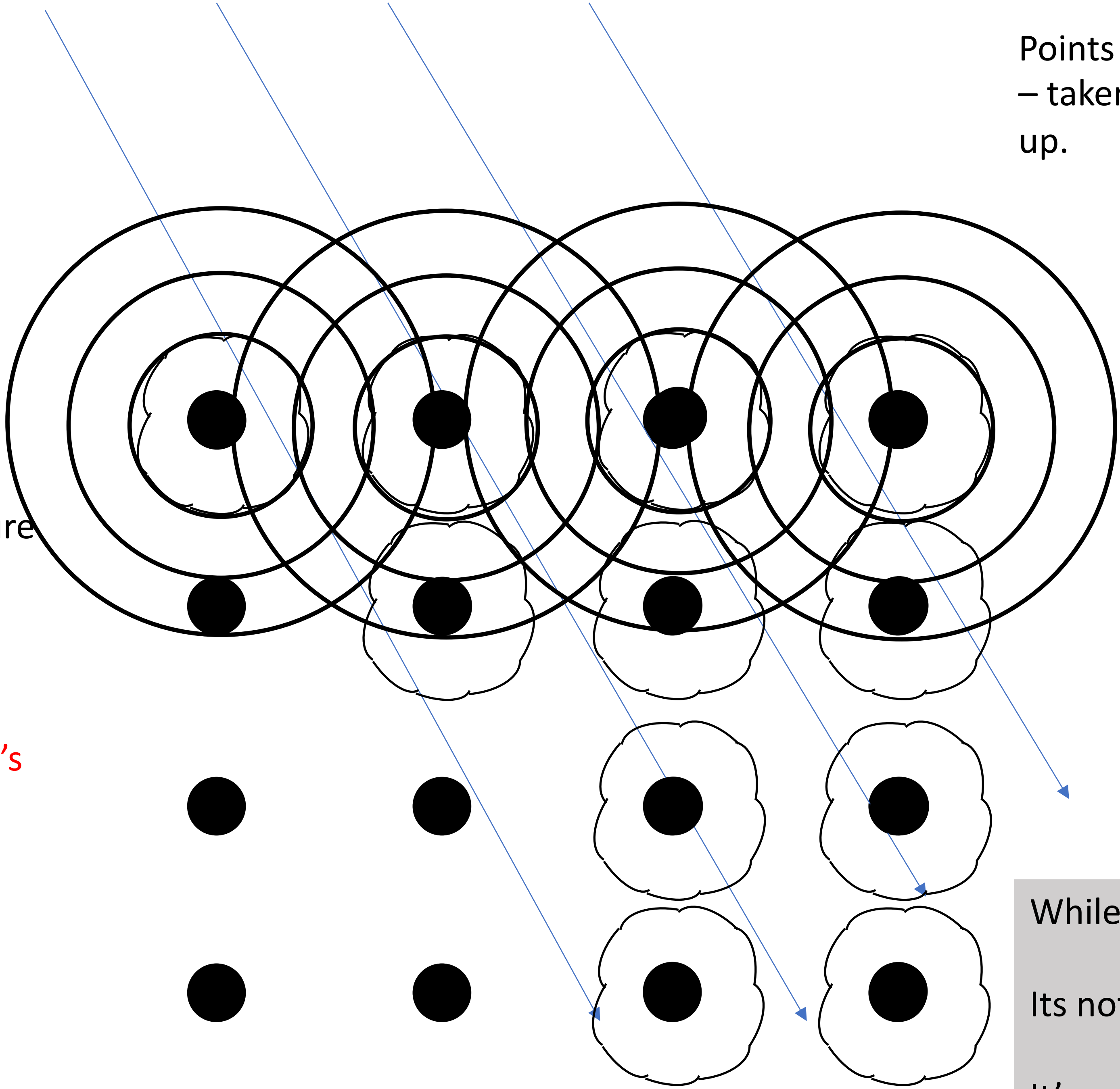


Bunch of X-Rays falling on sample.

A sequence of planes act as light sources.

Consider a periodic lattice

Points of intersection of the circl
– taken here to be say crests, ad
up.



While the surface atoms ensure that the reflection law is satisfied,

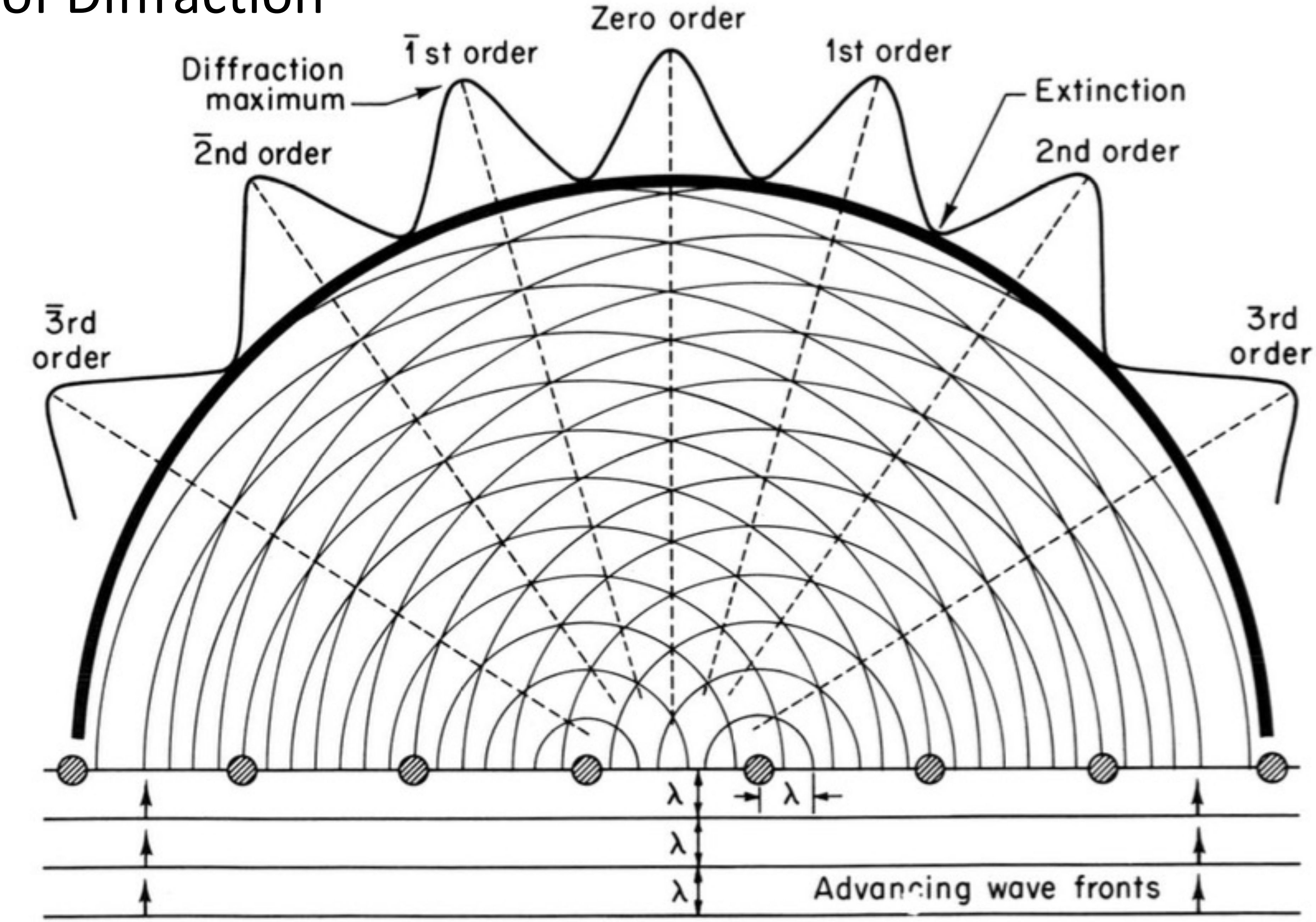
The subsequent planes in the sample ensure that the Bragg's law is satisfied

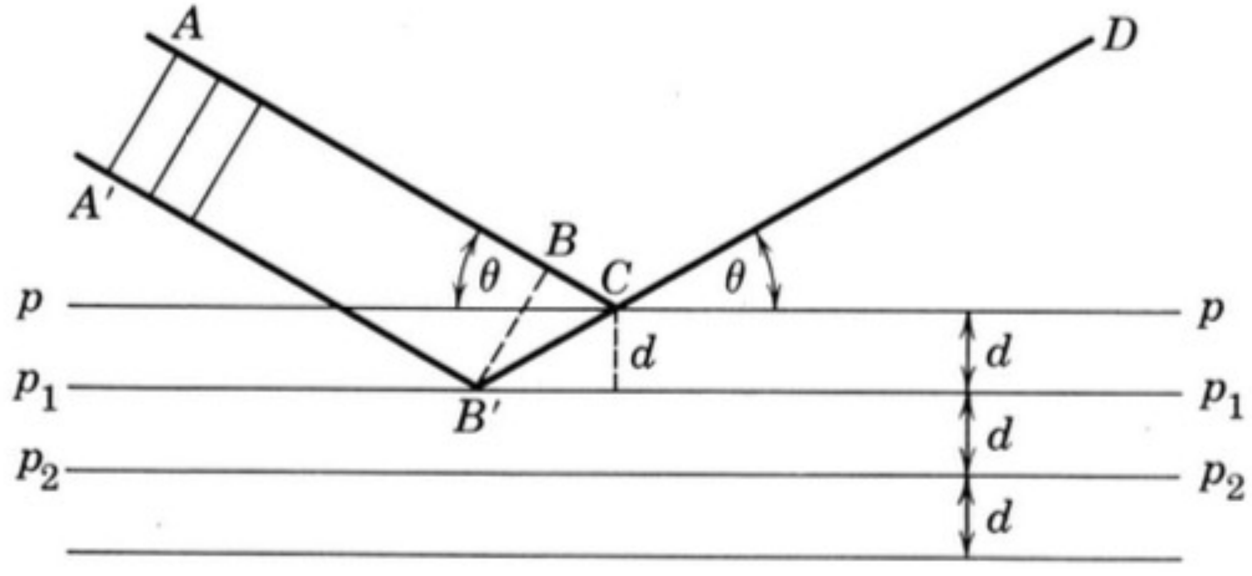
While, its is indeed reflection.

Its not purely reflection.

It's a diffraction!

Orders of Diffraction





Path difference:

$$B'C - BC = \frac{d}{\sin\theta}\,[1 - \cos 2\theta]$$

$$= \frac{\mathrm{d}}{\sin\theta}\,2\sin^2\theta$$

The condition for constructive interference: $B'C - BC = n\lambda$

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

The essential condition for diffraction

So, we write the Bragg's law for reflection as

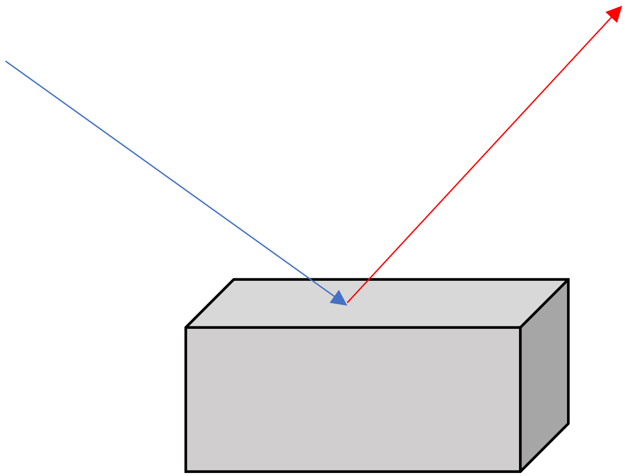
$$\lambda = 2d_{nh,nk,nl}\sin\theta$$

Remember h,k,l are inverse of planar intercepts.

Higher orders (nk,nl,nh) have a smaller d-spacing

For cubic systems

Where $d_{nh,nk,nl} = \frac{a}{\sqrt{n^2h^2+n^2k^2+n^2l^2}} = \frac{d_{h,k,l}}{n}$



For every diffracted beam with angle θ, we associate a set of planes with spacing d.

From here to identification of the plane is the idea of solving the structure.

Bragg’s law dictates the angle at which diffracted beam can be found.

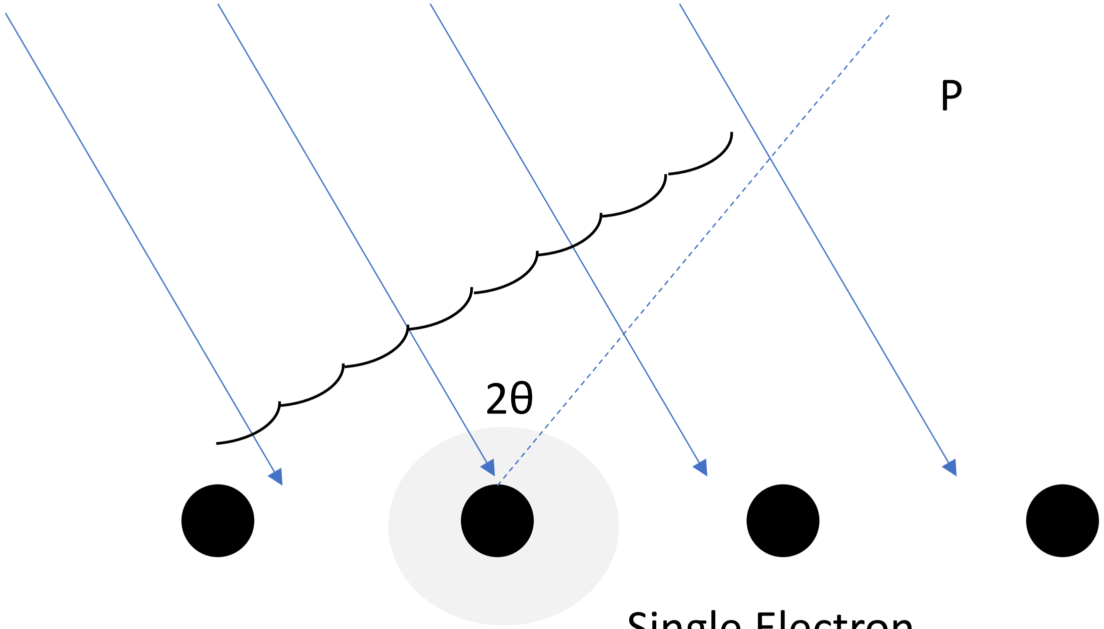
Can we estimate the intensity ?

Diffracted beam intensity depends on

1. Polarization factor
2. Lorentz/velocity factor
3. Atom scattering factor
4. Scattering inside a unit cell (structure factor)
5. Multiplication factor
6. Lorentz factor
7. Absorption factor
8. Temperature factor

Electron Scattering factor

Polarization factor:



Single Electron wavefunction

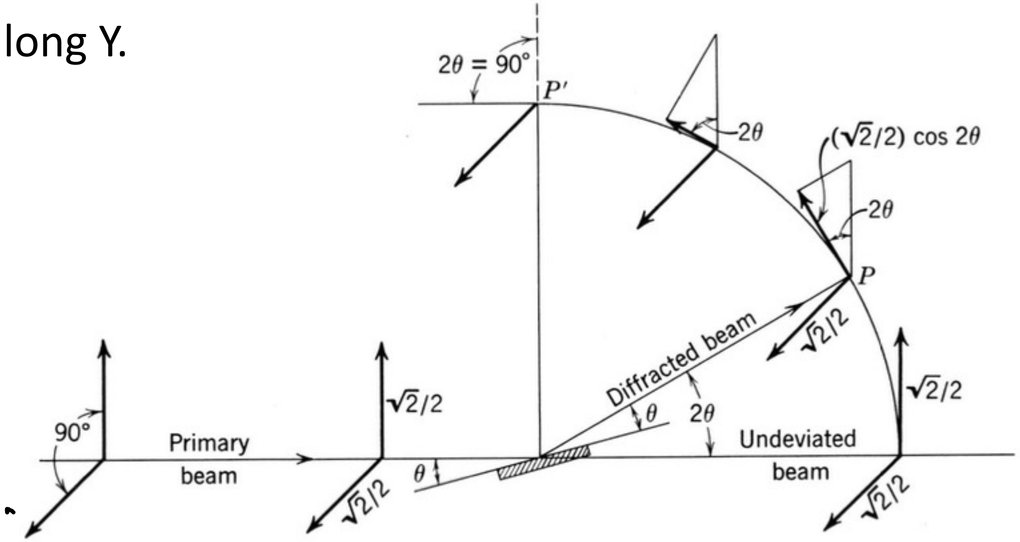
Incident beam of light is unpolarized.

However, the scattered light is polarized at higher angles.

Reason:

If electric field in incident light is along y axis,

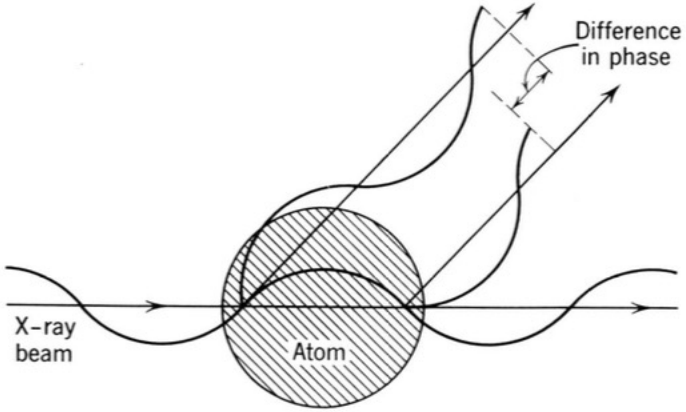
X-Rays scattered close to y-axis direction will have reduced E field along Y.



Scattering of the X-Ray from a single electron gives an intensity

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

Atomic Scattering Factor

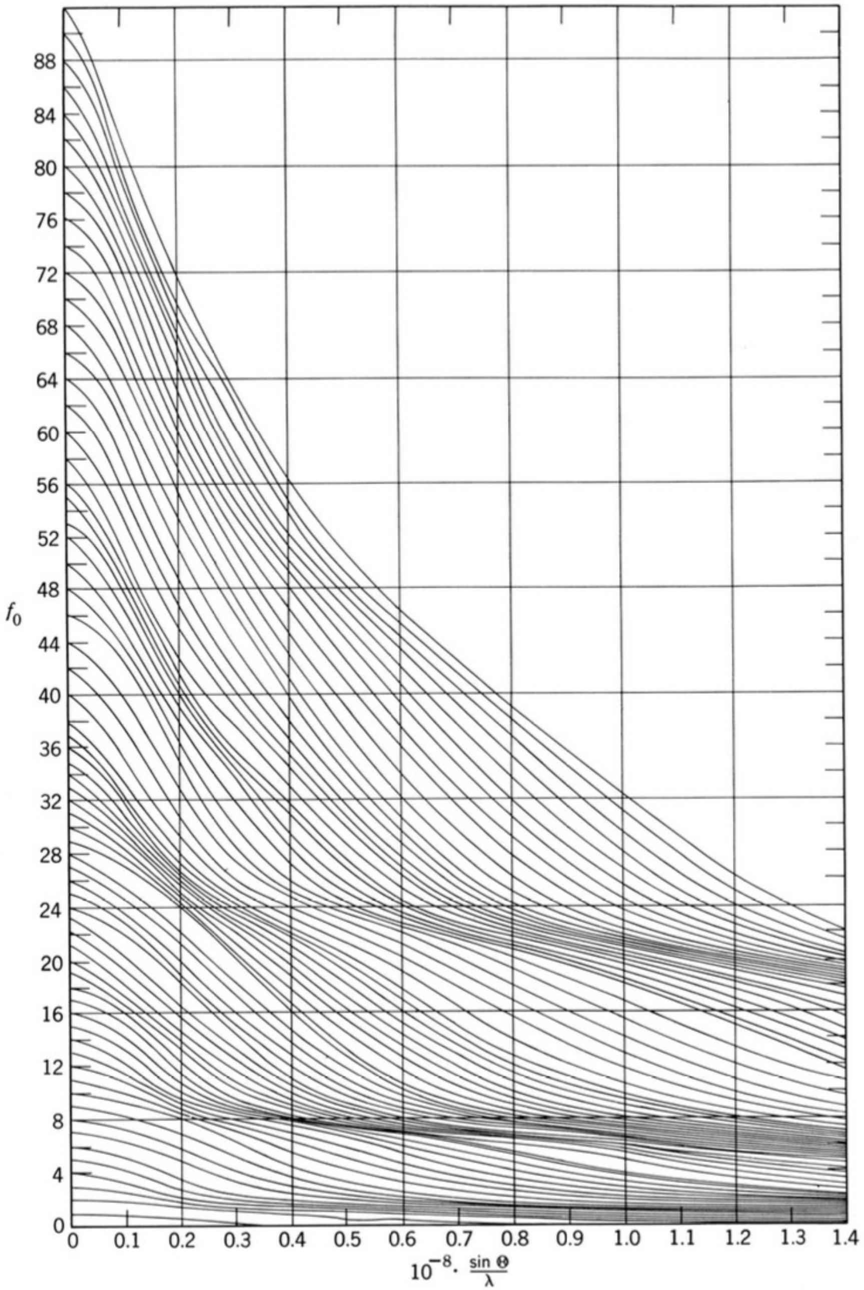


Atoms are not point sources!

If there are N electrons in an atom, the efficiency of all those electrons contributing to X-Ray scattering is represented by f_0

f_0 - ratio of scattering from the designated atom to that of a single electron at the same point.

$f_0 = Z$ at very small angles. It reduces sharpely at larger angles.



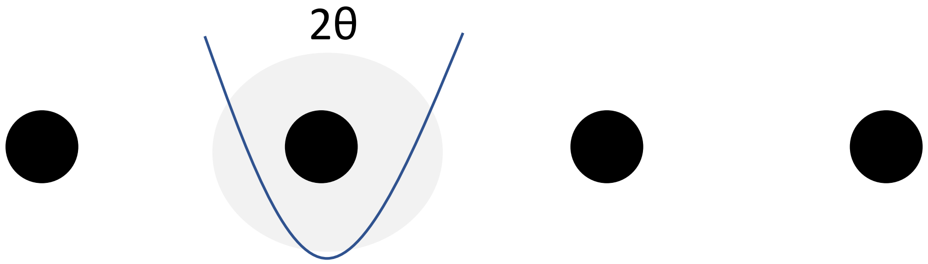
Lorentz Factor

The fraction of the sample interfacing with the X-Ray depends on θ

This is due to the slits, the fraction of crystals that can have their normals according to the Bragg’s condition

Lorentz Factor $L = \frac{1}{4 \sin^2 \theta \cos \theta}$

Temperature Factor



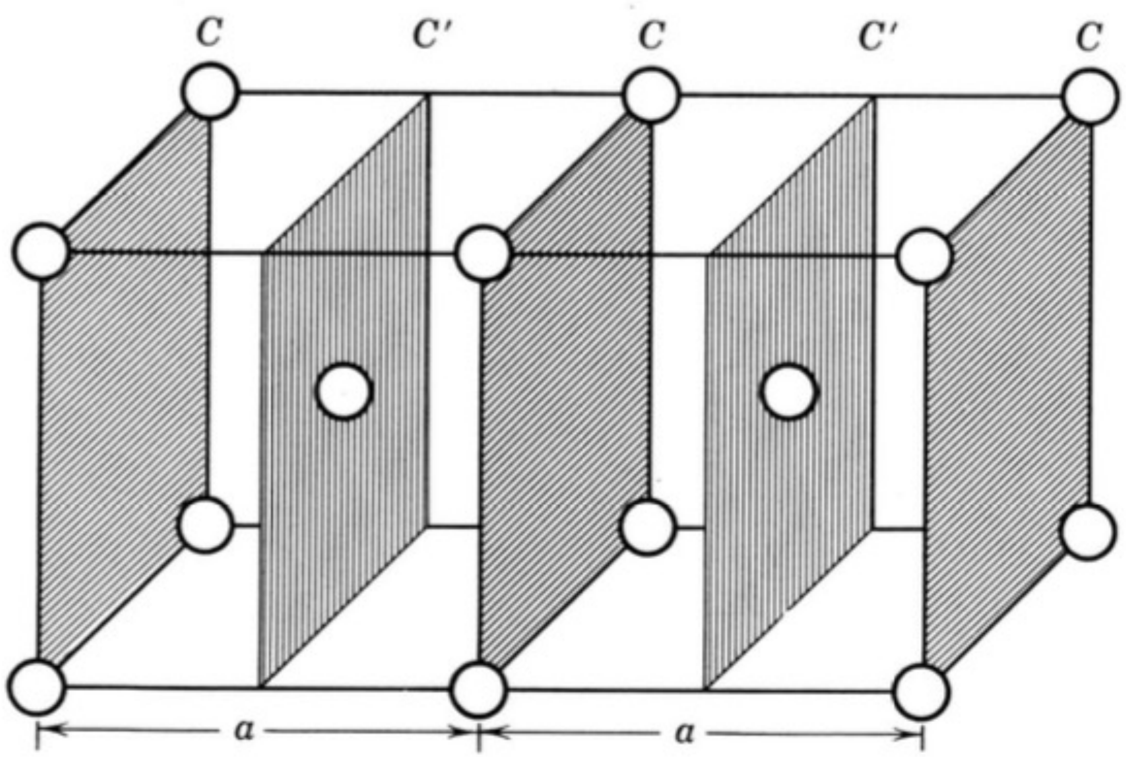
Harmonic potential

At any non-zero temperature, the atoms are vibrating about their mean position.

This disturbs the interplanar spacing and hence the total intensity of radiations in constructive interference.

Therefore, the atomic scatting factor can be scaled as $f_N \rightarrow F_N e^{-M}$

The curious case



Missing (100) planes ?

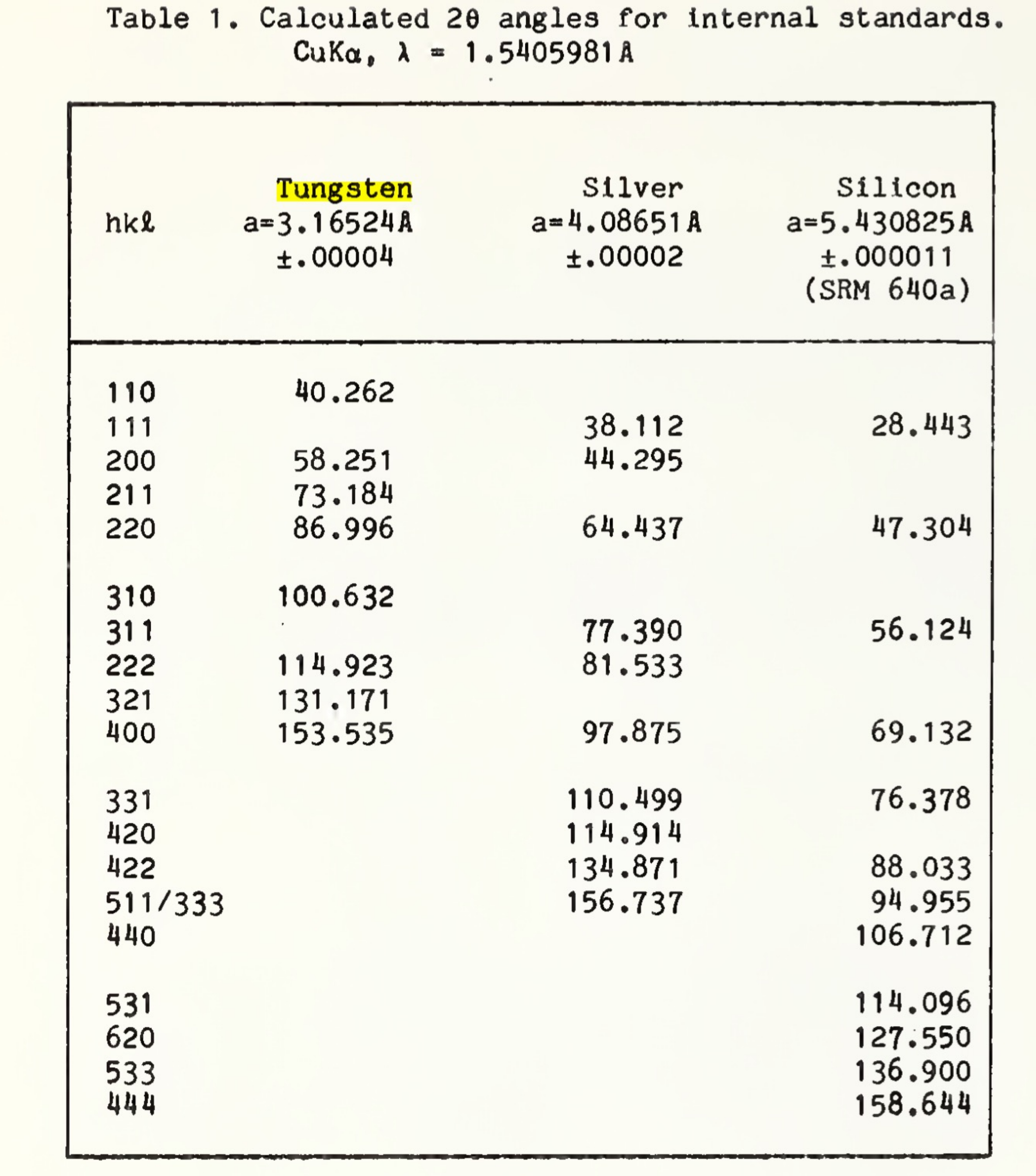
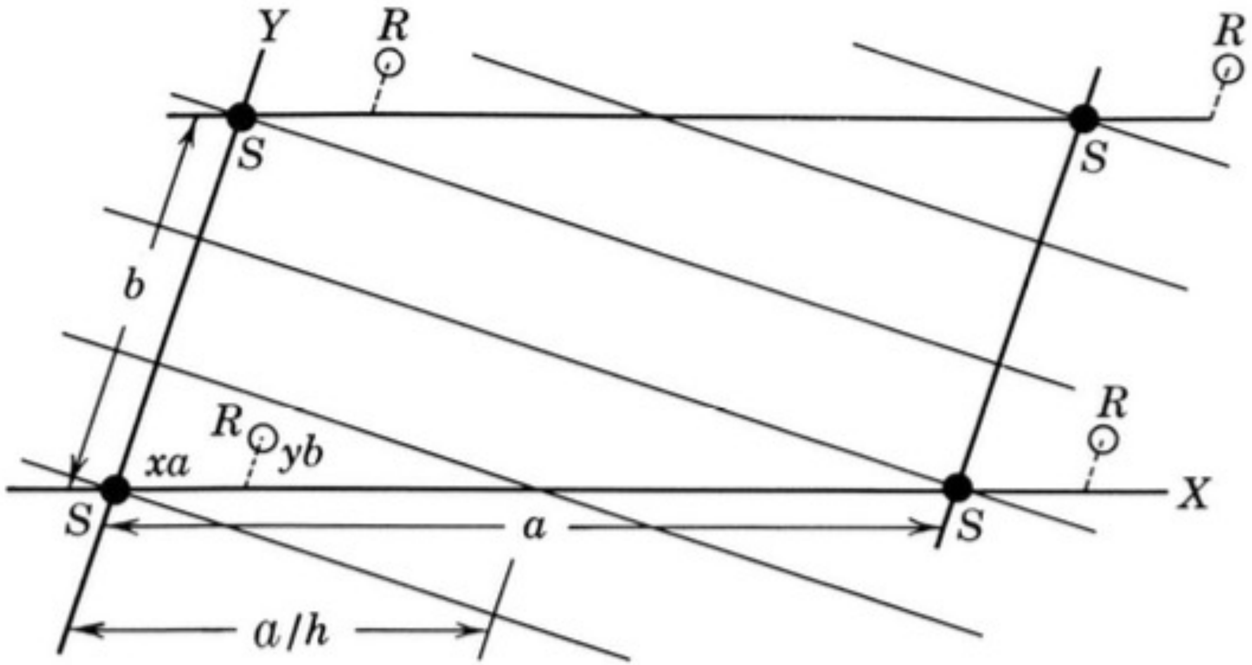


Table 1. Calculated 2θ angles for internal standards.
CuKα, λ = 1.5405981 A

hkℓ	Tungsten a=3.16524A ±.00004	Silver a=4.08651A ±.00002	Silicon a=5.430825A ±.000011 (SRM 640a)
110	40.262		
111		38.112	28.443
200	58.251	44.295	
211	73.184		
220	86.996	64.437	47.304
310	100.632		
311		77.390	56.124
222	114.923	81.533	
321	131.171		
400	153.535	97.875	69.132
331		110.499	76.378
420		114.914	
422		134.871	88.033
511/333		156.737	94.955
440			106.712
531			114.096
620			127.550
533			136.900
444			158.644



Consider a simple example in 2D:

Atom S, separated by lattice constants a and b

For any plane with index (h,k) seen in the example as (2,3) – divides the lattice constants by the same number.

For constructive interference – a phase difference of 2π is needed along $\vec{a}$ direction in distance $\frac{a}{h}$

a phase difference of 2π is needed along $\vec{b}$ direction in distance $\frac{b}{h}$

If we insert an additional atom at (xa,yb)

Phase difference added at Bragg's condition is : $xa * \frac{2\pi}{a/h}$ along $\vec{a}$

We define the additional phase to be $\phi_a = 2\pi h * xa/a$

In three dimensions, then the extra phase included due to an atom at xa,yb,zc is

$$\phi_R = 2\pi(hx + ky + lz)$$

Where $x = xa/a$ - is the lattice constant normalized x position of the new atom.

Structure Factor

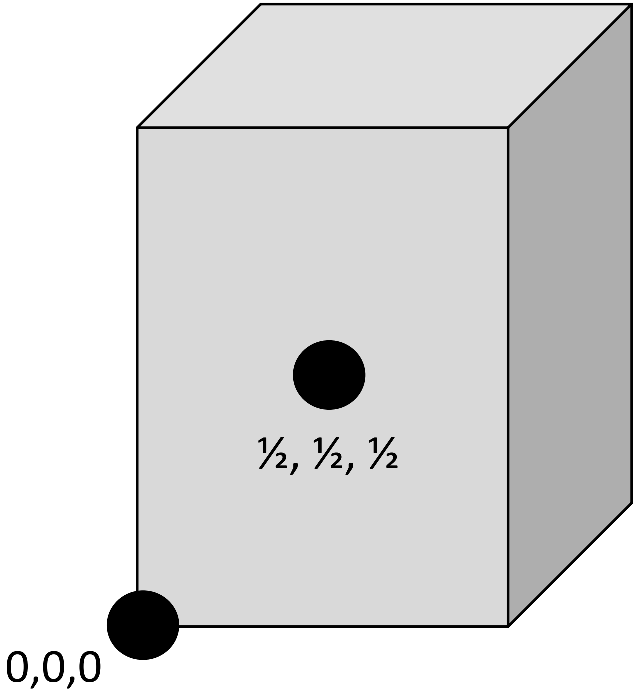
Consider the situation where

If there are n atoms in a unit cell;

With normalized offsets (u_i, v_i, w_i) from the cell origin.

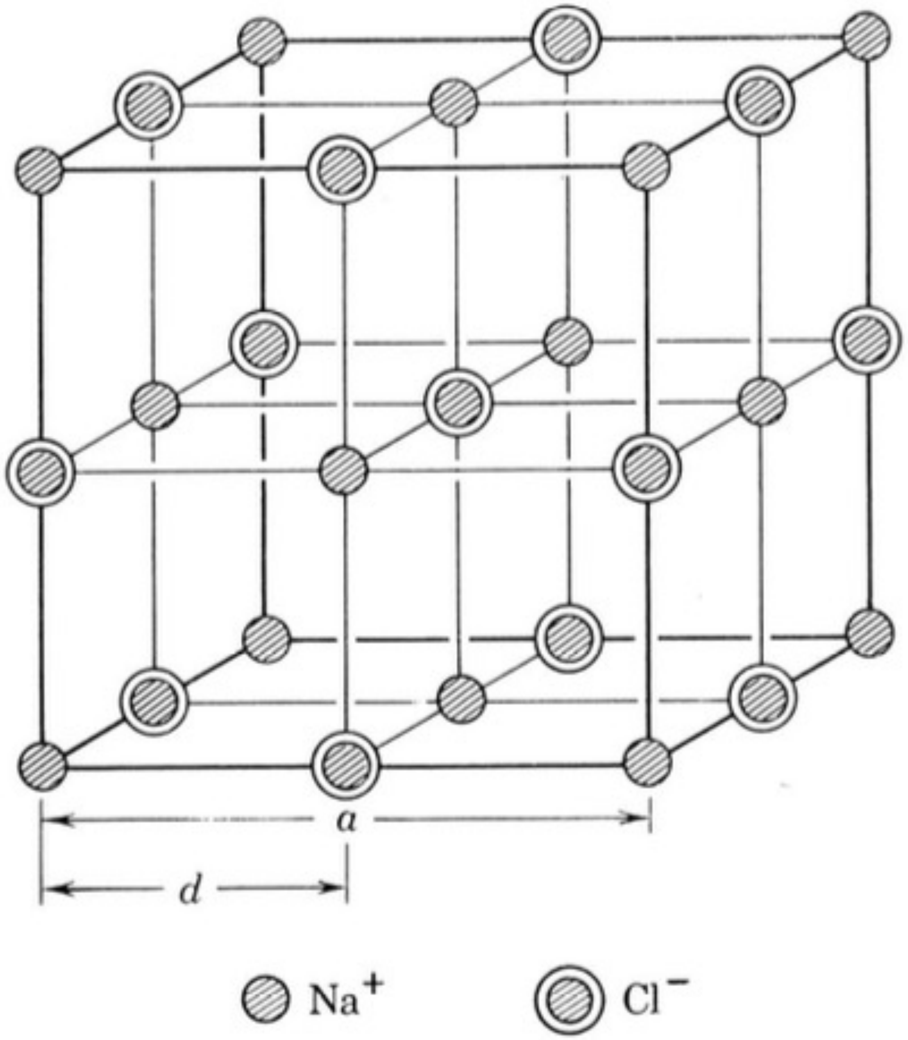
The phase difference $\phi_i = 2\pi(hu_i + kv_i + lw_i)$

Total phase difference $F = \sum_1^n f_n e^{i\phi_i}$

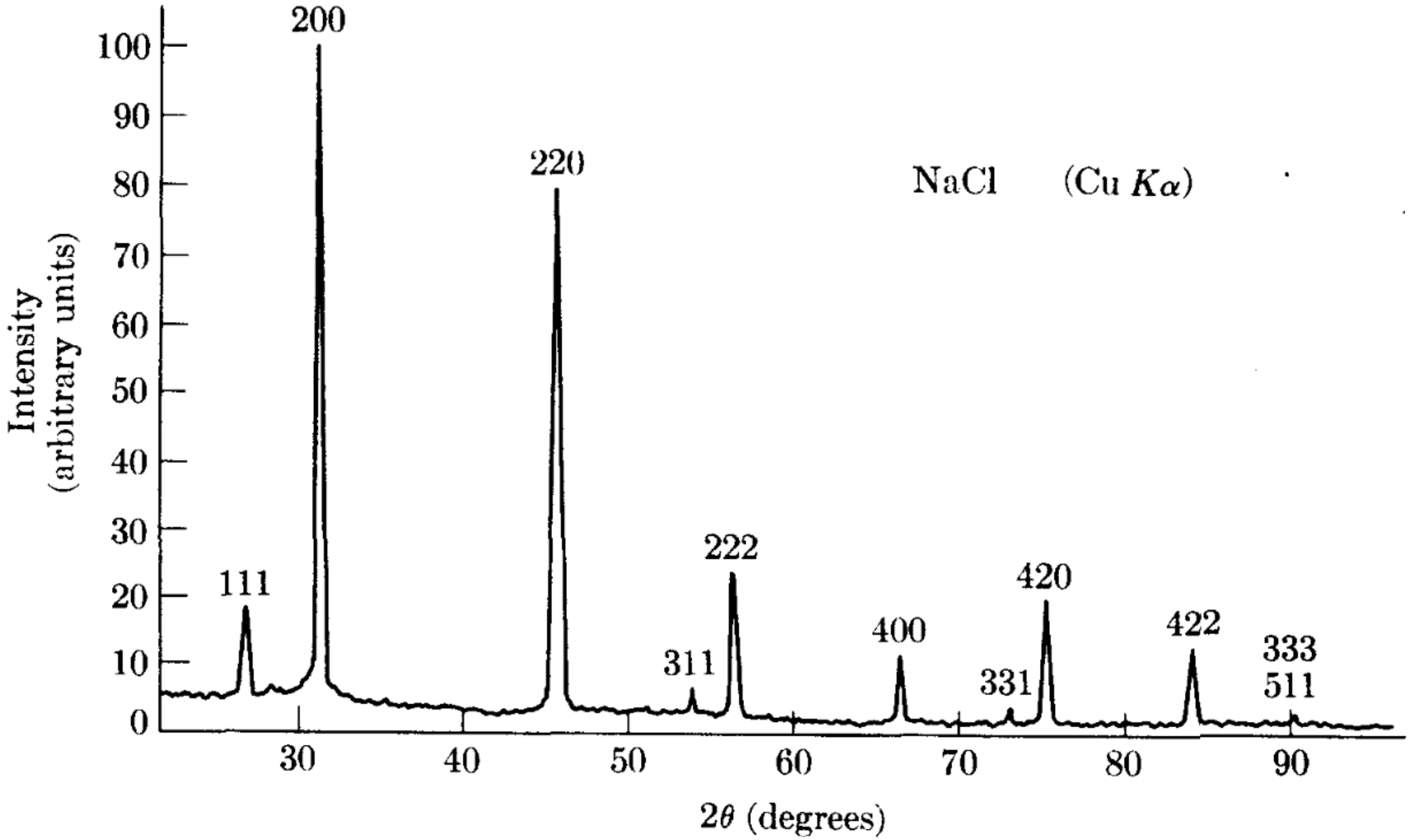


Therefore, for h,k,l = 100, the structure factor for BCC -> 0

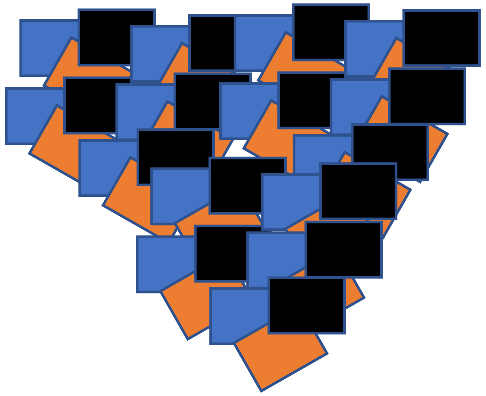
Structure factor for NaCl:



X-Ray Measurements on NaCl



Multiplicity in polycrystal



In a polycrystalline film, different grains with varying orientation are possible.

In a truly random mixture, (100),(010),(001), (-1,0,0),(0,-1,0),(0,0,-1) will occur with equal probability.

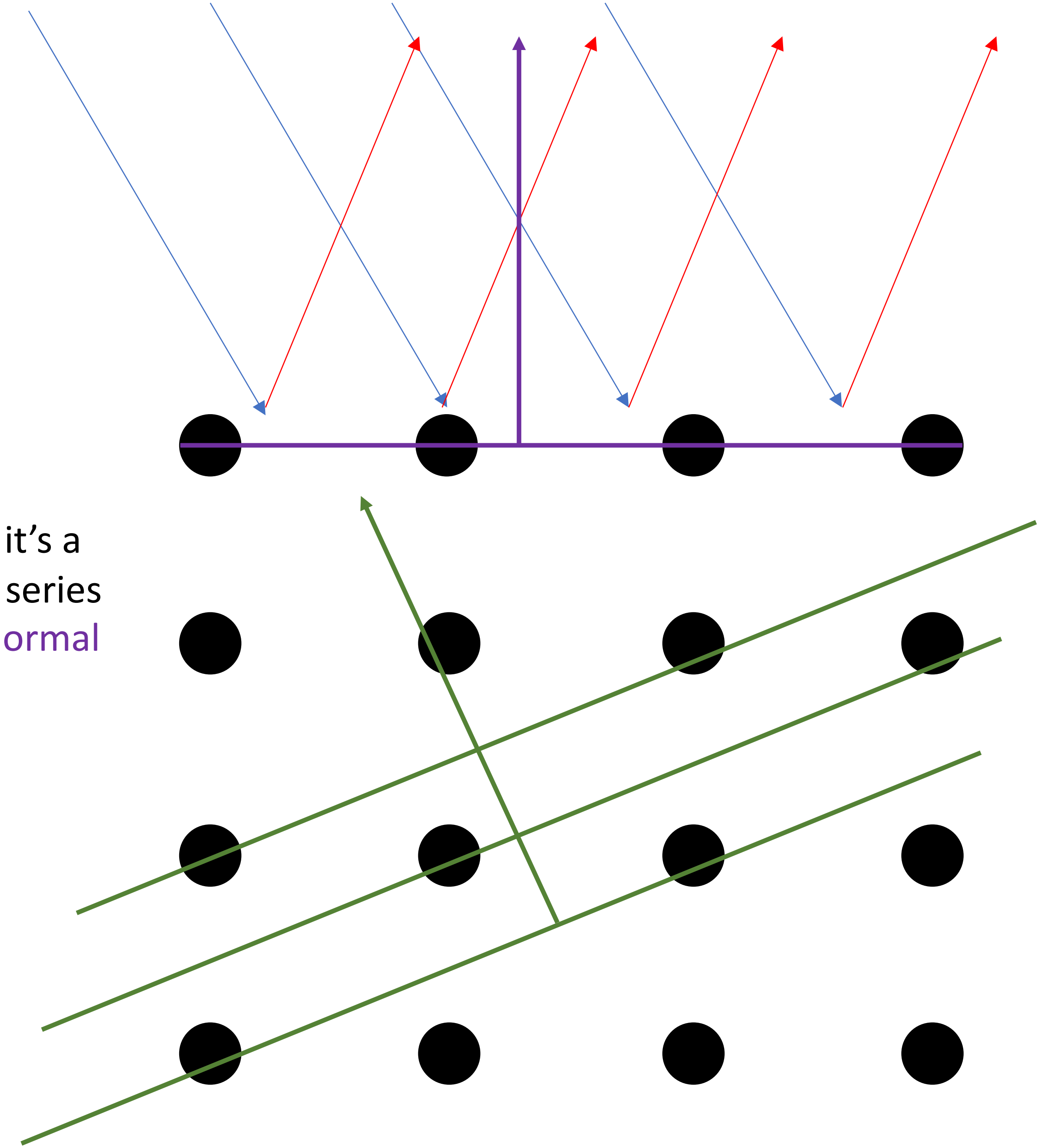
However, independent of what is the orientation, all of them will diffract at same 2θ.

Thus, the multiplicity $p\{100\} = 6$

On similar lines the multiplicity of $P\{111\} = 8$

The ratio of peak intensity of 111 / 100 = 4/3

The total intensity is then given by $I = |F|^2 p \, \frac{\left(1+\cos^2 2\theta\right)}{\sin^2 \theta \cos \theta} e^{-2M}$



Bragg's Idea:

A set of plane diffracts such that it's a specific case of reflection from a series of planes, with a defined plane normal

Is that the only plane that can diffract as if its reflection ?

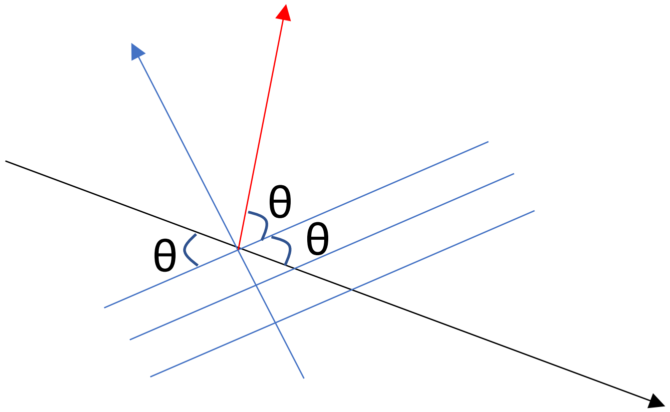
NO!

There can be infinitely many possibilities. Each of which has a different plane normal and the diffracted beam appears to be specularly reflected.

Experimental XRD

Bragg’s condition is necessary!

The incident beam is reflected at some plane normal!



If θ is the angle between incident ray with the planes, the diffracted beams are always at 2θ to the transmitted beam.

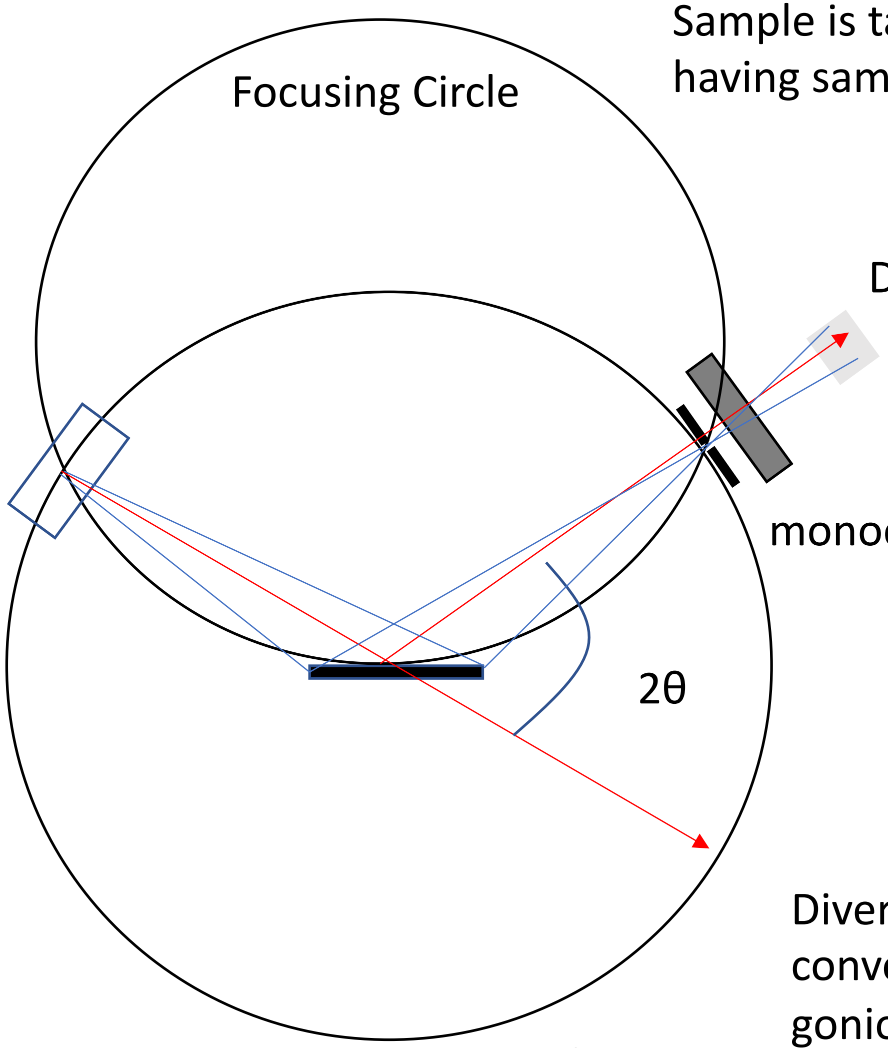
How do we now construct a device to identify all the planes in the system ?

1. Set the source and detector always at Bragg’s condition and look for the beam
2. Keep the source constant and rotate a crystal to expose all the planes
3. Send in a broad band X-Ray source and record on a photographic plate!

Geometries of measurement

The source and the detector moves on the goniometer circle

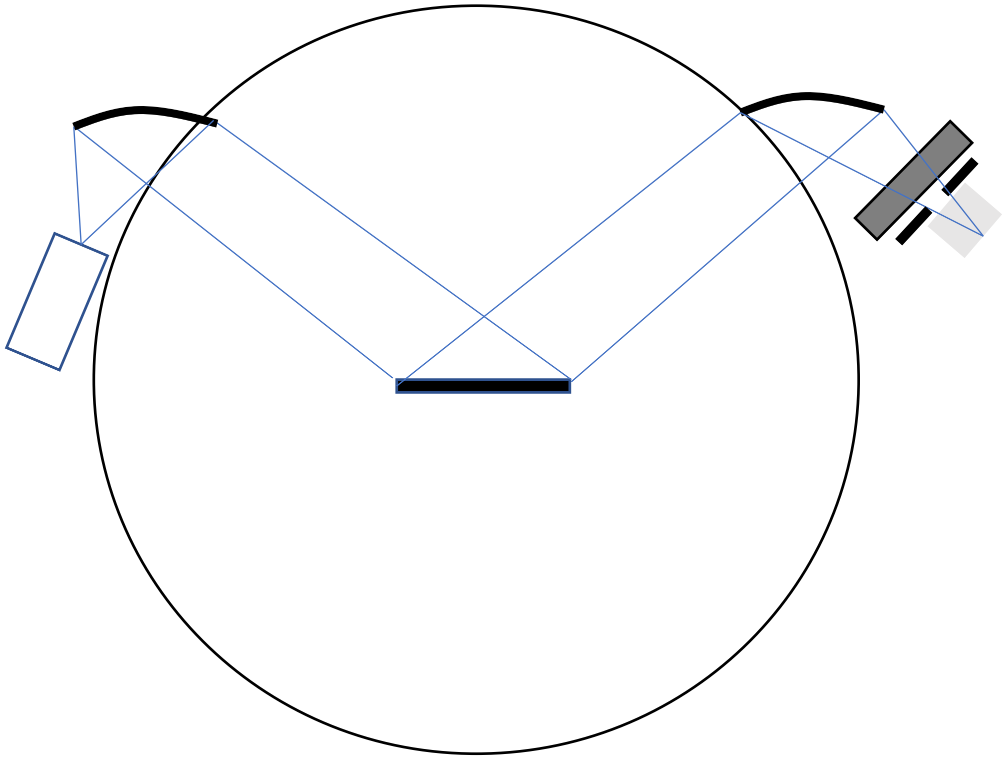
Bragg-Brentano



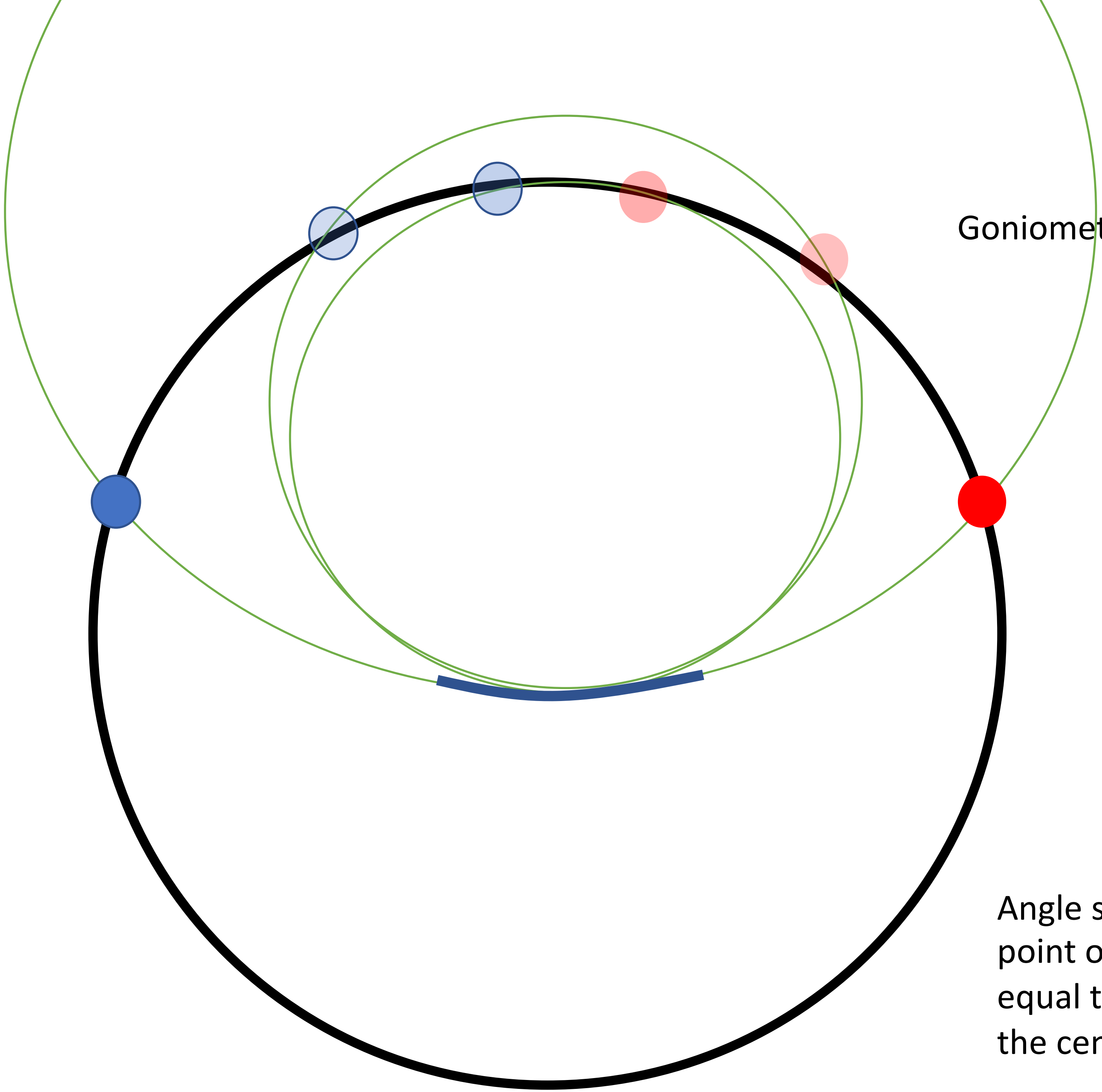
Sample is tangential to the focusing circle having sample, source and the detector slits

Divergent rays are converged again on the goniometer circle

Parallel beam



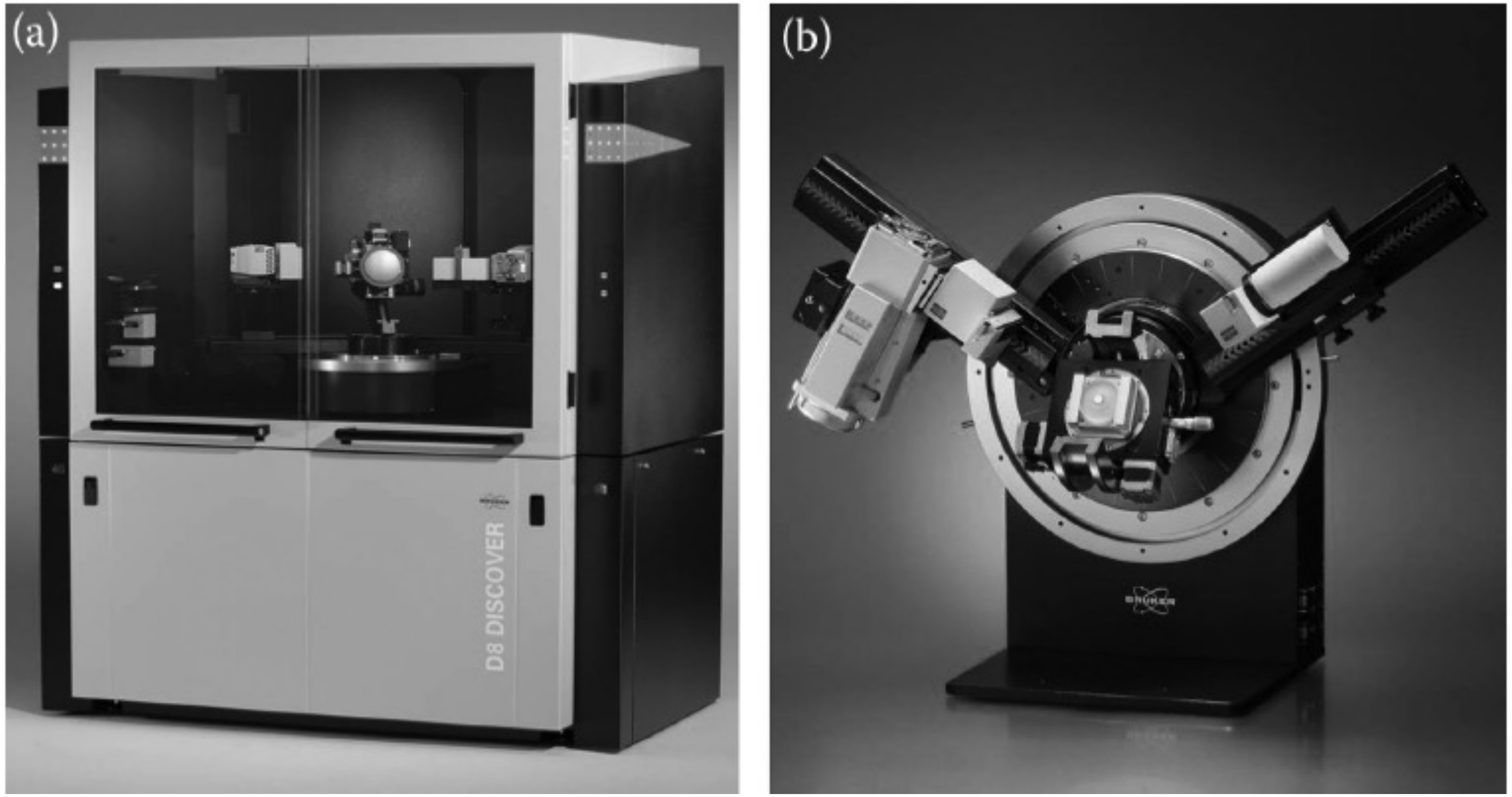
Parafocusing



The incident beam though diverging subtends closely similar angles to the entire sample

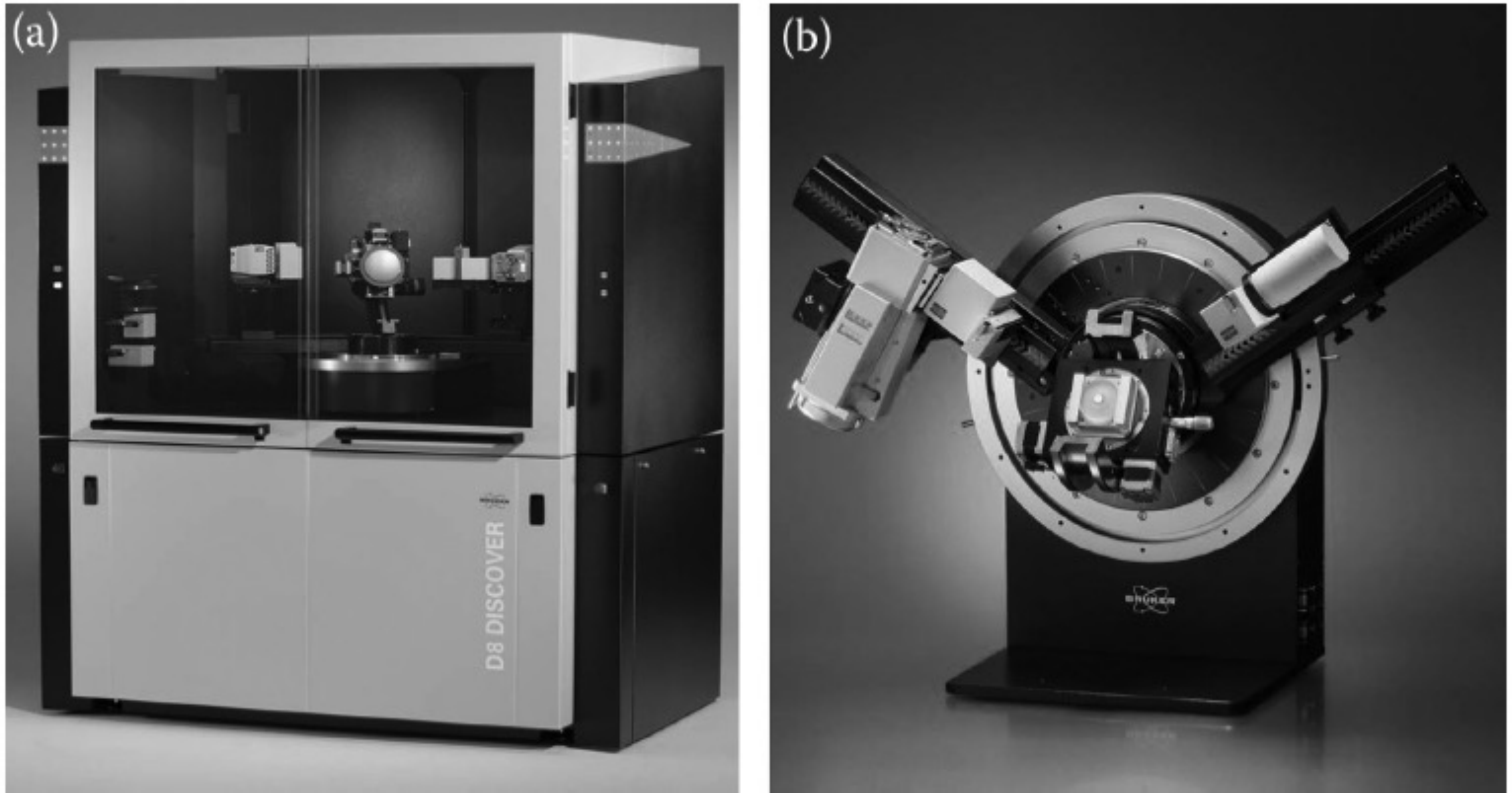
Angle subtended by an arc on any point on the remaining circle is equal to half that it subtends at the center

Typical commercial X-Ray diffractometer

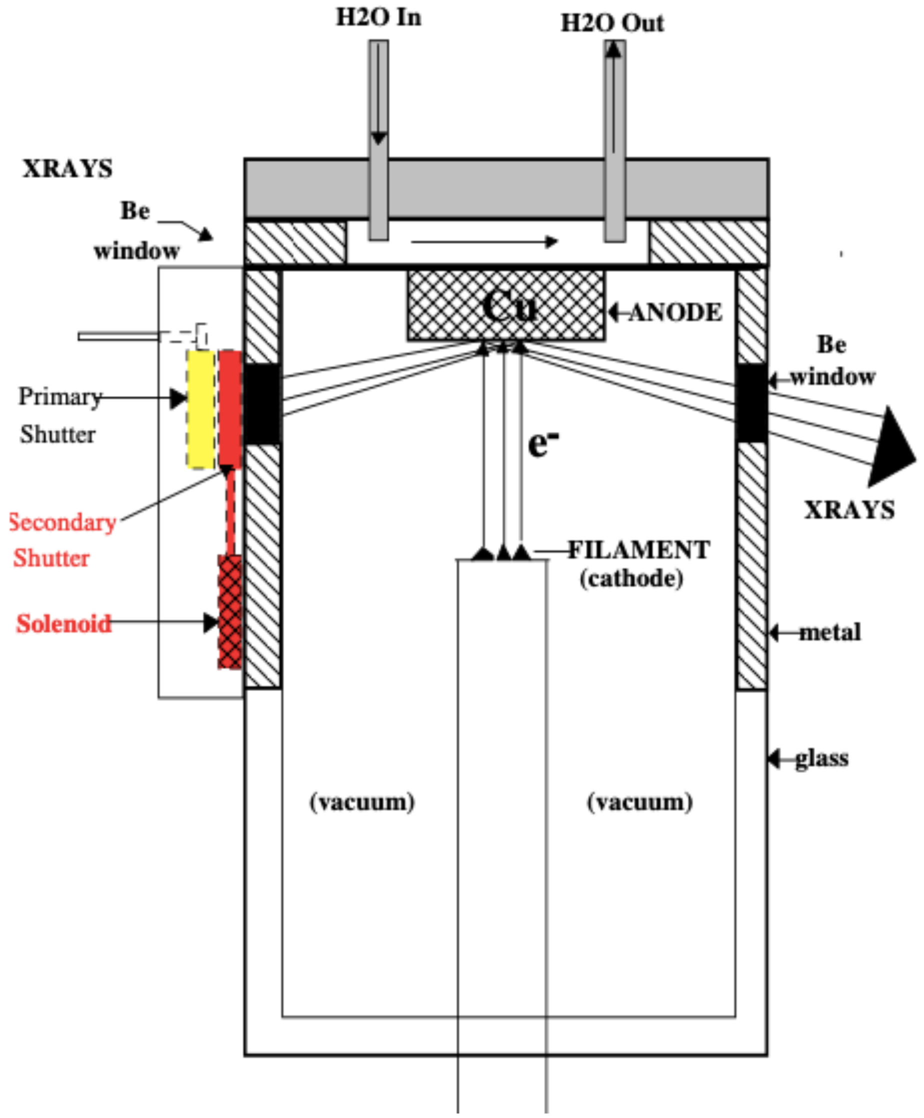


Parts of a typical X-Ray diffractometer

- X-Ray source
- Monochromators
- Ray optics
- X-Ray detectors
- Stage holders



Xray tube



- Xrays exit the tube via the Be windows.
  - Because Be has low mass absorption coefficient
  - Shutters are present at the exit to protect the users.
  - The walls, windows are cooled to prevent radiation damage.

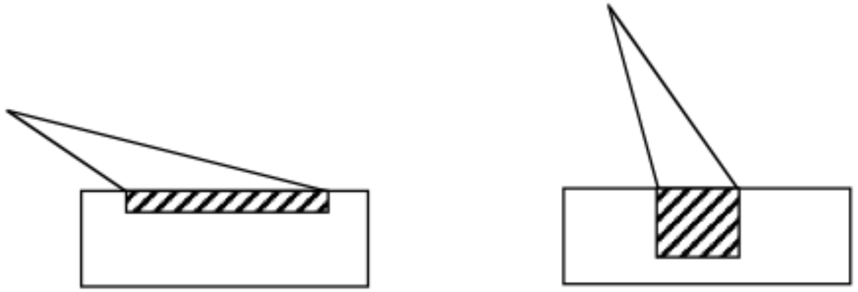
Beam Conditioners

X-Rays are divergent from the source and has different wavelengths.

Divergence is controlled by divergence slits

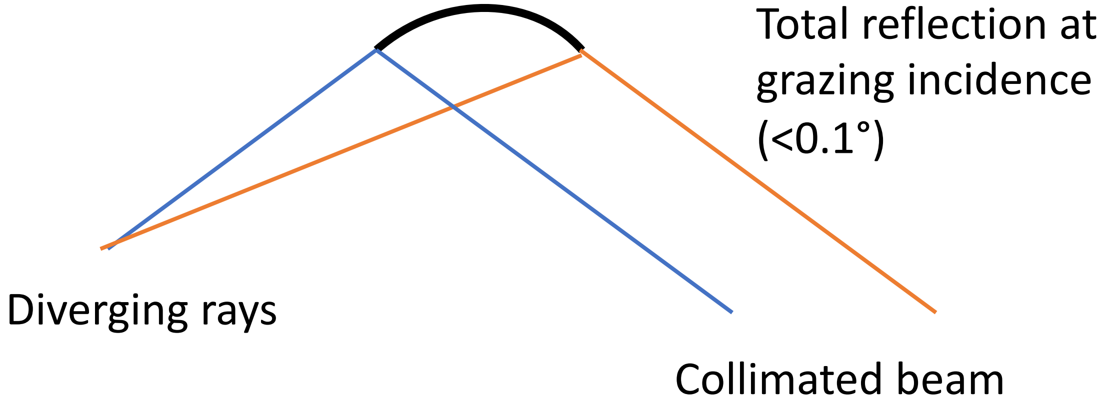
1. Divergence slits are used to limit the extent of X-Rays
   1. Smaller slit widths leads to smaller divergence, better resolution but lower intensity

Divergence also leads to difference x-ray interaction volume at different angles.



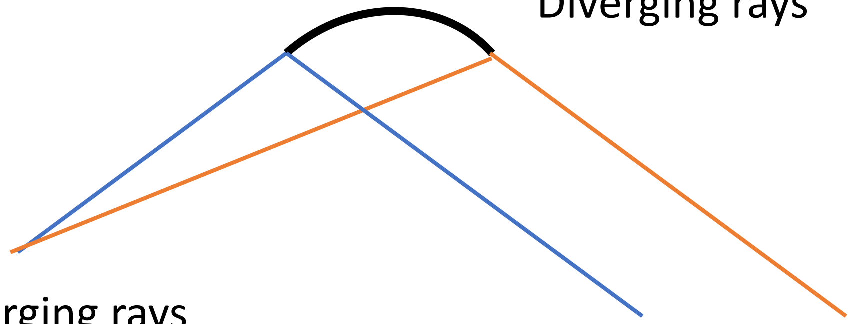
A diverging ray can be made parallel by several means.

parallel plate collimators
Soller slits
Parabolic mirrors and capillary lenses



Collimators

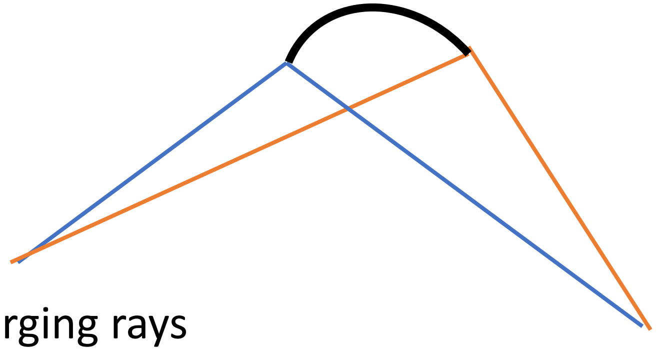
Parabolic Mirrors



Diverging rays

Collimated beam

Elliptical Mirrors

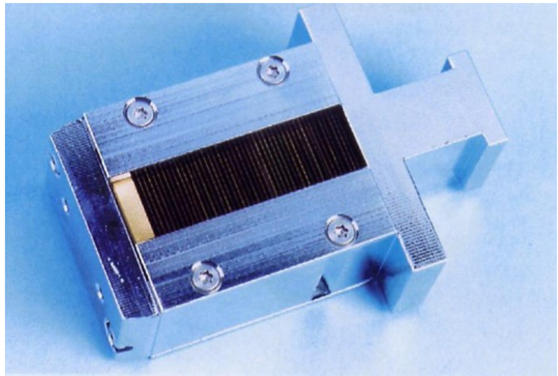


Diverging rays

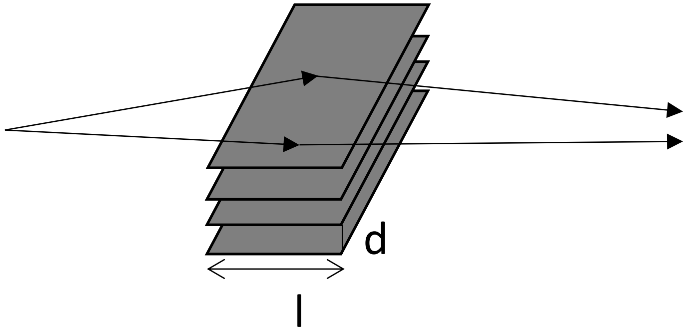
Converging beam

Total reflection at grazing incidence (<0.1°)

Soller Slits:

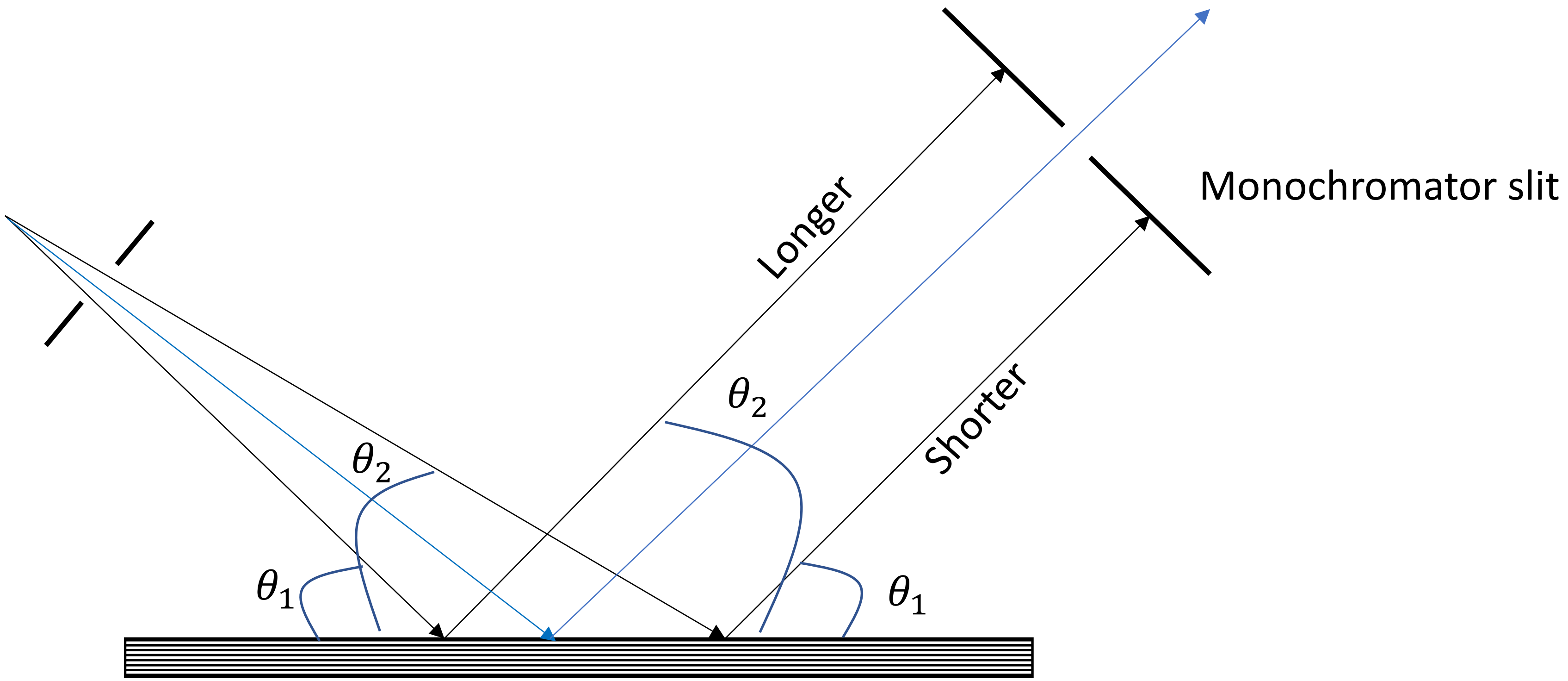


Reduce vertical divergence



Typical beam divergence $\alpha = \frac{2d}{l}$

Monochromators

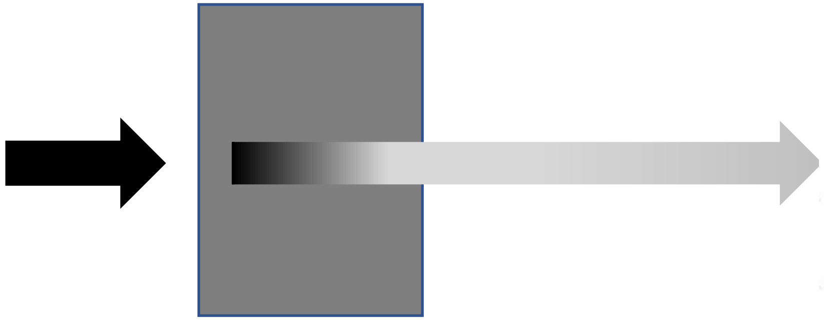


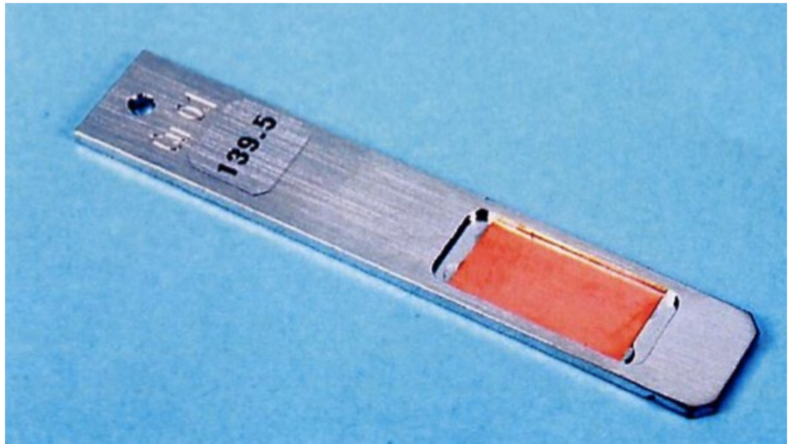
A properly aligned substrate such that its in Bragg's angle $2dsin\theta = \lambda$

Beam Absorbers and Attenuators

If µ is the absorption coefficient

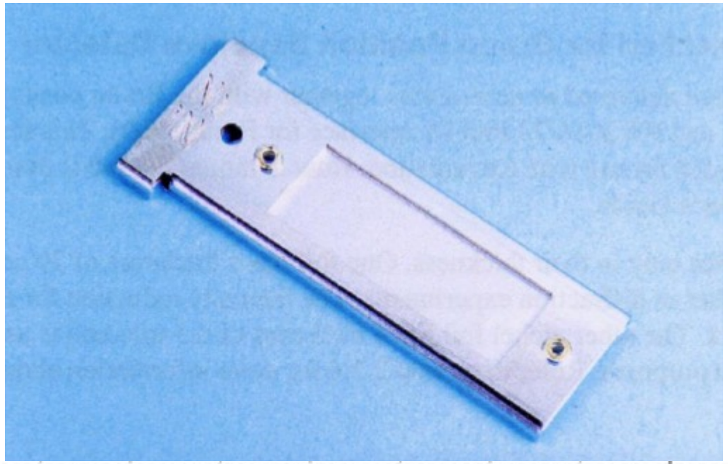
$$I = I_0 e^{-\mu x}$$

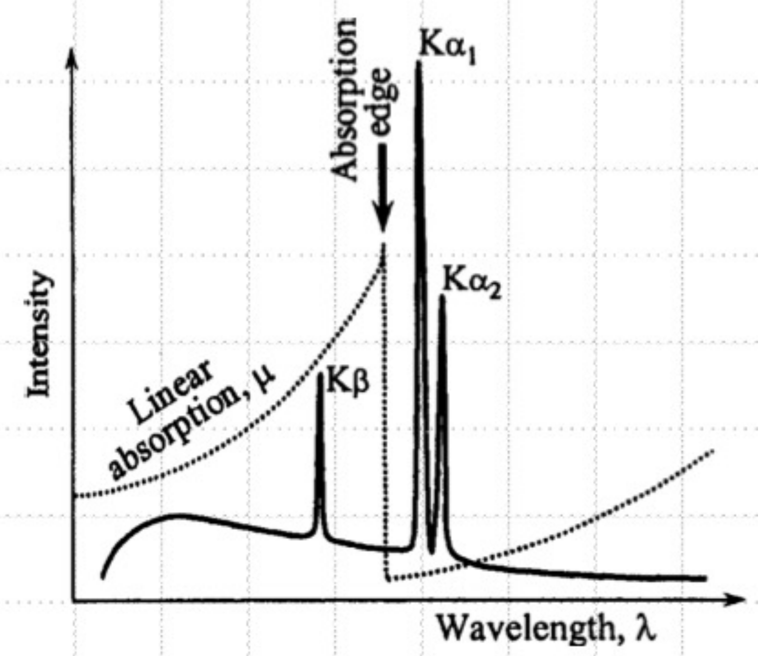


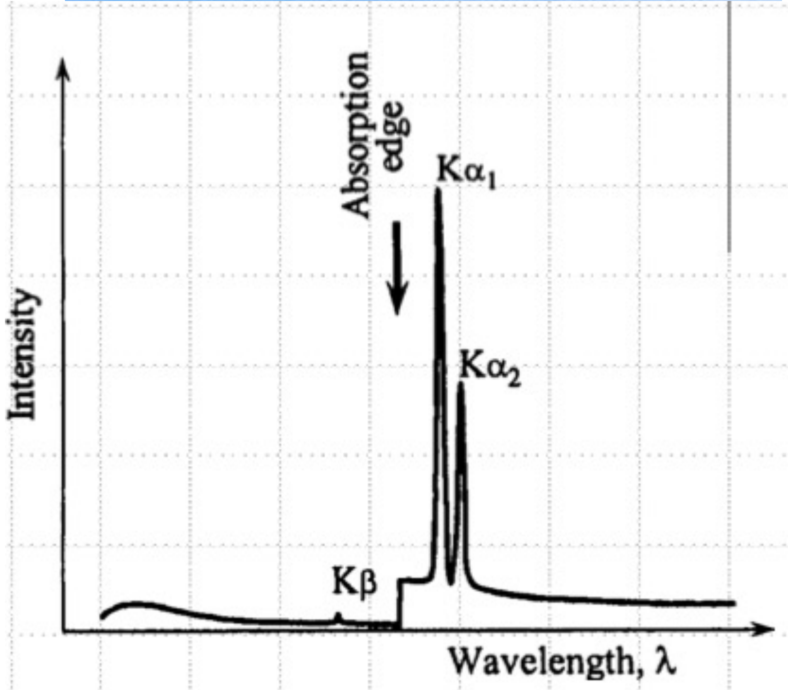


Selective filters

β filters







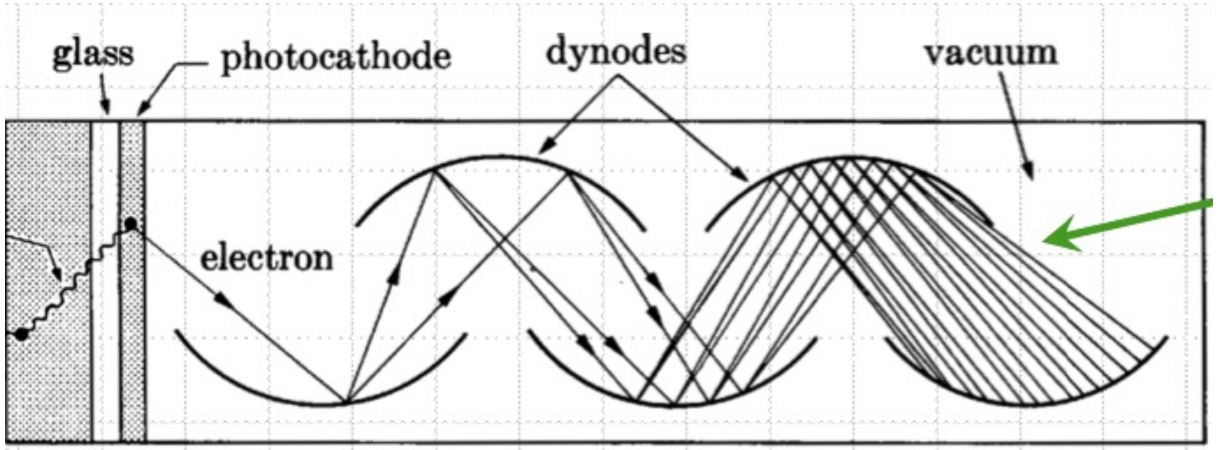
Xray filters

Gun Material	Filter	Thickness (µm)	Kβ Reduction	Kα Reduction
Mo	Zr	75	97	54
Cu	Ni	20	99	58
Co	Fe	16	99	51
Cr	V	13	98	45

X-Ray Detectors

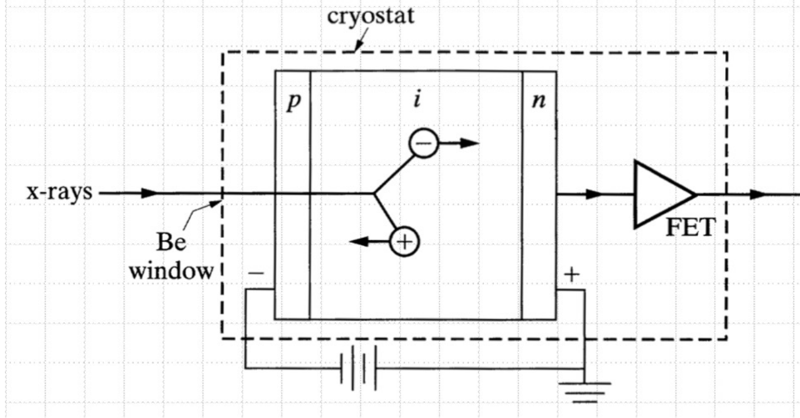
- Single photon detectors
  - Scintillators
  - Proportional counters
  - Semiconductor detectors
- Detectors with spatial resolution
  - Charge coupled device (CCD)
  - Wire detectors

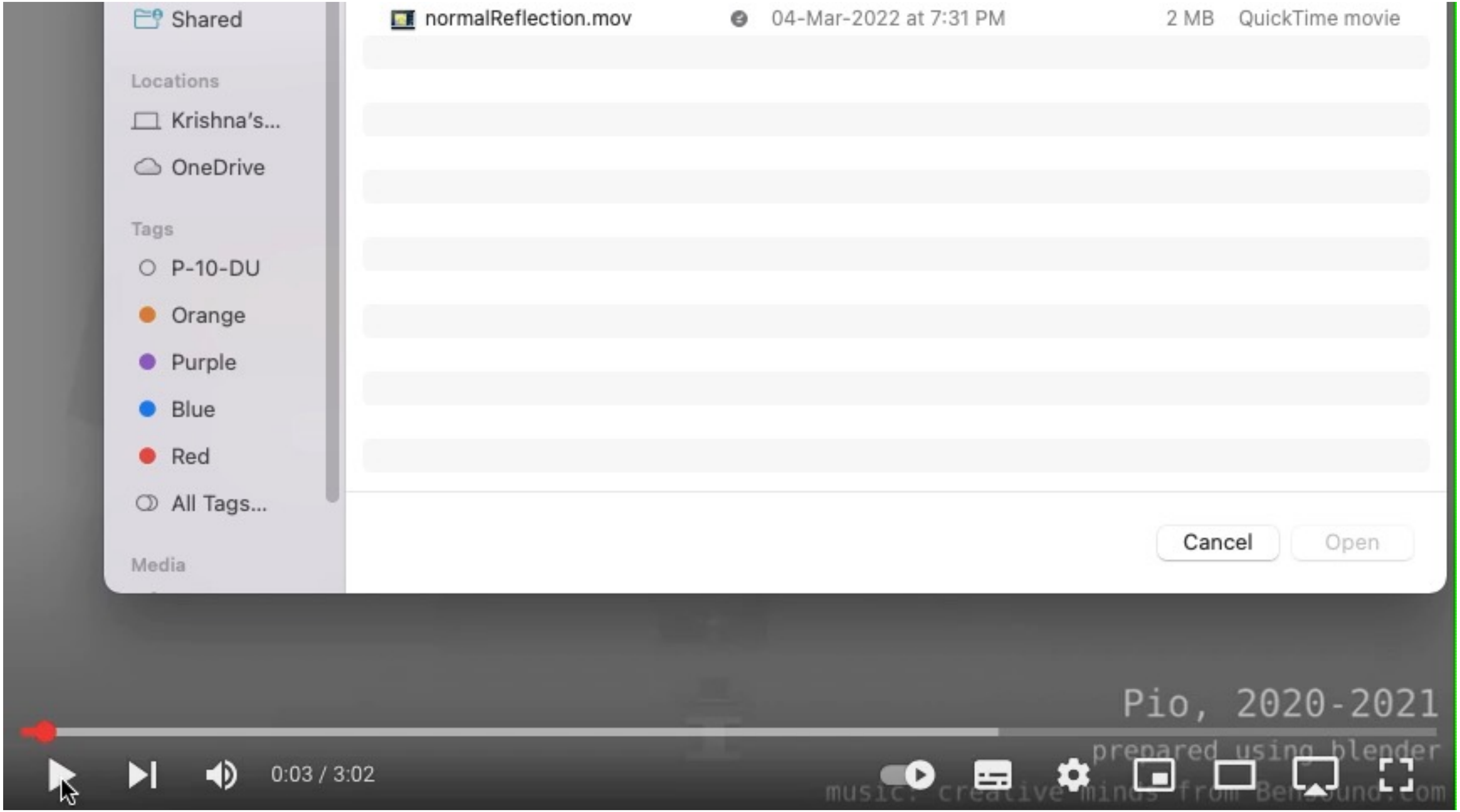
Scintillator with PMT



Proportional Wire detector

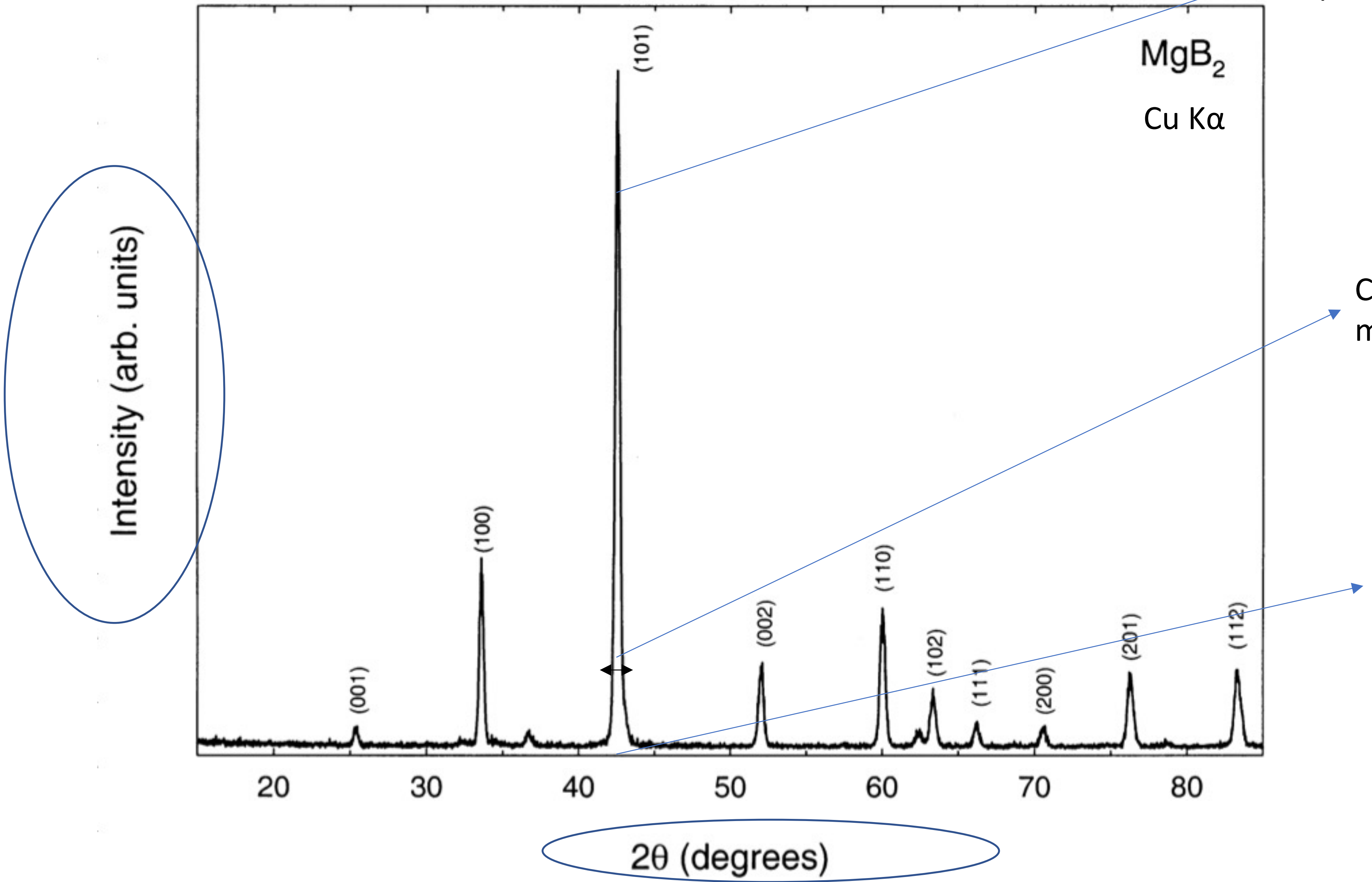
Semiconductor detector





normalReflection.mov 04-Mar-2022 at 7:31 PM 2 MB QuickTime movie

A sample measurement



Site occupancy and phase fraction

Crystallite size and micro strain

2θ position of the peak

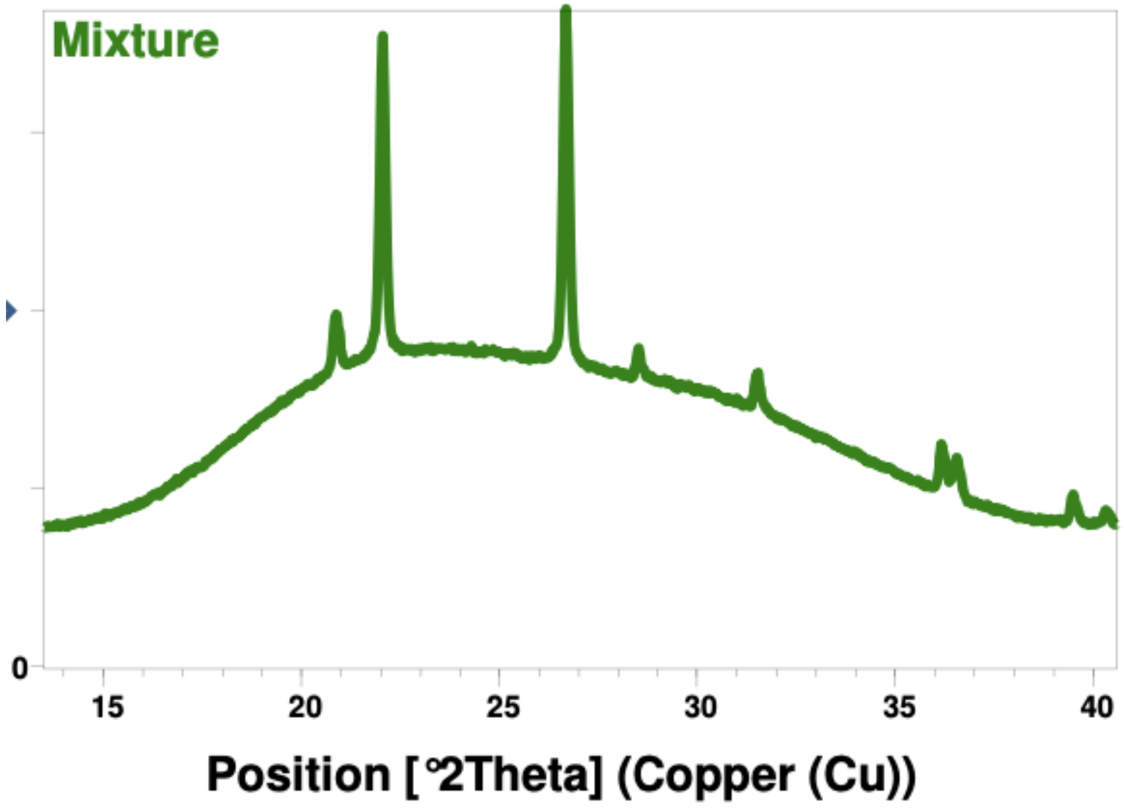
Gives spacing between planes

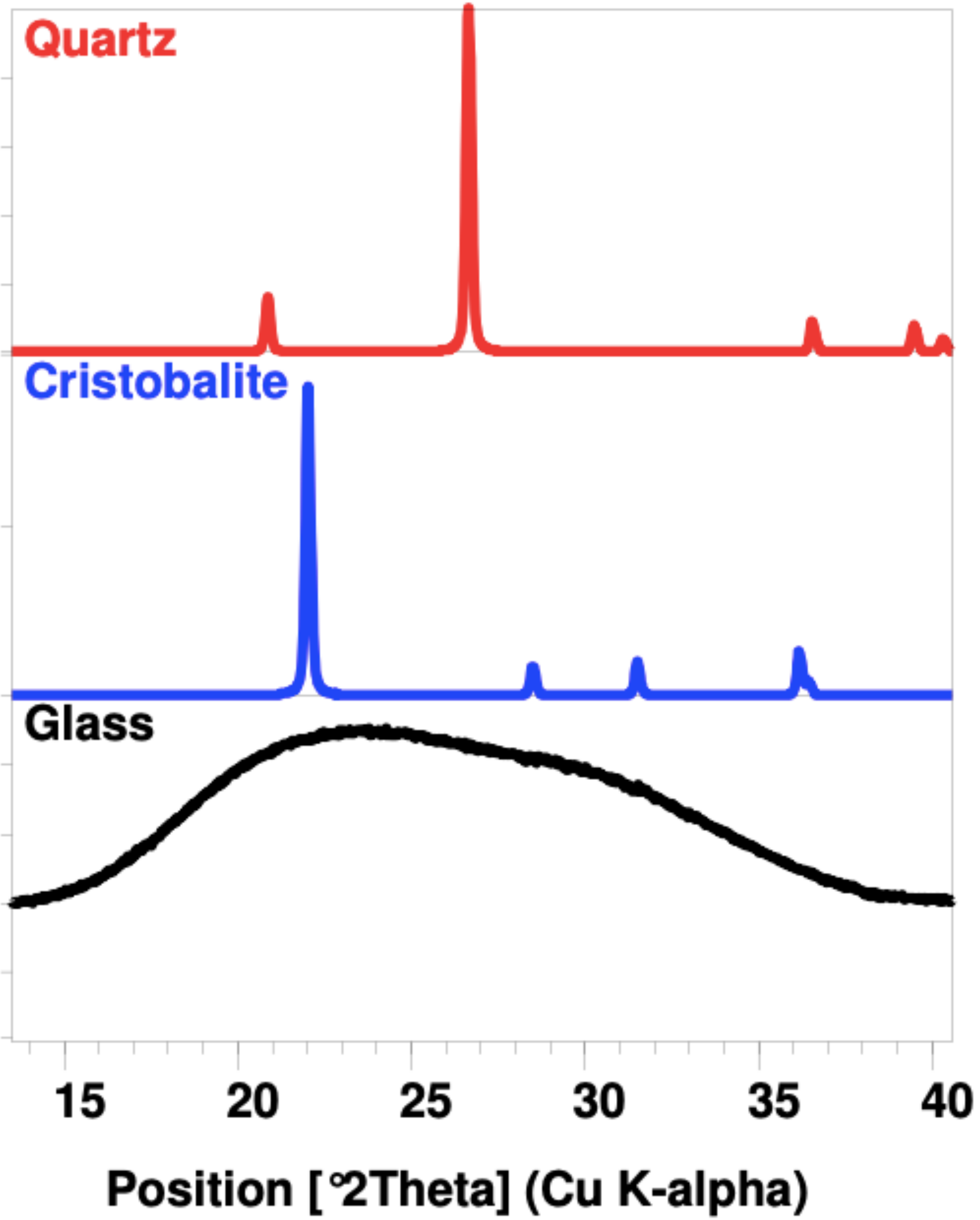
$$2d\sin\theta = \lambda$$

Phases and composites

All these are different phases of SiO_2

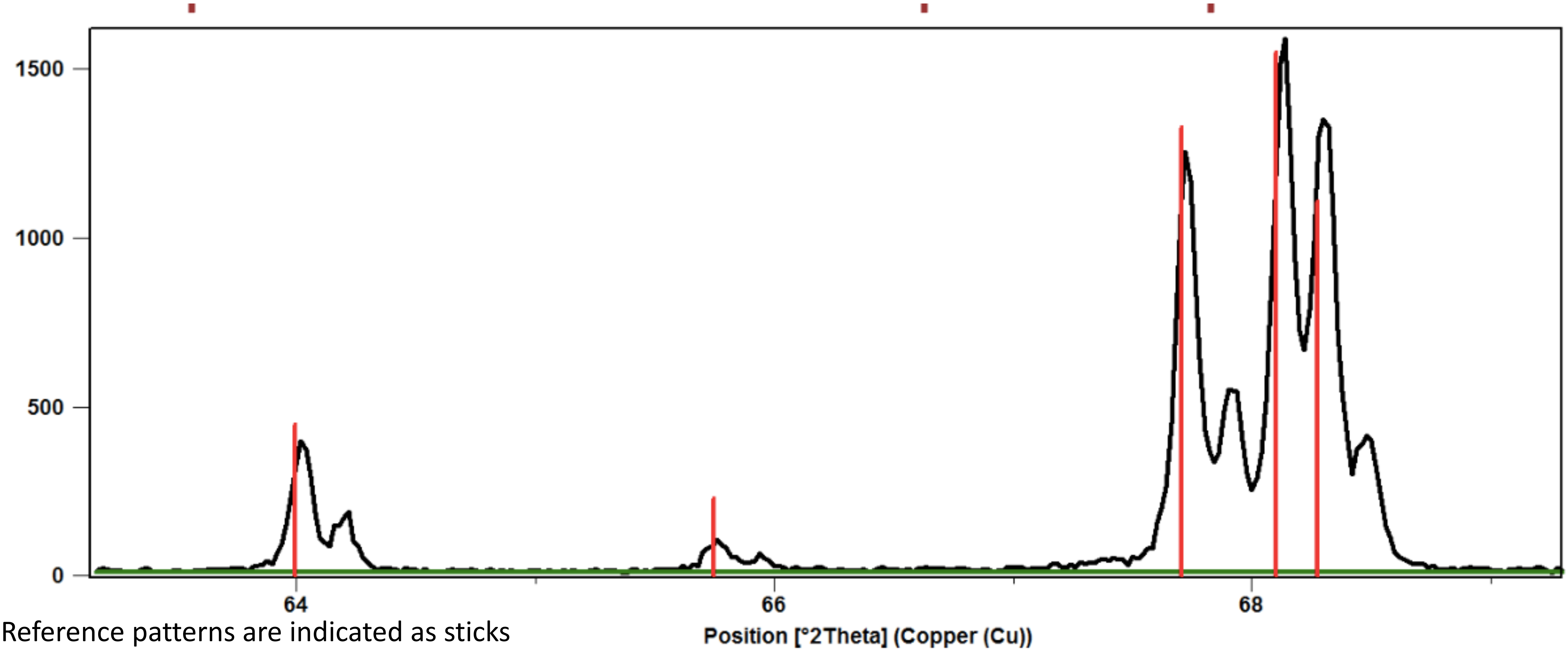
Chemically identical, but with different atomic arrangement





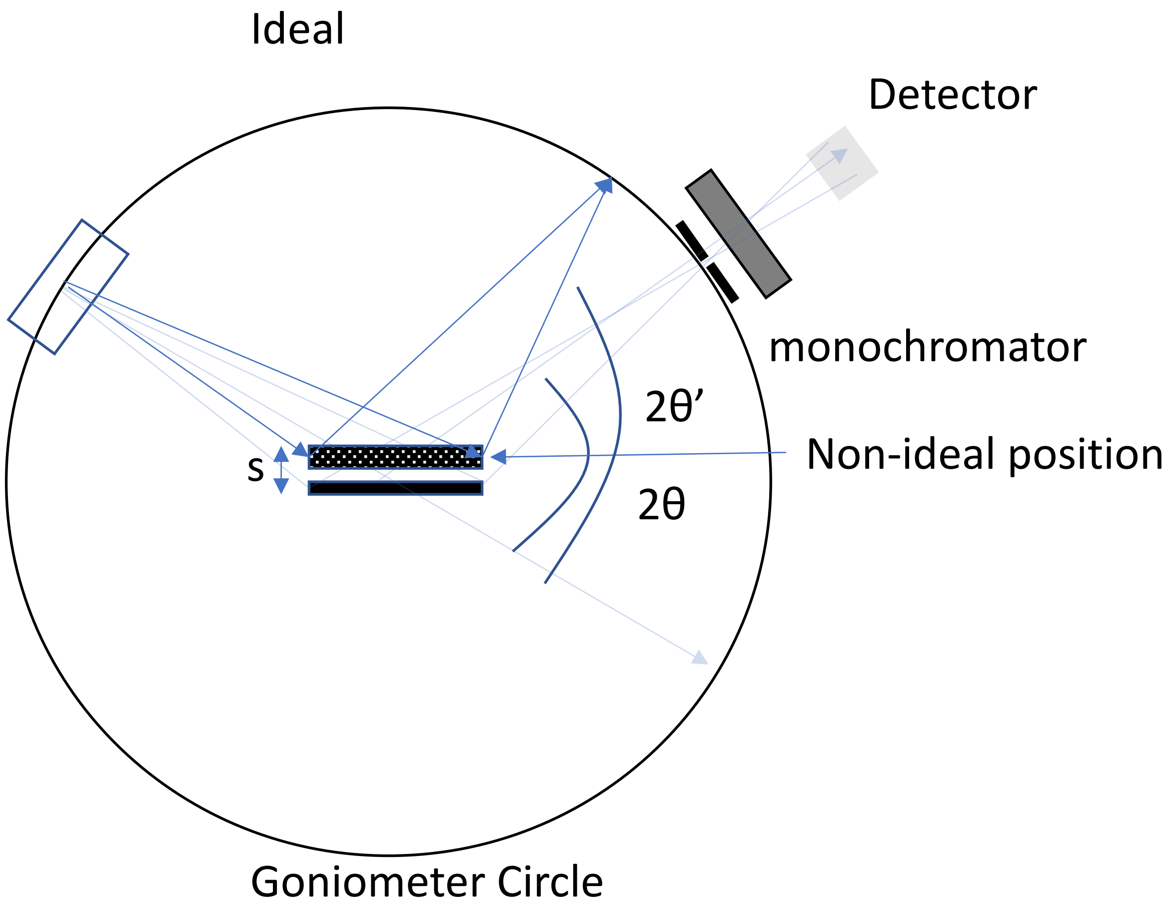
Quantitative Analysis

For the material, the peak intensities and the position should match

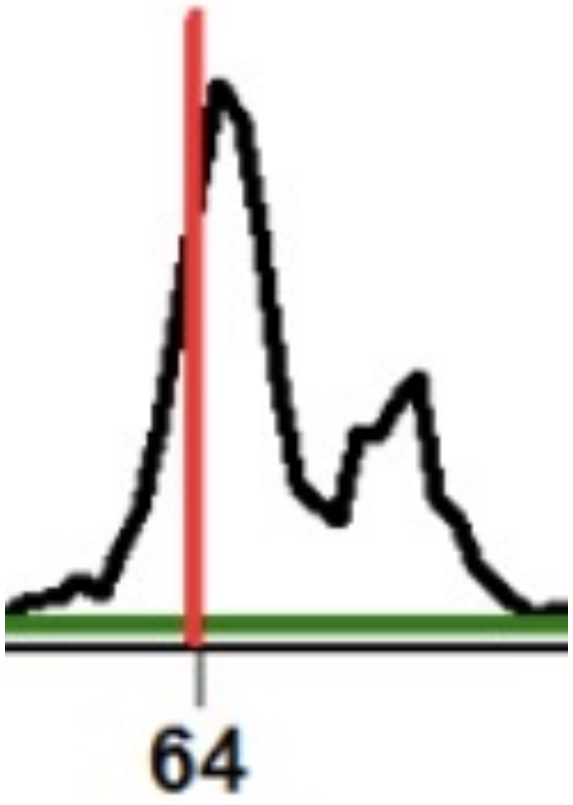


Reference patterns are indicated as sticks

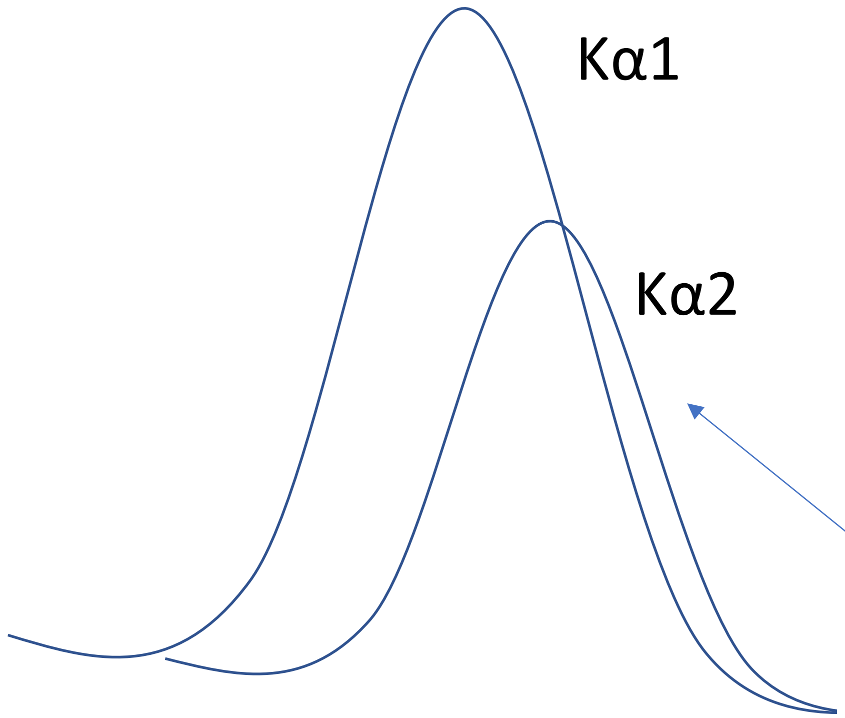
Specimen position errors



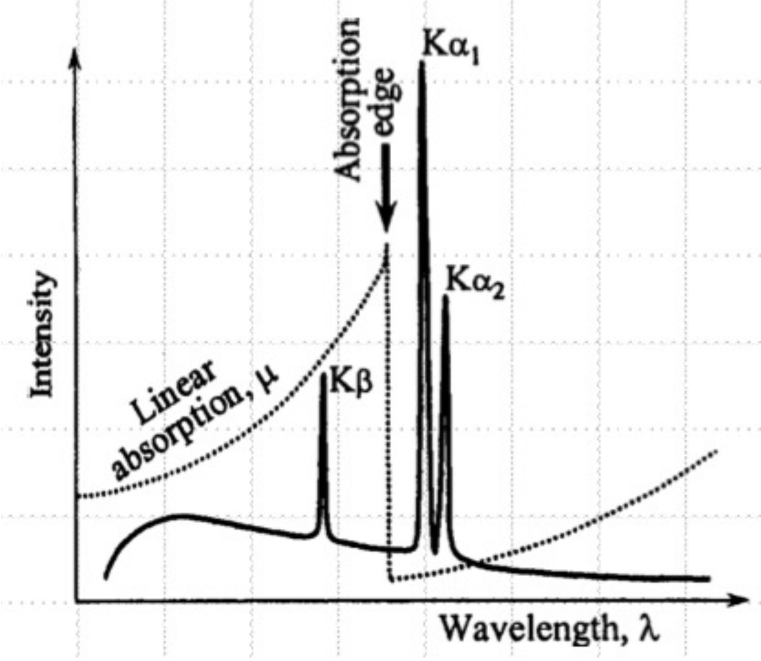
$$\theta' - \theta = \frac{S\cos\theta}{R}$$

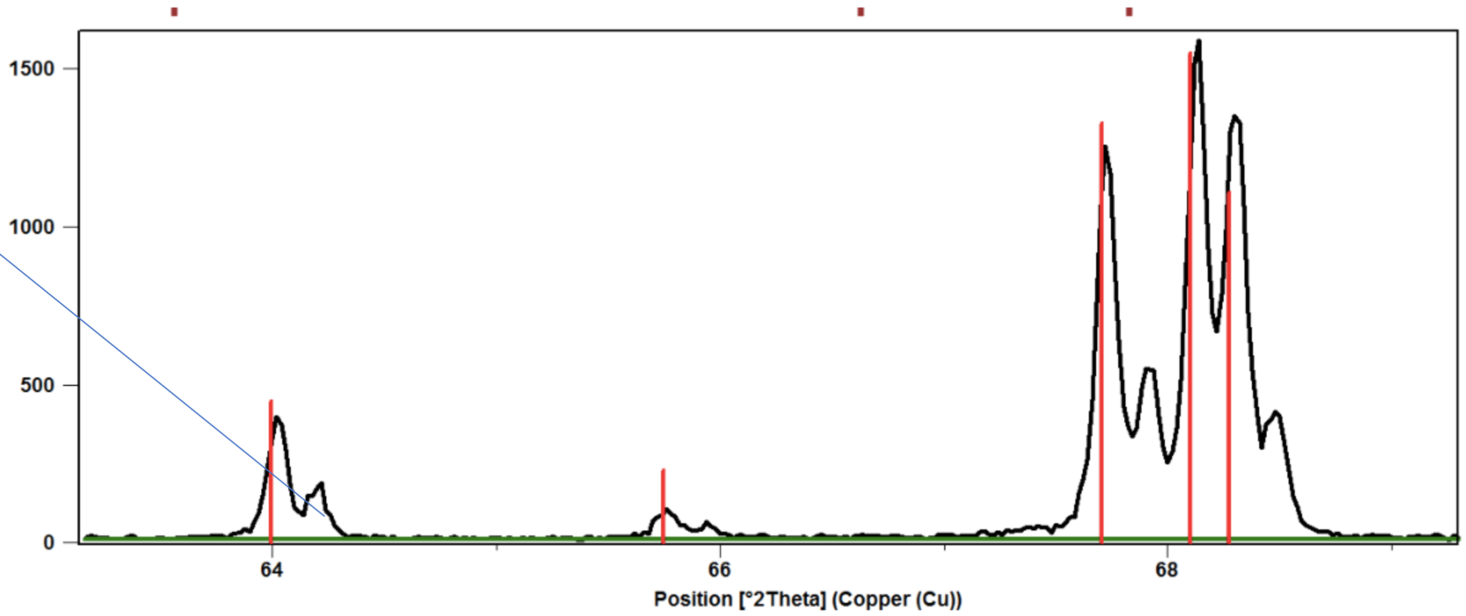


Truly non-monochromatic light



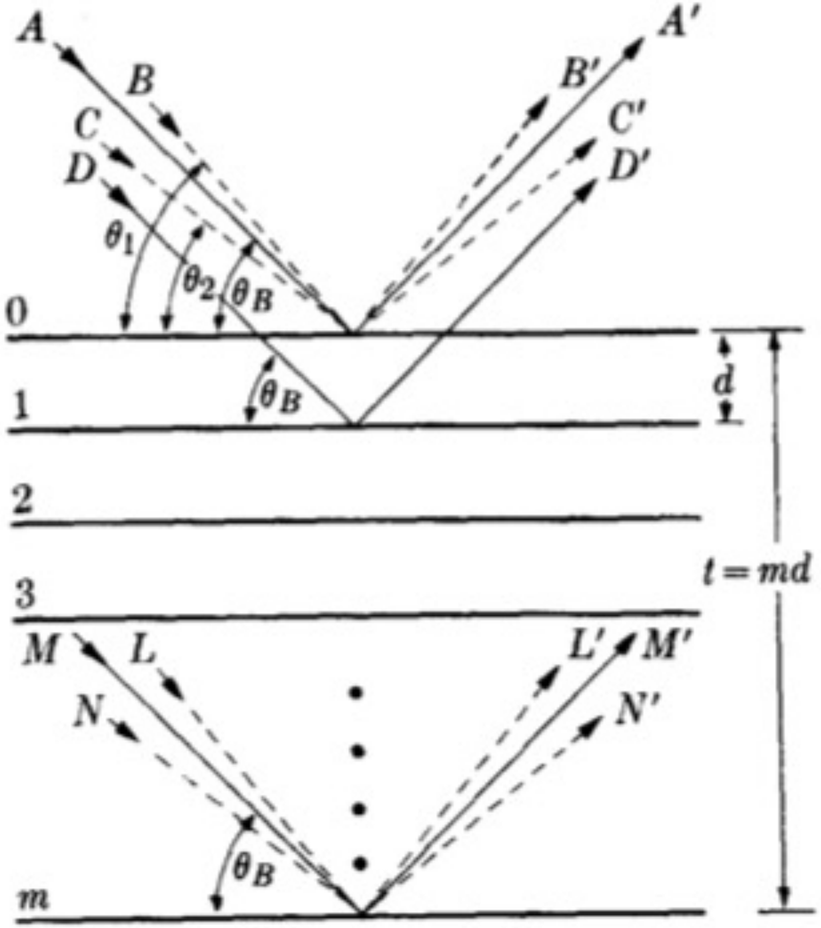
$$d = \frac{\lambda_{K\alpha_!}}{2\sin\theta_1} = \frac{\lambda_{K\alpha_2}}{2\sin\theta_2}$$

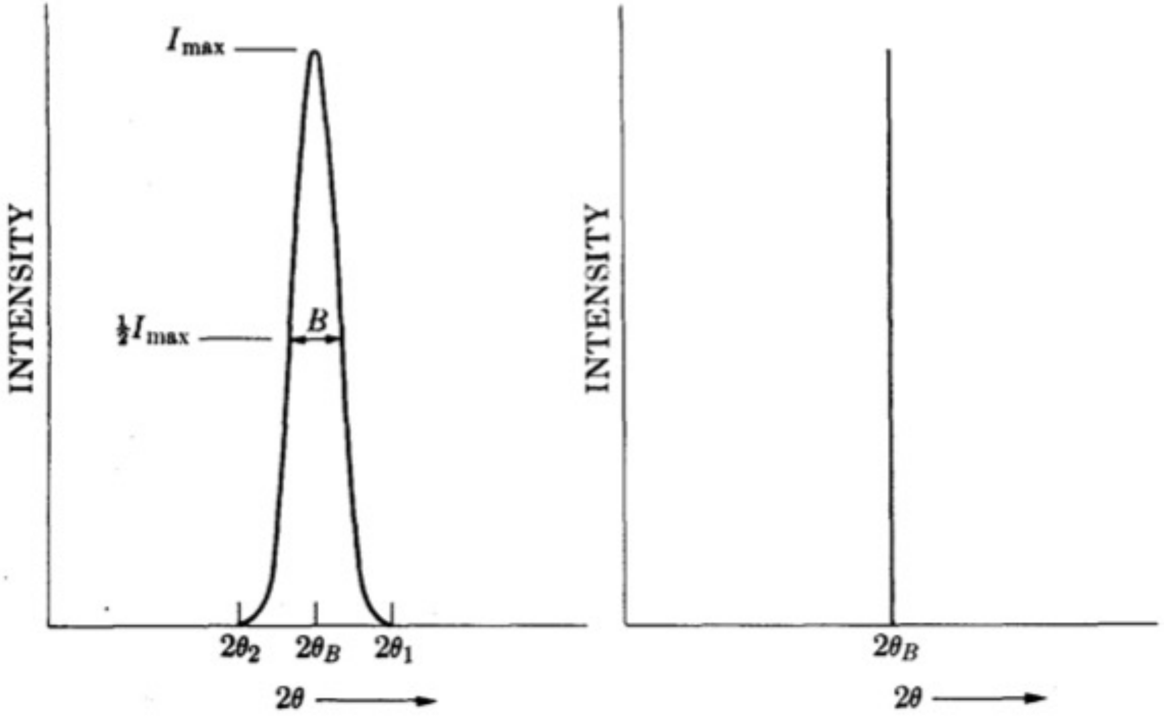




Peak Width

The diffraction peaks are broadened due to lack of infinite atomic planes to produce perfect destructive interfence.



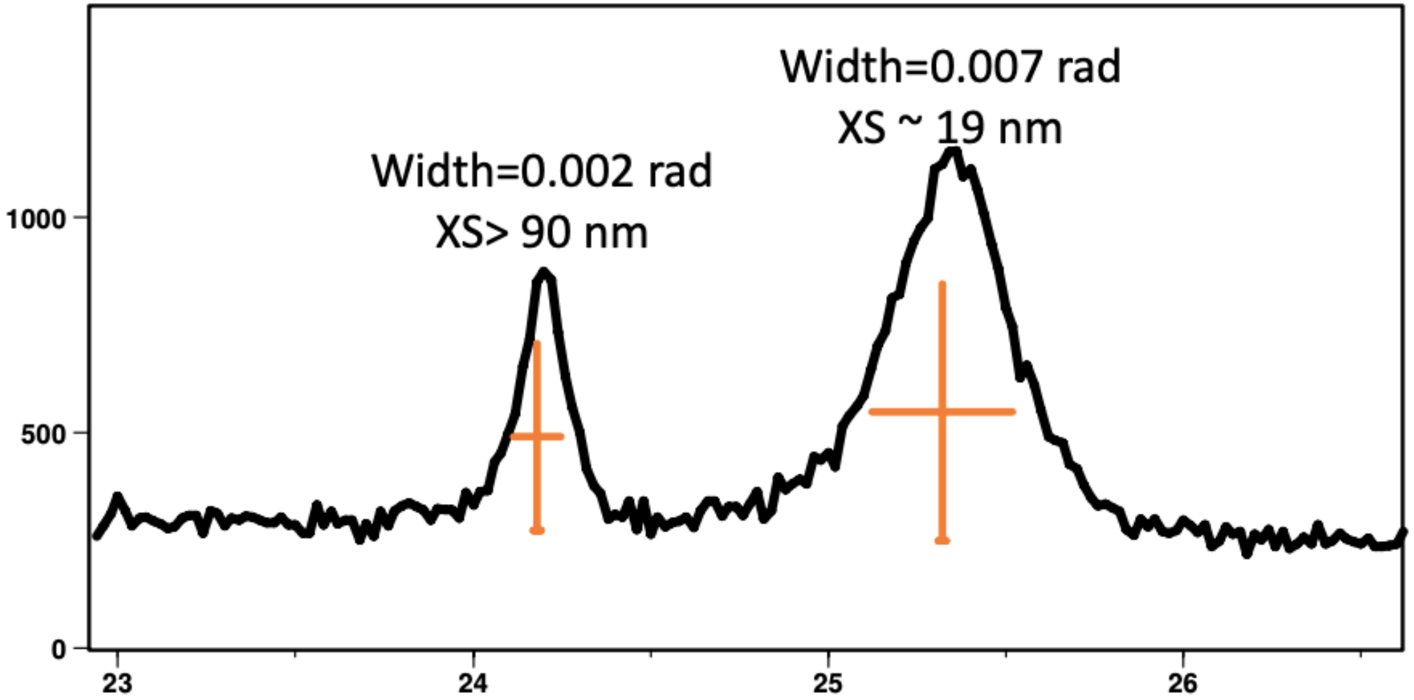


Lack of destructive interference leds to peak broadening

Size of crystallite size (Scherrer's Formula)

$$\tau = \frac{k\lambda}{B \sin\theta_B}$$

w – full width half maximum of the peak
k – constant ~= 0.9



However, non-uniform lattice strain can also lead to peak broadening

Hence one needs to fit a Gaussian/Lorentzian function to obtain the true FWHM.

Therefore from Powder XRD,

Collect the peak list (position and intensity).

1. Unit cell lattice parameters from the peak positions
2. Observed peaks can be indexed and absences to be noted. This gives the crystal system
3. Get the reference pattern and compare to get phase composition
4. Crystallite size and microstrain: Peak width and/or shape

Elements of Single crystal XRD

The necessary condition for XRAY peak – Bragg reflection.

The source, plane normal and the detector should be in a plane!

In a pure single crystal, there atomic planes are perfectly aligned, a single strong normal exists.

The difficulty now is in getting this normal in the plane of the source and the detector.