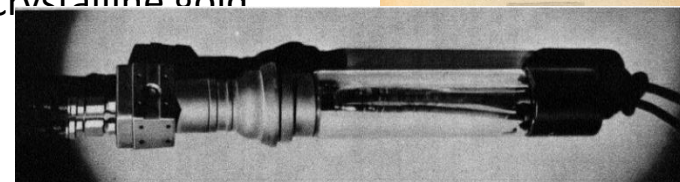
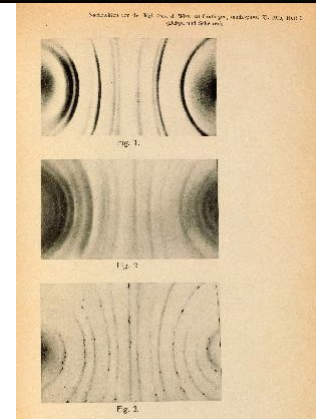
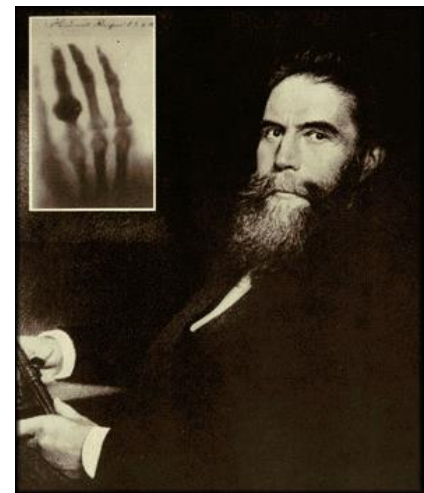


# X-ray Diffraction

# A Brief History of XRD

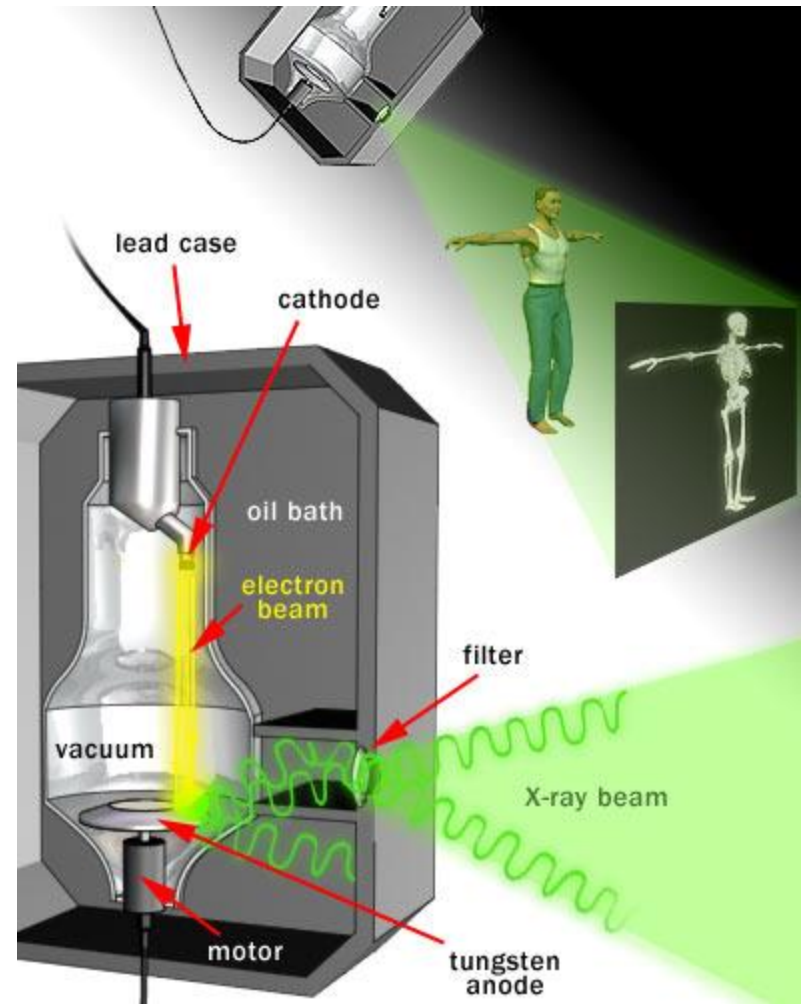
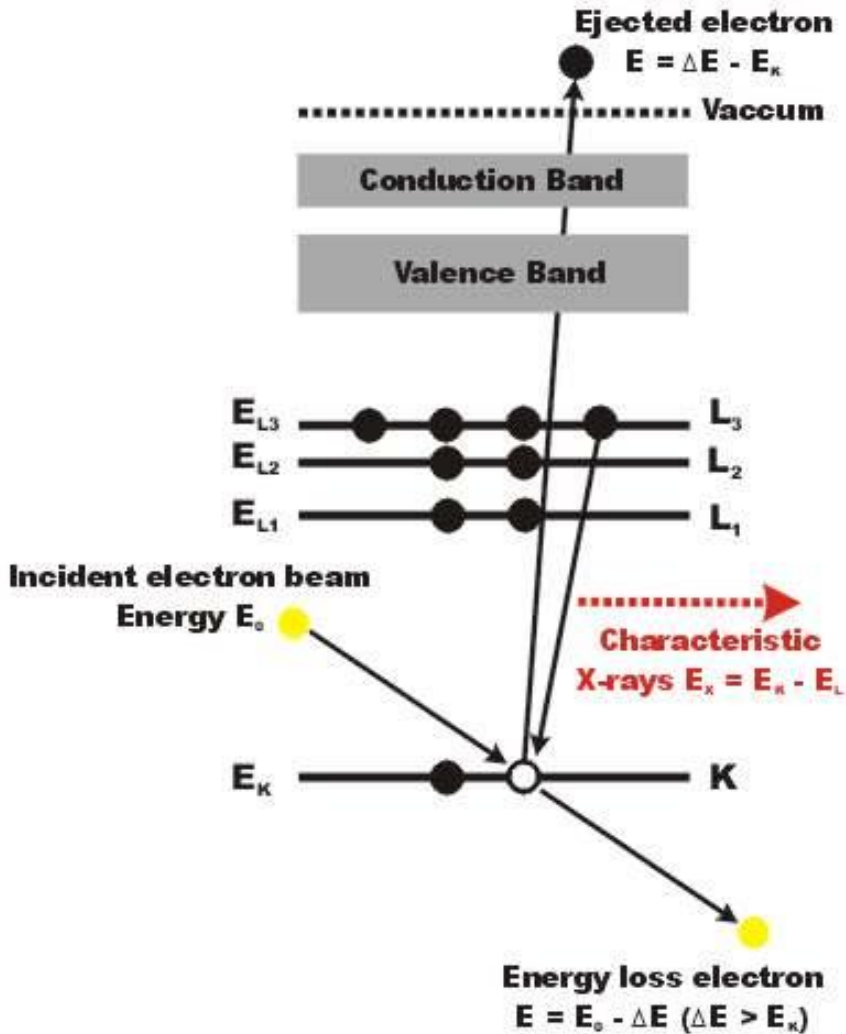
- 1895: Röntgen discovers X-Rays
  - received the first Nobel prize in physics in 1901
- 1912: Laue diffracts X-Rays from single crystal
  - 1914 Nobel prize in Physics
- 1912: Bragg analyzes crystal structures
  - 1915 Nobel prize in physics
- 1917: Ewald develops dynamical theory of X-Ray diffraction
- 1918: Scherrer uses X-Rays to determine crystallite size of nanocrystalline gold
- 1935: X-Ray powder diffractometer developed by Le Galley



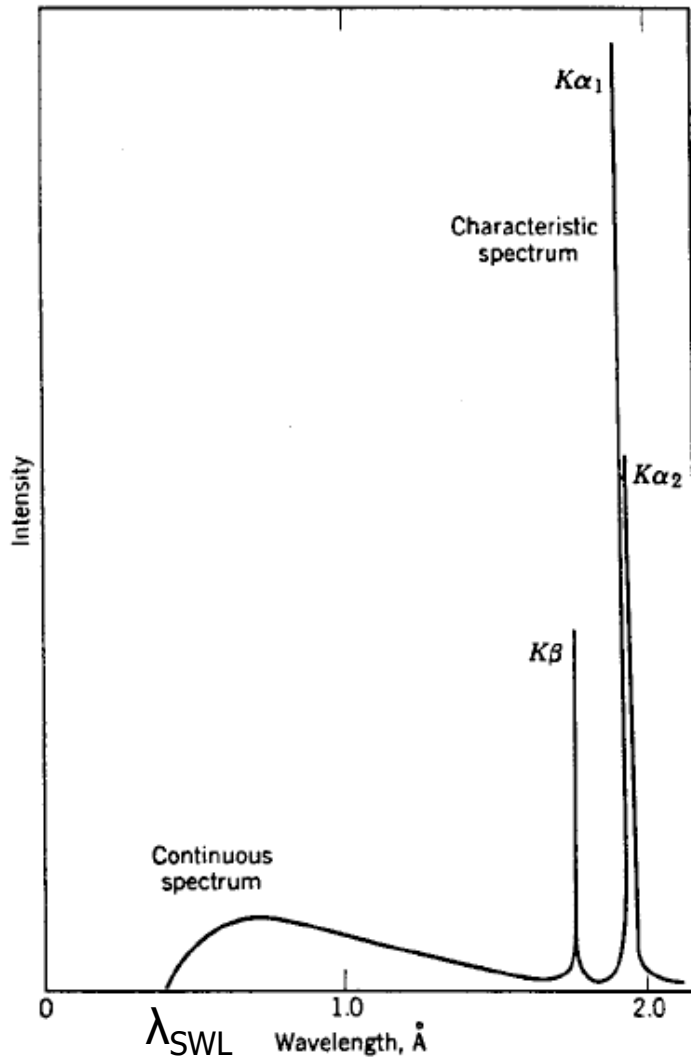
- 1947: First commercial powder diffractometer

- 1969: Establishment of the Joint Committee on Powder Diffraction Standards (JCPDS), now International Center for Diffraction Data (ICDD)

# Generation of X-rays



# X-ray Spectrum from an Iron target



- Short Wavelength Limit  $\lambda_{SWL}$  (nm) =  $\frac{12400}{V}$
- Continuous spectrum  $I_{CS} = AiZV^m$
- Characteristic X-ray Moseley's Law

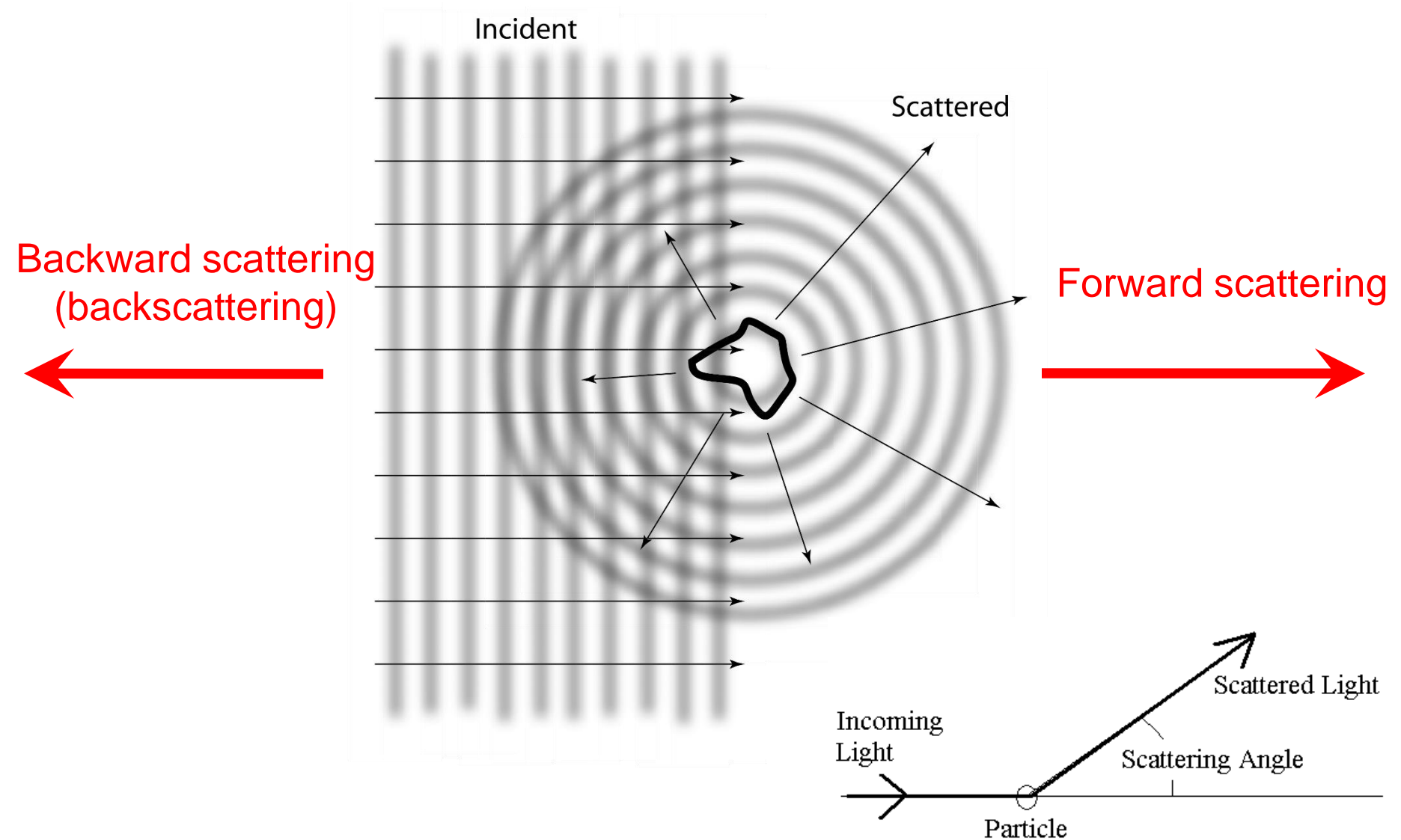
$$\sqrt{\nu} = C(Z - \sigma)$$

$$I_K = Bi(V - V_k)^n$$

# Scattering fundamentals

- *Scattering* can be broadly defined as the *redirection of radiation out of the original direction of propagation*, usually due to interactions with molecules and particles
- Reflection, refraction, diffraction etc. are actually all just forms of scattering
- Matter is composed of discrete electrical charges (atoms and molecules – dipoles)
- Light is an oscillating EM field – excites charges, which radiate EM waves
- These radiated EM waves are *scattered waves*, excited by a source external to the scatterer
- The *superposition of incident and scattered EM waves* is what is observed

# Scattering geometry

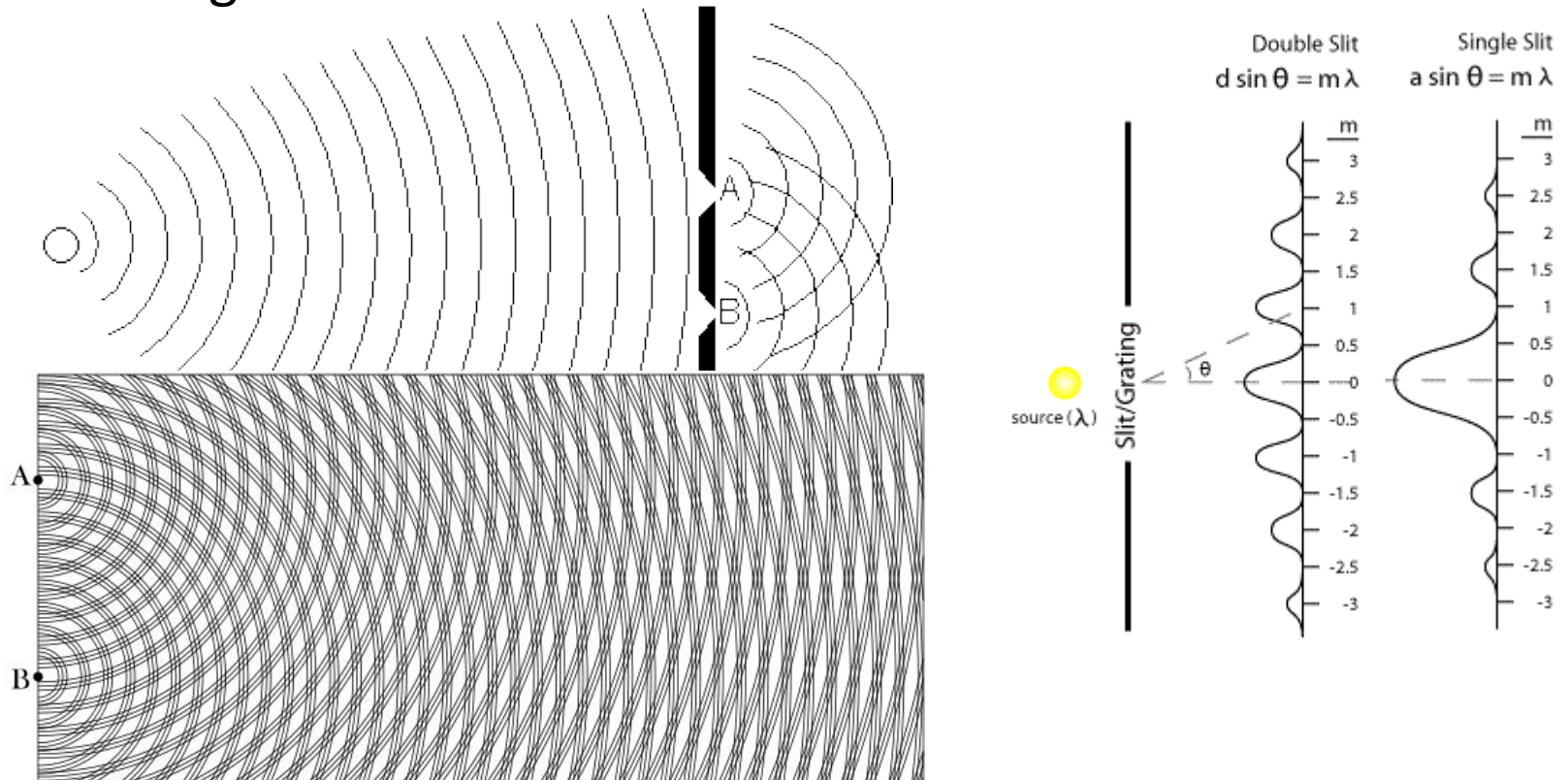


# Types of scattering

- *Elastic scattering* – the wavelength (frequency) of the scattered light is the same as the incident light (*Rayleigh and Mie scattering*)
- *Inelastic scattering* – the emitted radiation has a wavelength different from that of the incident radiation (*Raman scattering, fluorescence*)
- *Quasi-elastic scattering* – the wavelength (frequency) of the scattered light shifts (e.g., in moving matter due to Doppler effects)

# How Diffraction occurs

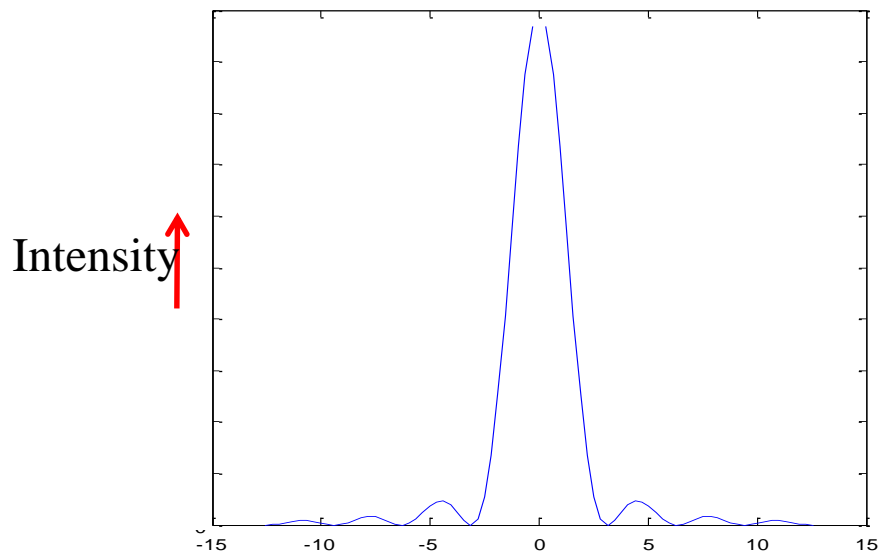
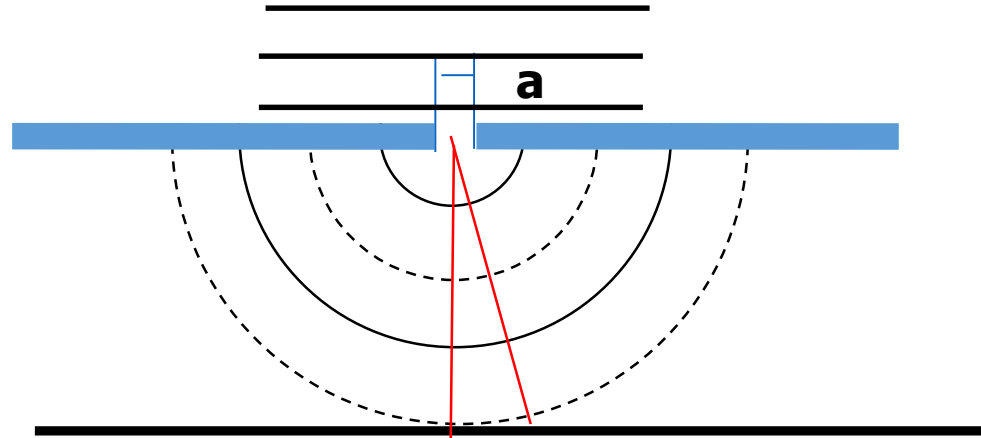
- Diffraction occurs when objects in a periodic array scatter radiation coherently, producing constructive interference at specific angles

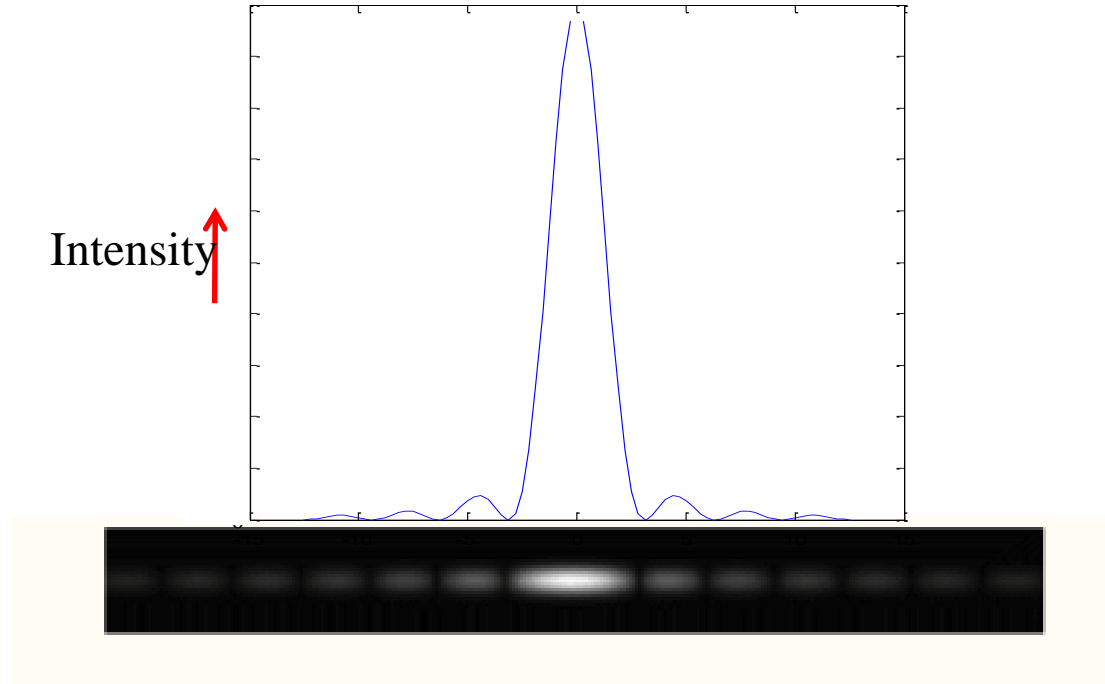


- X-Rays can diffract from a periodic array of elastic scatterers, such as atoms in a crystal



# Diffraction of light through an aperture





Minima

$$\frac{\sin \theta}{\lambda} = \frac{n}{a}$$

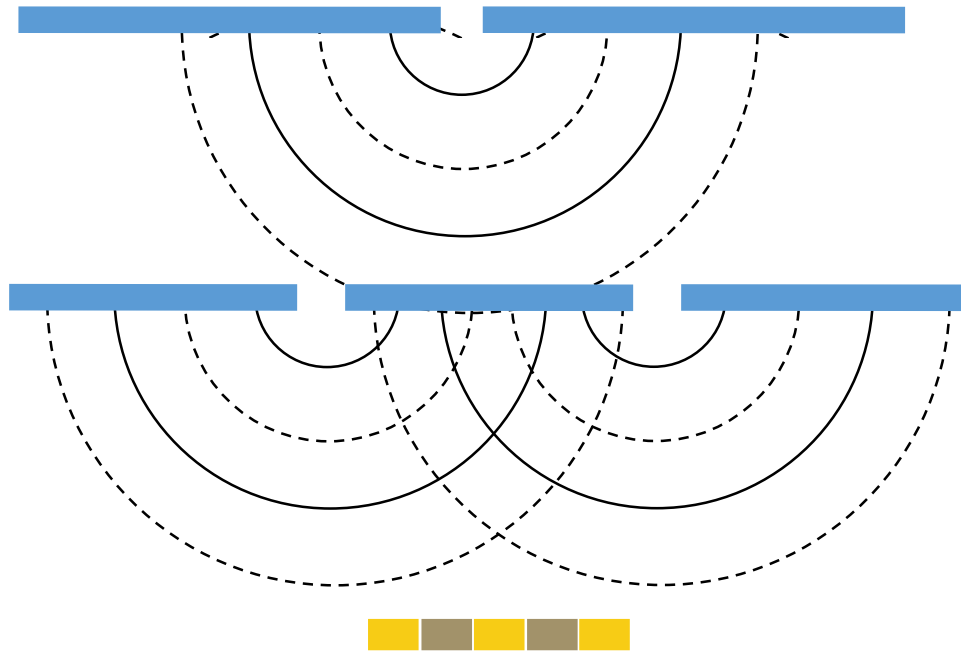
$$n = 0, 1, \dots$$

Maxima

$$\frac{\sin \theta}{\lambda} = \frac{2n+1}{2a}$$

$$n = 1, 2, \dots$$

# Young's Double slit experiment



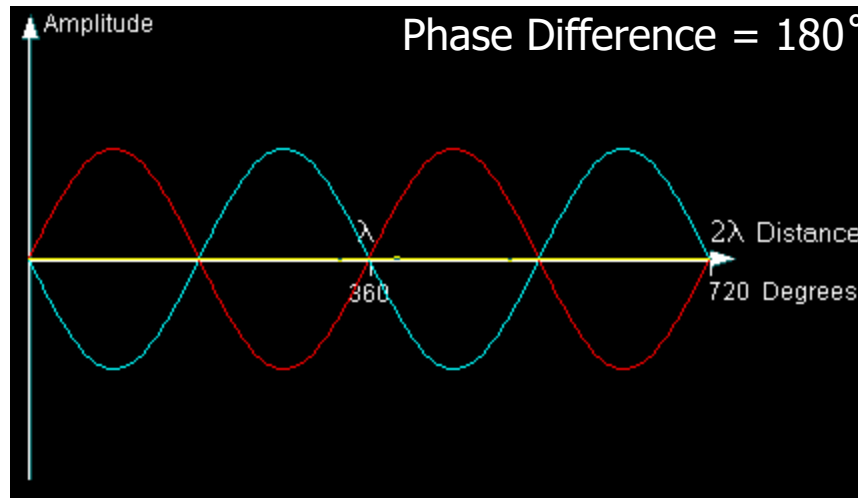
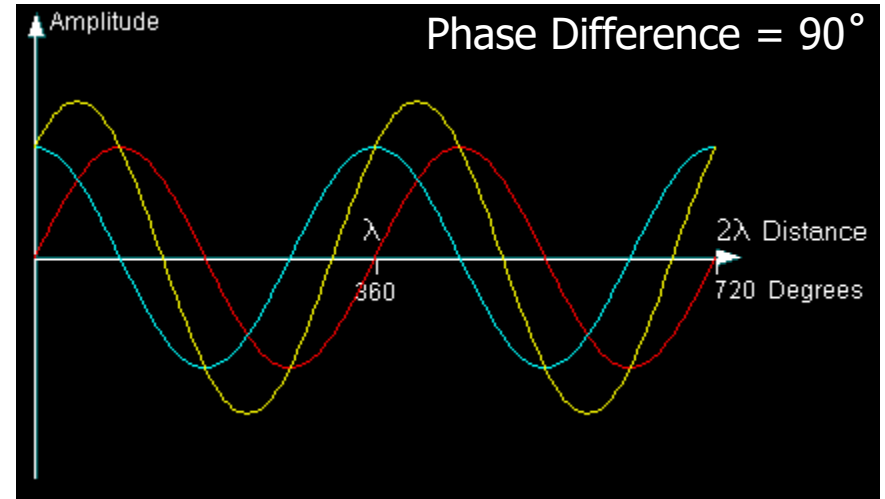
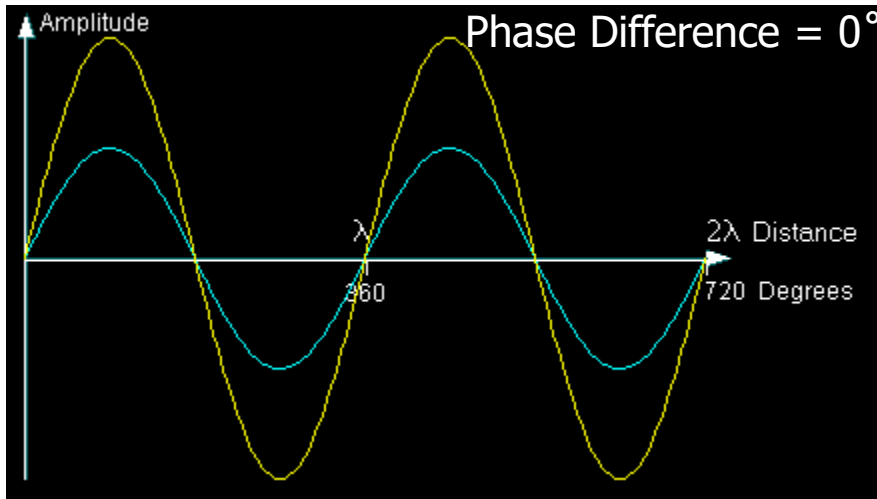
$$d \sin\theta = m\lambda, m = 1, 2, 3, \dots$$

Constructive Interference

$$d \sin\theta = (m + \frac{1}{2})\lambda, m = 1, 2, 3, \dots$$

Destructive Interference

# Interference



# Elastic Scattering

- When x-rays or electrons interact with matter, the dominant effect is *scattering*.
- Considering x-rays and electrons as waves we deal with elastic scattering (rather than as particles, where we deal with inelastic scattering)
- For elastic scattering, x-rays and electrons are scattered with no loss of energy, and give rise to scattered radiation of the same wavelength

# Constructive Interference

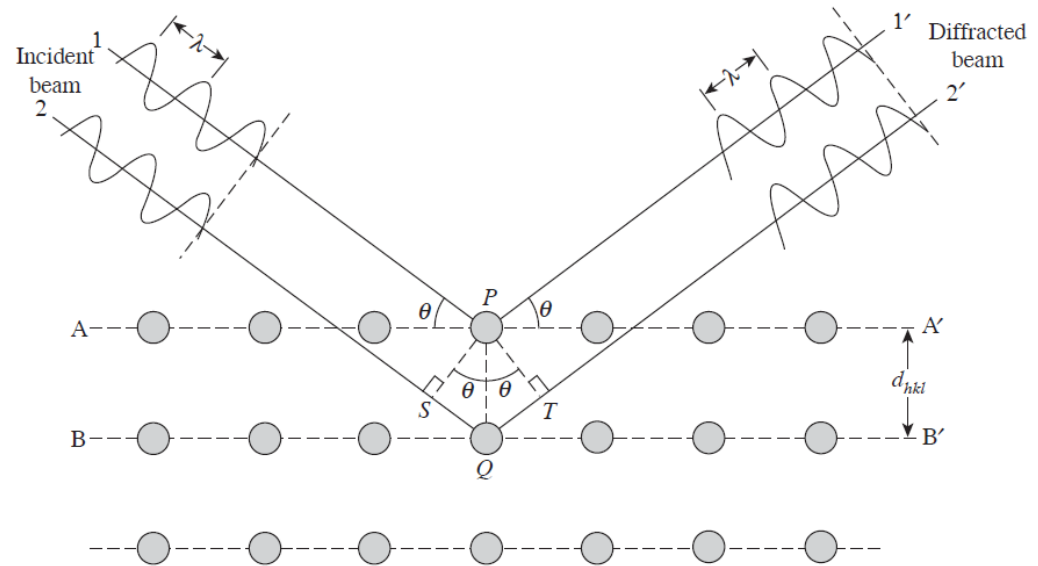
- The distance between atoms ( $d_{hkl}$ ) are on the same order of size as the wavelength of an x-ray (Cu K $\alpha$  = 1.54 Å)
- Interference phenomena is concentrated in directions related to the crystal lattice
- The intensity of the diffracted x-rays gives rise to peaks for each set of wave vectors which make up diffraction patterns
- The positions of the atoms in the material (the crystal lattice of the solid) and the wavelength of the x-rays determine the positions and intensities of the diffracted peaks.

Another kind of scattering, incoherent (Compton), is easiest understood in terms of the particle nature of photons: the photon deviates from path and electron takes part of its energy. The scattered photon has lost energy (so has a longer wavelength), and there is no relationship between the phases of the two waves. There is no interference and of little significance here (though it is for XRF) and we will not consider it further.

# Conditions Required for X-Ray Diffraction

Bragg's law - a model to describe the position of observed diffraction peaks

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



- Constructive interference only occurs when Bragg's law is satisfied for parallel planes of atoms, with a space  $d_{hkl}$  between them
- Each plane of atoms produces a diffraction peak at a specific angle  $\theta$
- Wavelengths of the excited filament material should be similar in dimension with the interplanar spacing  $d$  (most common emission being copper  $K_{\alpha}$  1.5418 Å)

# Conditions Required for X-Ray Diffraction

Miller indices (hkl) define a series of parallel planes in a crystal with interplanar spacing  $d$

The interplanar distance is dependent on the Miller indices. When combined with Bragg's law:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

This equation helps us determine the Miller indices of crystal planes that diffract x-rays

For example: {001} is the planar index for  $(h^2+k^2+l^2)=1$

Or {110} is the planar index for  $(h^2+k^2+l^2)=2$

This calculation is not practical because Miller indices for the diffracting planes and the diffraction angles for a known wavelength are presented for all crystalline materials by the International Center for Diffraction Data (ICDD)

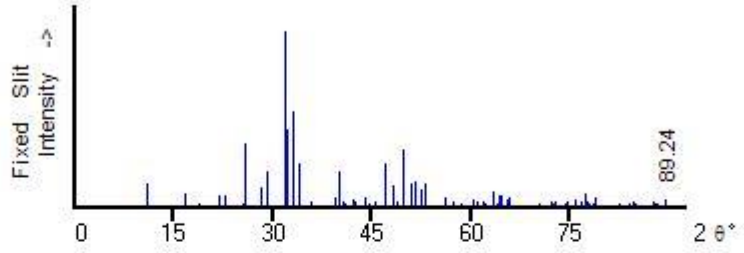


# Diffraction Data is Essential

PDF # 860740, Wavelength = 1.54060 (Å)

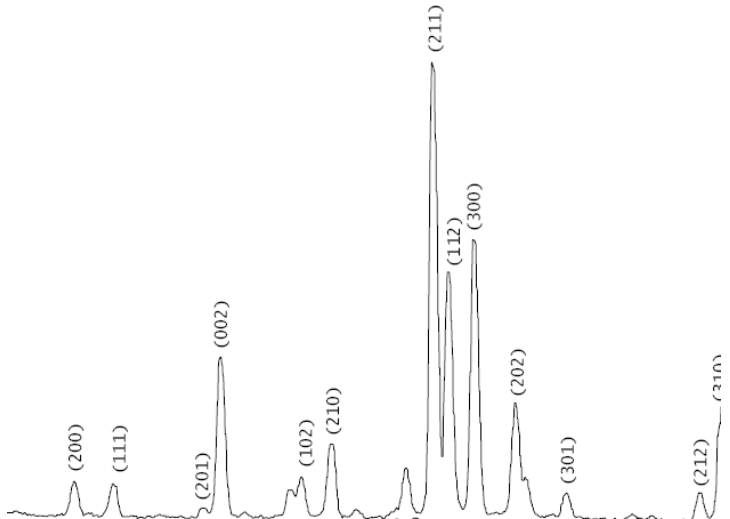
86-0740 Quality: C  
 CAS Number:  
 Molecular Weight: 502.32  
 Volume[CD]: 521.26  
 Dx: 3.200 Dm:  
 Sys: Hexagonal  
 Lattice: Primitive  
 S.G.: P63/m (176)  
 Cell Parameters:  
 a 9.352 b c 6.882  
 α β γ

Ca5 ( P O4 )3 ( O H )  
 Calcium Phosphate Hydroxide  
 Ref: Calculated from ICSD using POWD-12+, (1997)  
 Ref: Tomita, K et al., J. Mineral. Petrol. Econ. Geol., 91, 11 (1996)



I/Cor: 1.04  
 Rad: CuKα1  
 Lambda: 1.54060  
 Filter:  
 d-sp: calculated  
 ICSD #: 081442  
 Mineral Name:  
 Hydroxylapatite

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
10.915	125	1	0	0	45.402	32	2	0	3	63.950	17	5	1	0
16.892	69	1	0	1	46.947	248	2	2	2	64.134	64	3	0	4
18.964	22	1	1	0	48.350	116	1	3	2	64.485	58	3	2	3
21.931	66	2	0	0	48.985	33	2	3	0	65.537	44	5	1	1
22.976	64	1	1	1	49.620	323	2	1	3	65.714	46	3	3	2
25.501	14	2	0	1	50.861	134	2	3	1	66.761	7	4	1	3
25.872	361	0	0	2	51.679	139	1	4	0	66.846	8	4	2	2
28.154	112	1	0	2	52.388	102	4	0	2	67.543	1	2	2	4
29.149	198	2	1	0	53.195	135	0	0	4	68.660	4	1	3	4
31.973	999*	2	1	1	54.479	4	1	0	4	69.176	1	1	0	5
32.275	437	1	1	2	56.218	54	3	2	2	69.593	2	6	0	0
33.157	542	3	0	0	56.790	2	5	0	0	70.188	16	1	5	2
34.167	245	2	0	2	56.988	6	1	1	4	70.694	2	4	3	0
35.697	31	3	0	1	57.364	25	3	1	3	71.204	2	5	0	3
38.473	2	2	2	0	58.215	1	2	0	4	71.378	2	1	1	5
39.364	51	2	1	2	58.490	12	5	0	1	71.963	5	4	0	4
40.110	203	1	3	0	58.678	8	4	1	2	72.209	29	4	3	1
40.726	30	2	2	1	59.234	3	3	3	0	72.469	15	2	0	5
40.852	19	1	0	3	60.434	43	2	4	0	72.877	27	5	2	0
42.290	41	1	3	1	60.891	30	3	3	1	73.380	3	3	3	3
42.528	29	3	0	2	61.806	33	1	2	4	74.373	17	5	2	1
43.928	52	1	1	3	62.071	12	2	4	1	74.459	23	2	4	3
44.722	13	4	0	0	63.418	83	5	0	2	75.205	7	2	3	4



# Conditions Required for X-Ray Diffraction

Not all diffracted lights from crystal planes that satisfy Bragg's law are detectable. Detection of the diffracted light depends on its intensity

X-ray diffraction in a crystal happens in all direction from all atoms within the crystal that satisfy the Bragg's law

All these atoms contribute to the intensity of the diffracted light

An X-ray can be scattered by an electron in all directions in space

The intensity of the scattered light is a function of the angle ( $2\theta$ ) between the incident photon and the scattered:

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

- $I_o$  is the intensity of the incident photon
- $r$  is the distance between the electron and the detector
- $K$  is a constant depending on the properties of the atom
- The mathematical term represents the effect of the scattering angle on intensity – Polarization factor

# Conditions Required for X-Ray Diffraction

Total intensity of the scattered (diffracted) X-rays from an atom at a specific scattering angle is less than the theoretical intensity of X-rays generated by the electrons

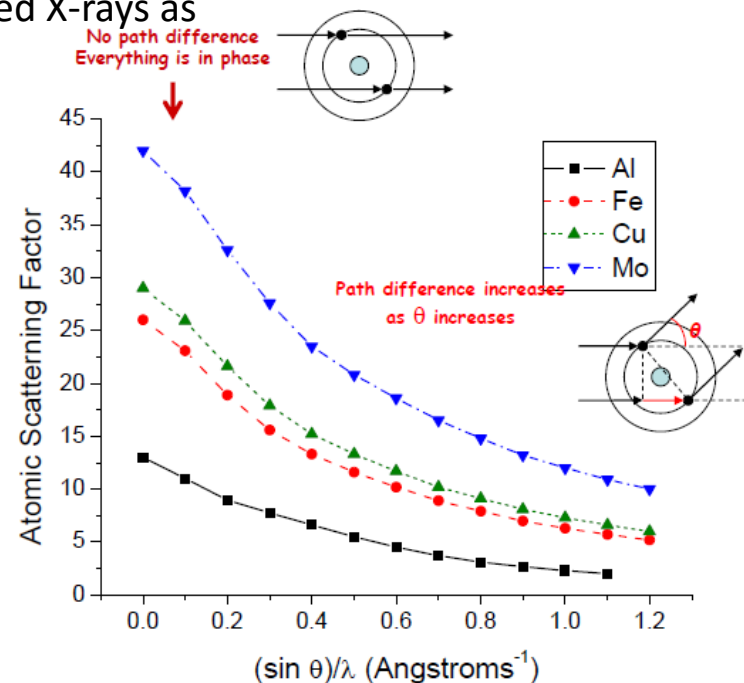
The reason is absorption (fluorescence) of some of the diffracted X-rays by electrons at suitable positions around the atom

Scattered X-rays follow different paths with different path lengths for each diffraction angle

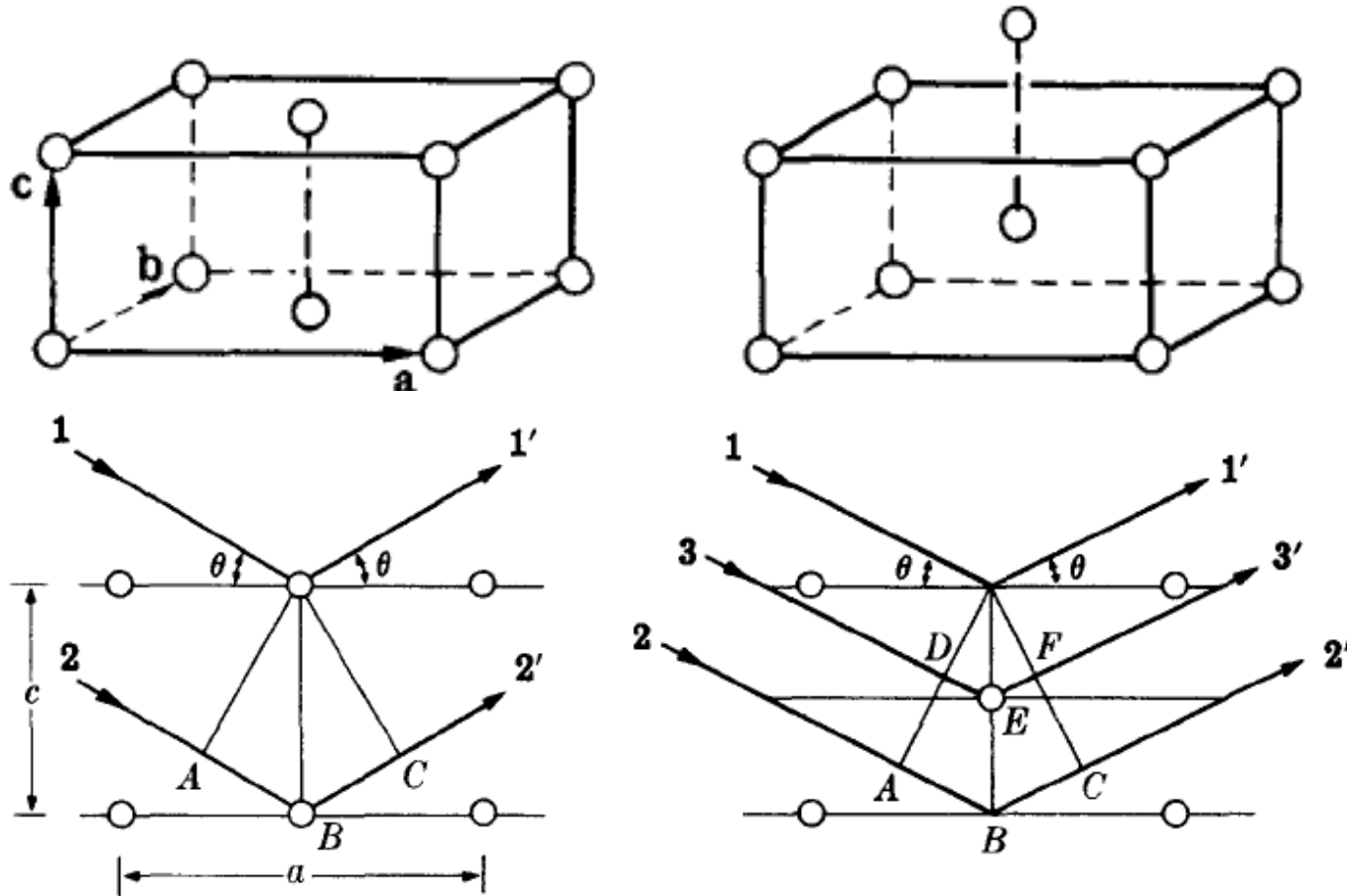
Atomic scattering factor determines the intensity of the diffracted X-rays as

$f =$  Number of X-rays scattered from an atom/

Number of X-rays scattered from all electrons in the atom



# Structural photon absorption



(a) Base-centered and (b) body-centered orthorhombic unit cells.

# Conditions Required for X-Ray Diffraction

Structural absorption of diffracted X-ray intensity is determined from the Structural factor (F)

$$F_{hkl} = \sum_n^N f_n \exp [2\pi i(hu_n + kv_n + lw_n)]$$

It is independent of the shape (cubic, hexagonal, etc) or size of the crystal structure

In a unit cell within the (hkl) plane and consisting of N atoms, the position of the nth atom is defined as  $u_n, v_n, w_n$

Structural factor can be calculated if the atomic scattering factor  $f_n$  is known

# Structure Factor

Structural absorption of diffracted X-ray intensity is determined from the Structural factor (F)

$$F_{hkl} = \sum_n^N f_n \exp [2\pi i(hu_n + kv_n + lw_n)]$$

For a plane within a body centered cubic crystal, the structural factor in the (001) and (002) planes are found as:

$$\begin{aligned} F_{001} &= f \exp [2\pi i(0 + 0 + 1 \times 0)] + f \exp [2\pi i(0 \times 0.5 + 0 \times 0.5 + 1 \times 0.5)] \\ &= f + f \exp [\pi i] = 0 \end{aligned}$$

$$\begin{aligned} F_{002} &= f \exp [2\pi i(0 + 0 + 2 \times 0)] + f \exp [2\pi i(0 \times 0.5 + 0 \times 0.5 + 2 \times 0.5)] \\ &= f + f \exp [2\pi i] = 2f \end{aligned}$$

Simple crystal structures like BCC, FCC, SC have the same structural factors in general

# Systematic Absences

$$F_{hkl} = \sum_1^N f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

Intensity of the diffracted beam  $\propto |F|^2$

- $h, k, l$ : indices of the diffraction plane under consideration
- $u, v, w$ : co-ordinates of the atoms in the lattice
- $N$ : number of atoms
- $f_n$ : scattering factor of a particular type of atom

Bravais Lattice	Reflections possibly present	Reflections absent
Simple	All	None
Body Centered	$(h+k+l)$ : Even	$(h+k+l)$ : Odd
Face Centered	$h, k,$ and $l$ unmixed i.e. all odd or all even	$h, k,$ and $l$ : mixed

## Permitted Reflections

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Simple Cubic	(100), (110), (111), (200), (210), (211), (220), (300), (221) .....
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BCC	(110), (200), (211), (220), (310), (222)....
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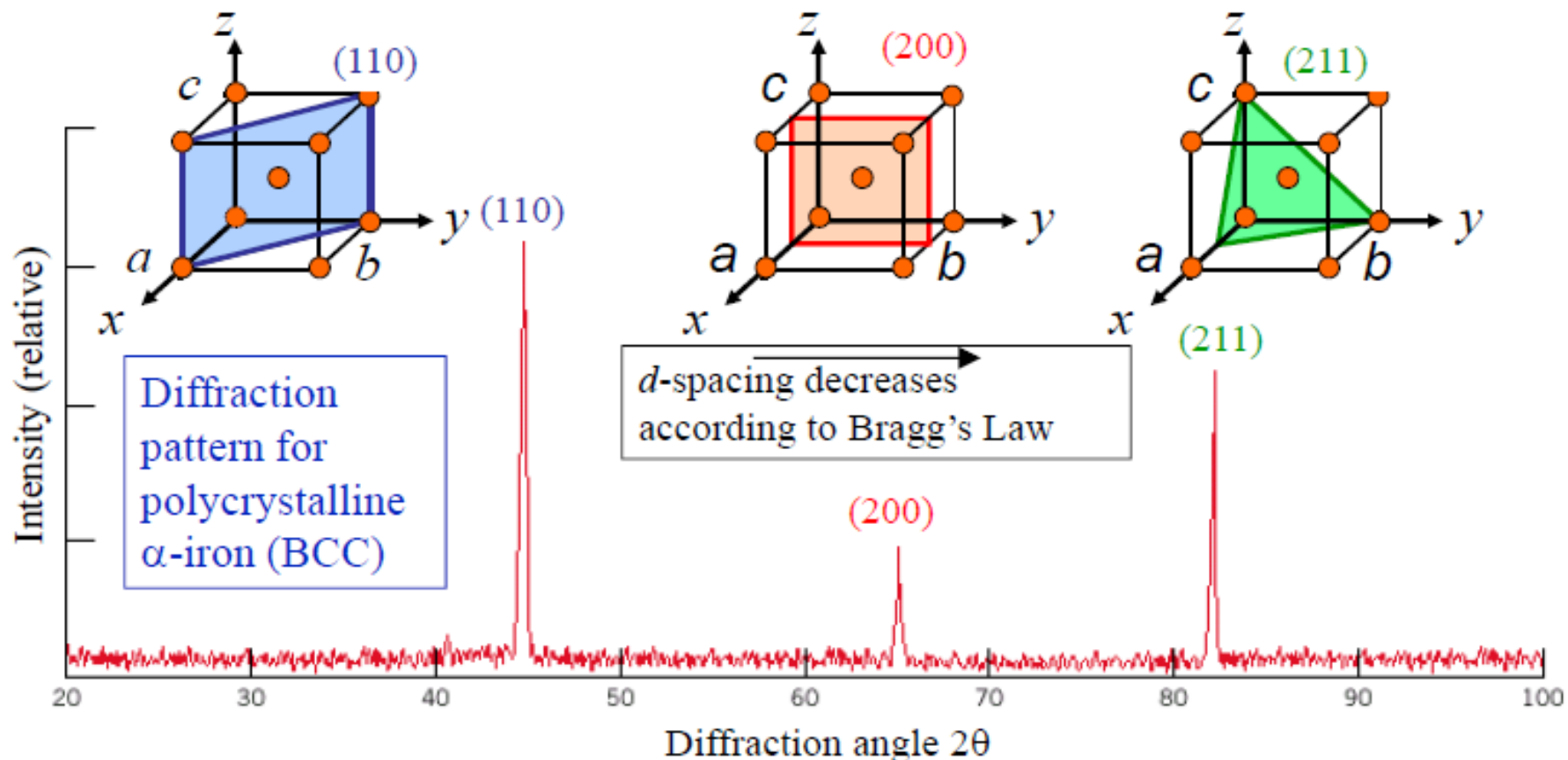
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FCC	(111), (200), (220), (311).....
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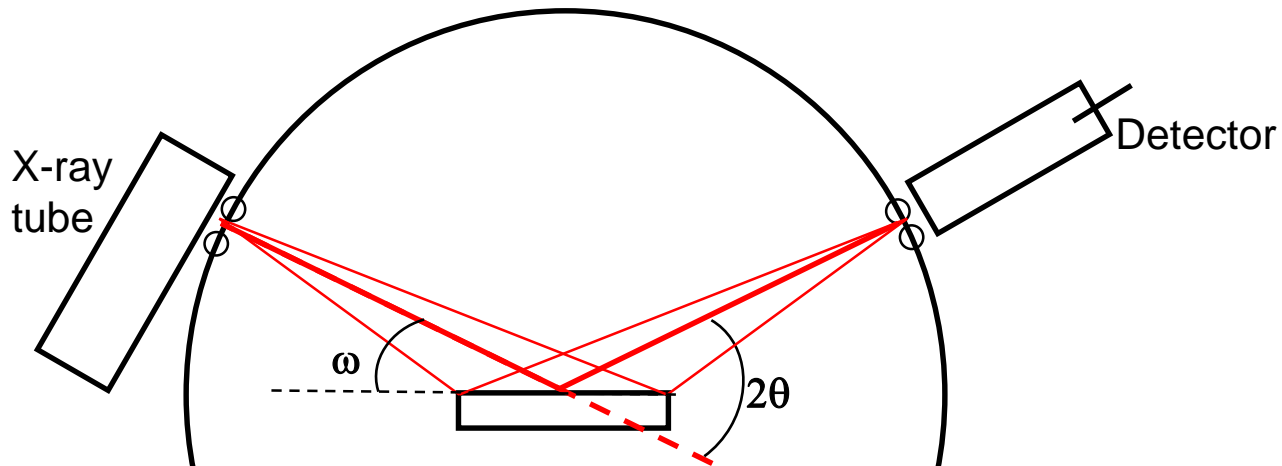
# The result of structural absorption



→  $h+k+l$  even are only allowed according to previously shown selection rules for BCC.

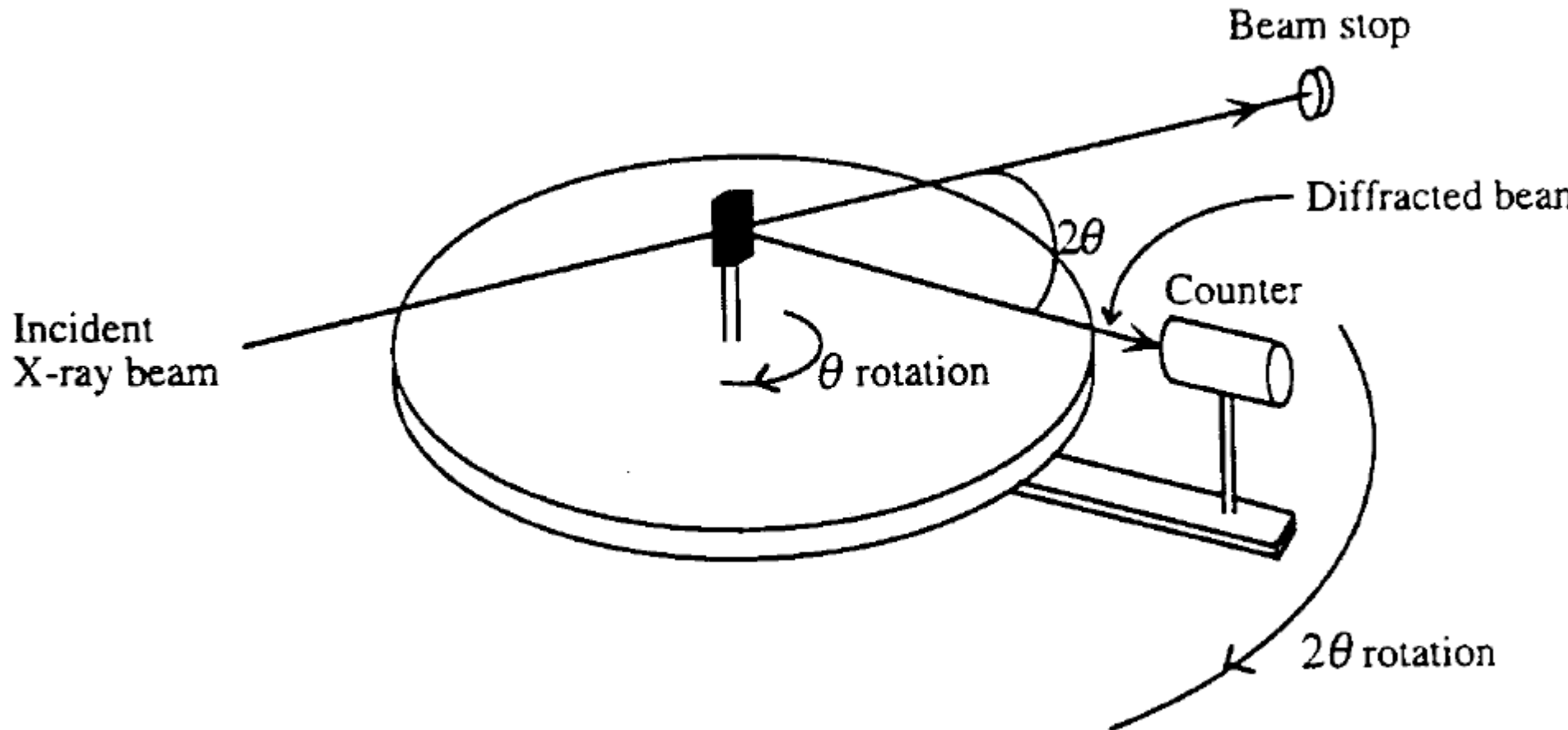
# Diffraction Instrument

- Modern powder diffractometers typically use the Bragg-Brentano parafofocusing geometry
- The incident angle between the X-Ray source and the sample is  $\omega$   
The diffraction angle, between the incident beam and the detector angle, is  $2\theta$
- The Bragg-Brentano geometry constrains  $\omega$  to be always  $\frac{1}{2}$  of the detector angle  $2\theta$
- Two main diffractometer models: The tube is fixed, sample and detector rotate – The sample is fixed, tube and detector rotate



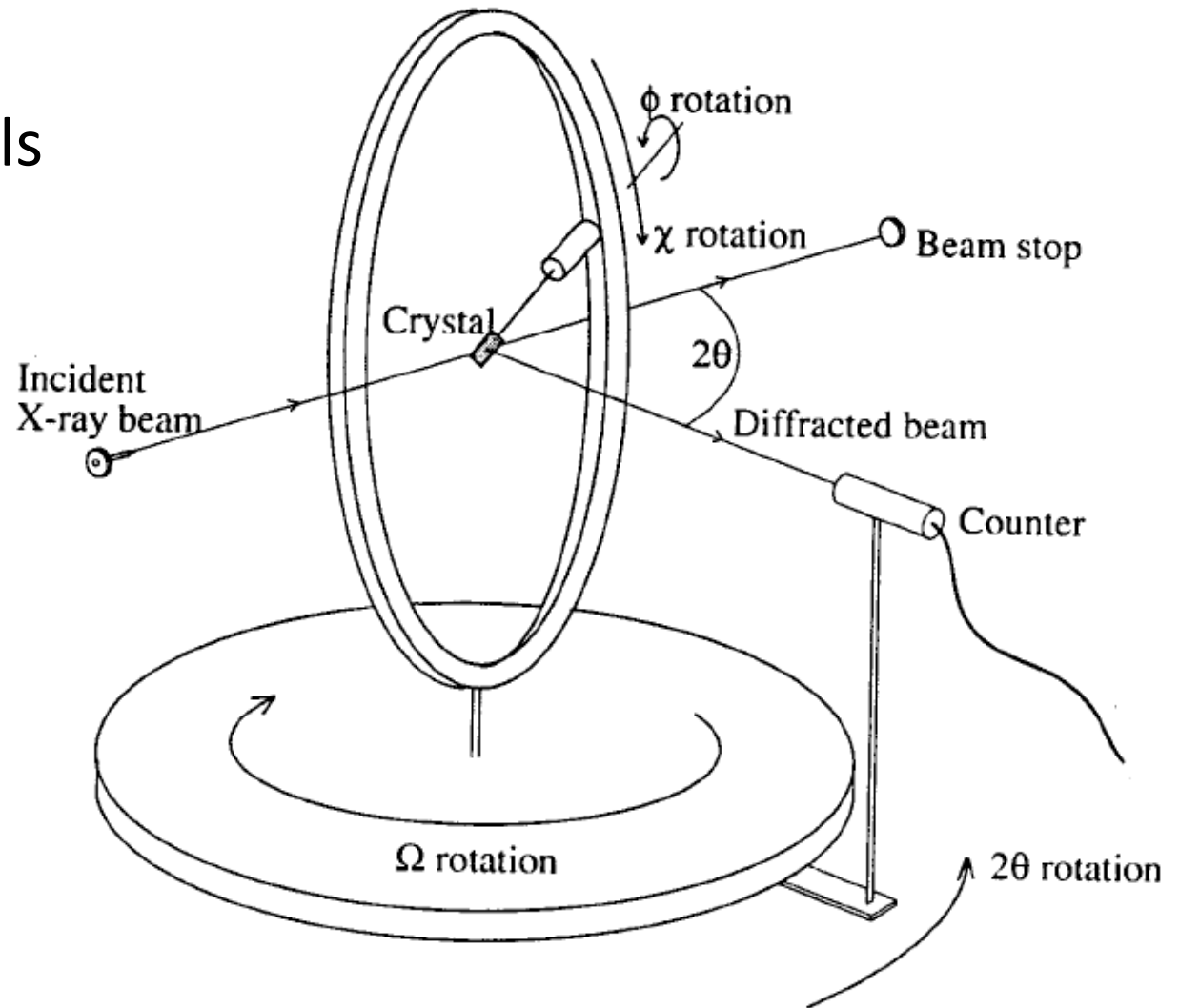
# Two Circle Diffractometer

- For polycrystalline Materials



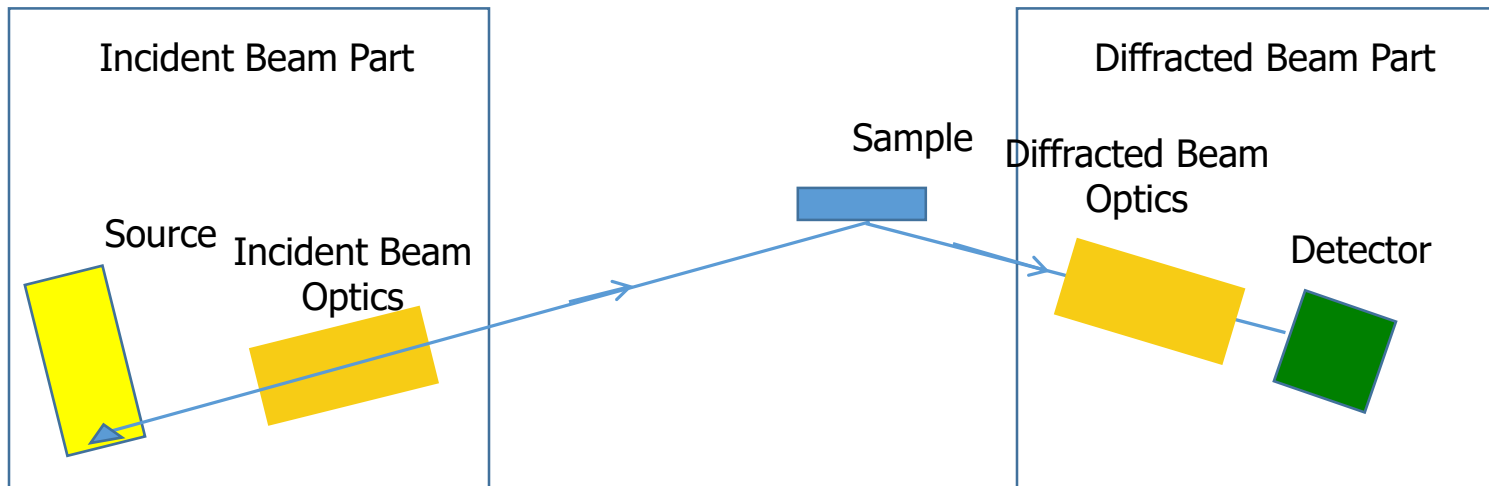
# Four Circle Diffractometer

For single crystals



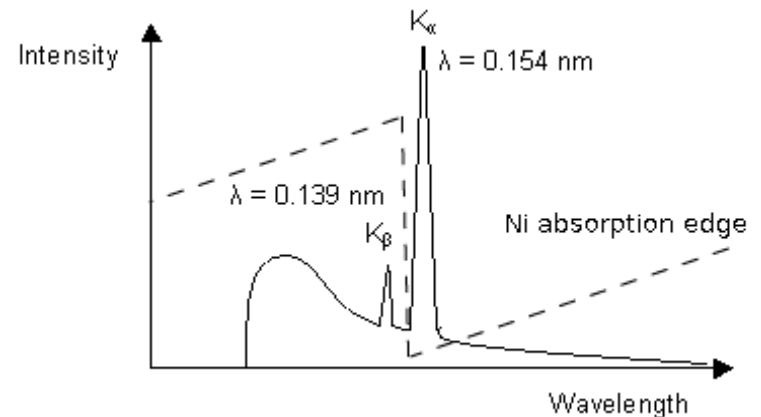
# Geometry and Configuration

- Theta-Theta → Source and detector move  $\theta$ , sample fixed
- Theta-2Theta → Sample moves  $\theta$  and detector  $2\theta$ , source fixed



# Beam Optics

- A material with an absorption edge between the K-alpha and K-beta wavelengths can be used as a beta filter.
- This is often the element just below the target material on the periodic table –For example, when using Cu radiation,
  - Cu K-alpha = 1.541 Å
  - Cu K-beta = 1.387 Å
  - The Ni absorption edge = 1.488 Å
- Choice of proper thickness
- The Ni absorption of Cu radiation is:
  - 50% of Cu K-alpha
  - 99% of Cu K-beta



H																	He						
Li	Be																	B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
Fr	Ra	A																					

## Fluorescence

- Some atoms absorb incident X-rays and fluoresce them as X-rays of a different wavelength
  - The absorption of X-rays decreases the diffracted signal
  - The fluoresced X-rays increase the background noise
- The increased background noise from fluoresced X-rays can be removed by using:
  - a diffracted-beam monochromator
  - an energy sensitive detector
- The diffracted beam signal can only be increased by using a different wavelength of radiation
- The most problematic materials are those two and three below the target material:
  - For Cu, the elements that fluoresce the most are Fe and Co

The X-ray beam produced by the X-ray tube is divergent.  
Incident-beam optics are used to limit this divergence

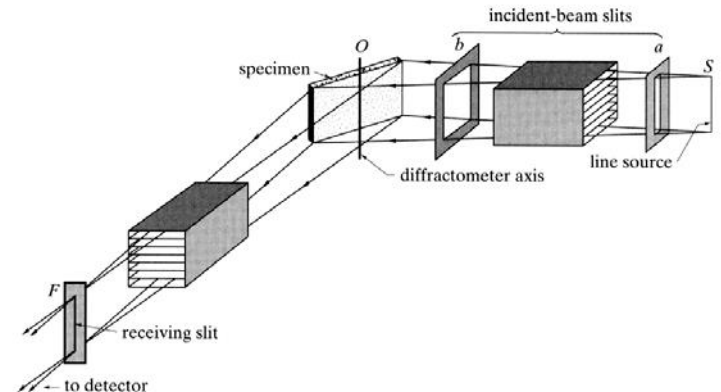
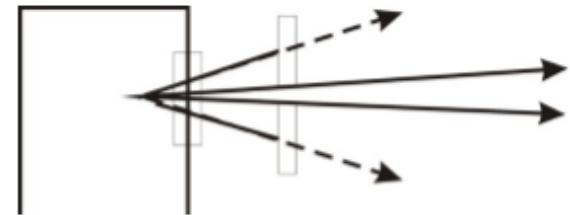
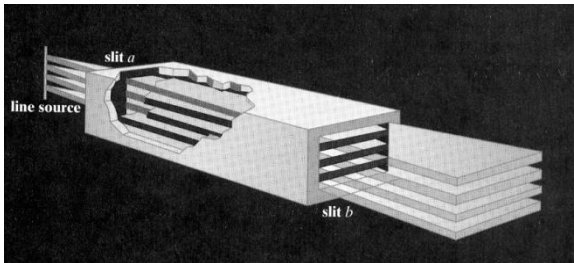
$$\lambda = 2d_{hkl} \sin \theta$$

- X Rays from an X-ray tube are:
  - divergent
  - contain multiple characteristic wavelengths as well as Bremsstrahlung radiation
- neither of these conditions suit our ability to use X rays for analysis
  - the divergence means that instead of a single incident angle  $\theta$ , the sample is actually illuminated by photons with a range of incident angles.
  - the spectral contamination means that the sample does not diffract a single wavelength of radiation, but rather several wavelengths of radiation.
    - Consequently, a single set of crystallographic planes will produce several diffraction peaks instead of one diffraction peak.
- Optics are used to:
  - limit divergence of the X-ray beam
  - refocus X rays into parallel paths
  - remove unwanted wavelengths



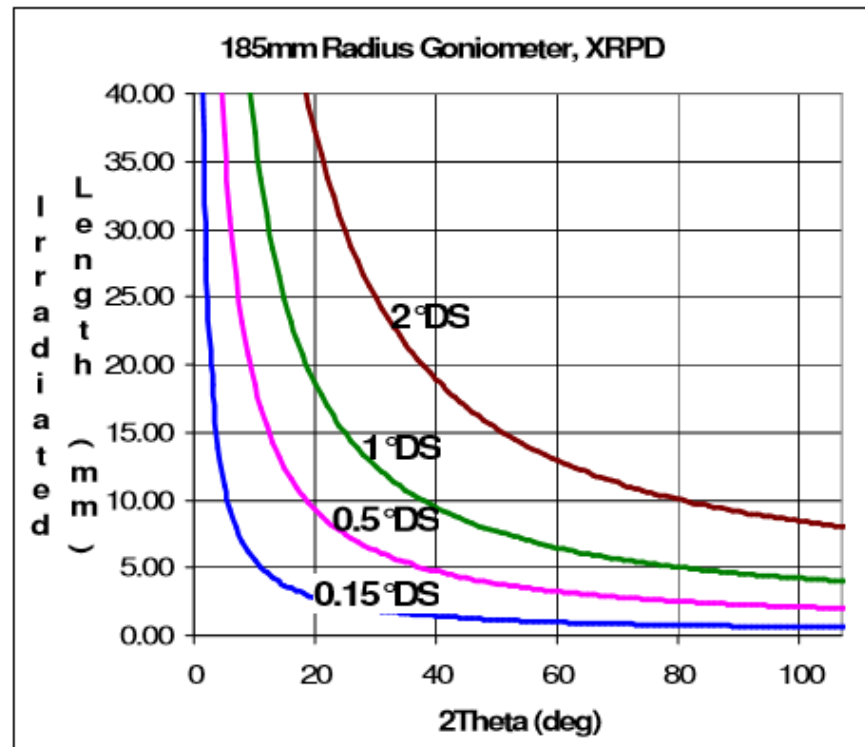
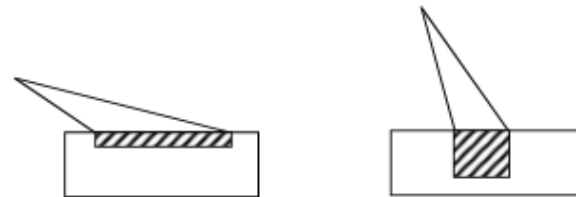
# Divergence slits are used to limit the divergence of the incident X-ray beam.

- The slits block X-rays that have too great a divergence.
- The size of the divergence slit influences peak intensity and peak shapes.
- Narrow divergence slits:
  - reduce the intensity of the X-ray beam
  - reduce the length of the X-ray beam hitting the sample
  - produce sharper peaks
    - the instrumental resolution is improved so that closely spaced peaks can be resolved.



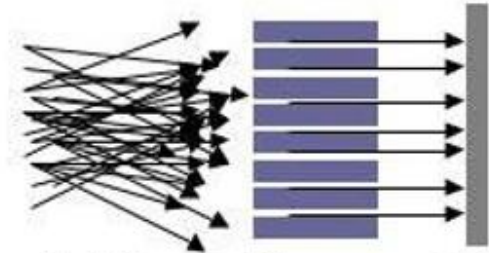
One by-product of the beam divergence is that the length of the beam illuminating the sample becomes smaller as the incident angle becomes larger.

- The length of the incident beam is determined by the divergence slit, goniometer radius, and incident angle.
- This should be considered when choosing a divergence slits size:
  - if the divergence slit is too large, the beam may be significantly longer than your sample at low angles
  - if the slit is too small, you may not get enough intensity from your sample at higher angles
  - Appendix A in the SOP contains a guide to help you choose a slit size.
- The width of the beam is constant: 12mm for the Rigaku RU300.

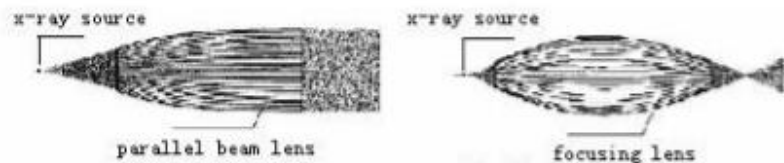
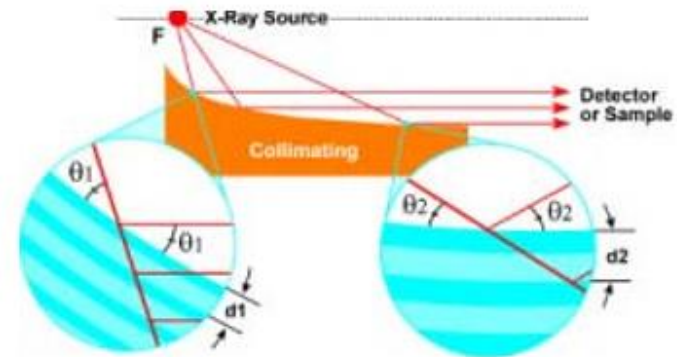


## Other optics:

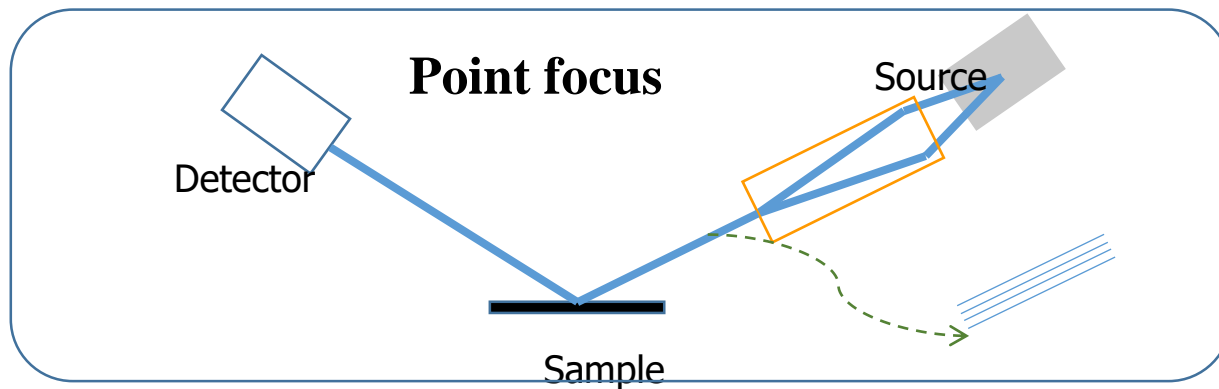
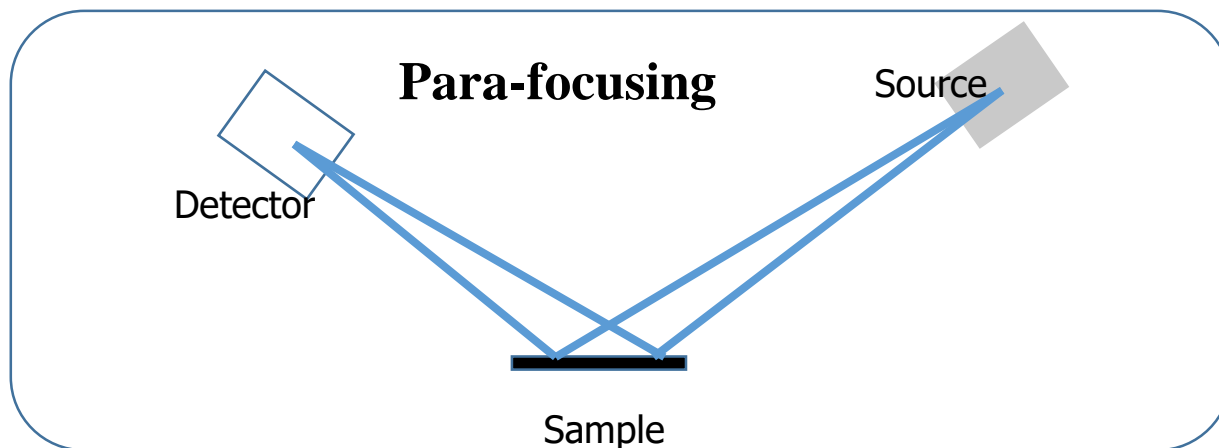
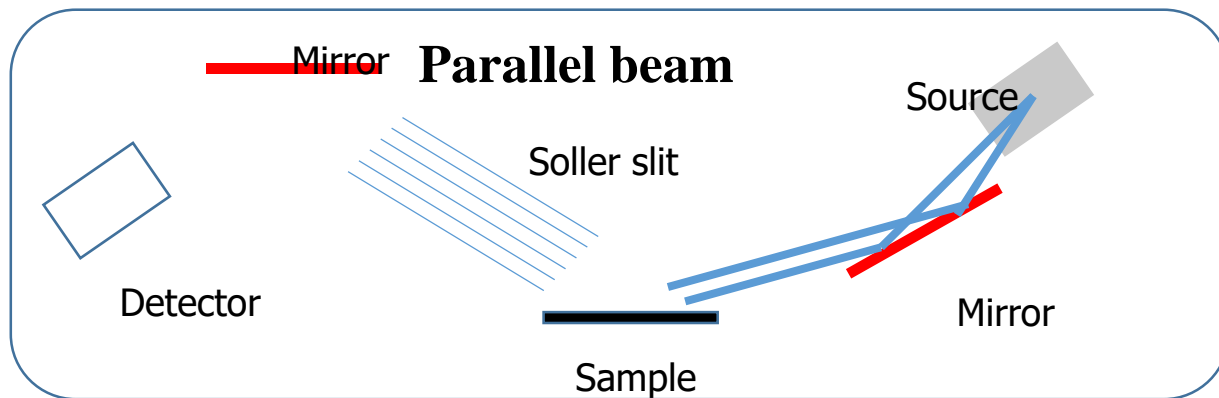
- limit divergence of the X-ray beam
  - Divergence limiting slits
  - Parallel plate collimators
  - Soller slits
- refocus X rays into parallel paths
  - “parallel-beam optics”
  - parabolic mirrors and capillary lenses
  - focusing mirrors and lenses
- remove unwanted wavelengths
  - monochromators
  - $K\beta$  filters



Parallel Plate Collimator & Soller Slits block divergent X-rays, but do not restrict beam size like a divergent slit



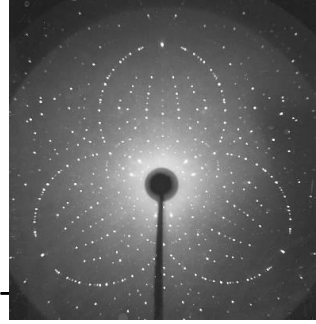
Göbel Mirrors and capillary lenses collect a large portion of the divergent beam and refocus it into a nearly parallel beam



# Comparison

<b>Parallel beam</b>	<b>Para-focusing</b>
X-rays are aligned	X-rays are diverging
Lower intensity for bulk samples	Higher intensity
Higher intensity for small samples	Lower intensity
Instrumental broadening independent of orientation of diffraction vector with specimen normal	Instrumental broadening dependent of orientation of diffraction vector with specimen normal
Suitable for GI-XRD	Suitable for Bragg-Brentano
Texture, stress	Powder diffraction

# Diffraction Methods

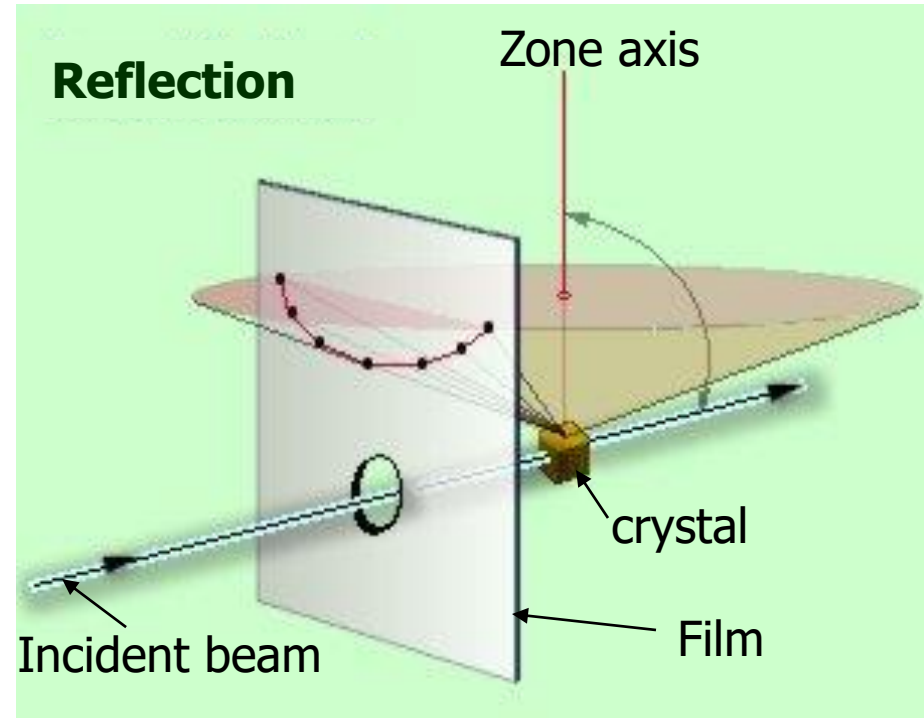
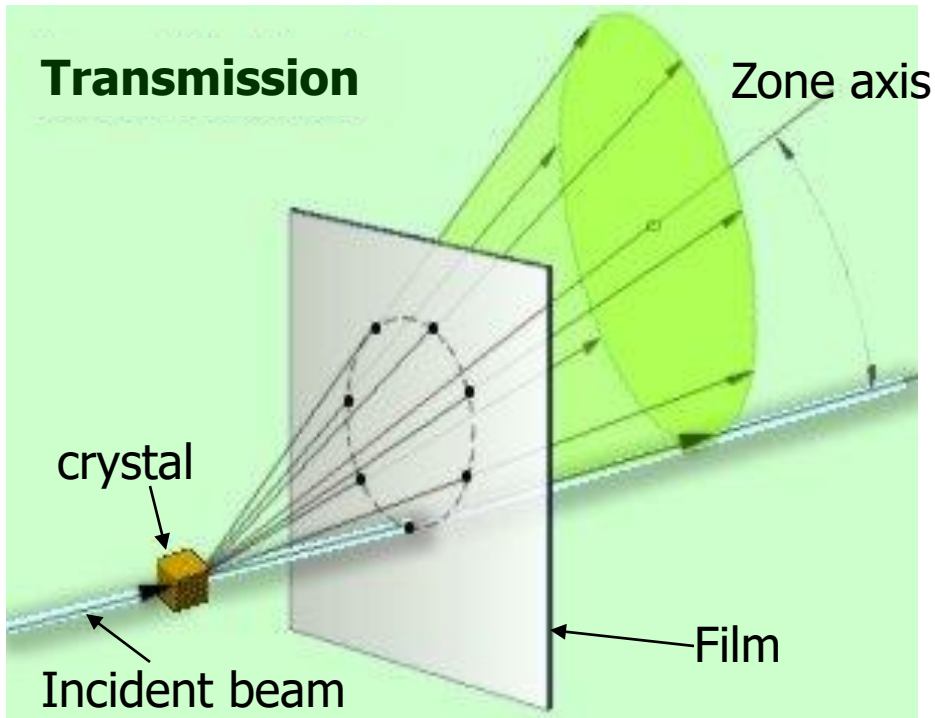


1. Laue method: a single crystal is held stationary in a beam of x-ray white radiation. The crystal diffracts the discrete values of  $l$  for which  $\{hkl\}$  planes exist of spacing  $d_{hkl}$  and incidence angle  $\theta$  for each wavelength. Used to determine symmetry of a crystal.
2. Rotating-crystal method: a single crystal is rotated about a fixed axis in a beam of monochromatic x-rays. The variation in  $\theta$  brings different atomic planes into position for reflection.
3. Powder (Debye-Scherrer-Hull) method: a finely powdered sample is placed in a holder in a monochromatic x-ray beam, with the angle  $\theta$  gradually changing due synchronous movement of holder and detector. Assuming random orientation of the tiny crystallites, there will be diffraction off of different  $\{hkl\}$  planes at specific angles.

# Diffraction Methods

Method	Wavelength	Angle	Specimen
Laue	Variable	Fixed	Single Crystal
Rotating Crystal	Fixed	Variable (in part)	Single Crystal
Powder	Fixed	Variable	Powder

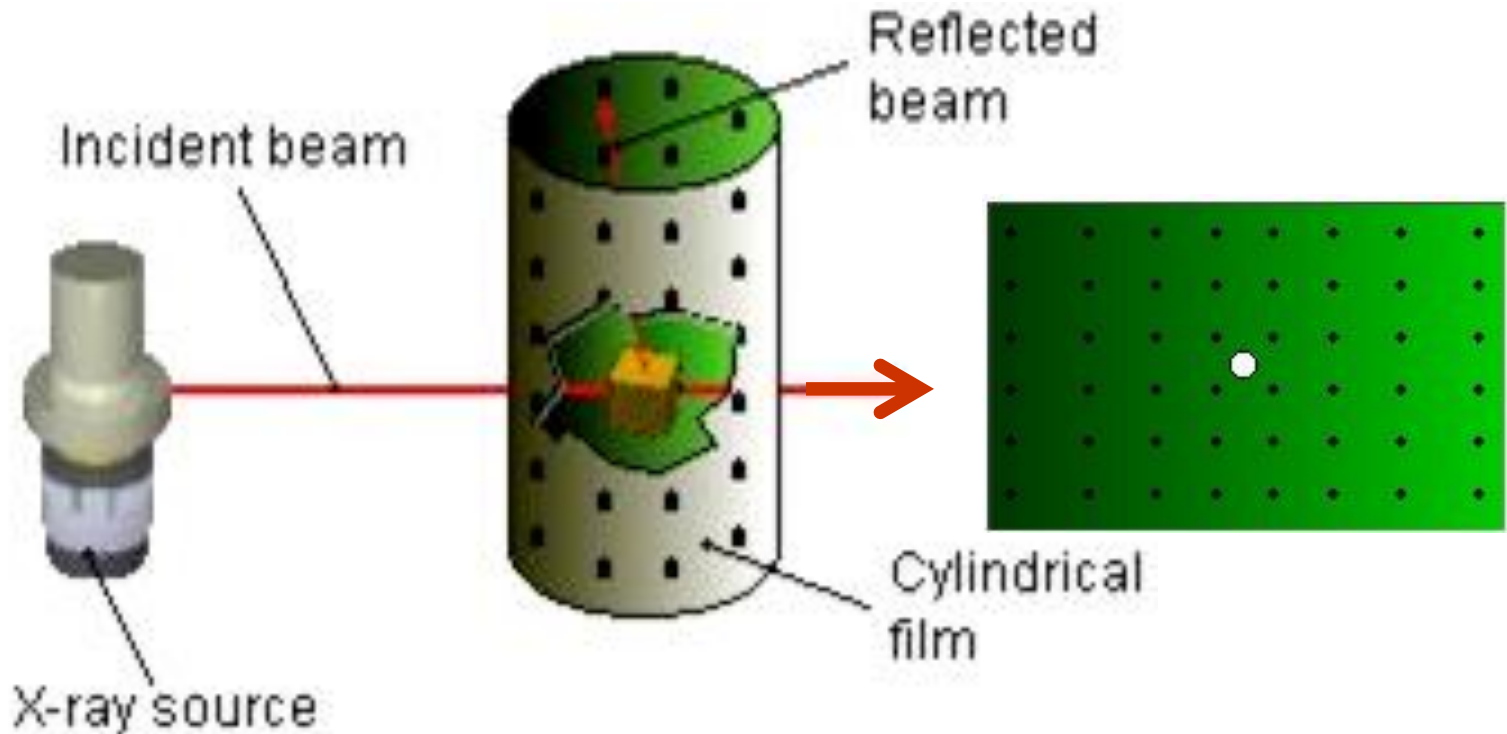
# Laue Method



- Uses Single crystal
- Uses White Radiation
- Used for determining crystal orientation and quality

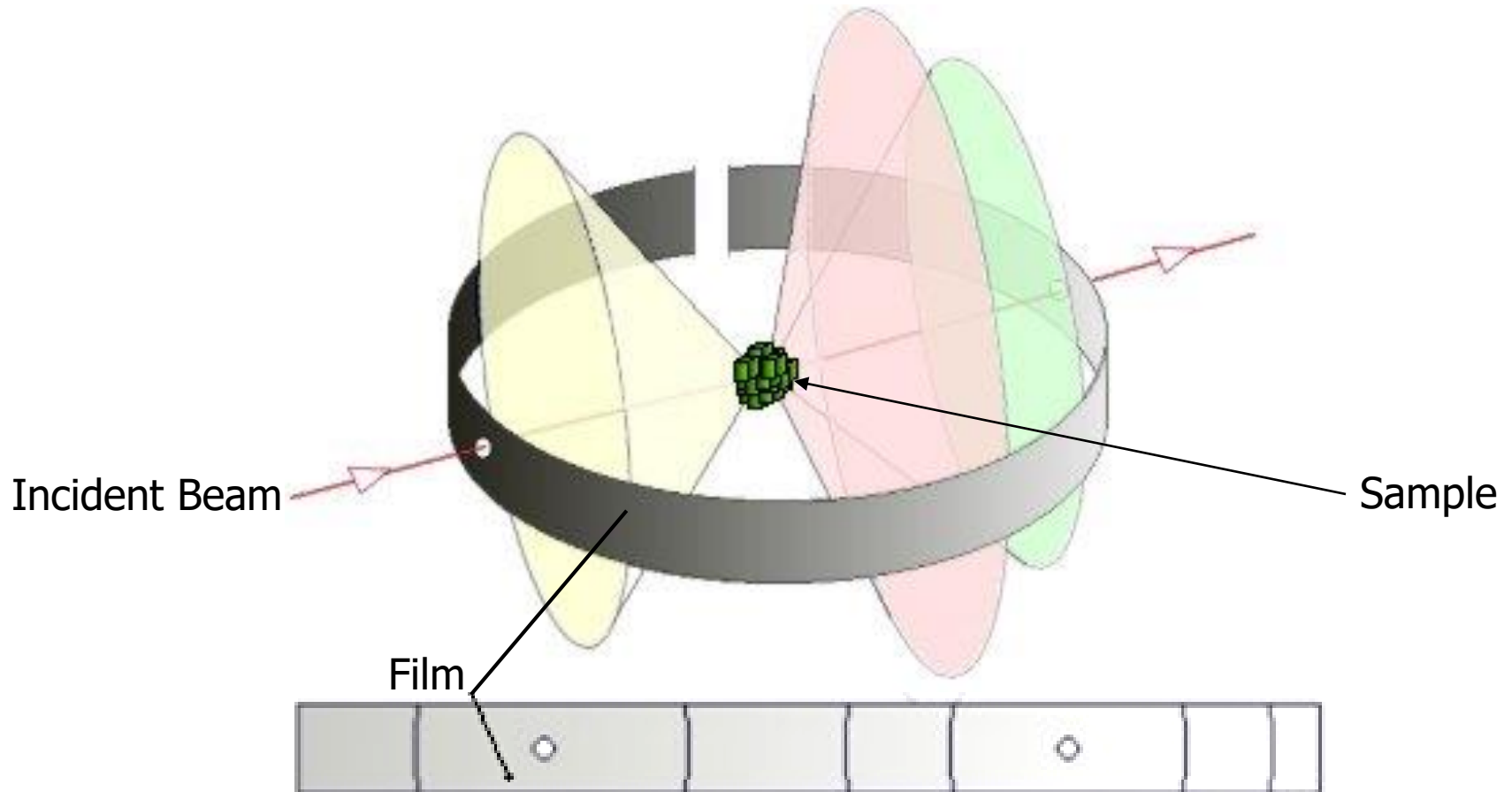


# Rotating Crystal Method



- Used for determination of unknown crystal structures

# Powder Method



- Useful for determining lattice parameters with high precision and for identification of phases

# X-rays are scattered in a sphere around the sample

- A cone along the sphere corresponds to a single Bragg angle  $2\theta$ 
  - The tens of thousands of randomly oriented crystallites in an ideal sample produce a Debye diffraction cone.
- The linear diffraction pattern is formed as the detector scans through an arc that intersects each Debye cone at a single point; thus giving the appearance of a discrete diffraction peak.

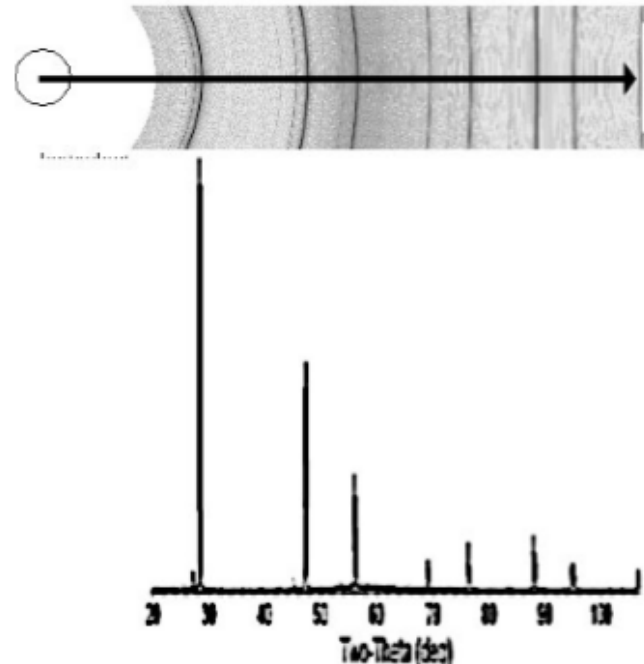
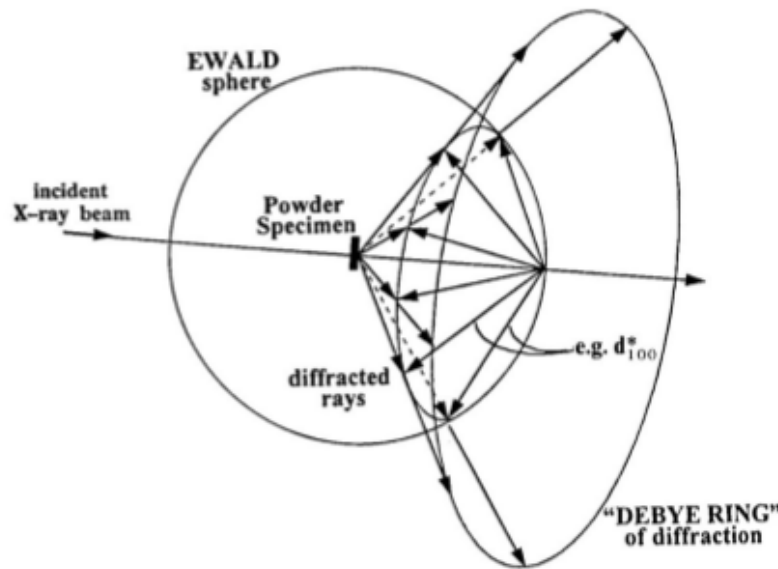
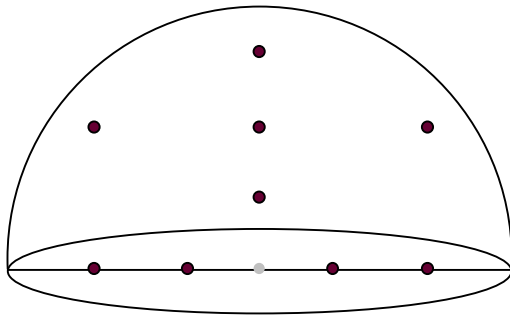
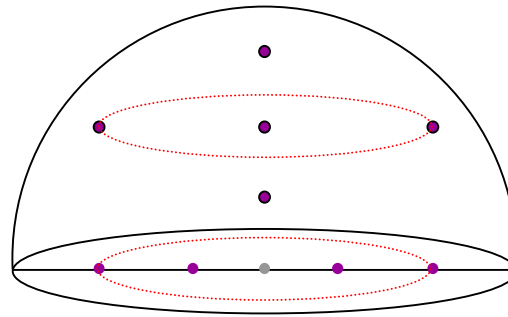
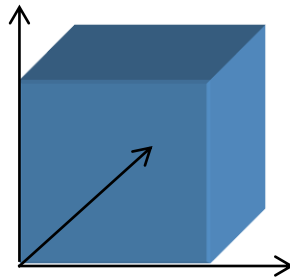


Figure 3.9. The intersection of  $d_{100}^*$  vectors from a powder with the Ewald sphere.

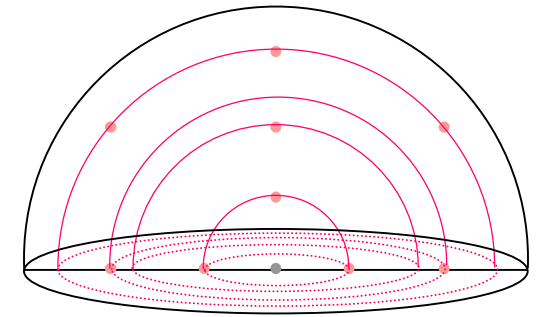
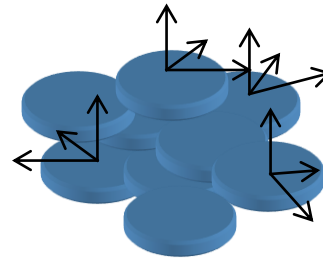
# What does a powder really mean?



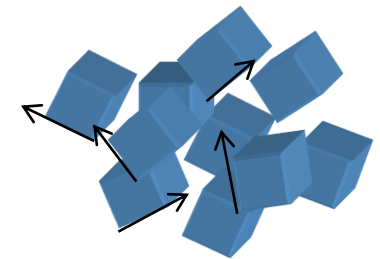
Single



Oriented

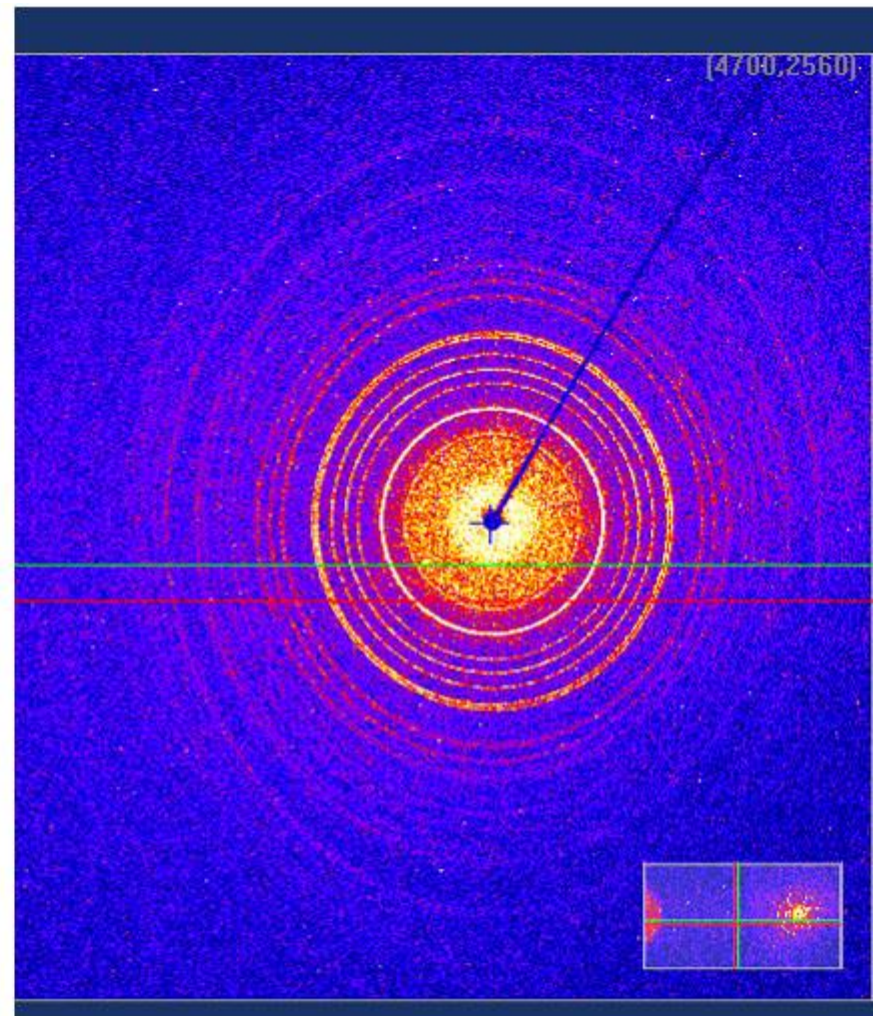
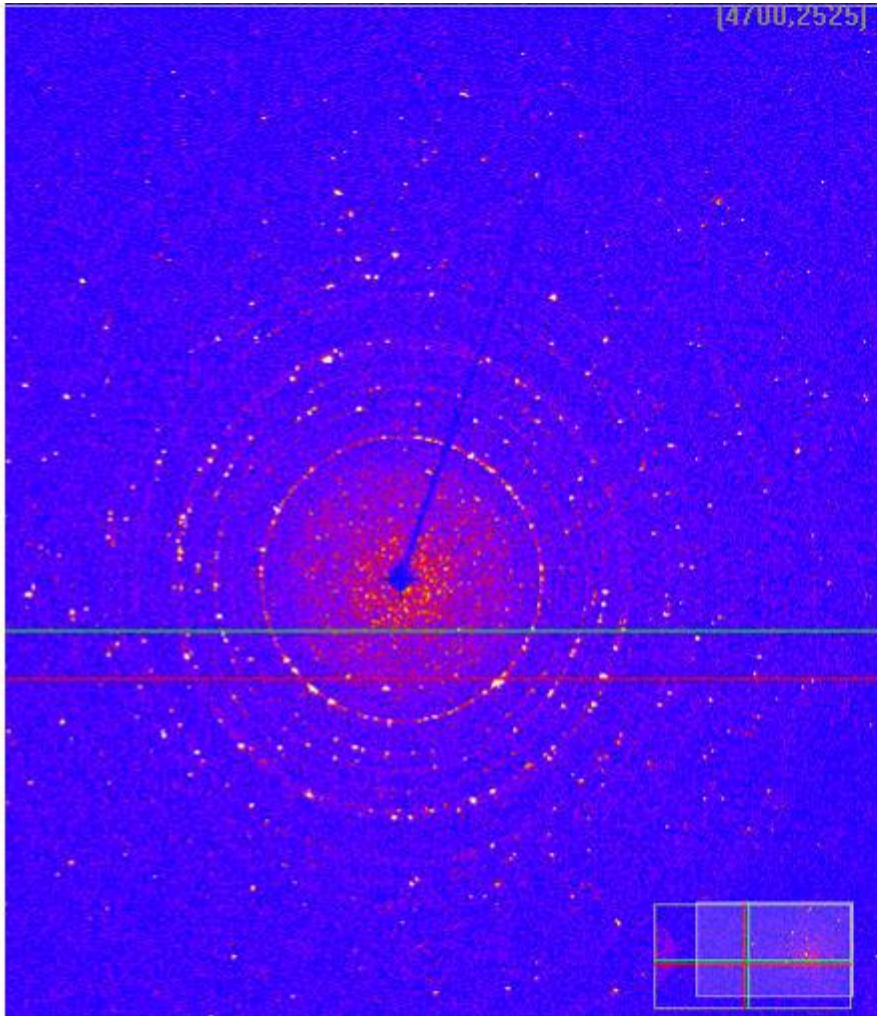


Random





# Limited crystals vs. many crystals



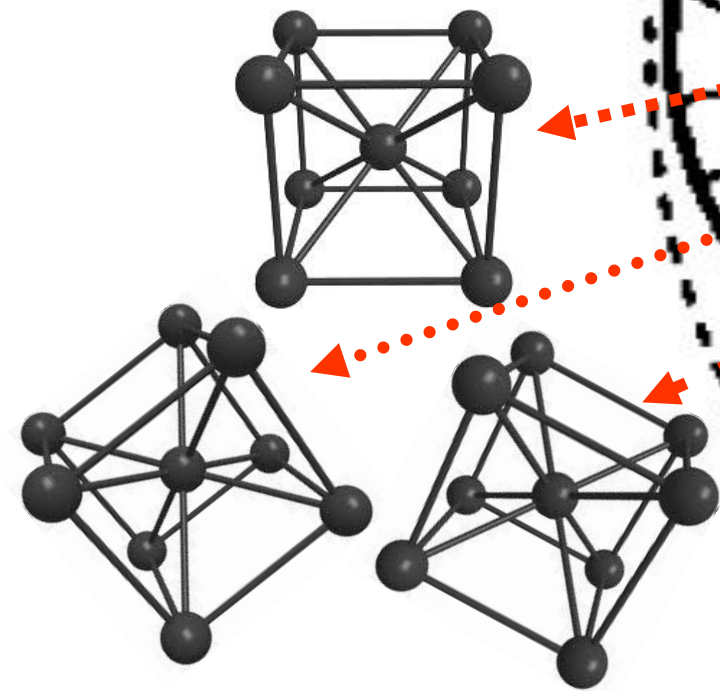
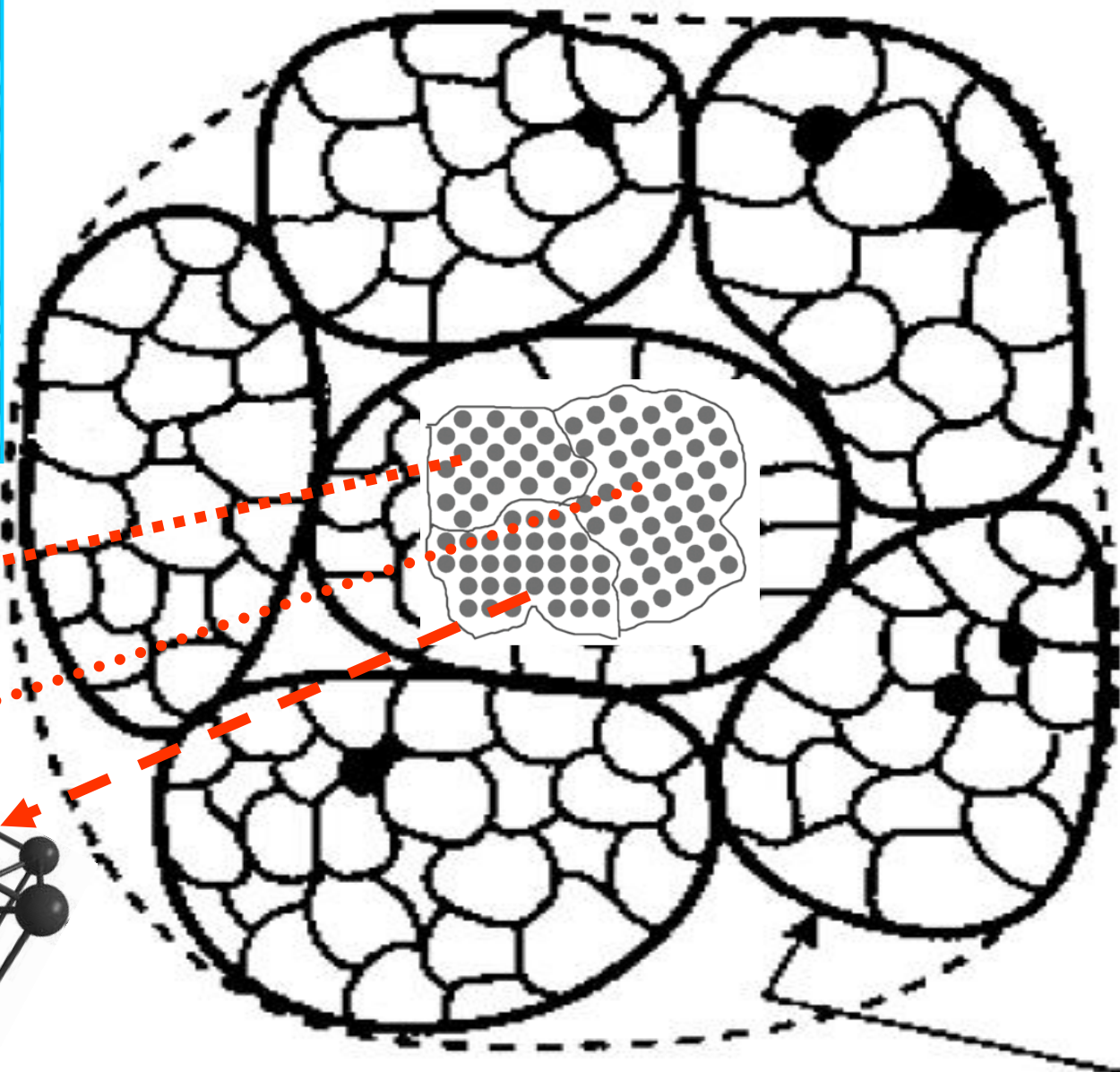
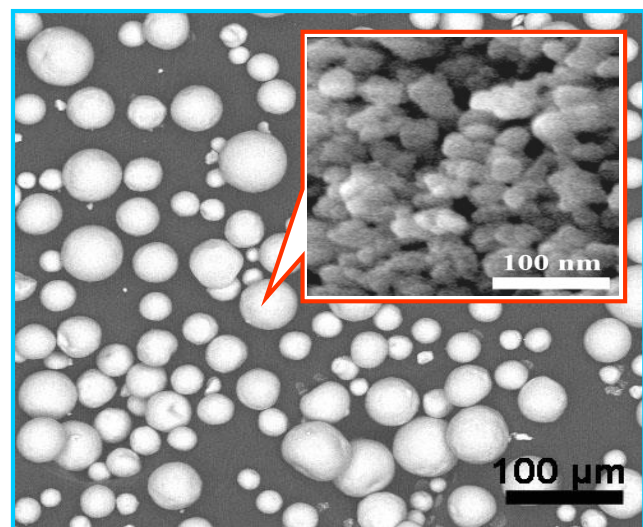
# X-Ray Powder Diffraction

- Each crystallite in the powder is a small single crystal with a random orientation
- There is roughly equal statistically relevant number of crystallites for every set of randomly oriented planes that will diffract the incident beam
- Samples can be powder, sintered pellets, coatings on substrates, engine block
- The resultant XRD pattern is a unique fingerprint of the polycrystalline material which contains a lot of information
- The position, intensity, width, and shape of the observed diffraction peaks tells us about the crystal structure and, in some cases, microstructure of the sample

## X-Ray Powder Diffraction (XRPD) is a somewhat inefficient measurement technique

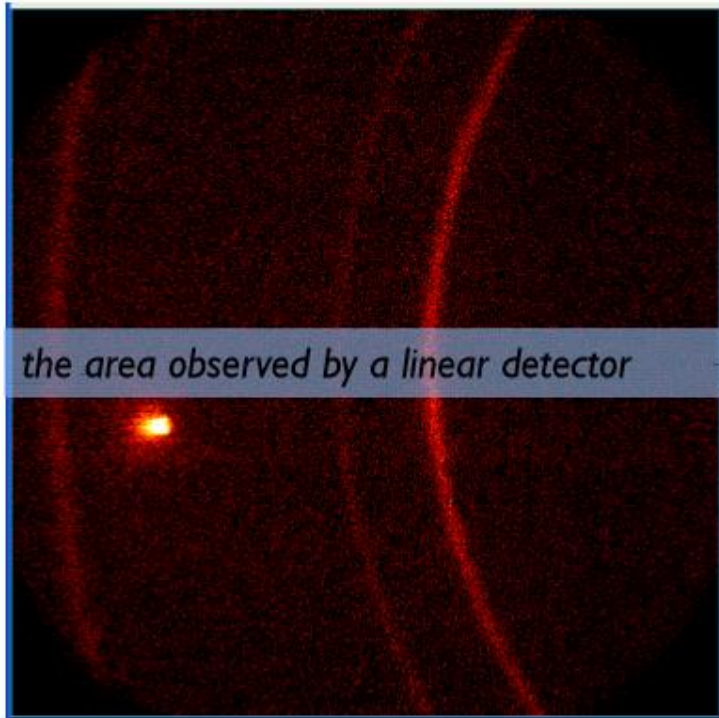
- Only a small fraction of crystallites in the sample actually contribute to the observed diffraction pattern
  - Other crystallites are not oriented properly to produce diffraction from any planes of atoms
  - You can increase the number of crystallites that contribute to the measured pattern by spinning the sample
- Only a small fraction of the scattered X-rays are observed by the detector
  - A point detector scanning in an arc around the sample only observes one point on each Debye diffraction cone
  - You can increase the amount of scattered X-rays observed by using a large area (2D) detector



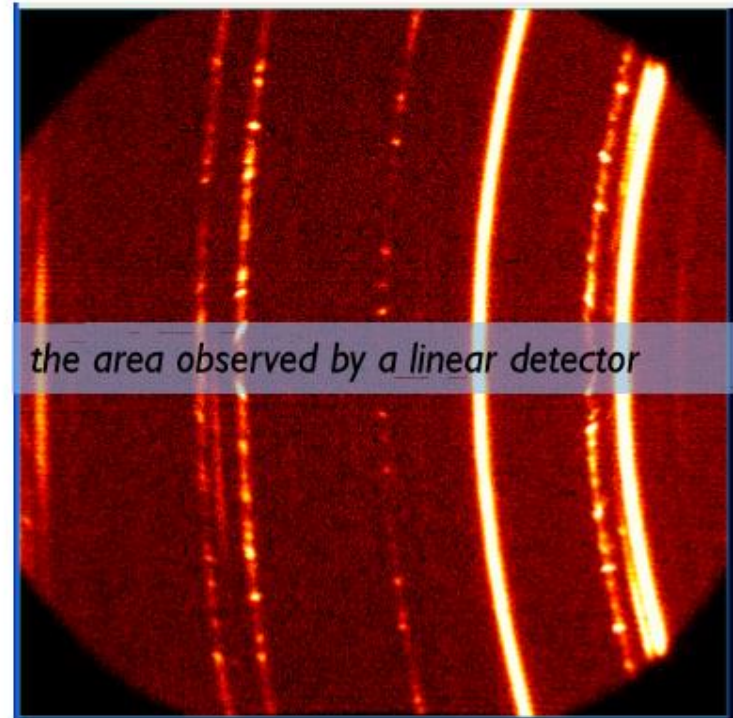




Area (2D) Diffraction allows us to image complete or incomplete (spotty) Debye diffraction rings



Polycrystalline thin film on a single crystal substrate

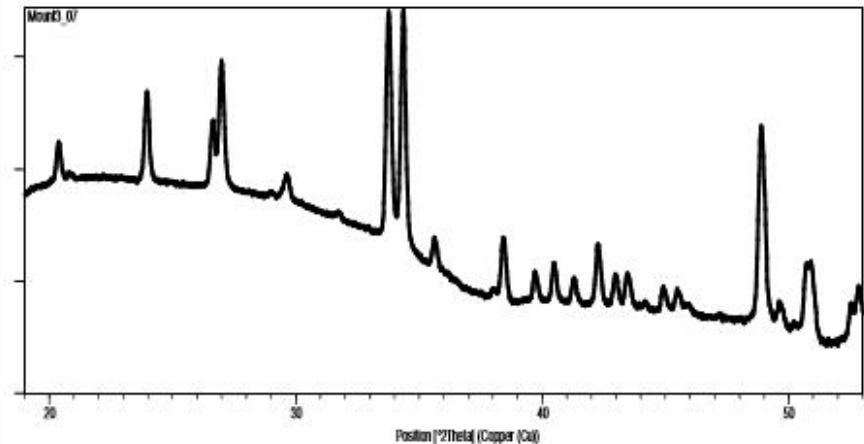
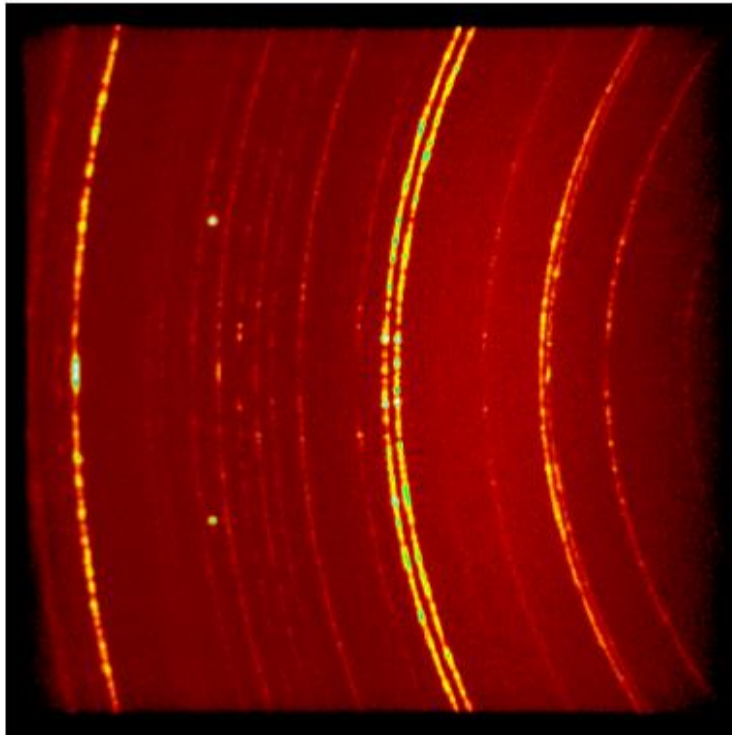


Mixture of fine and coarse grains in a metallic alloy

Conventional linear diffraction patterns would miss information about single crystal or coarse grained materials

## Non-Ideal Samples: a “spotty” diffraction pattern

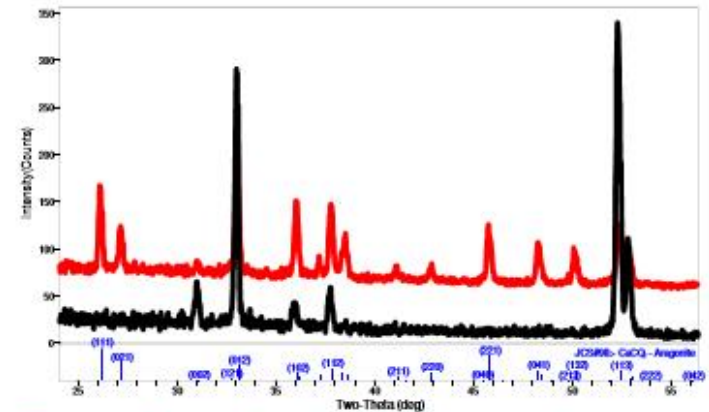
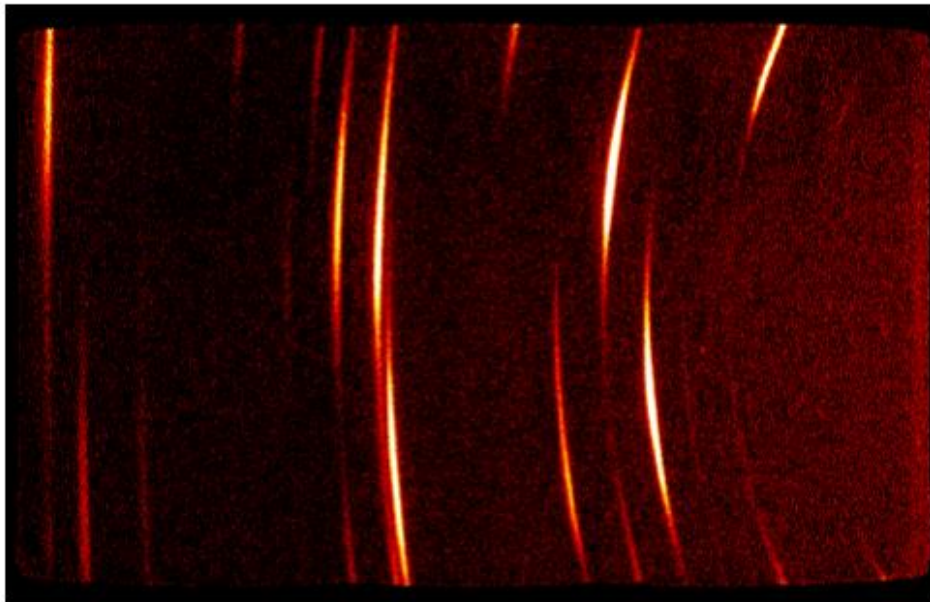
- The sample does not contain tens of thousands of grains
  - The Debye diffraction cone is incomplete because there are not a statistically relevant number of grains being irradiated



**The poor particle statistics cause random error in the observed diffraction peak intensities.**

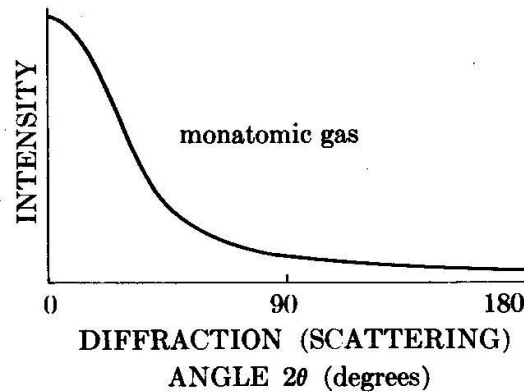
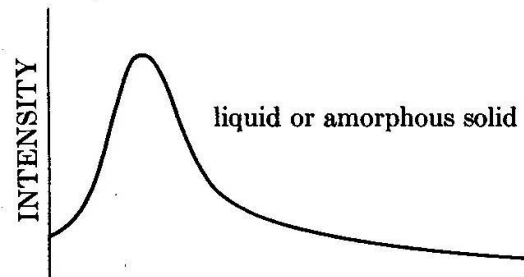
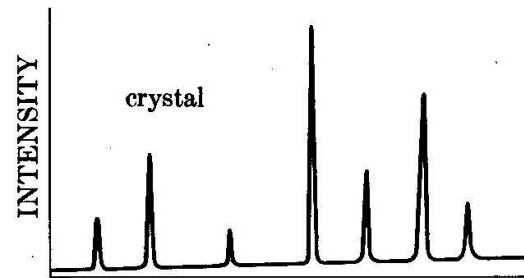
## Non-ideal samples: Texture (i.e. preferred crystallographic orientation)

- The samples consists of tens of thousands of grains, but the grains are not randomly oriented
  - Some phenomenon during crystallization and growth, processing, or sample preparation have caused the grains to have preferred crystallographic direction normal to the surface of the sample



The preferred orientation creates a systematic error in the observed diffraction peak intensities.

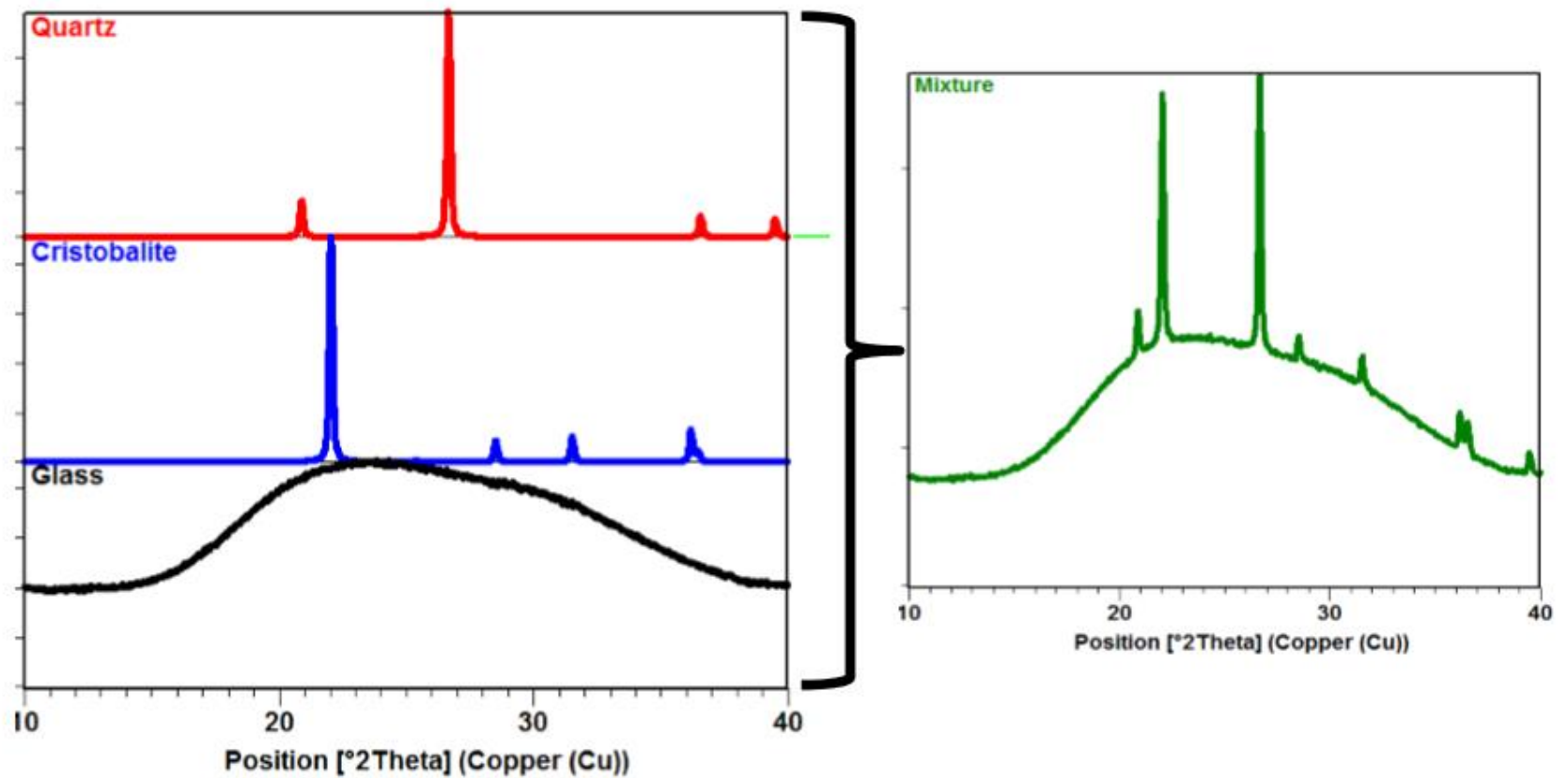
# Diffraction from a variety of materials



(From "Elements of X-ray Diffraction", B.D. Cullity, Addison Wesley)



The diffraction pattern of a mixture is a simple sum of the scattering from each component phase

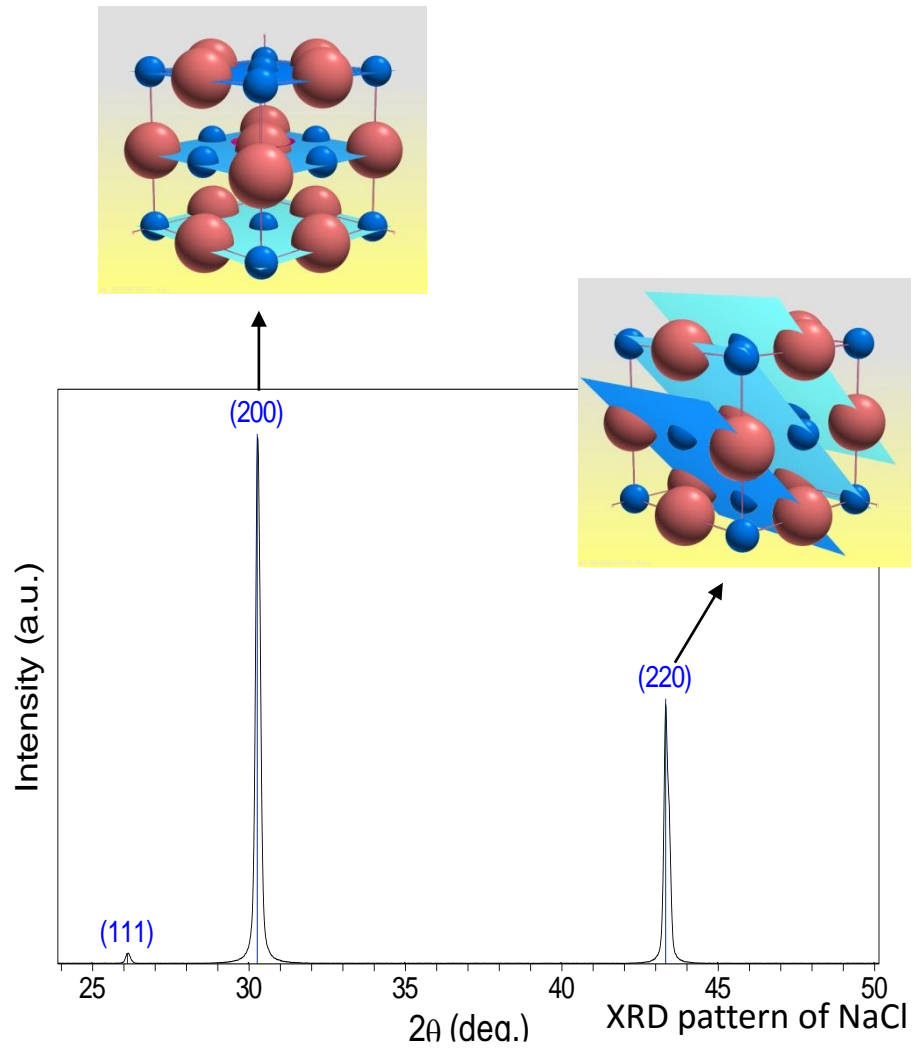


# What can be done with XRD?

- Identify phase composition
- Measure unit cell lattice parameters
- Estimate crystallite size, microstrain
- Measure residual stress
- Measure texture and/or epitaxy
- Evaluate thin film quality
- Measure multilayer thin film thickness, roughness, and density
- Determine orientation of single crystals
- Solve or refine crystal structures
- Analyze ordered meso- and nanostructures

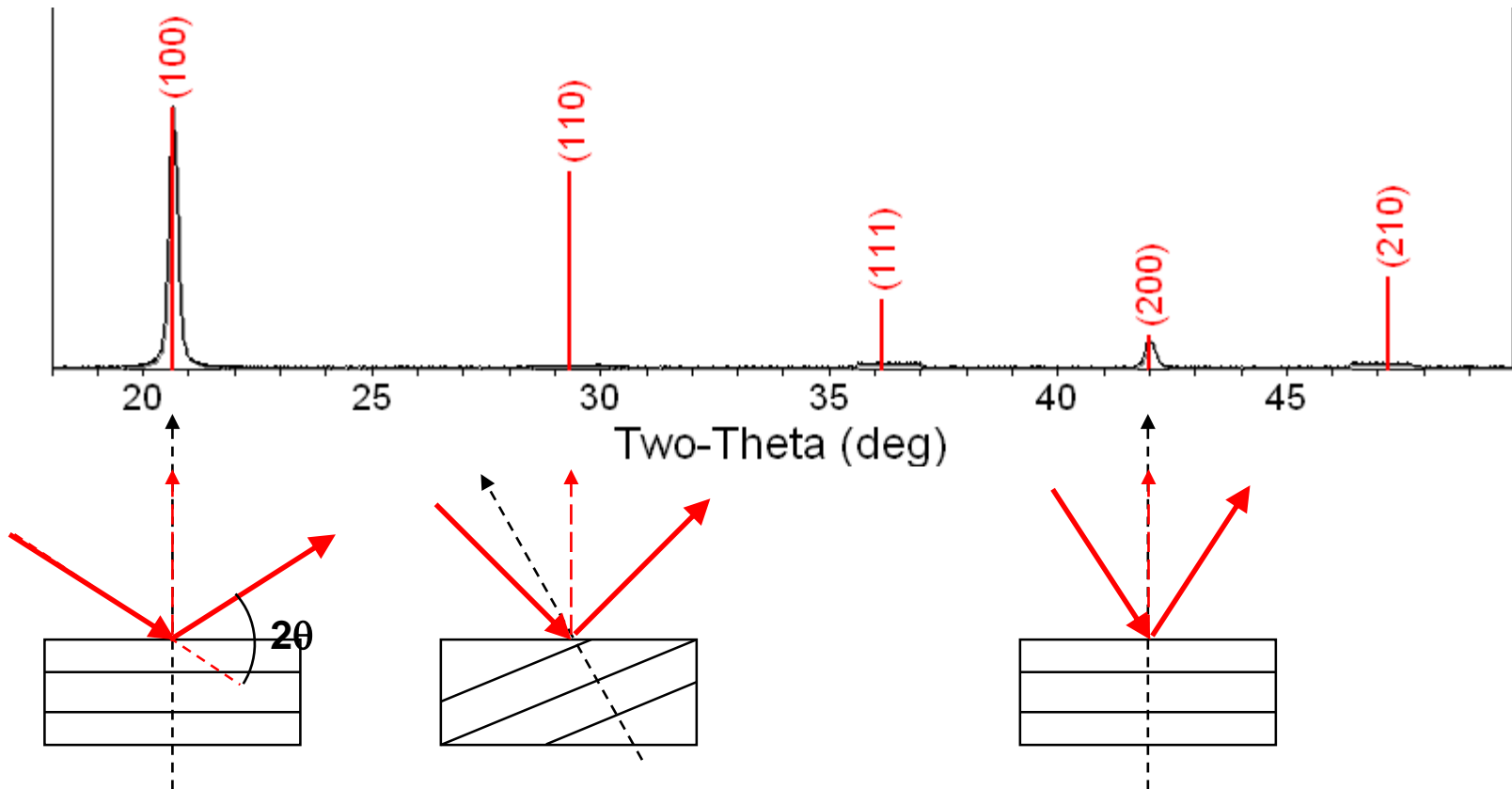
# Diffraction Pattern

- Diffraction peak positions and intensity contain information about the crystal structure of a material
- Each diffraction peak is produced by a family of atomic planes.
- The position of the diffraction peak indicates the length  $d_{hkl}$  between those atomic planes
  - this ultimately correlates to the bond distances between atoms
- The intensity of the diffraction peak is determined by what atoms are present on the diffracting plane, their scattering factors, and the structure factor



# Diffraction of a Single Crystal

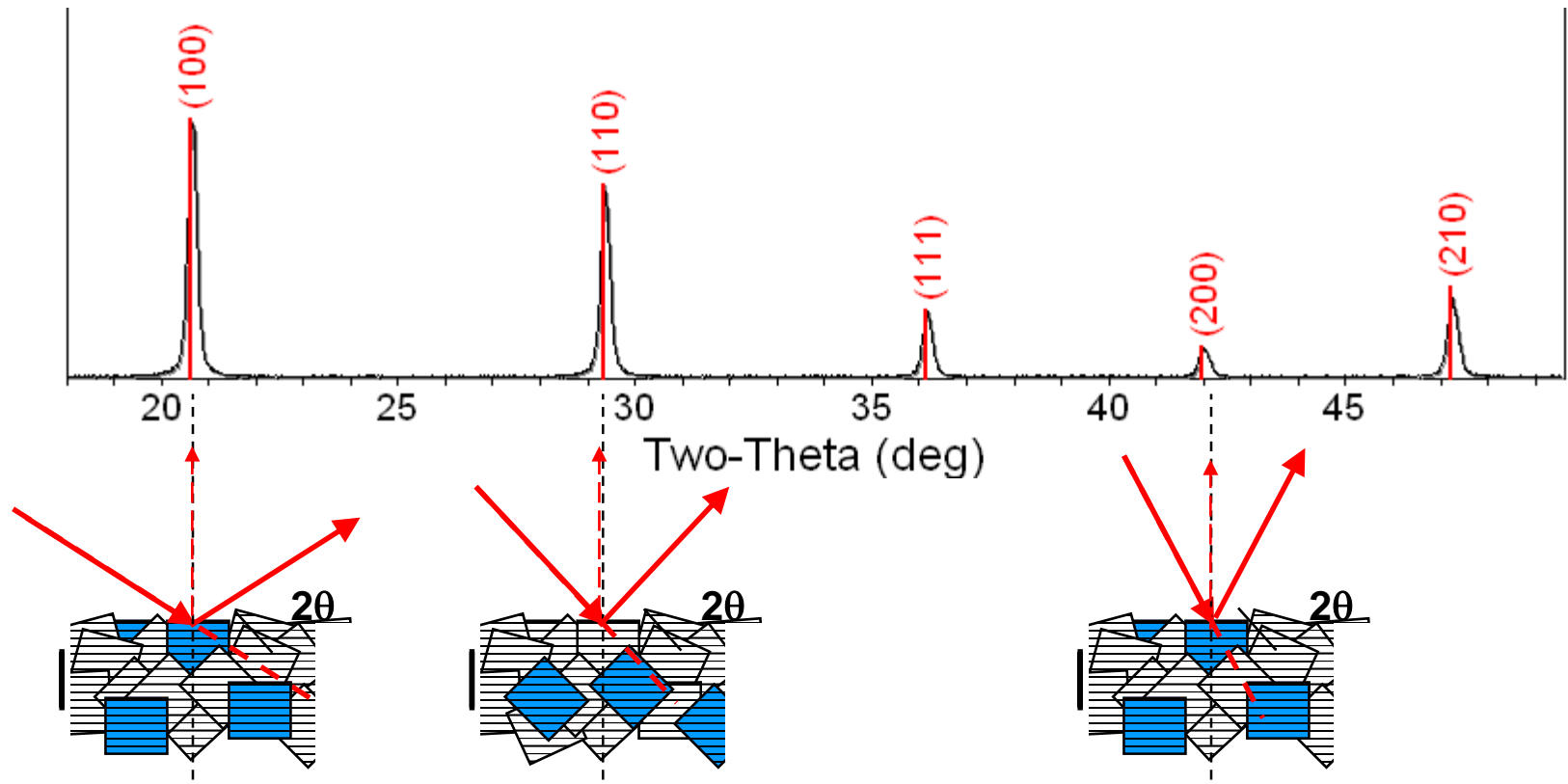
- A single crystal in a Bragg-Brentano diffractometer produces one family of peaks in the diffraction pattern





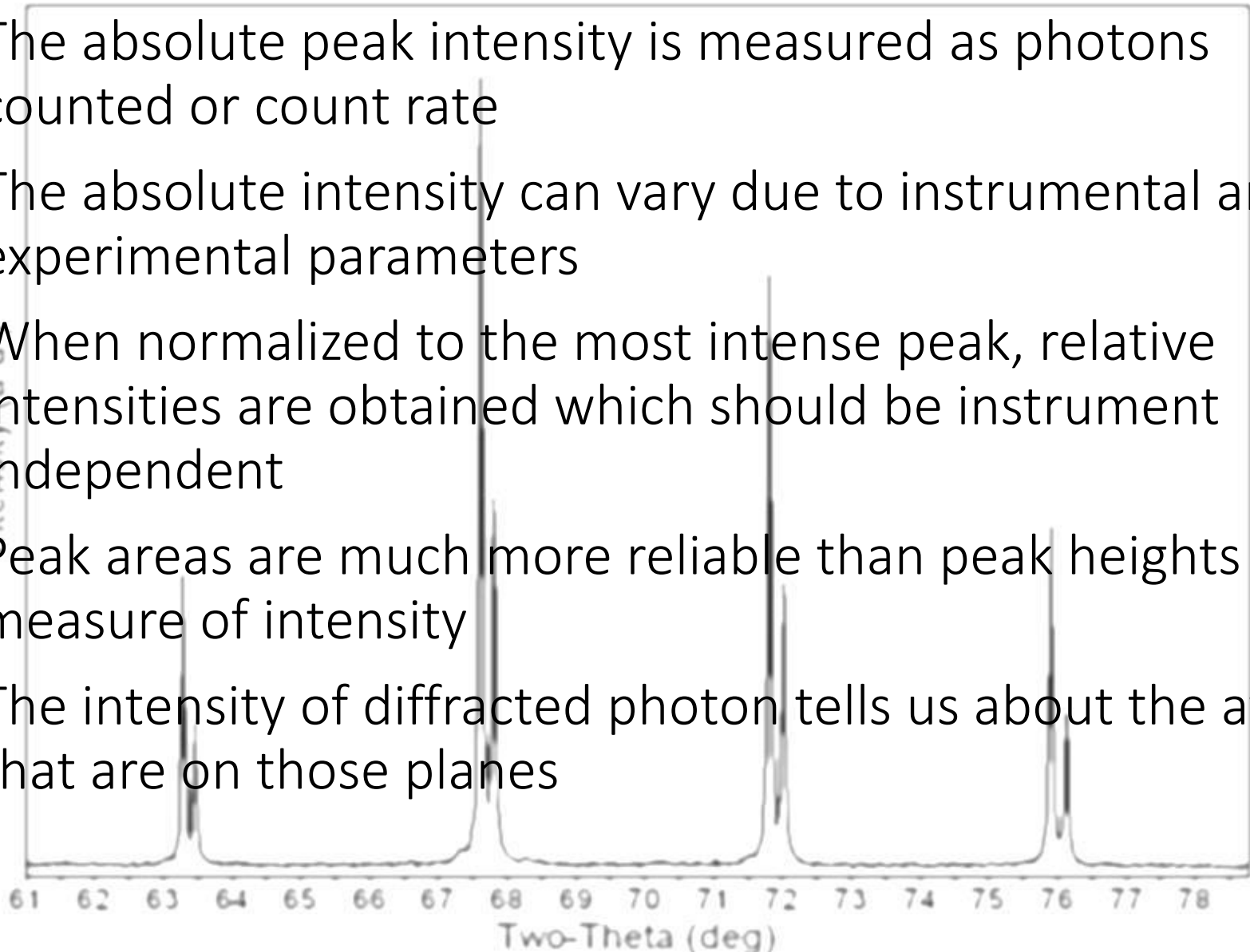
# Diffraction of a Polycrystalline Sample

- A polycrystalline sample contains thousands of crystallites
- All diffraction peaks should be observed
- There will be a small percentage of crystallites that are properly oriented to diffract for every set of planes

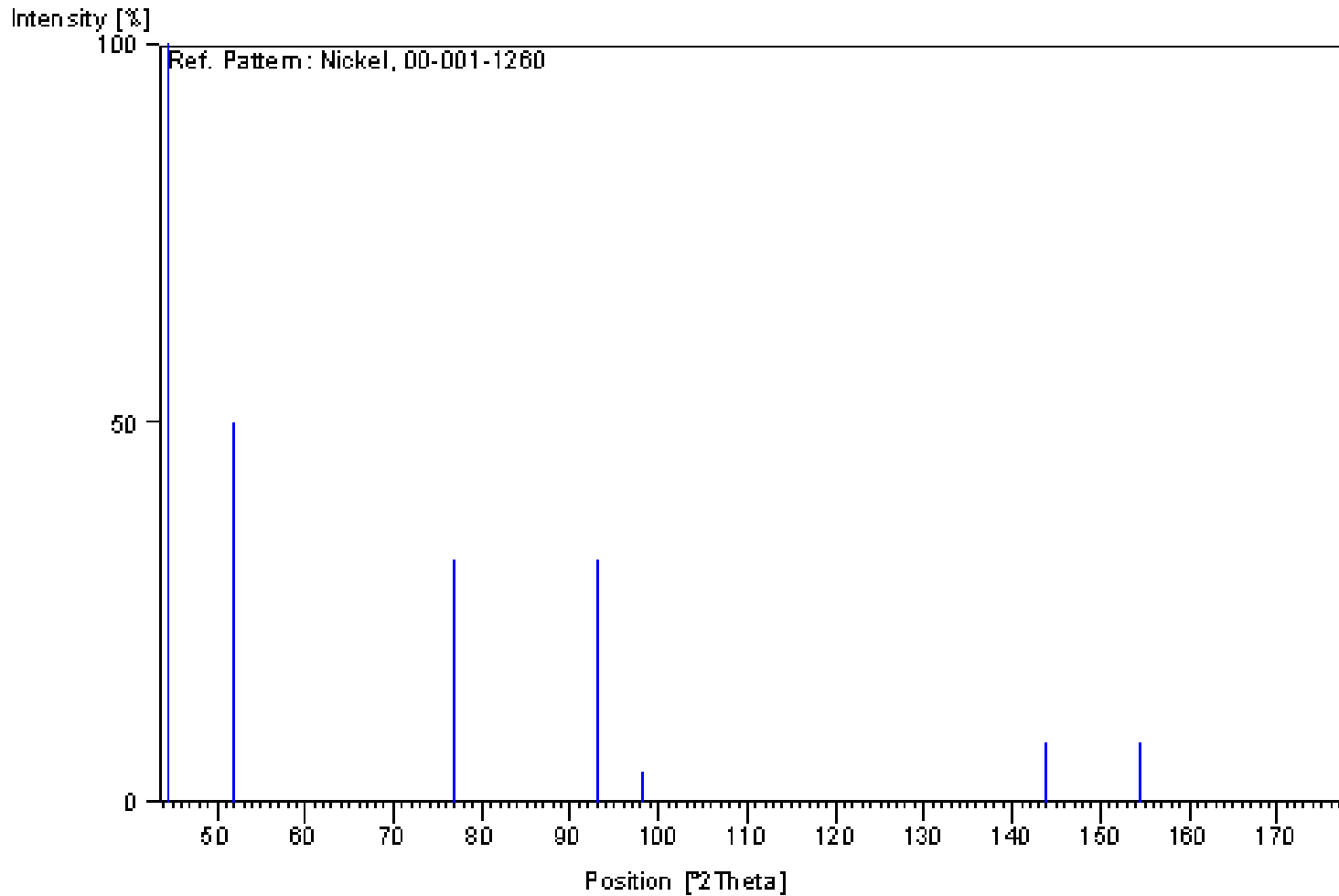


# Diffraction Peaks

- The absolute peak intensity is measured as photons counted or count rate
- The absolute intensity can vary due to instrumental and experimental parameters
- When normalized to the most intense peak, relative intensities are obtained which should be instrument independent
- Peak areas are much more reliable than peak heights as a measure of intensity
- The intensity of diffracted photon tells us about the atoms that are on those planes

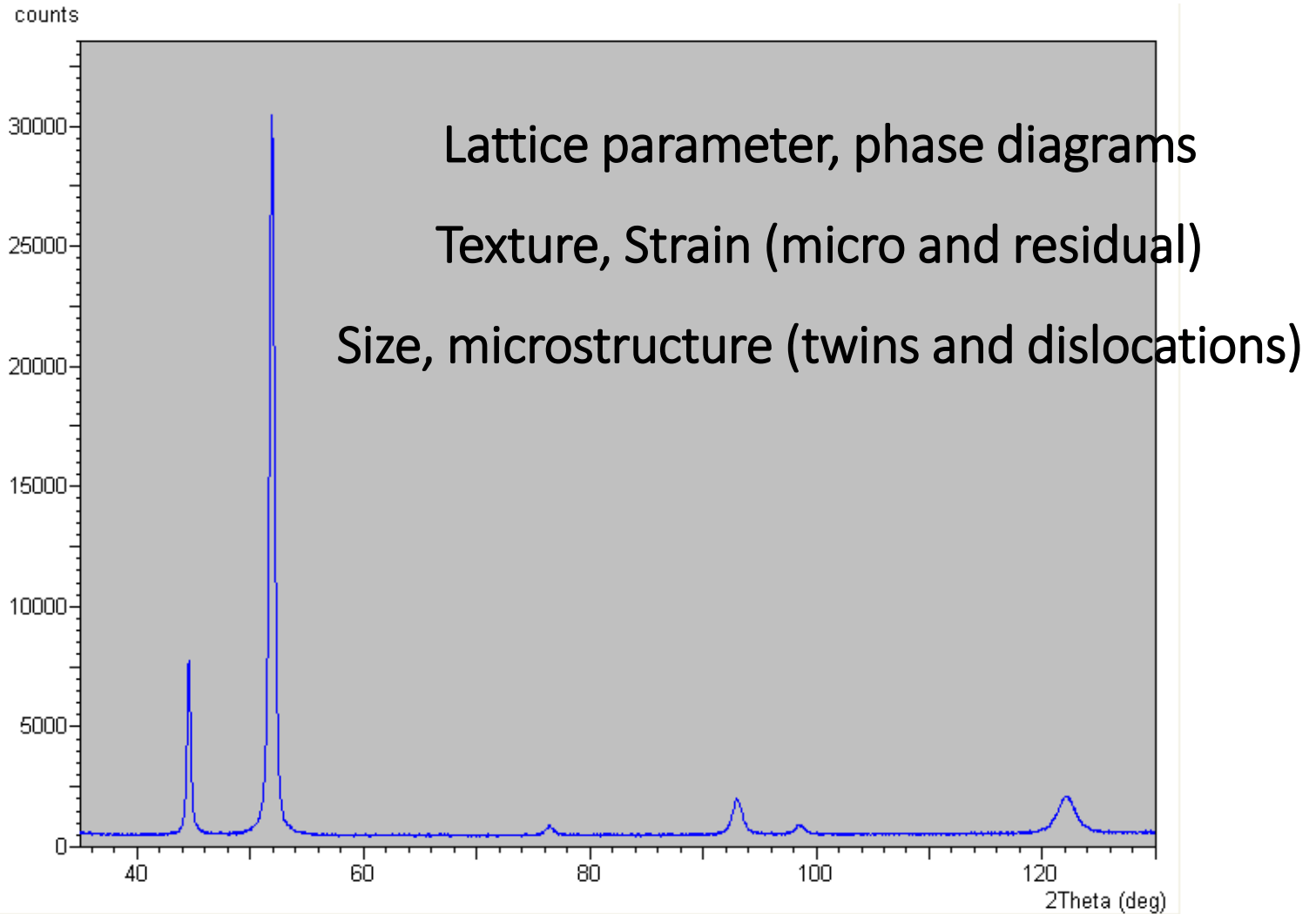


# Stick pattern from JCPDS



<http://ww1.iucr.org/cww-top/crystal.index.html>

# Actual Pattern



Bulk electrodeposited nanocrystalline nickel

# Qualitative Phase Identification

- Mostly used for analysis of processes and quality control

When

You found something in the laboratory and want to know what it is

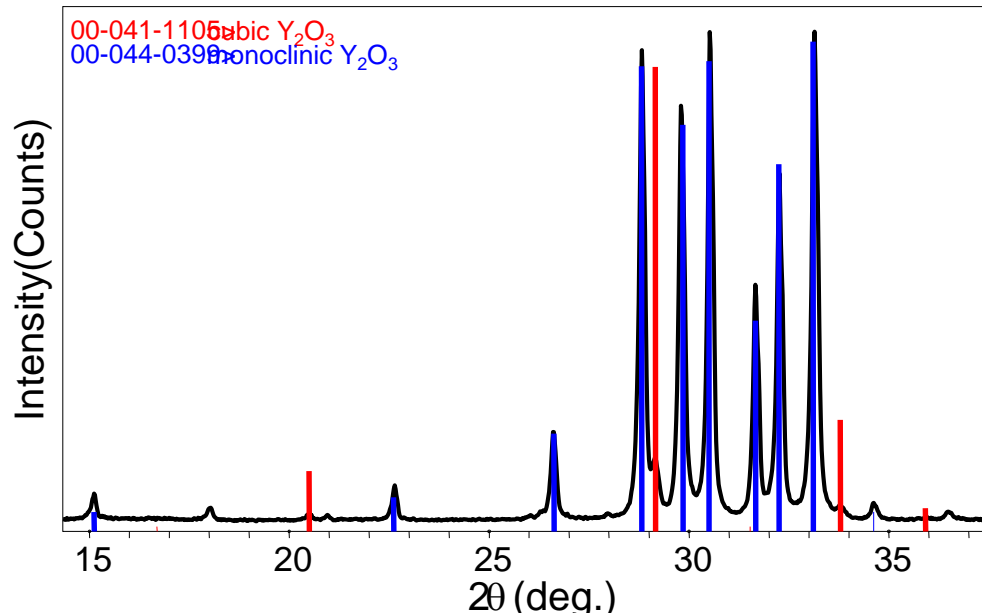
or

You tried to synthesize a material and want to know if you really did

or

You want to check if your raw materials are pure

Example: You have some monoclinic  $Y_2O_3$  in the lab for a long time and want to see if it degraded in time

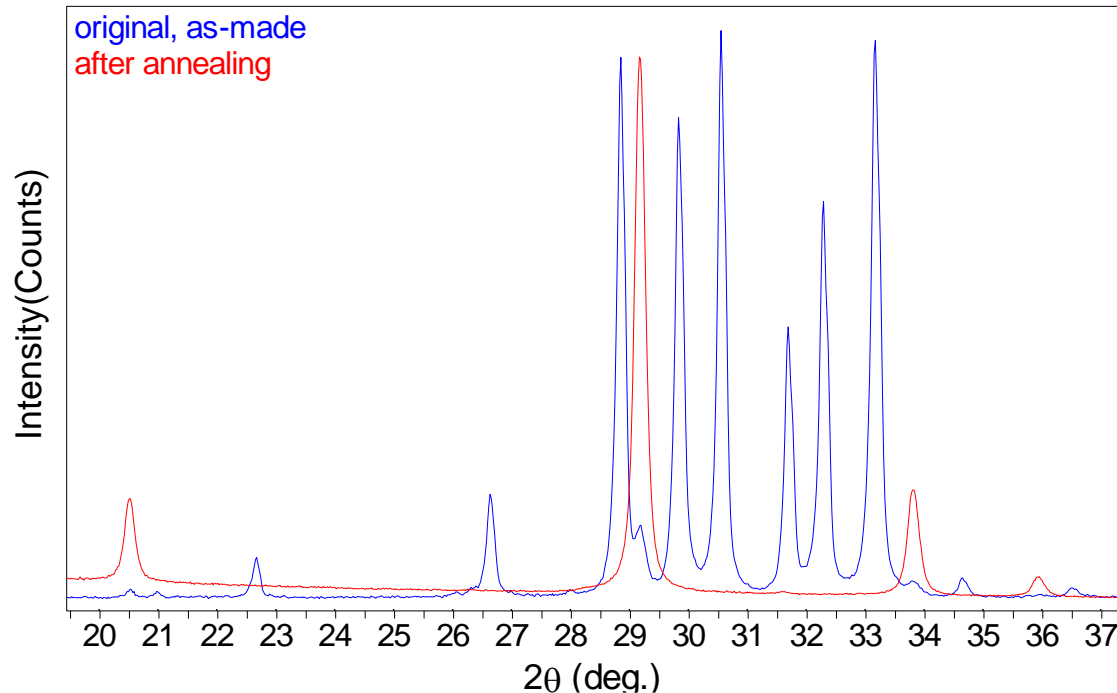


# Qualitative Phase Identification can be used to study reactions *ex situ*

- Comparing and identifying the XRD patterns of a material before and after a phase changing reaction

Example: You heated the monoclinic  $Y_2O_3$  to 1000 °C and want to see the level of degradation

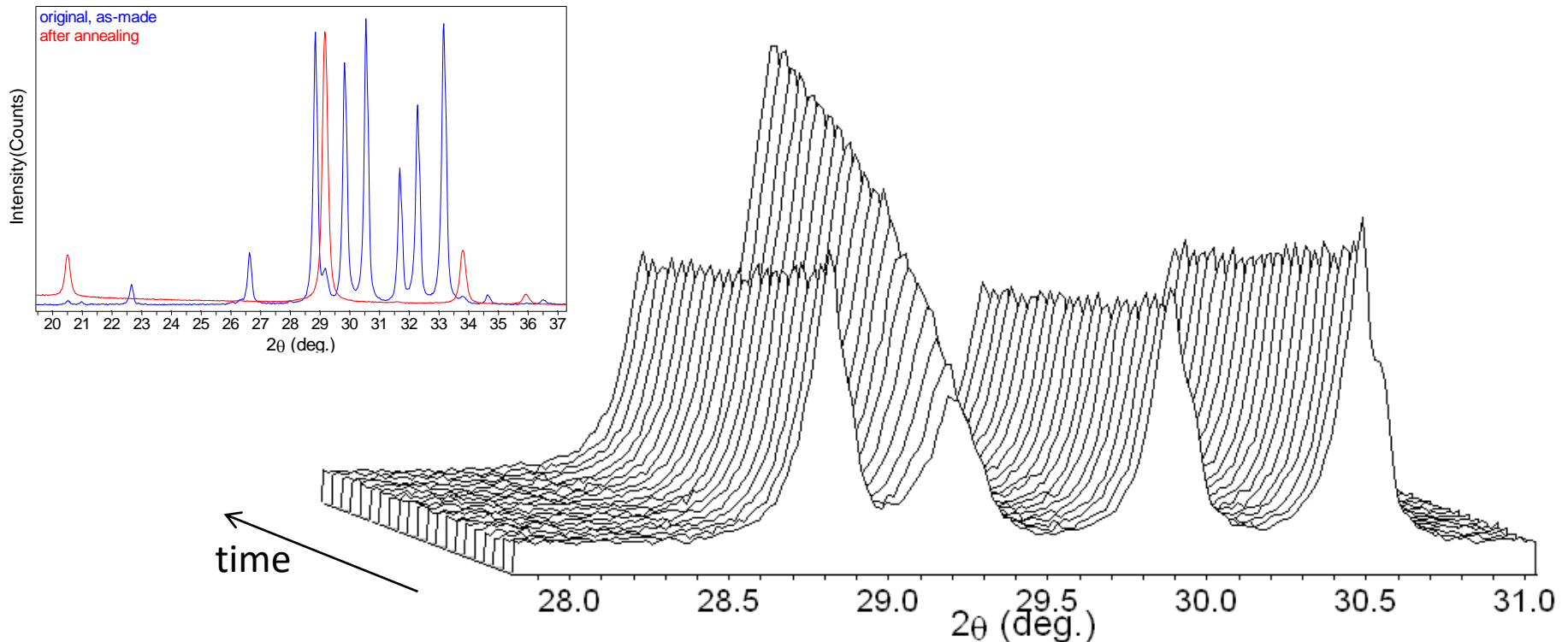
Heat treatment converted all of the monoclinic  $Y_2O_3$  into cubic  $Y_2O_3$



# Qualitative Phase Identification can also be used to study reactions *in situ*

- A phase changing reaction such as heat treatment is monitored directly by the attached X-Ray diffractometer

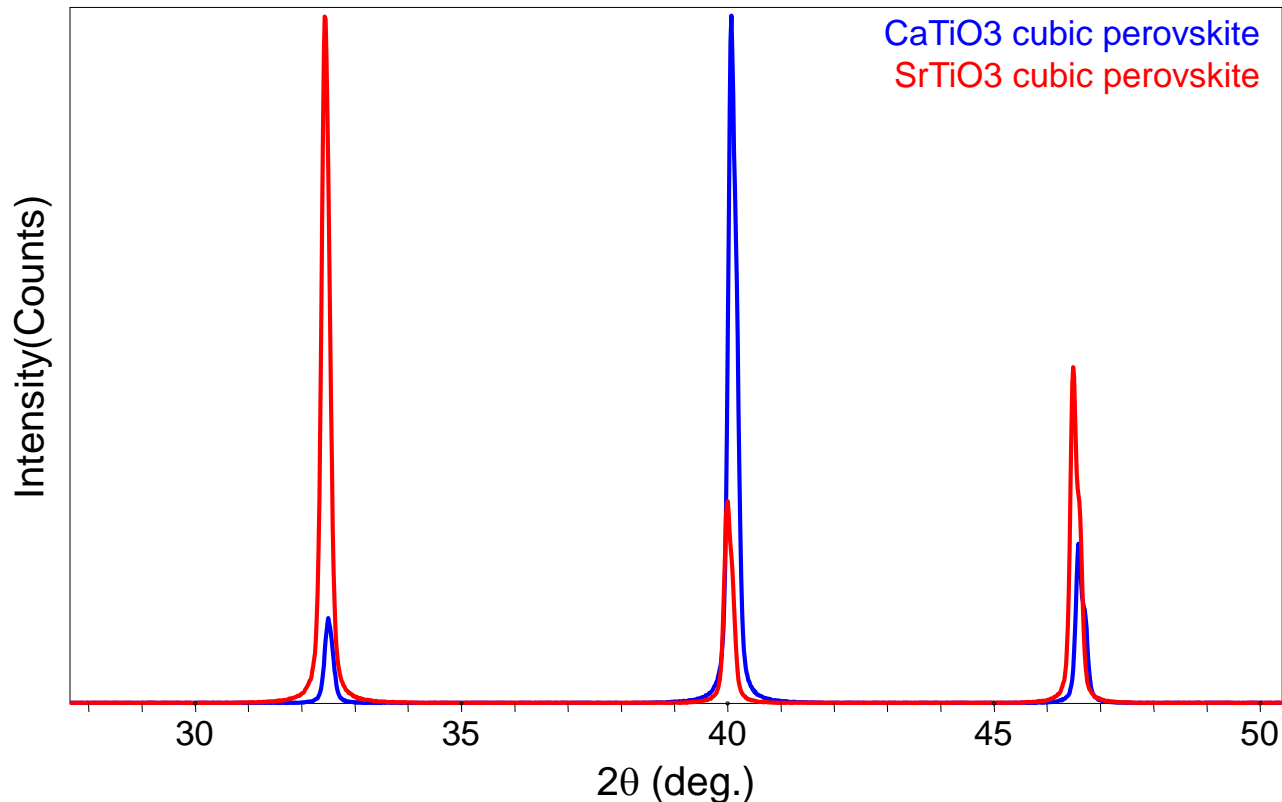
Example: You heat the monoclinic  $Y_2O_3$  to 1000 °C and want to see the rate of degradation



Qualitative Phase Identification can also be used to discern between isostructural compounds and polymorphs

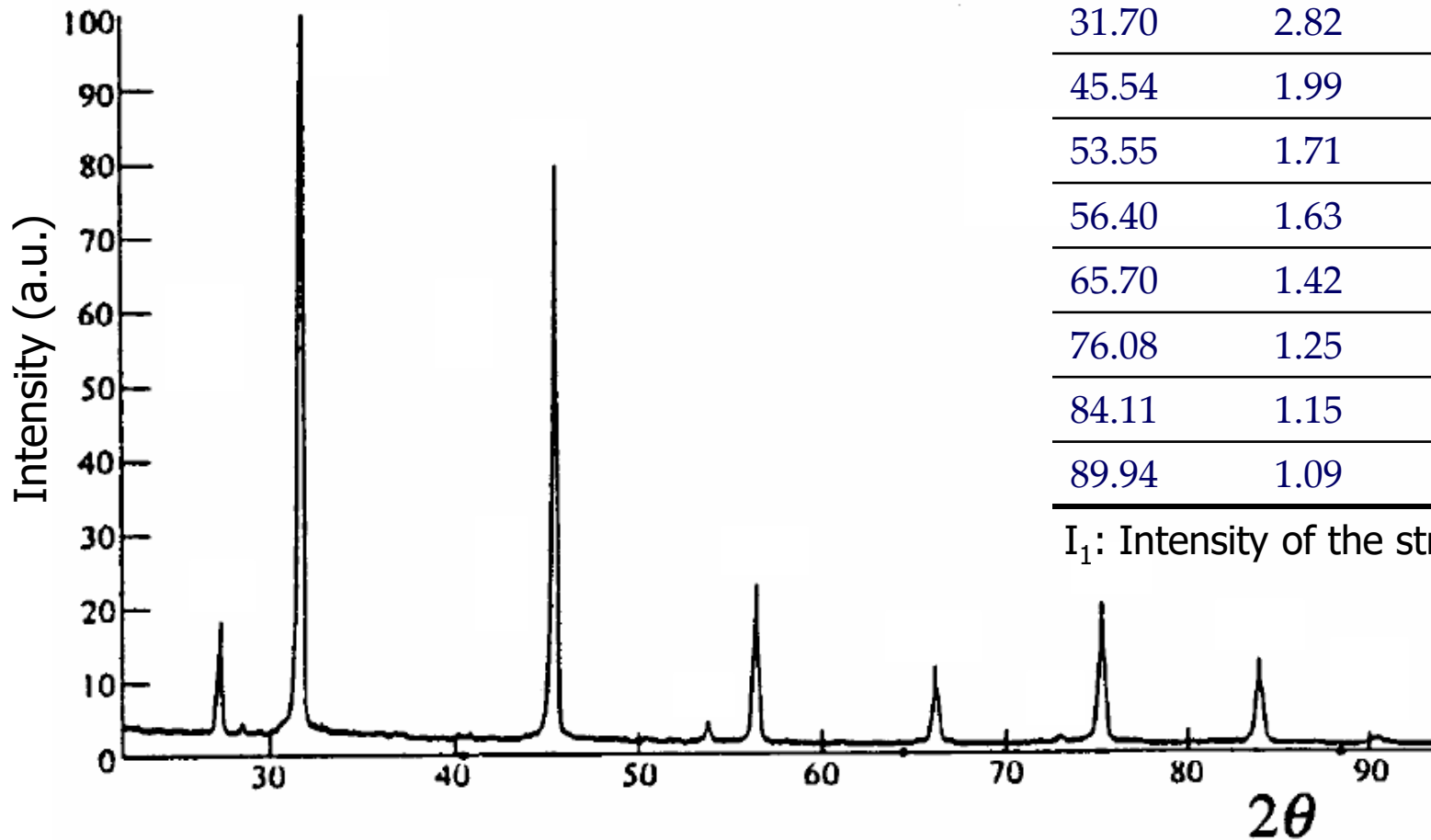
- Differences in electron density can be mapped because X-Rays scatter proportionally to  $Z^2$

Example: the cubic phases of  $\text{CaTiO}_3$  and  $\text{SrTiO}_3$  have identical crystal structures, with the cation replaced by Ca or Sr respectively





# Analysis of Single Phase



2θ(°)	d (Å)	(I/I <sub>1</sub> )*100
27.42	3.25	10
31.70	2.82	100
45.54	1.99	60
53.55	1.71	5
56.40	1.63	30
65.70	1.42	20
76.08	1.25	30
84.11	1.15	30
89.94	1.09	5

I<sub>1</sub>: Intensity of the strongest peak

# Procedure

- Note first three strongest peaks at  $d_1$ ,  $d_2$ , and  $d_3$
- In the present case:  $d_1$ : 2.82;  $d_2$ : 1.99 and  $d_3$ : 1.63 Å
- Search JCPDS manual to find the d group belonging to the strongest line: between 2.84-2.80 Å
- There are 17 substances with approximately similar  $d_2$  but only 4 have  $d_1$ : 2.82 Å
- Out of these, only NaCl has  $d_3$ : 1.63 Å
- **It is NaCl**

Specimen and Intensities	Substance	File Number
2.82 <sub>9</sub> 1.99 <sub>9</sub> 2.26 <sub>x</sub> 1.61 <sub>9</sub> 1.51 <sub>9</sub> 1.49 <sub>9</sub> 3.57 <sub>8</sub> 2.66 <sub>8</sub>	(ErSe) <sub>2</sub> Q	19-443
2.82 <sub>x</sub> 1.99 <sub>6</sub> 1.63 <sub>2</sub> 3.26 <sub>1</sub> 1.26 <sub>1</sub> 1.15 <sub>1</sub> 1.41 <sub>1</sub> 0.89 <sub>1</sub>	NaCl	5-628
2.82 <sub>4</sub> 1.99 <sub>4</sub> 1.54 <sub>x</sub> 1.20 <sub>4</sub> 1.19 <sub>4</sub> 2.44 <sub>3</sub> 5.62 <sub>2</sub> 4.89 <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> WO <sub>2</sub> Cl <sub>4</sub>	22-65
2.82 <sub>x</sub> 1.99 <sub>8</sub> 1.26 <sub>3</sub> 1.63 <sub>2</sub> 1.15 <sub>2</sub> 0.94 <sub>1</sub> 0.89 <sub>1</sub> 1.41 <sub>1</sub>	(BePd)2C	18-225

**Caution:** It could be much more tricky if the sample is oriented or textured or your goniometer is not calibrated

# Presence of Multiple phases

- More Complex
- Several permutations combinations possible
- e.g.  $d_1$ ;  $d_2$ ; and  $d_3$ , the first three strongest lines show several alternatives
- Then take any of the two lines together and match
- It turns out that 1<sup>st</sup> and 3<sup>rd</sup> strongest lines belong to Cu and then all other peaks for Cu can be separated out

Pattern for Cu	
d (Å)	I/I <sub>1</sub>
2.088	100
1.808	46
1.278	20
1.09	17
1.0436	5
0.9038	3
0.8293	9
0.8083	8

d (Å)	I/I <sub>1</sub>
3.01	5
2.47	72
2.13	28
2.09 *	100
1.80 *	52
1.50	20
1.29	9
1.28 *	18
1.22	4
1.08 *	20
1.04 *	3
0.98	5
0.91	4
0.83 *	8
0.81 *	10

# Presence of Multiple phases

- Now separate the remaining lines and normalize the intensities
- Look for first three lines and it turns out that the phase is  $\text{Cu}_2\text{O}$
- If more phases, harder to solve

Pattern of $\text{Cu}_2\text{O}$	
d (Å)	I/I <sub>1</sub>
3.020	9
2.465	100
2.135	37
1.743	1
1.510	27
1.287	17
1.233	4
1.0674	2
0.9795	4

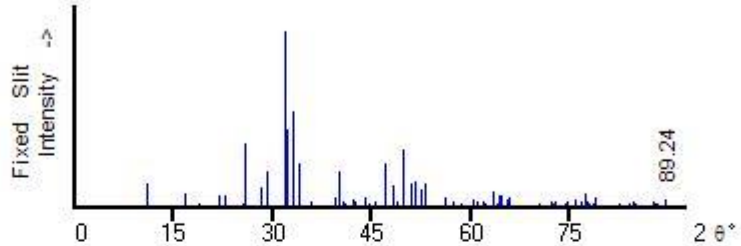
Remaining Lines		
d (Å)	I/I <sub>1</sub>	
	Observed	Normalized
3.01	5	7
2.47	72	100
2.13	28	39
1.50	20	28
1.29	9	13
1.22	4	6
0.98	5	7

# Diffraction Data is Essential

PDF # 860740, Wavelength = 1.54060 (Å)

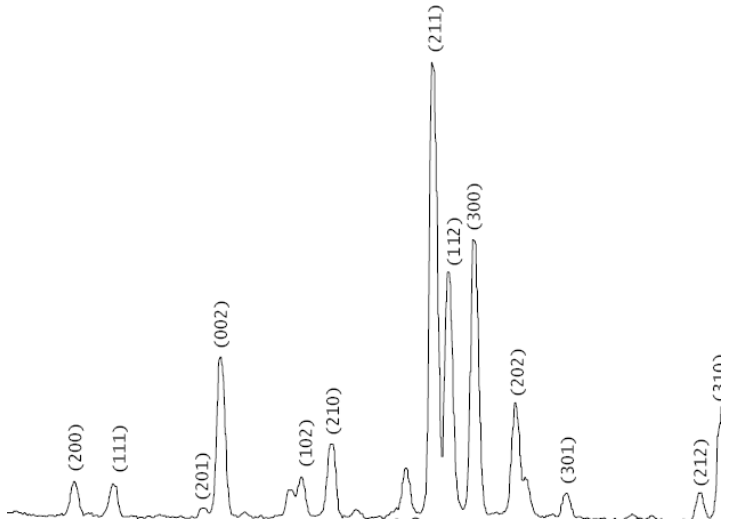
86-0740 Quality: C  
 CAS Number:  
 Molecular Weight: 502.32  
 Volume[CD]: 521.26  
 Dx: 3.200 Dm:  
 Sys: Hexagonal  
 Lattice: Primitive  
 S.G.: P6<sub>3</sub>/m (176)  
 Cell Parameters:  
 a 9.352 b c 6.882  
 α β γ

Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)  
 Calcium Phosphate Hydroxide  
 Ref: Calculated from ICSD using POWD-12+, (1997)  
 Ref: Tomita, K et al., J. Mineral. Petrol. Econ. Geol., 91, 11 (1996)



I/Cor: 1.04  
 Rad: CuKα1  
 Lambda: 1.54060  
 Filter:  
 d-sp: calculated  
 ICSD #: 081442  
 Mineral Name:  
 Hydroxylapatite

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
10.915	125	1	0	0	45.402	32	2	0	3	63.950	17	5	1	0
16.892	69	1	0	1	46.947	248	2	2	2	64.134	64	3	0	4
18.964	22	1	1	0	48.350	116	1	3	2	64.485	58	3	2	3
21.931	66	2	0	0	48.985	33	2	3	0	65.537	44	5	1	1
22.976	64	1	1	1	49.620	323	2	1	3	65.714	46	3	3	2
25.501	14	2	0	1	50.861	134	2	3	1	66.761	7	4	1	3
25.872	361	0	0	2	51.679	139	1	4	0	66.846	8	4	2	2
28.154	112	1	0	2	52.388	102	4	0	2	67.543	1	2	2	4
29.149	198	2	1	0	53.195	135	0	0	4	68.660	4	1	3	4
31.973	999*	2	1	1	54.479	4	1	0	4	69.176	1	1	0	5
32.275	437	1	1	2	56.218	54	3	2	2	69.593	2	6	0	0
33.157	542	3	0	0	56.790	2	5	0	0	70.188	16	1	5	2
34.167	245	2	0	2	56.988	6	1	1	4	70.694	2	4	3	0
35.697	31	3	0	1	57.364	25	3	1	3	71.204	2	5	0	3
38.473	2	2	2	0	58.215	1	2	0	4	71.378	2	1	1	5
39.364	51	2	1	2	58.490	12	5	0	1	71.963	5	4	0	4
40.110	203	1	3	0	58.678	8	4	1	2	72.209	29	4	3	1
40.726	30	2	2	1	59.234	3	3	3	0	72.469	15	2	0	5
40.852	19	1	0	3	60.434	43	2	4	0	72.877	27	5	2	0
42.290	41	1	3	1	60.891	30	3	3	1	73.380	3	3	3	3
42.528	29	3	0	2	61.806	33	1	2	4	74.373	17	5	2	1
43.928	52	1	1	3	62.071	12	2	4	1	74.459	23	2	4	3
44.722	13	4	0	0	63.418	83	5	0	2	75.205	7	2	3	4



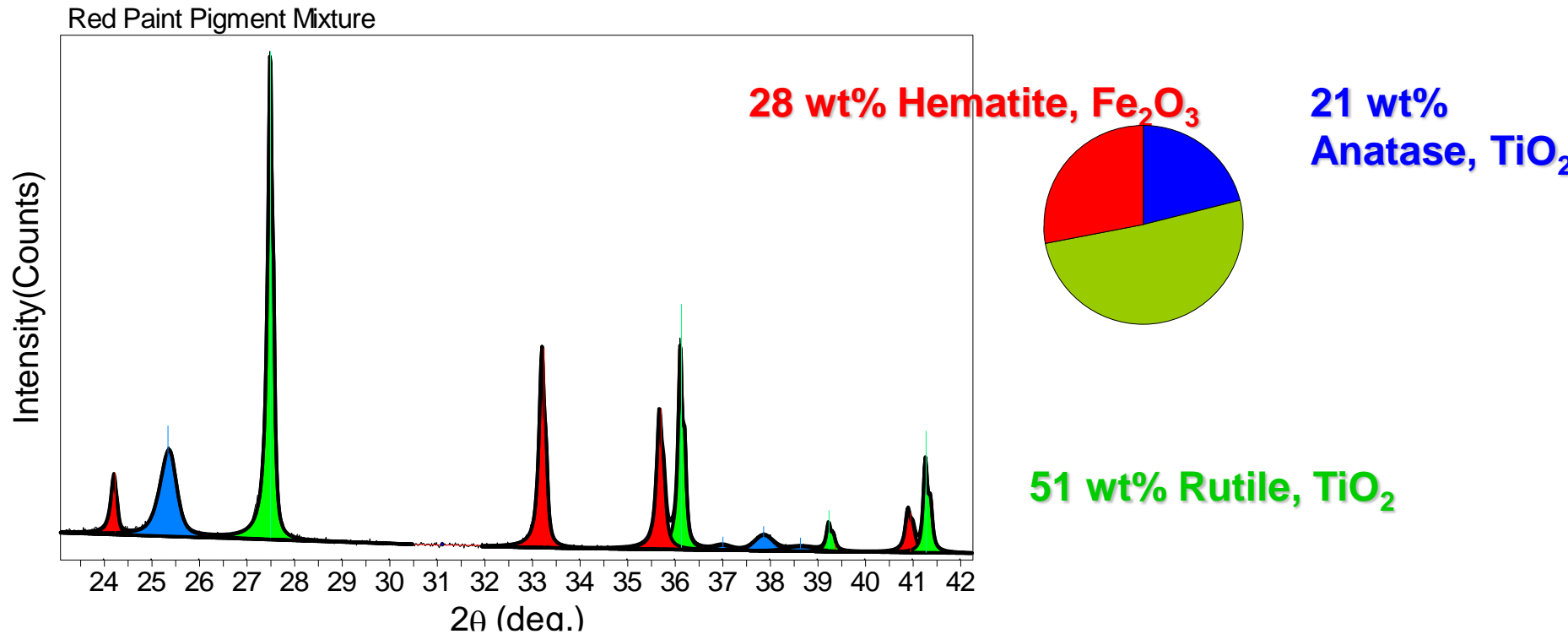
# Quantitative Phase Identification

- In depth analysis for precise monitoring of phase composition

When

You know which phases are present and want to know how much

Example: You mix certain powders to make a red paint pigment then wonder how much of each is present



# Relative Intensity Approach

- The ratio of peak intensities varies linearly with the ratio of weight fractions

$$\frac{I_{\alpha}}{I_{\beta}} = K \frac{X_{\alpha}}{X_{\beta}}$$

- K is determined from the mass absorption coefficients of all phases in the sample
  - Not the most accurate and reliable way
- Simplification of the ratio of the general intensity equation

$$I_{(hkl)\alpha} = \left[ \frac{I_0 \lambda^3}{64\pi r} \left( \frac{e^2}{m_e c^2} \right)^2 \right] \left[ \frac{M_{hkl}}{V_{\alpha}} \right] \left[ F_{(hkl)\alpha} \right]^2 \left[ \frac{1 + \cos 2\theta^2 \cos 2\theta_m^2}{\sin \theta^2 \cos \theta} \right] \left[ \frac{X_{\alpha}}{\rho_{\alpha}(\mu/\rho)_s} \right]$$

Constant for an experimental setup (points to the first bracketed term)  
 Multiplicity factor (points to  $M_{hkl}/V_{\alpha}$ )  
 Structure factor (points to  $F_{(hkl)\alpha}$ )  
 Lorentz polarization factor (points to the fraction with  $\theta$ )  
 Absorption factor (points to the final fraction with  $X_{\alpha}$ )

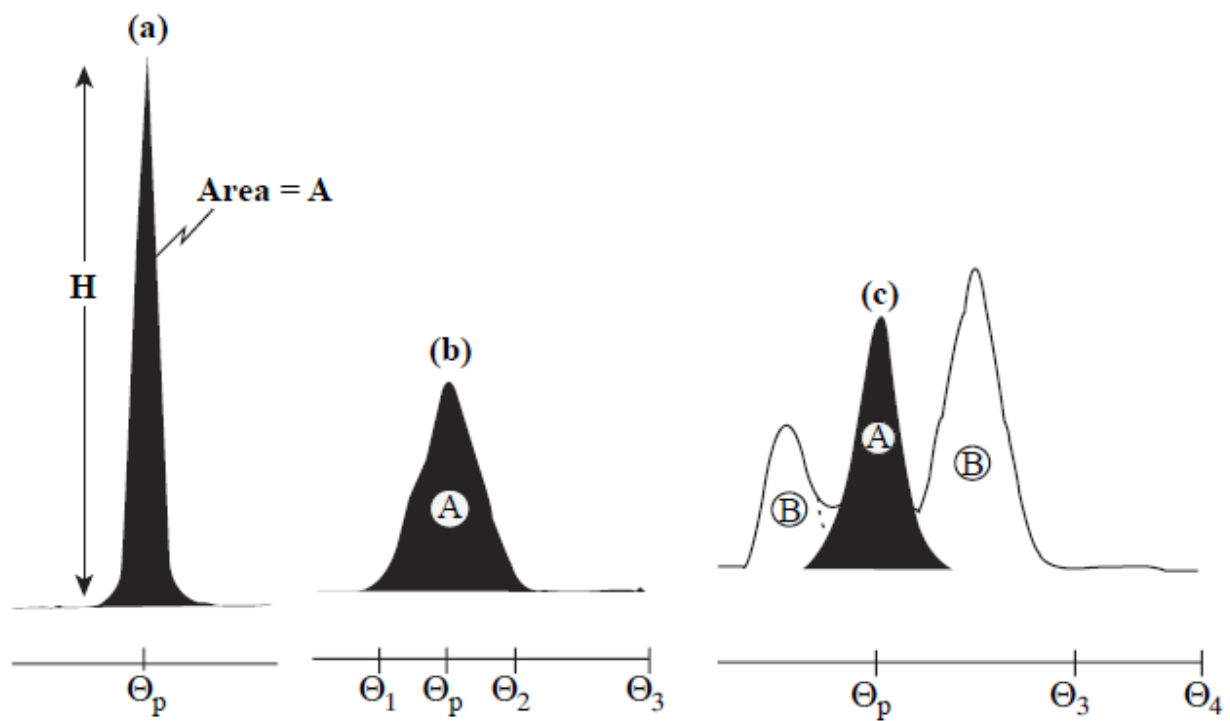
$$I_{(hkl)\alpha} = \frac{K_{\theta} K_{(hkl)\alpha} X_{\alpha}}{\rho_{\alpha}(\mu/\rho)_s}$$

# Relative Intensity Approach

- K can be determined :
  - by using published relative intensity values ( $I/I_c$ ) → External Standard Method
  - empirically, by building calibration curves → Internal Standard Method
  - by simulating the diffraction pattern: whole pattern refinement → Reitveld Analysis
- To equate the concentration of a given phase with the intensity of the peaks in the multiphase pattern,
  - a single peak, → least precision
  - a number of peaks, → considerable precision
  - all of the peaks → ultimate precision (Reitveld analysis)can be utilized
- The shape of the peaks is decisive in choosing the intensity measurement method
  - When the diffraction peak is sharp and non-overlapped, peak height is taken as the representative value as it is considered proportional to the peak area
- Background corrected integrated intensities are measured by subtracting the background intensity from the peak height



- a) Peak height is proportional to peak area. Peak height is measured
  - b) Peak height not proportional to peak area. Combined intensity is calculated
  - c) Peak area is overlapped by other peaks
- This is a common case. Peak profiles should be adjusted



# External Standard Method

$$W_{\alpha} = \frac{I_{\alpha}}{I_{\alpha}^P} \cdot \frac{(\mu/\rho)_m}{(\mu/\rho)_{\alpha}}$$

- The complexity of the analysis of multiple phases in a mixture is greatly reduced by referring all of the pure phase peak intensities to a single standard

$$\frac{W_{\alpha}}{W_s} = 1, \text{ so } \frac{I_{\alpha}^P}{I_s^P} = RIR_{\alpha} = \frac{(\mu/\rho)_{\alpha}}{(\mu/\rho)_s}$$

where  $I_{\alpha}$  is the intensity of the 100% peak of phase  $\alpha$ , and  $I_s$  is the intensity of the 100% peak of a reference phase  $s$ , taken by convention to be  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, corundum, in a 50:50 mixture by weight

$$W_{\alpha} = \frac{I_{\alpha}}{I_s^P} \cdot \frac{(\mu/\rho)_m}{(\mu/\rho)_s} \cdot \frac{1}{RIR_{\alpha}}$$

$$W_{\alpha} = \left[ \frac{I_{\alpha}^{hkl}}{I_{\alpha}^{REL}} \right] \cdot \left[ \frac{(\mu/\rho)_m}{(\mu/\rho)_s} \right] \cdot \left[ \frac{1}{I_s^P \cdot RIR_{\alpha}} \right]$$

Generalized External Standard Equation

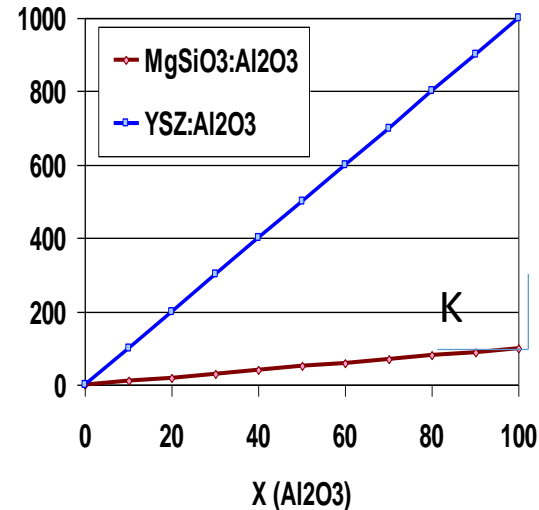
0-0.999

The use of RIR values is much faster and less prone to error than the determination of all of the weight fractions from the starting equation which would require reference to the integrated intensities of the 100% peak of each phase in its pure form

# Internal Standard Method

- The proportionality constant  $K$  is determined empirically by building calibration curves from mixtures containing known quantities of internal standard

$$\frac{I_{\alpha}}{I_{\beta}} = K \frac{X_{\alpha}}{X_{\beta}}$$



Example – Three component mixture consisting of predetermined concentrations of MgSiO<sub>3</sub>, YSZ, Al<sub>3</sub>O<sub>2</sub>

Sample	MgSiO <sub>3</sub> wt%	YSZ wt%	Al <sub>3</sub> O <sub>2</sub> wt%
1	30	50	20
2	30	30	40
3	30	10	60
4	10	10	80

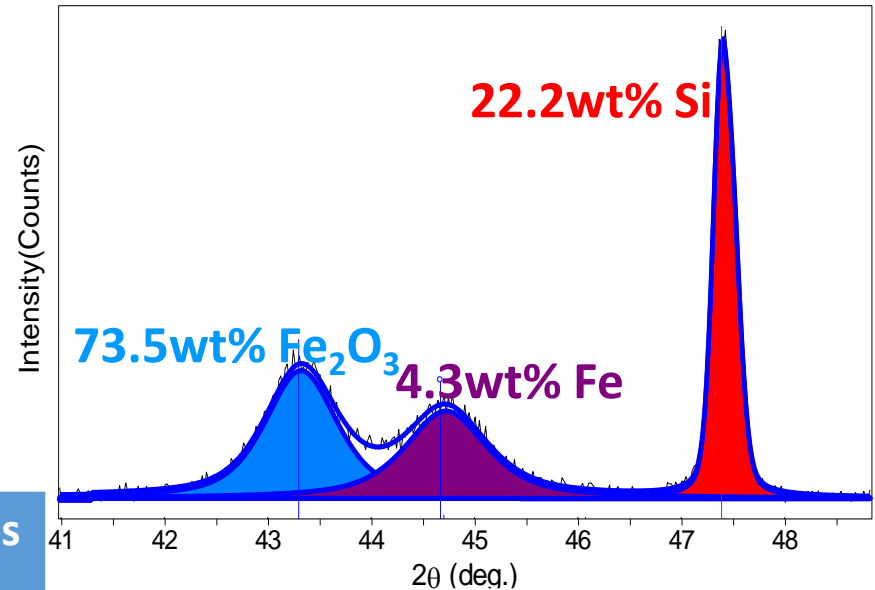
# Determining Crystallinity using Standard Additions

- Adding a predetermined amount of well crystallized standard to a sample containing amorphous phases
- Calculate the observed amount of all phases using any of the quantitative analysis methods, ignoring the amorphous content
- Apply a normalization to all calculated amounts based on the initial standard amount

Example – Fe, Fe<sub>2</sub>O<sub>3</sub> mixture with 17% Si standard

the discrepancy due to the amorphous content

Sample	Fe wt%	Fe <sub>2</sub> O <sub>3</sub> wt%	Si wt%	Amorphous
Calculated	4.3	73.5	22.2	0
Actual	3	55	17	25



# Determining Crystallinity without Standard Additions

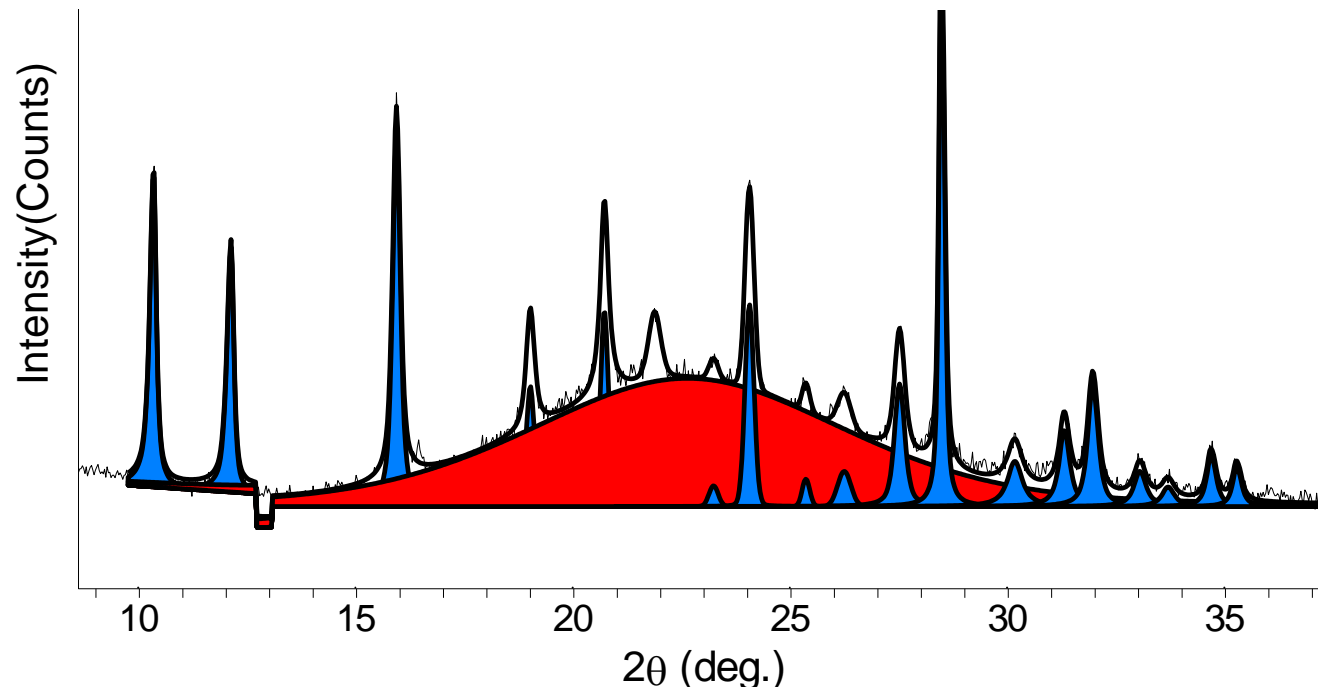
- If the mass absorption coefficient of an amorphous phase is the same as the crystalline content, the ratio of intensities can be used to determine % crystallinity

**Area Crystalline Peaks: 108322 cts**

**% Crystalline: 46.5%**

**Area Amorphous Hump: 124621 cts**

**% Amorphous: 53.5%**

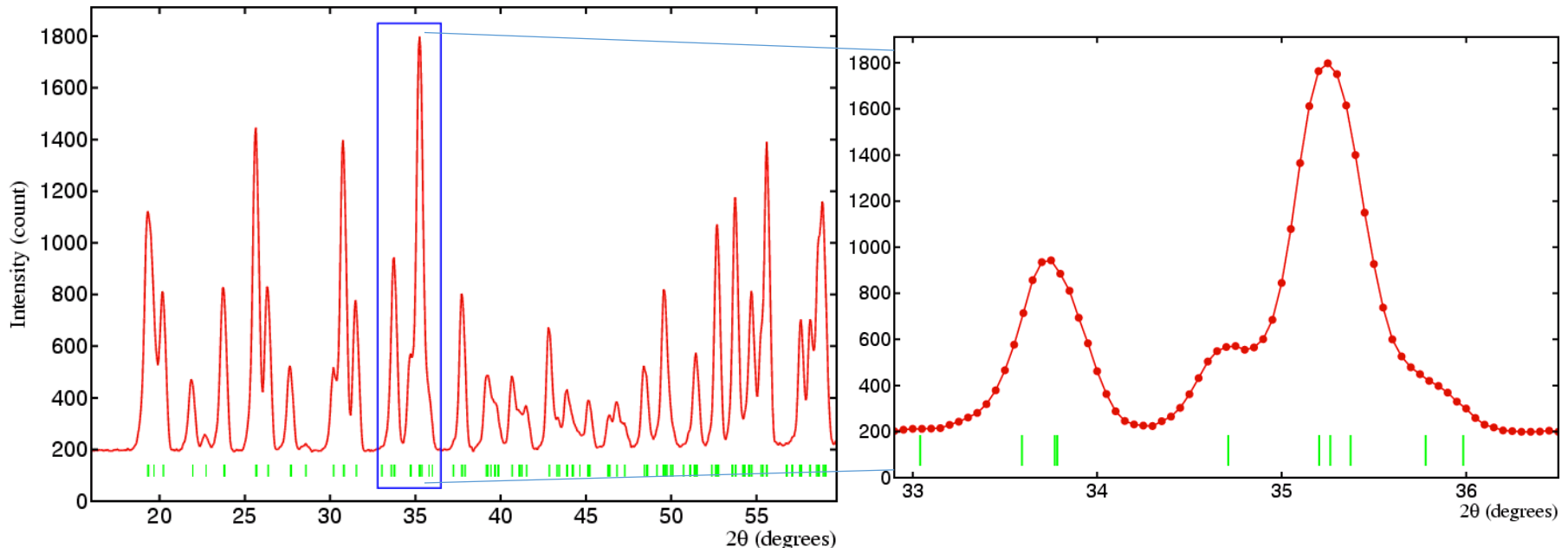


# Rietveld Refinement

- Rietveld realised that the detailed profile of a powder-diffraction pattern contained a lot more information than the extracted intensities of composite peaks and stated that

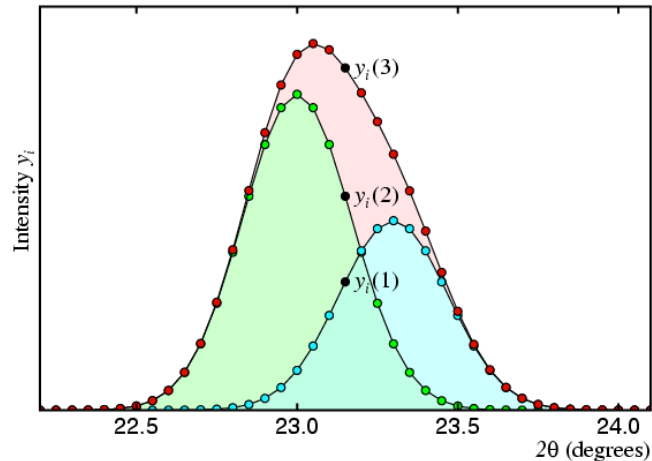
*"The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram."*

H. M. Rietveld



# Reitveld Refinement

- Reitveld found that the detailed profile could be fitted on a point by point basis using the simple Gaussian peak-shape function without any need to extract intensities of composite groups of reflections

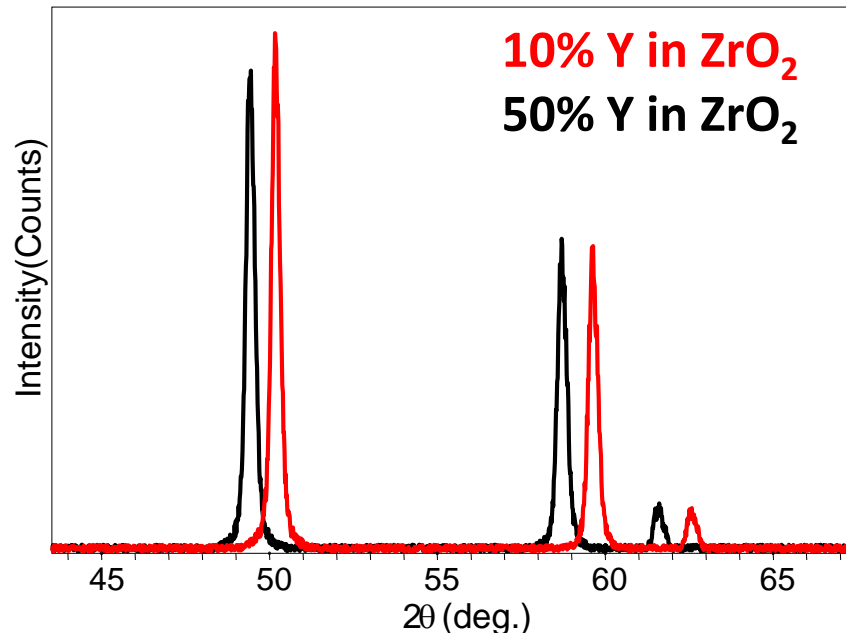


- Refinement implies taking an approximate model of the structure and converting it so that diffraction data calculated from the model structure has a closer resemblance to the measured data
- Many complex computer algorithms operating on the basis of using a least-squares procedure to refine the initial structure model in order to improve the agreement between the observed diffraction data and that calculated from the model
- In other words Reitveld refinement is a broad numerical technique used to make the XRD pattern as true and error-free as possible

# Lattice Parameter Determination

- Changes in the interplanar spacing of a material such as substitution of an atom can be detected by XRD
- The position of the diffraction peaks are a product of the space between planes of atoms
- The change in peak intensity due to substitution of atoms with similar Z is subtle, however peak angles which indicate the interplanar space change

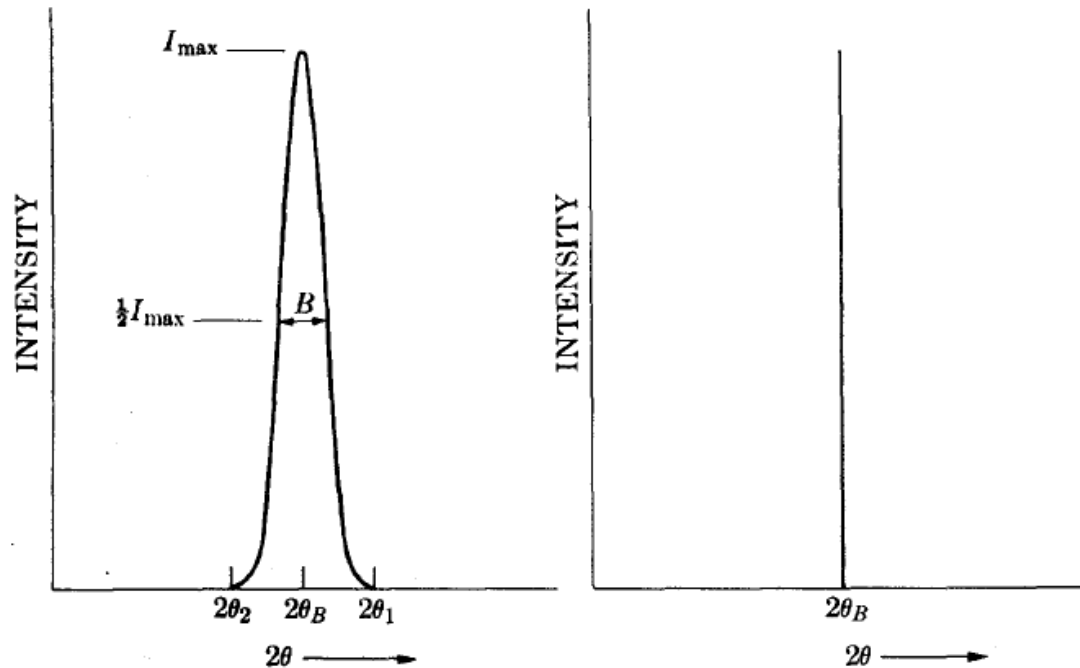
Example – Substitution of Zr in YSZ with Y





# Crystallite Size Broadening

Ideally a peak in the Bragg diffraction pattern is a line without a width. In reality the peaks have some width that originate from the instrument and the size of the crystals



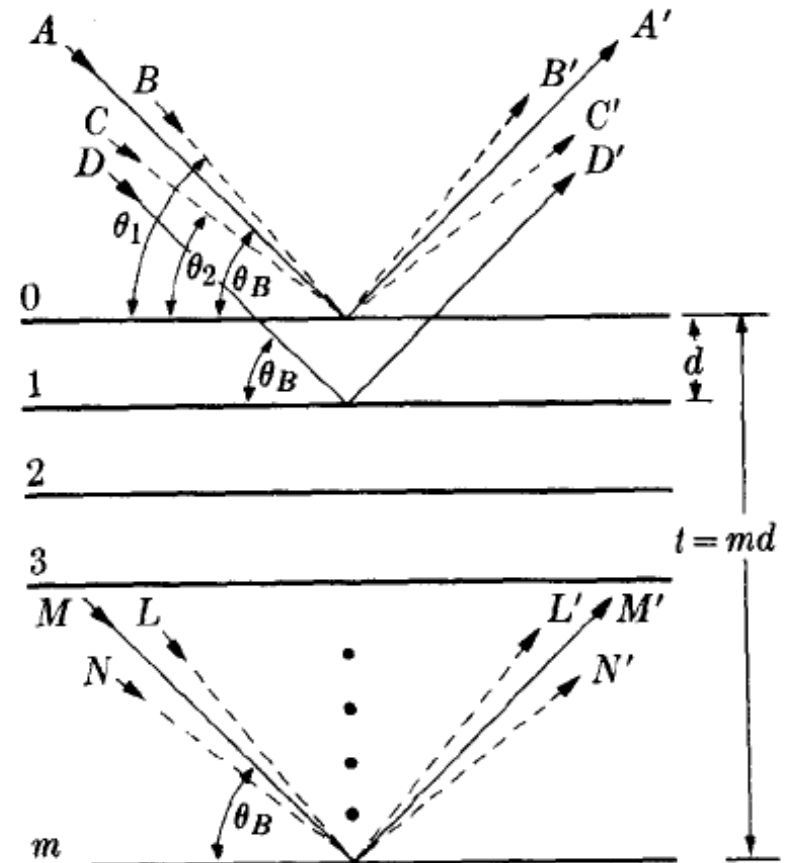
# Crystallite Size Broadening

A diffraction peak is produced by a plane with  $\theta_B$  that satisfies Bragg's law  
However X-ray beam in para-focusing geometry is not perfectly parallel and is diffracted at angles between  $\theta_1$  and  $\theta_2$ . So X-rays scattered at angles between  $\theta_1$  and  $\theta_2$  do not interfere with each other perfectly constructively or destructively

In this case X-rays scattered from plane 0 and 1 have angles  $\theta_1$  that correspond to Bragg's number  $n$  less than an integer

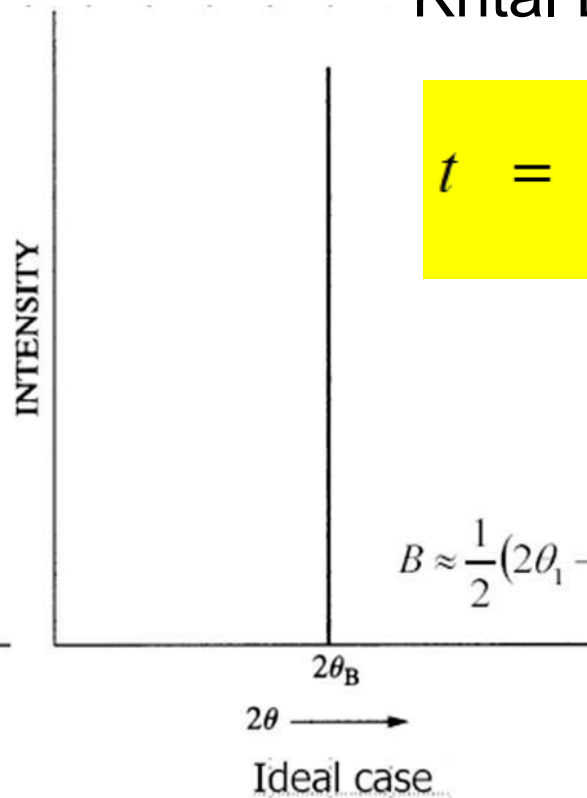
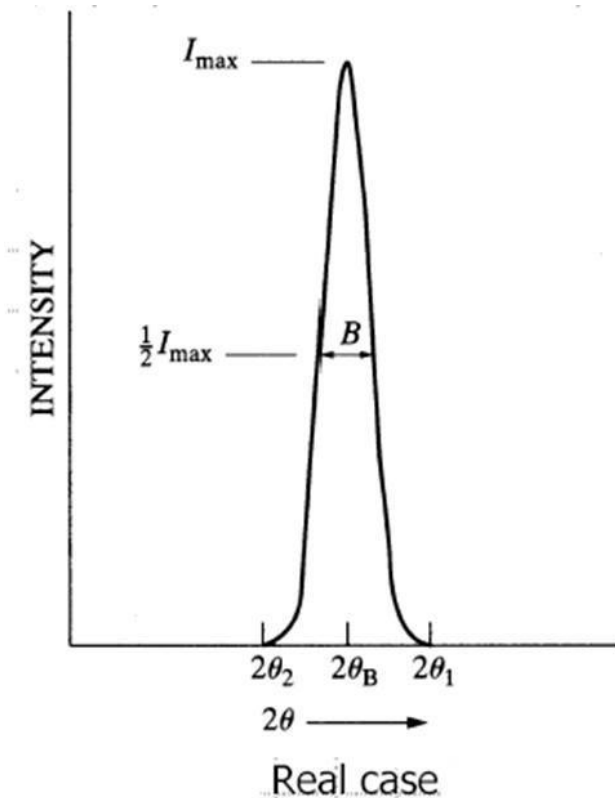
These X-rays will interfere with X-rays scattered from plane  $m$  that scatters rays with an angle that correspond to  $n/2$  (out of phase - destructive interference)

For very fine crystals the plane  $m$  is not present so that X-rays diffracted at  $\theta_1$  will be detected as peak broadening



# Kristal Boyutu

Peak genişliği ile kristal boyutu ters orantılıdır. Peak genişliği (B) arttıkça kristal boyutu küçülür.



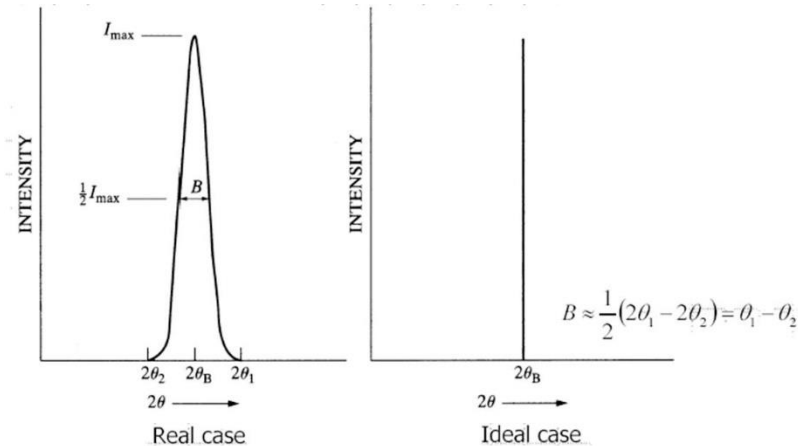
Krital Boyut hesabı (t) :

$$t = \frac{0.9 \lambda}{B \cos \theta_B}$$

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

# Crystallite Size Broadening

- No crystal is perfect due to its finite size
- The deviation from perfect crystallinity leads to a broadening of the diffraction peaks which is negligible above a certain size (~0.1 - 1 micron)
- Peak broadening occurs for powder samples with crystallites around 100 nm in diameter



$$L = \frac{K\lambda}{B(2\theta)\cos\theta} \quad K=0.87-1.00$$

Sherrer Equation for samples with fine crystallites

- Peak width is measured at the half of the maximum peak intensity (FWHM)
- Various methods to determine the crystallite size of an unknown fine powder mixed with a coarse standard powder

$$B^2 = B_U^2 - B_S^2$$

Warren's equation – the simplest form

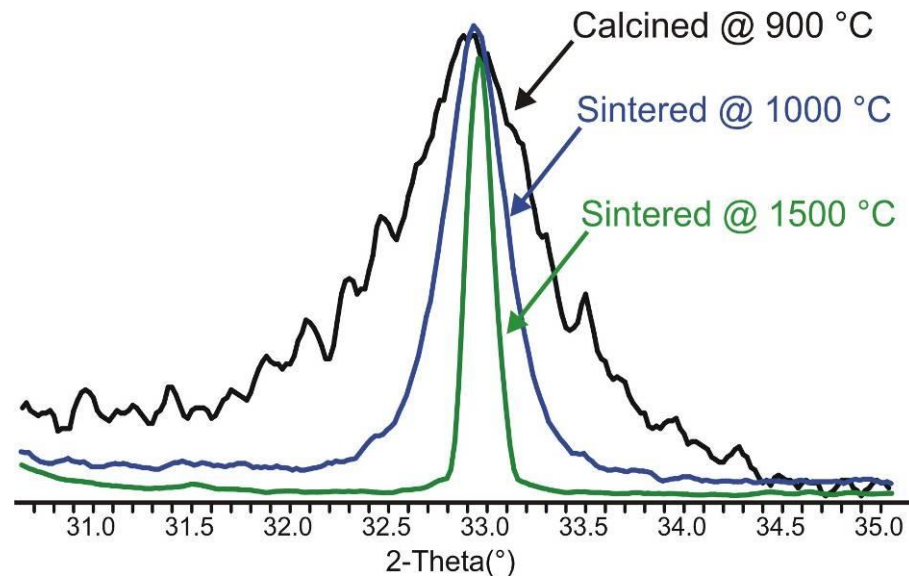
# Crystallite Size Broadening

Example - Sherrer analysis of the main peak for a heat treated polycrystalline  $\text{La}_2\text{Zr}_2\text{O}_7$  to estimate the crystallite size

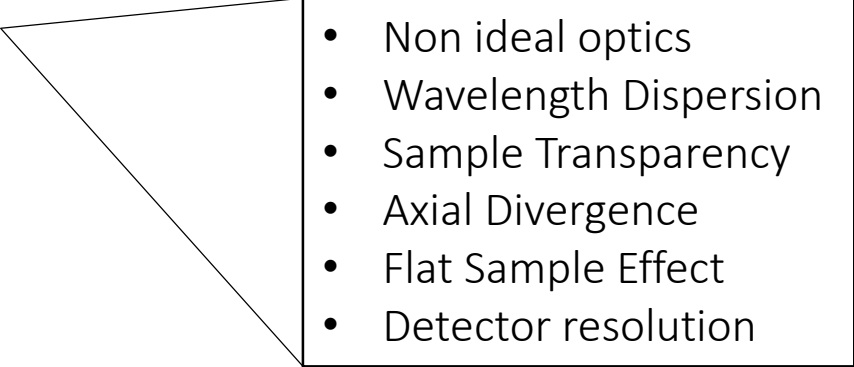
Calcined at 900 °C for 1 hr: ~10 nm average crystallite size

Sintered at 1000 °C for 96 hrs: ~30-40 nm average size

Sintered at 1500 °C for 2 hrs: >100 nm average crystallite size

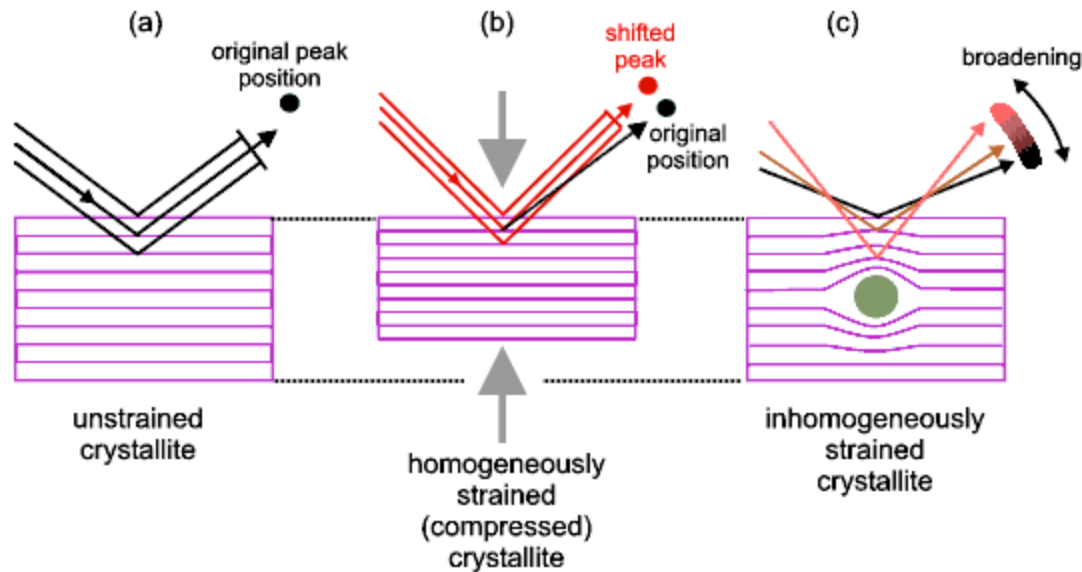


# Factors That Contribute to Crystallite Size Broadening

- Instrumental Broadening
  - Crystallite Size
  - Microstrain
  - Faulting
  - Dislocations
  - Antiphase Domain Boundaries
  - Grain Surface Relaxation
  - Solid Solution Inhomogeneity
  - Temperature Factors
- 
- Non ideal optics
  - Wavelength Dispersion
  - Sample Transparency
  - Axial Divergence
  - Flat Sample Effect
  - Detector resolution
- The peak profile is a combination of the profiles from all of these contributions
  - Peak broadening analysis is most accurate when the broadening due to crystallite size effects is at least twice the contribution due to instrumental broadening

# Microstrain Determination

- Inhomogeneous strain is the second main source of specimen broadening

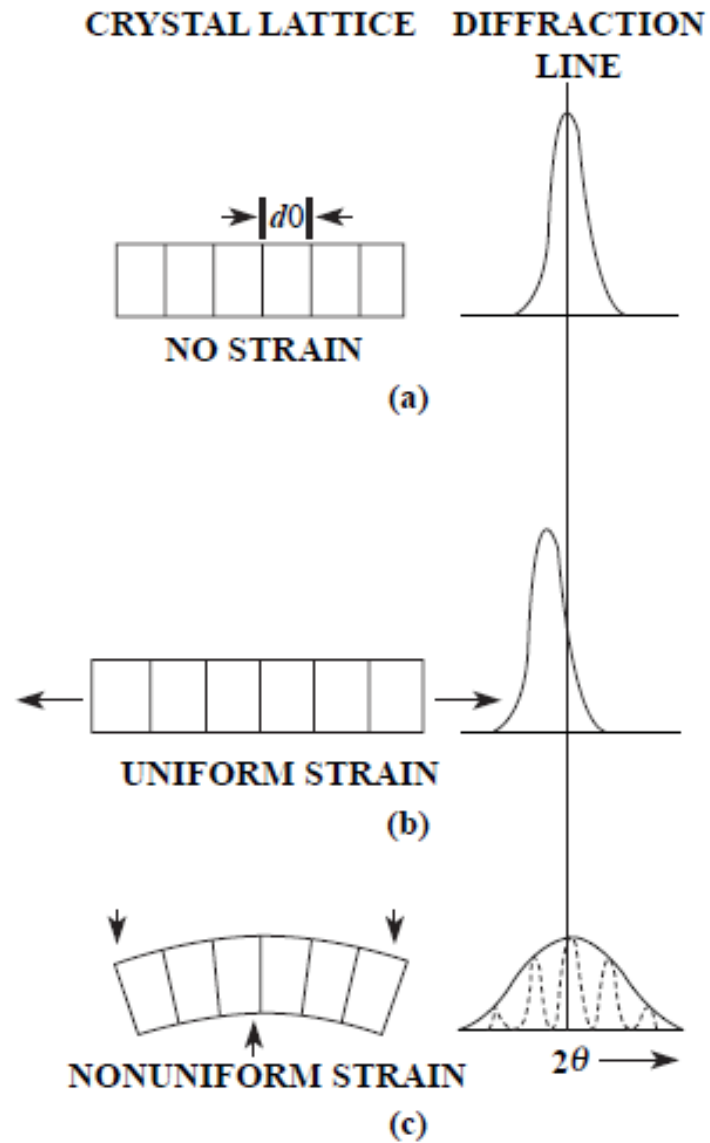


a compressive stress would make the  $d$  spacings smaller and a tensile stress would make the  $d$  spacings larger which would cause only peak shifting

if the strain is *inhomogeneous* then different crystallites will be strained by different amounts and the shifts in  $2\theta$  will be variable resulting in peak broadening

$$B(s) = C \tan\theta, \quad C=4-5$$

# Microstrains





# Separating the size and microstrain contributions to peak broadening

- Williamson and Hall simplified the contributions of size and strain to a basic sum or sum of squares

$$B(2\theta) = \frac{K\lambda}{L \cos \theta}$$

$$B(s) = C \tan \theta$$

$$B(\text{total}) = B(2\theta) + B(s) = \frac{K\lambda}{L \cos \theta} + C \tan \theta$$

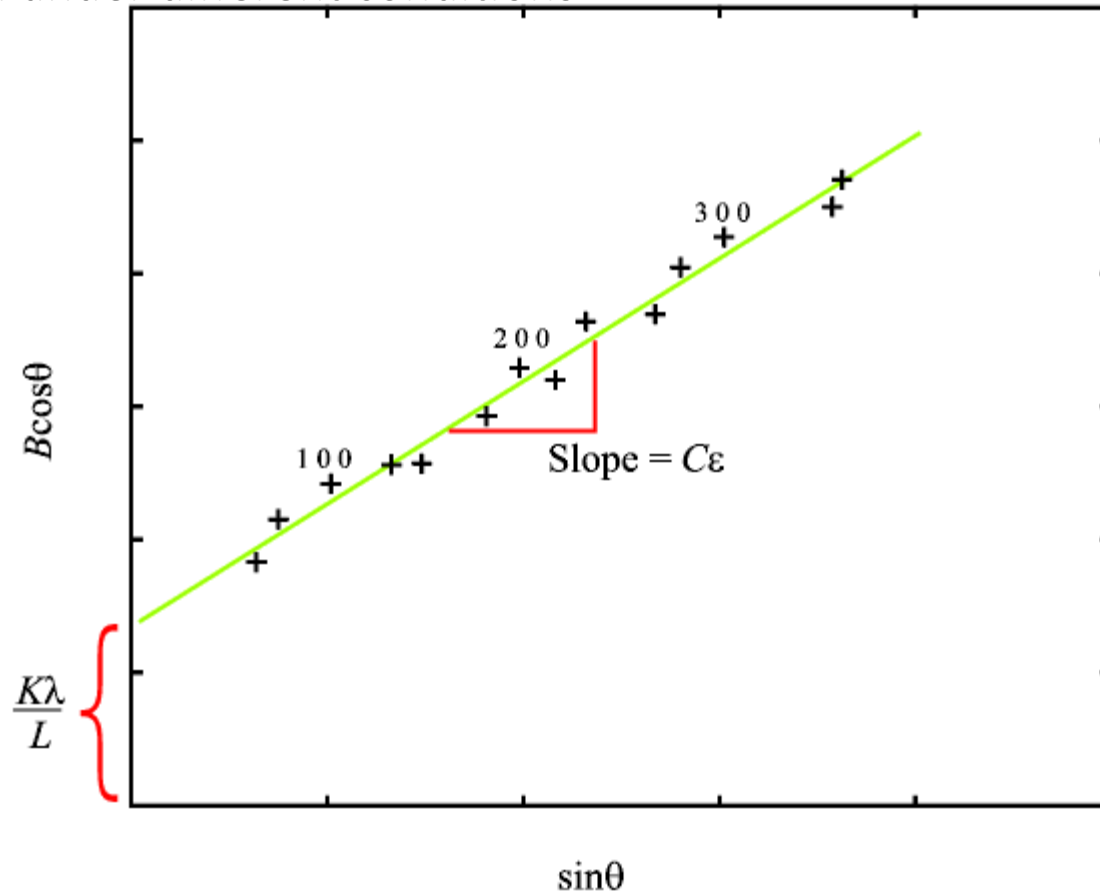
$$B(\text{total}) \cos \theta = \frac{K\lambda}{L} + C \sin \theta$$

By plotting a Williamson-Hall graph, where  $B(\text{total}) \cos \theta$  and  $\sin \theta$  are the axes, the strain component is obtained from the slope ( $C$ ) and the size component from ( $L$ ) the intercept

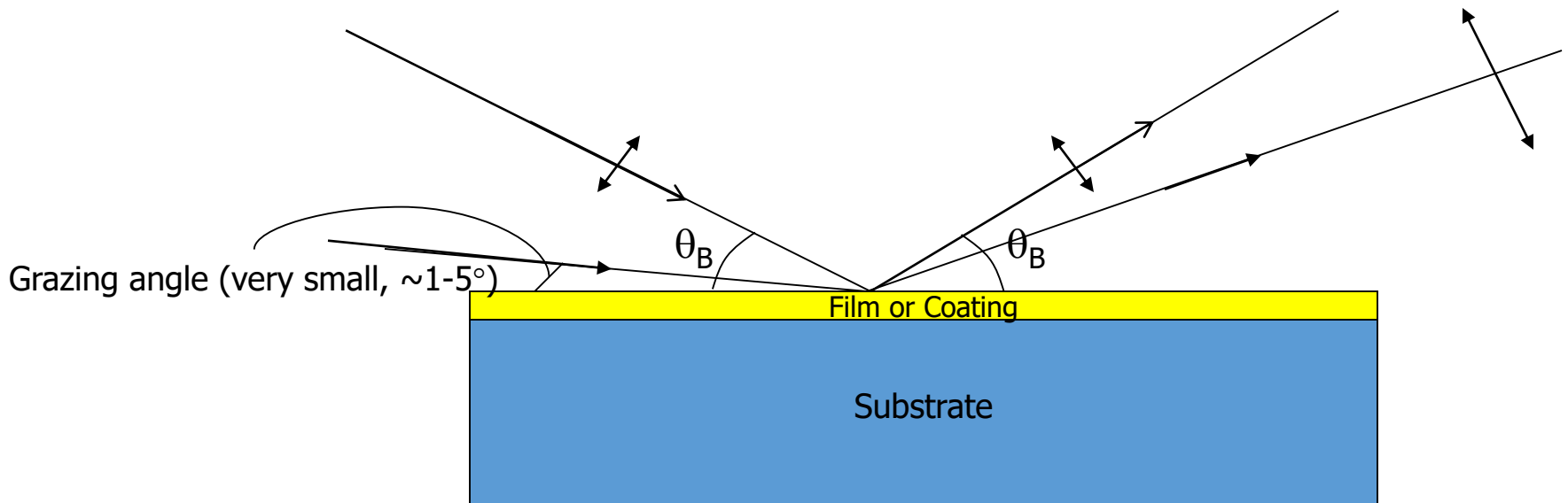
# Separating the size and microstrain contributions to peak broadening

- Williamson-Hall method lacks precision due to its simplifications but it can be a useful method if used to observe trends in the relative sense.

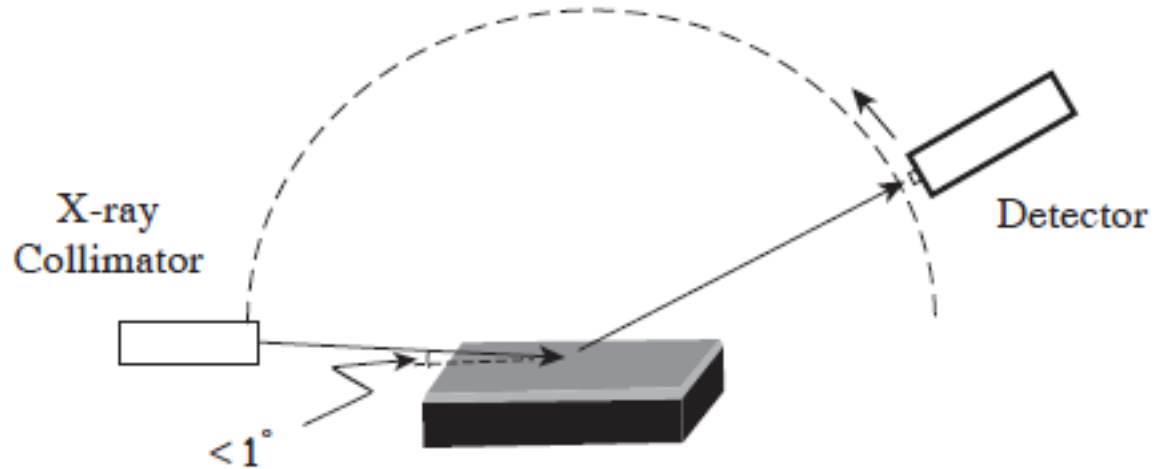
Example - a study of many powder patterns of the same chemical compound, but synthesized under different conditions



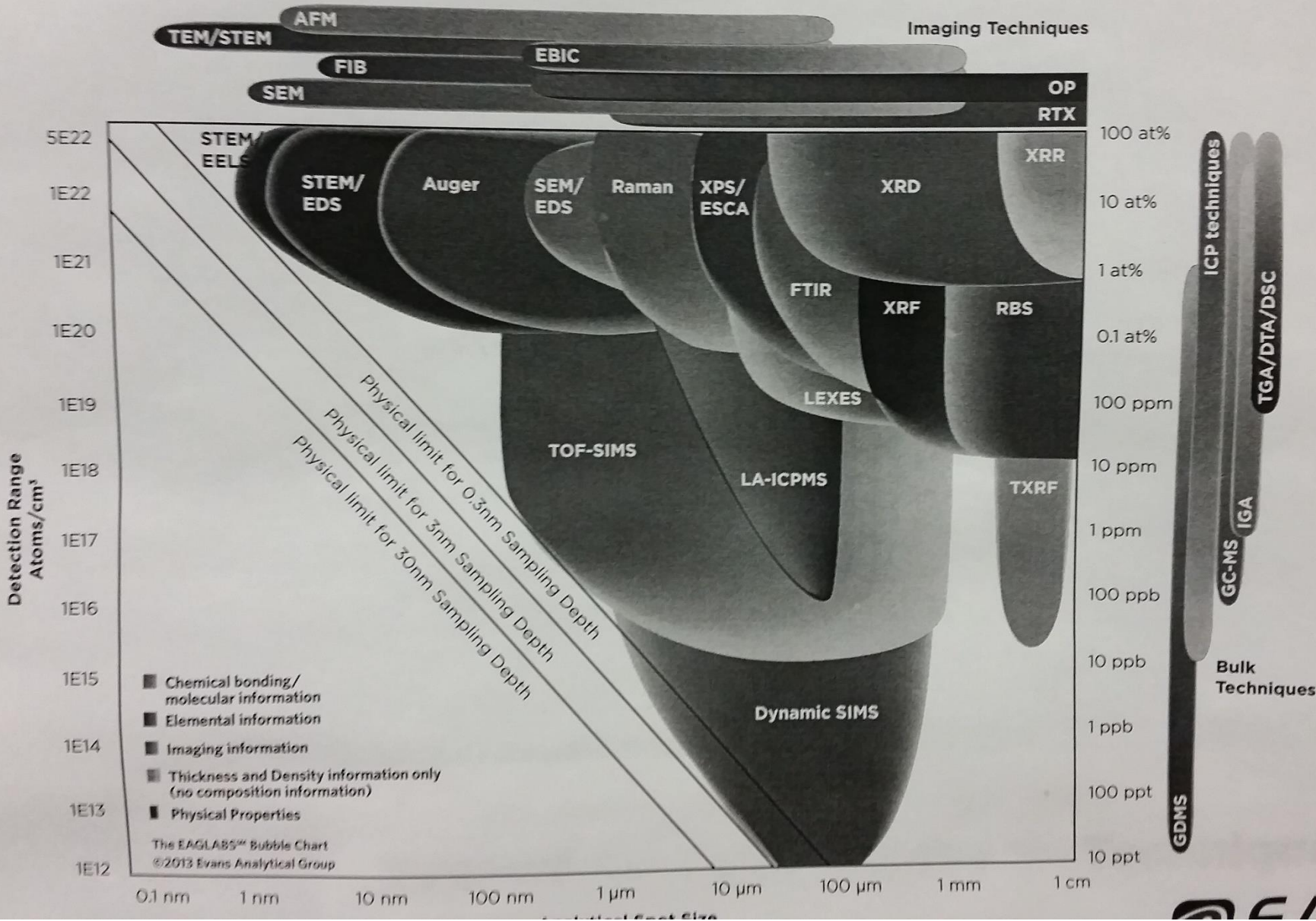
# Thin Film Specimen

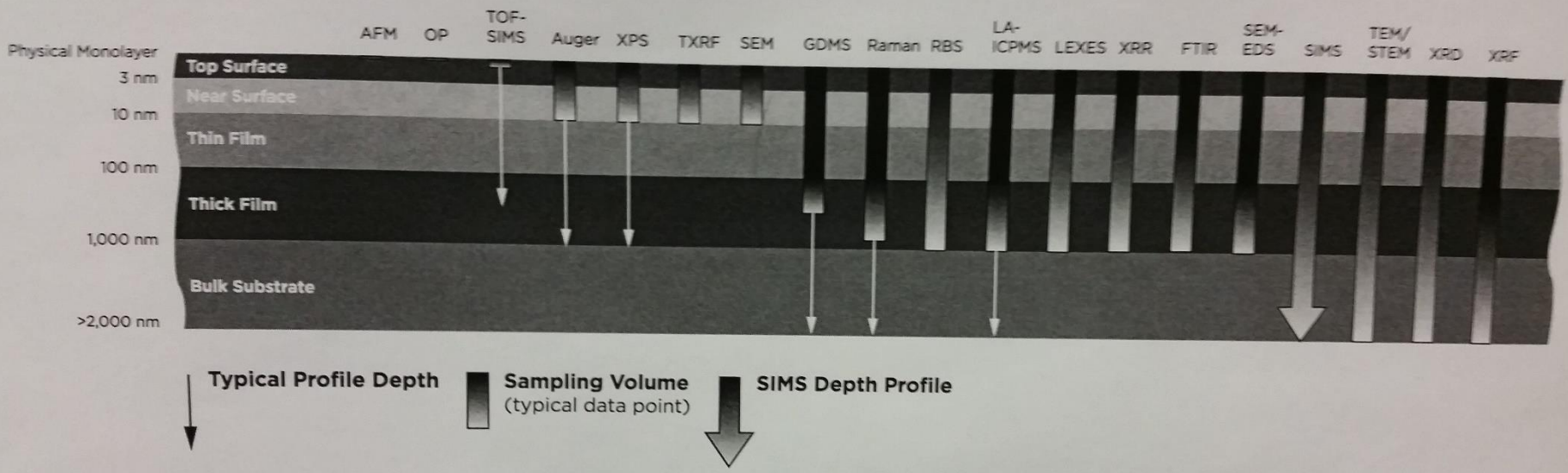


- Smaller volume *i.e.* less intensity of the scattered beam from the film
- Grazing angle
  - Useful only for polycrystalline specimens



# Analytical Resolution vs Detection Limit





# Data collection and analysis procedure

- Choose  $2\theta$  range
- Step size and time per step
- Hardware: slit size, filter, sample alignment
- Fast scan followed with a slower scan
- Look for fluorescence
- Collected data: Background subtraction,  $K_{\alpha 2}$  stripping
- Normalize data for comparison  $I/I_{\max}$

Thank you for your interest!

The following sources provide more information on X-Ray  
Diffraction:

Elements of X-Ray Diffraction (The Bible)  
by B. D. Cullity

Fundamentals of Powder Diffraction and Structural  
Characterization of Materials  
by V. K. Pecharsky et al.

Principles and Applications of Powder Diffraction  
by A. Clearfield et al.