X-Ray Diffraction (XRD)

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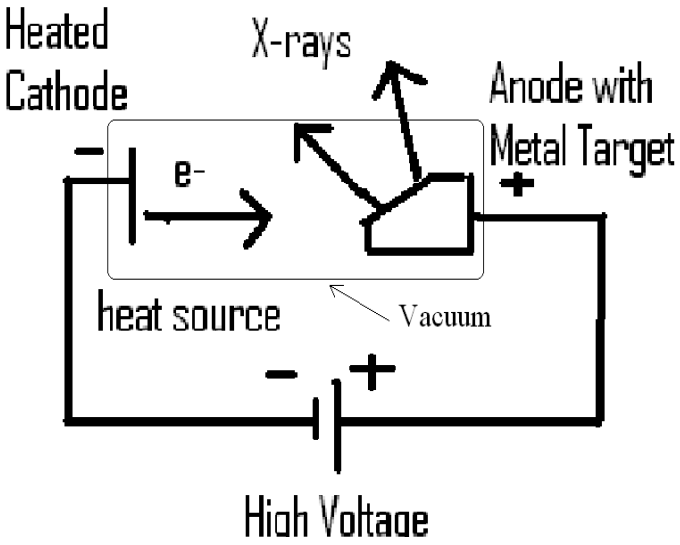
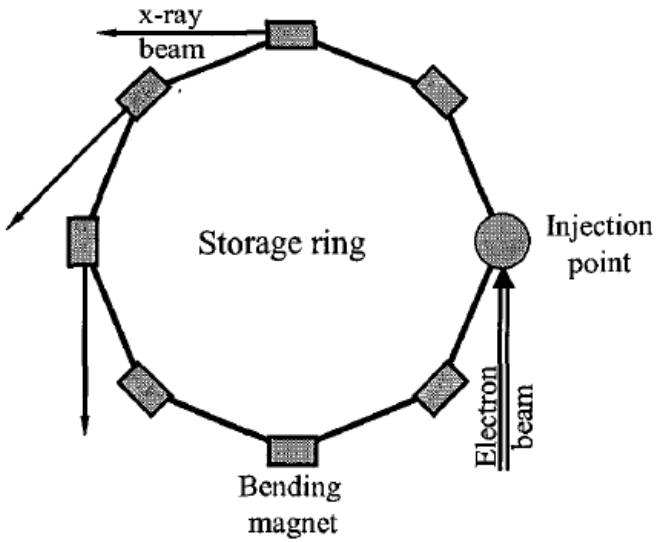
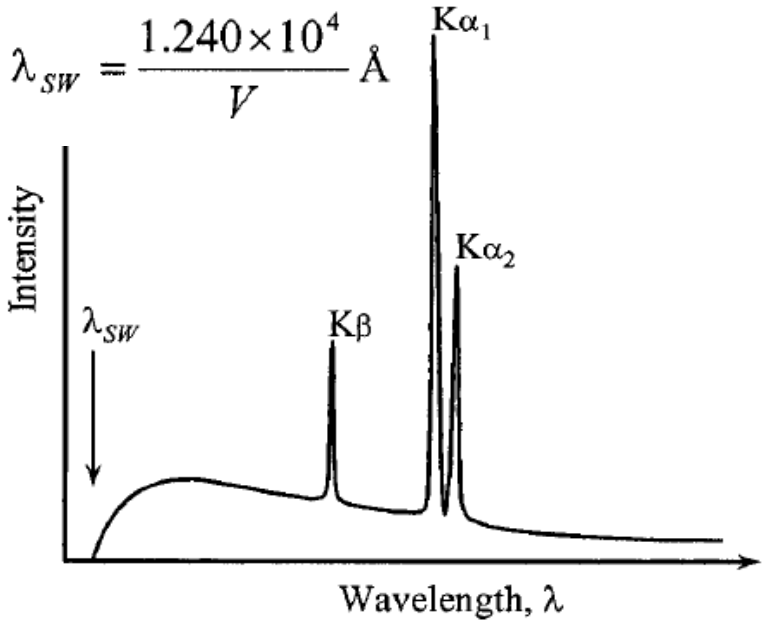
X-ray Generation & typical spectrum

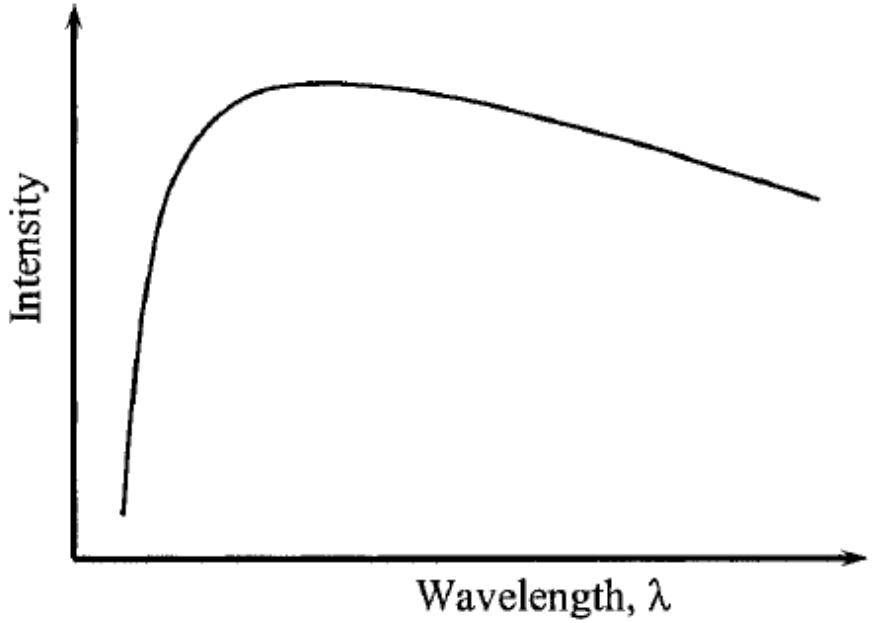
Conventional X-ray Source & Synchrotron:



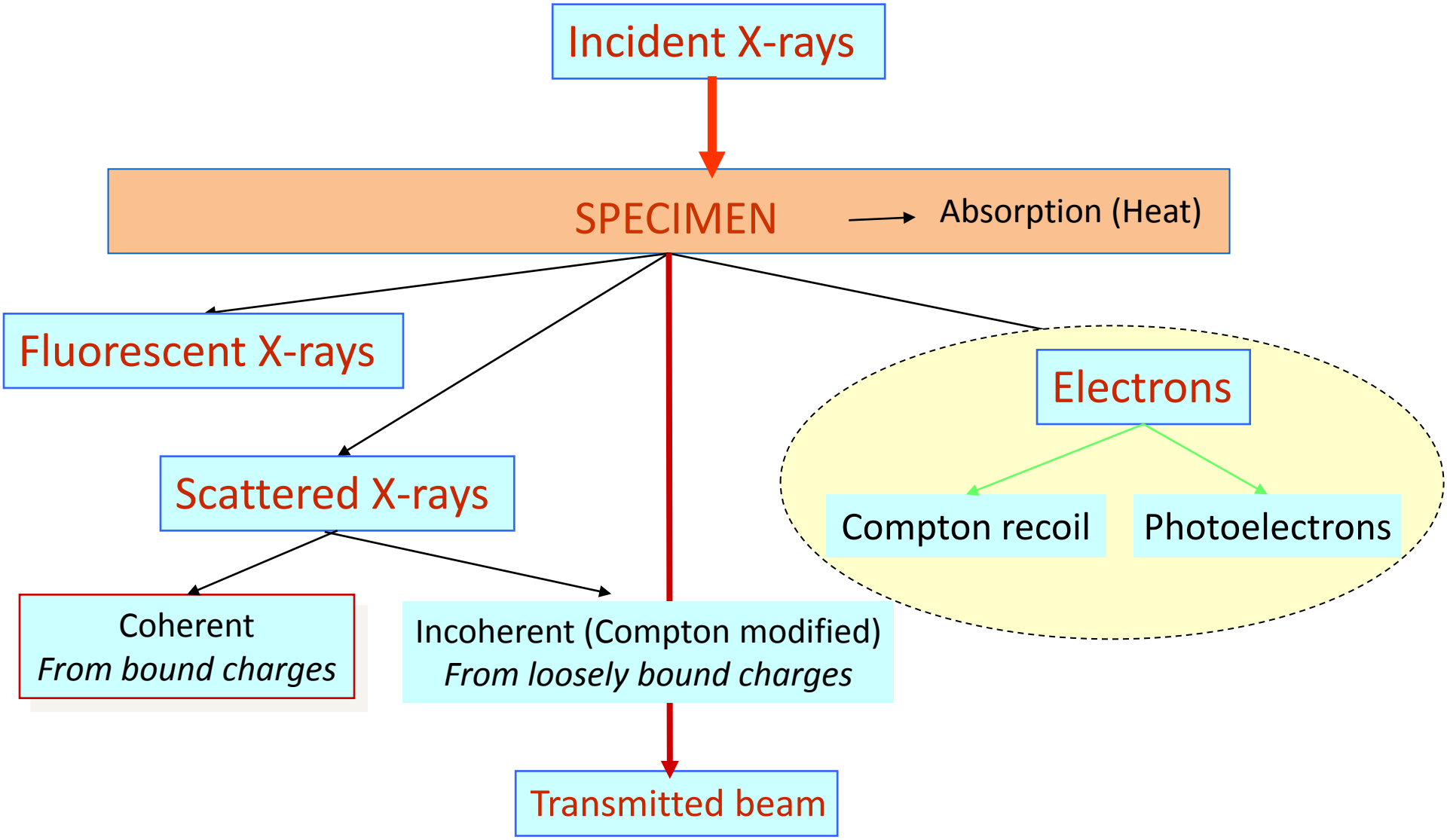


$$\lambda_{SW} = \frac{1.240 \times 10^4}{V} \text{ Å}$$



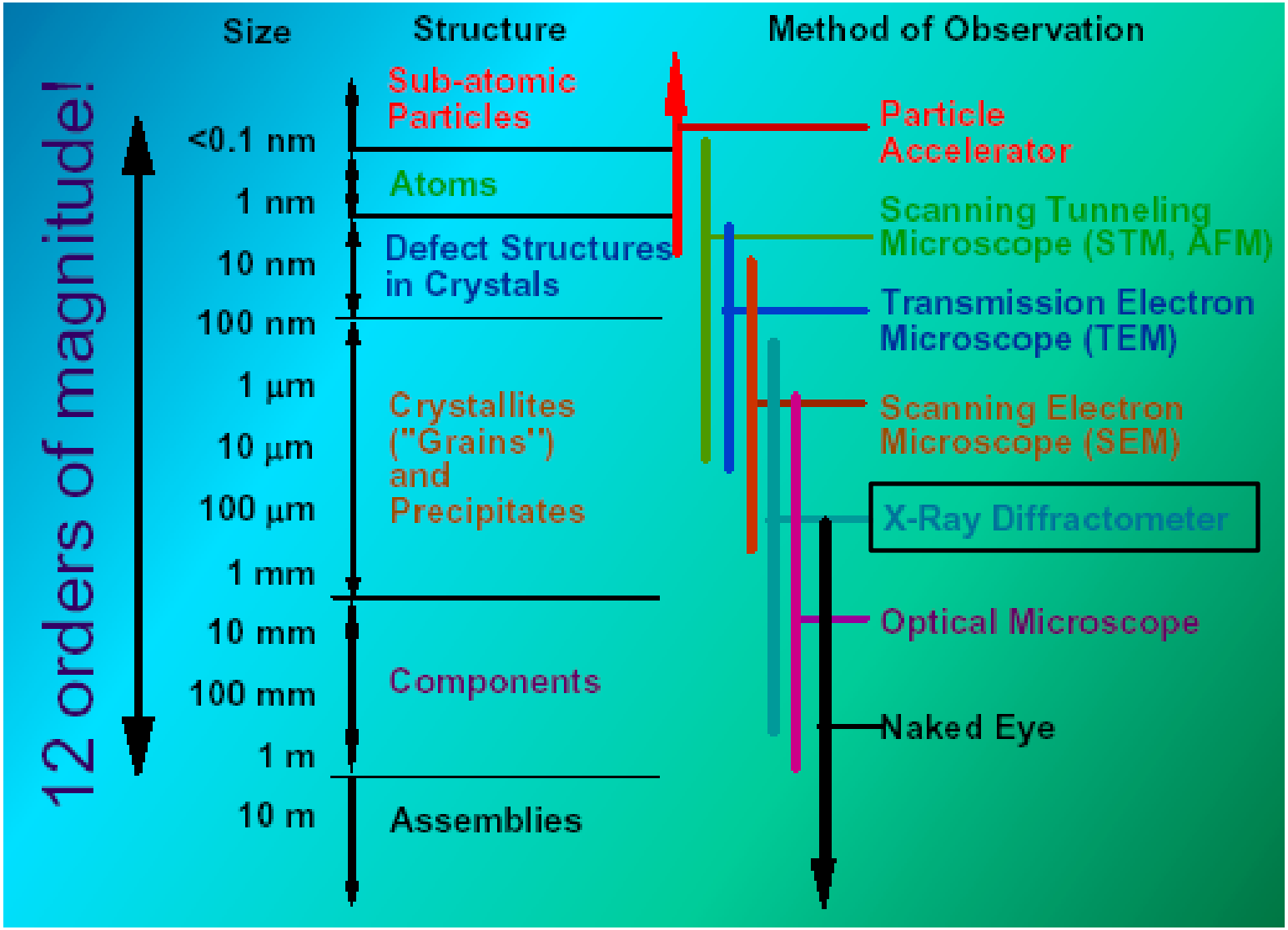


Interaction of X-rays with matter



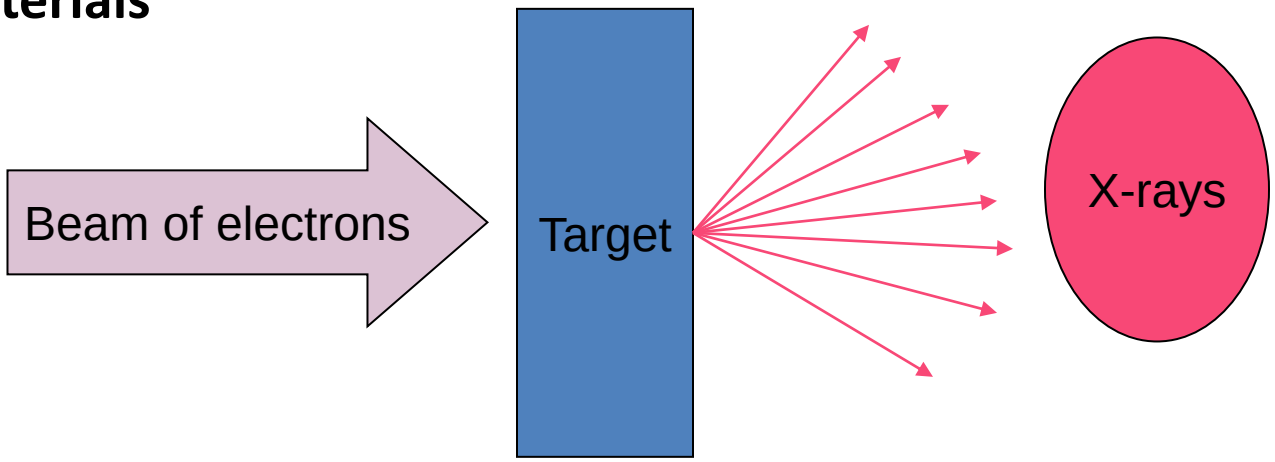
The coherently scattered X-rays are the ones that are important from XRD perspective.

Scale of Structure Organization



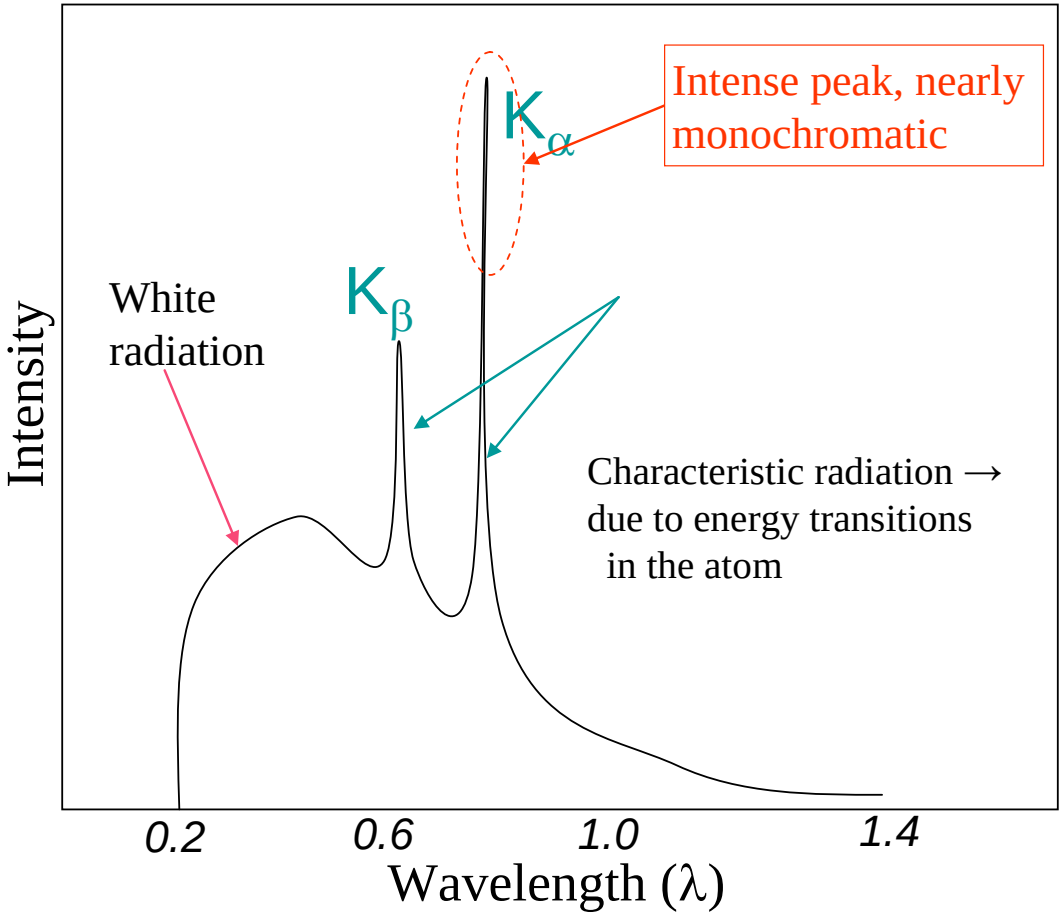
Diffraction Basics

- **For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength**
- **In crystals the typical interatomic spacing ~ 2-3 Å so the suitable radiation is X-rays**
- **Hence, X-rays can be used for the study of crystal structures**
- **Neutrons and Electrons are also used for diffraction studies from materials.**
- **Neutron diffraction is especially useful for studying the magnetic ordering in materials**



A accelerating charge radiates electromagnetic radiation

Mo Target impacted by electrons accelerated by a 35 kV potential shows the emission spectrum as in the figure below (schematic)



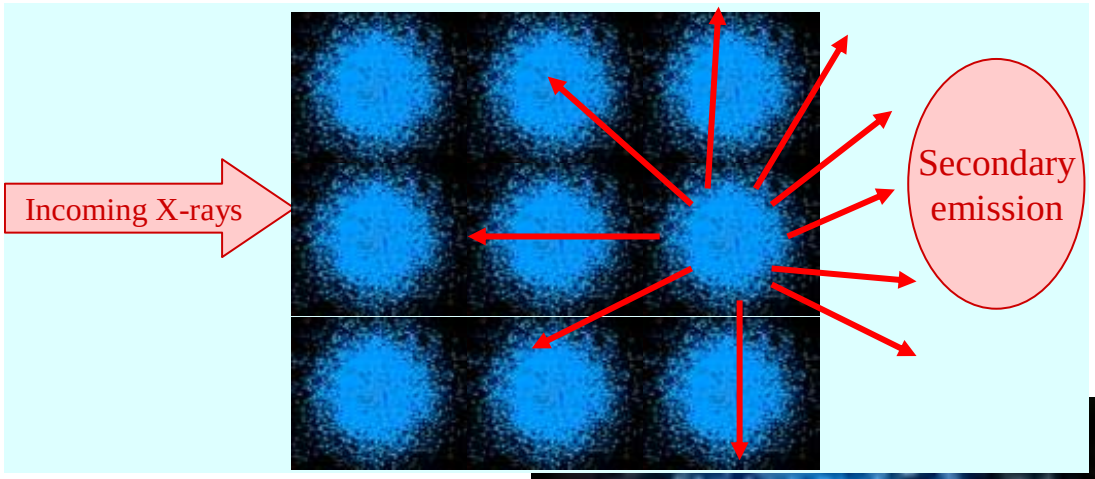
X-ray sources with different λ for doing XRD studies

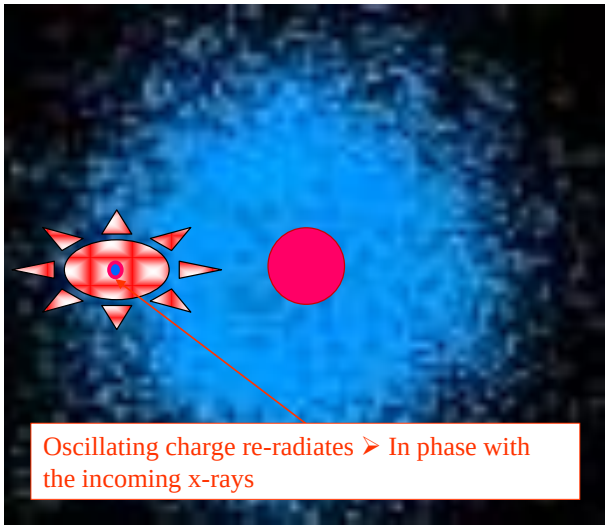
Target Metal	λ Of K_α radiation (Å)
Mo	0.71
Cu	1.54
Co	1.79
Fe	1.94
Cr	2.29

The high intensity nearly monochromatic K_α x-rays can be used as a radiation source for X-ray diffraction (XRD) studies ➢ a monochromator can be used to further decrease the spread of wavelengths in the X-ray

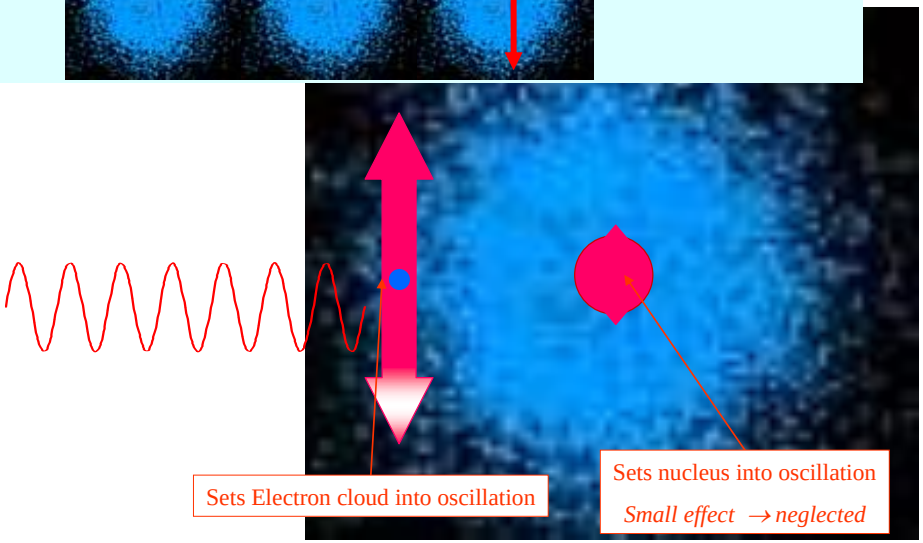
XRD → the first step

- **A beam of X-rays directed at a crystal interacts with the electrons of the atoms in the crystal.**
- **The electrons oscillate under the influence of the incoming X-Rays and become secondary sources of EM radiation.**
- **The secondary radiation is in all directions.**
- **The waves emitted by the electrons have the same frequency as the incoming X-rays ⇒ *coherent.***
- **The emission can undergo constructive or destructive interference.**



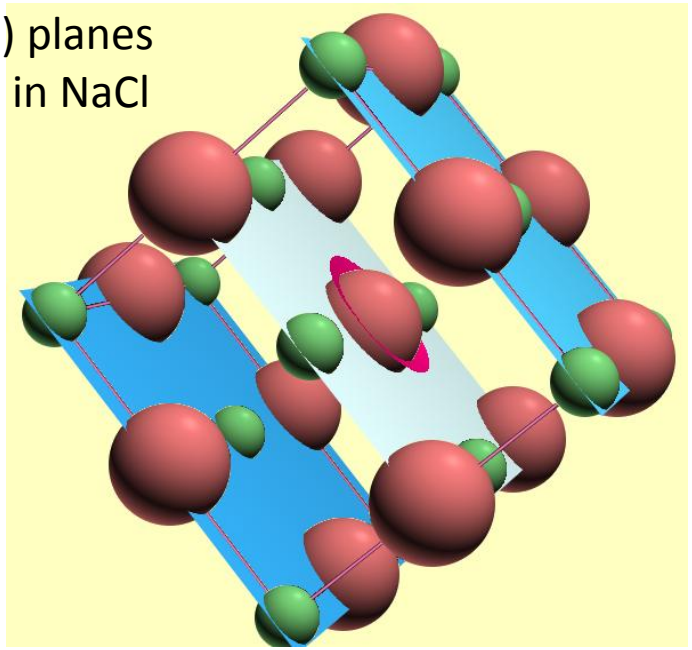


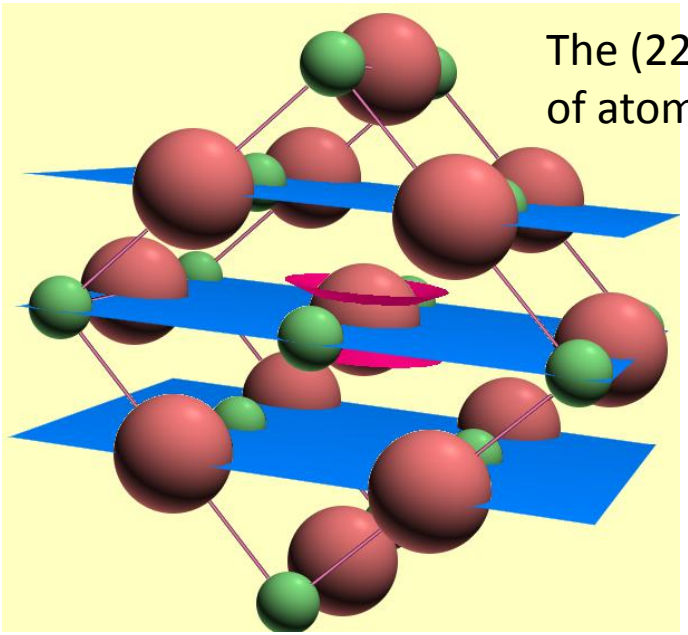
Schematics



Crystalline materials are characterized by the orderly periodic arrangements of atoms.

The (200) planes of atoms in NaCl





The (220) planes of atoms in NaCl

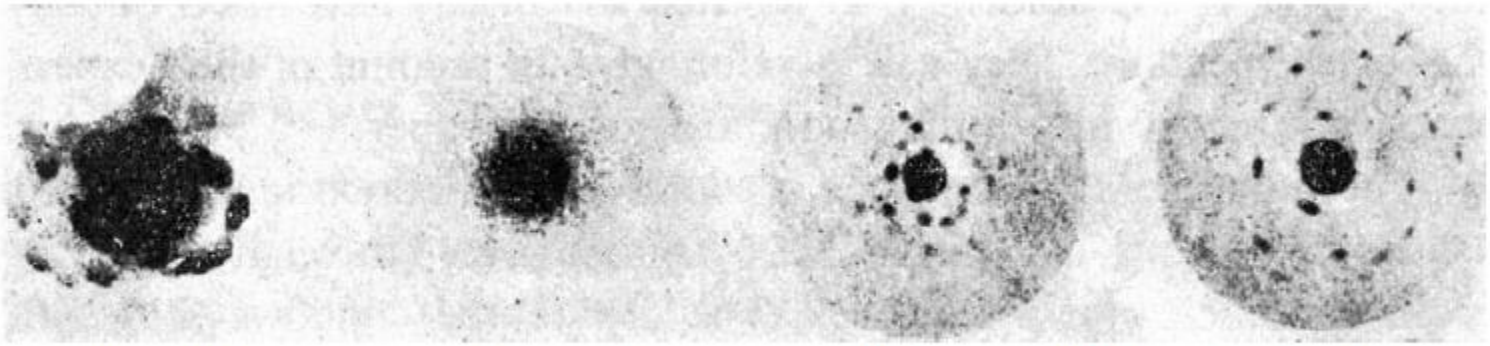
- The unit cell is the basic repeating unit that defines a crystal.
- Parallel **planes of atoms** intersecting the unit cell are used to define directions and distances in the crystal.
  - These crystallographic planes are identified by **Miller indices**.

The atoms in a crystal are a periodic array of coherent scatterers and thus can diffract light.

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

2012 was the 100th Anniversary of X-Ray Diffraction

- X-rays were discovered by WC Rontgen in 1895
- In 1912, PP Ewald developed a formula to describe the passage of light waves through an ordered array of scattering atoms, based on the hypothesis that crystals were composed of a space-lattice-like construction of particles.
- Maxwell von Laue realized that X-rays might be the correct wavelength to diffract from the proposed space lattice.
- In June 1912, von Laue published the first diffraction pattern in *Proceedings of the Royal Bavarian Academy of Science.*



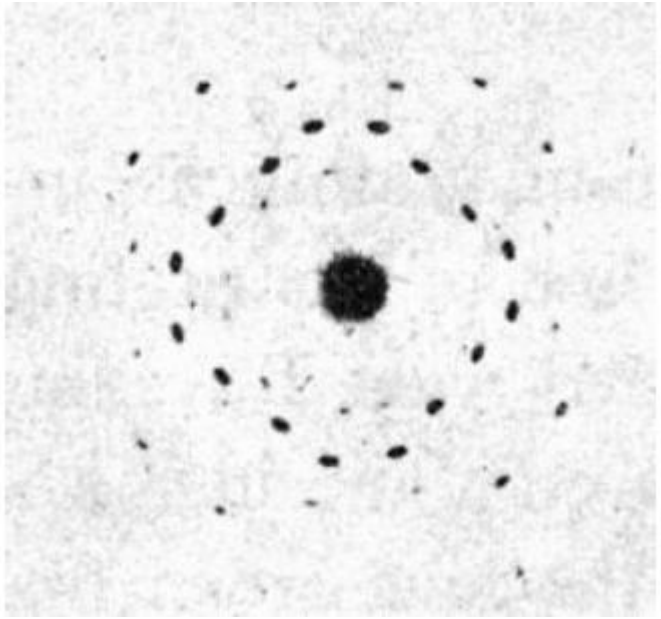
The diffraction pattern of copper sulfate, published in 1912

The Laue diffraction pattern

•Von Laue's diffraction pattern supported two important hypotheses

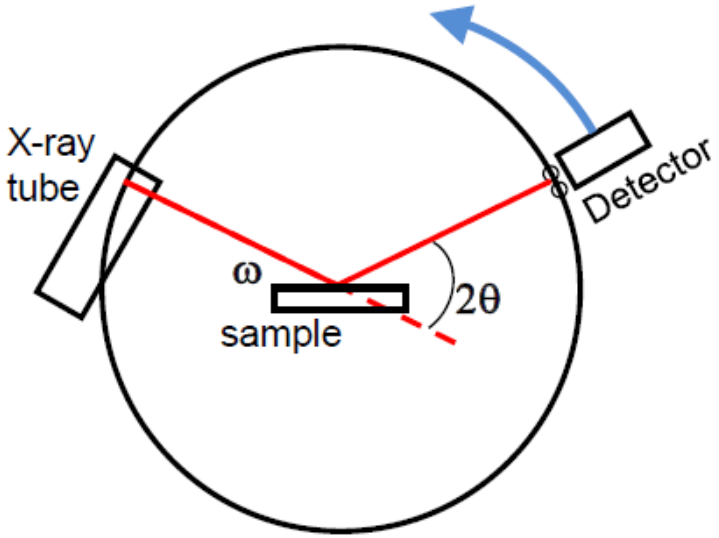
–X-rays were wavelike in nature and therefore were electromagnetic radiation
–The space lattice of crystals

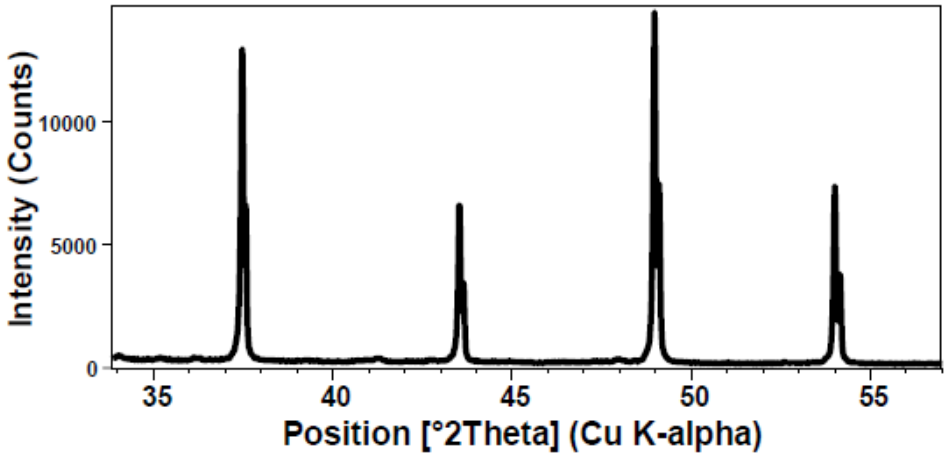
•Bragg consequently used X-ray diffraction to solve the first crystal structure, which was the structure of NaCl published in June 1913.
•Single crystals produce "spot" patterns similar to that shown to the right.
•*However, powder diffraction patterns look quite different*.



The second diffraction pattern published was of ZnS. Because this is a higher symmetry material, the pattern was less complicated and easier to analyze

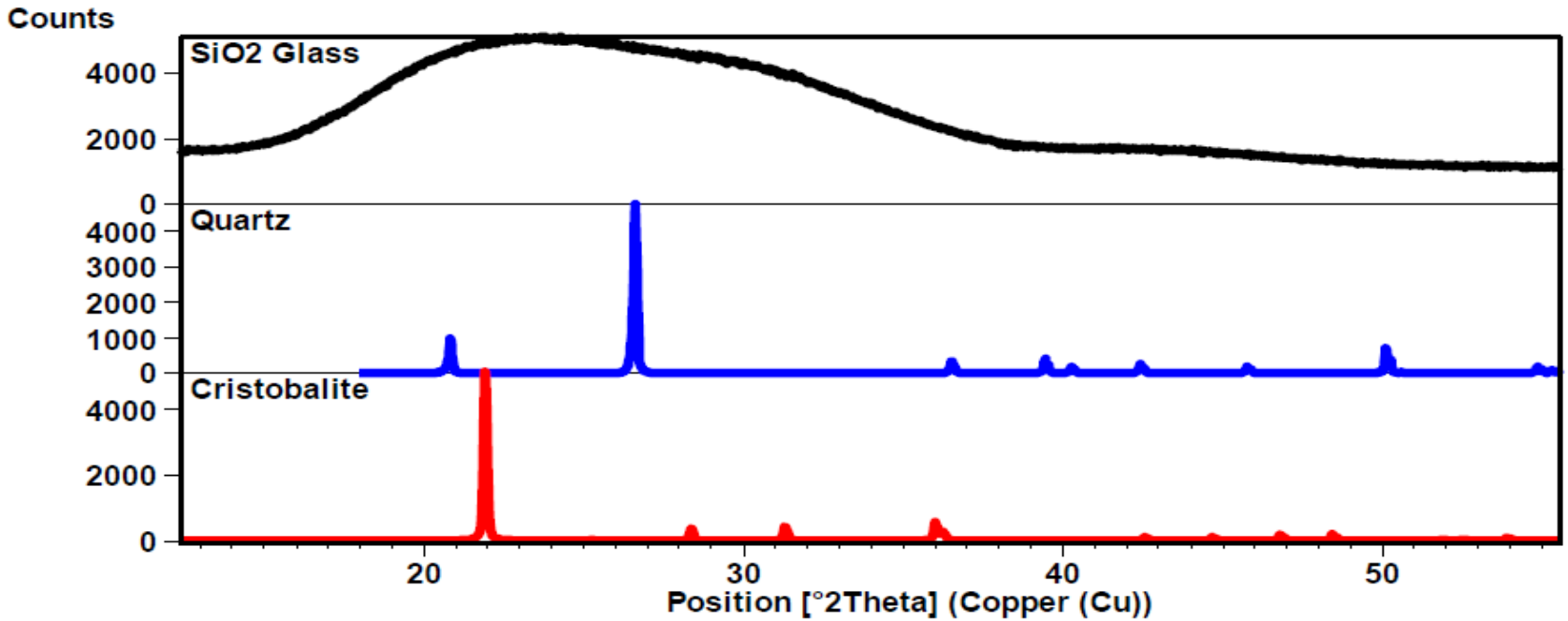
An X-ray powder diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample





- The detector moves in a circle around the sample
  - –The detector position is recorded as the angle 2theta (2θ)
  - –The detector records the number of X-rays observed at each angle 2θ
  - –The X-ray intensity is usually recorded as “counts” or as “counts per second”
- Many powder diffractometers use the Bragg-Brentano parafocusing geometry
  - –To keep the X-ray beam properly focused, the incident angle omega changes in conjunction with 2theta
  - –This can be accomplished by rotating the sample or by rotating the X-ray tube.

X-rays scatter from atoms in a material and therefore contain information about the atomic arrangement



- The three X-ray scattering patterns above were produced by three *chemically identical forms* SiO_2
- Crystalline materials like quartz and Cristobalite produce X-ray diffraction patterns
  - Quartz and Cristobalite have two different crystal structures
  - The Si and O atoms are arranged differently, but both have long-range atomic order
  - The difference in their crystal structure is reflected in their different diffraction patterns
- The amorphous glass does not have long-range atomic order and therefore produces only broad scattering features

Diffraction occurs when light is scattered by a periodic array with long-range order, producing constructive interference at specific angles

•The electrons in each atom coherently scatter light.
–We can regard each atom as a coherent point scatterer
–The strength with which an atom scatters light is proportional to the number of electrons around the atom.

•The atoms in a crystal are arranged in a periodic array with long-range order and thus can produce diffraction.

•The wavelength of X rays are similar to the distance between atoms in a crystal. Therefore, we use X-ray scattering to study atomic structure.

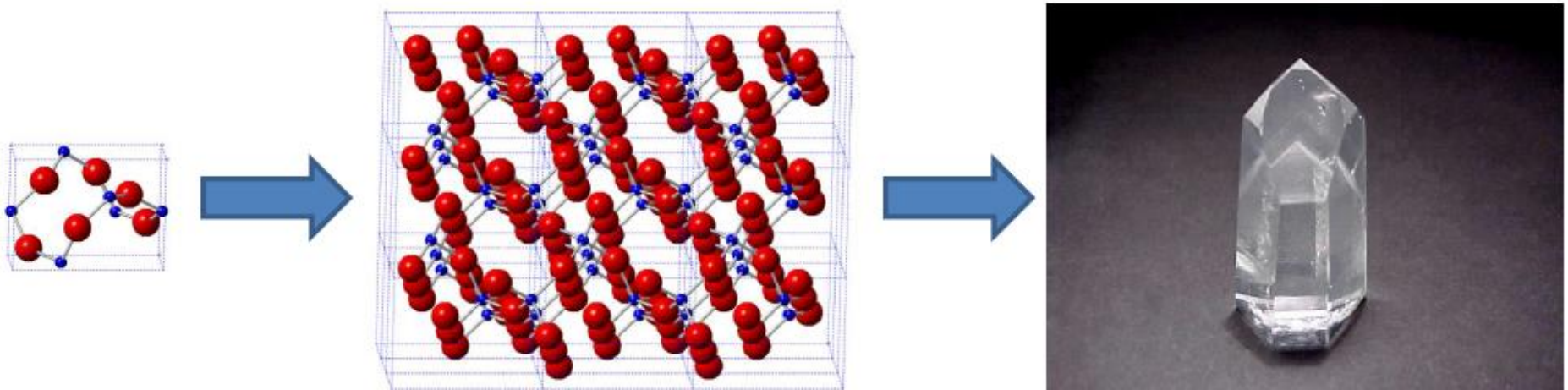
•**The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal**

•Amorphous materials like glass do not have a periodic array with long-range order, so they do not produce a diffraction pattern. Their X-ray scattering pattern features broad, poorly defined amorphous ‘humps’.

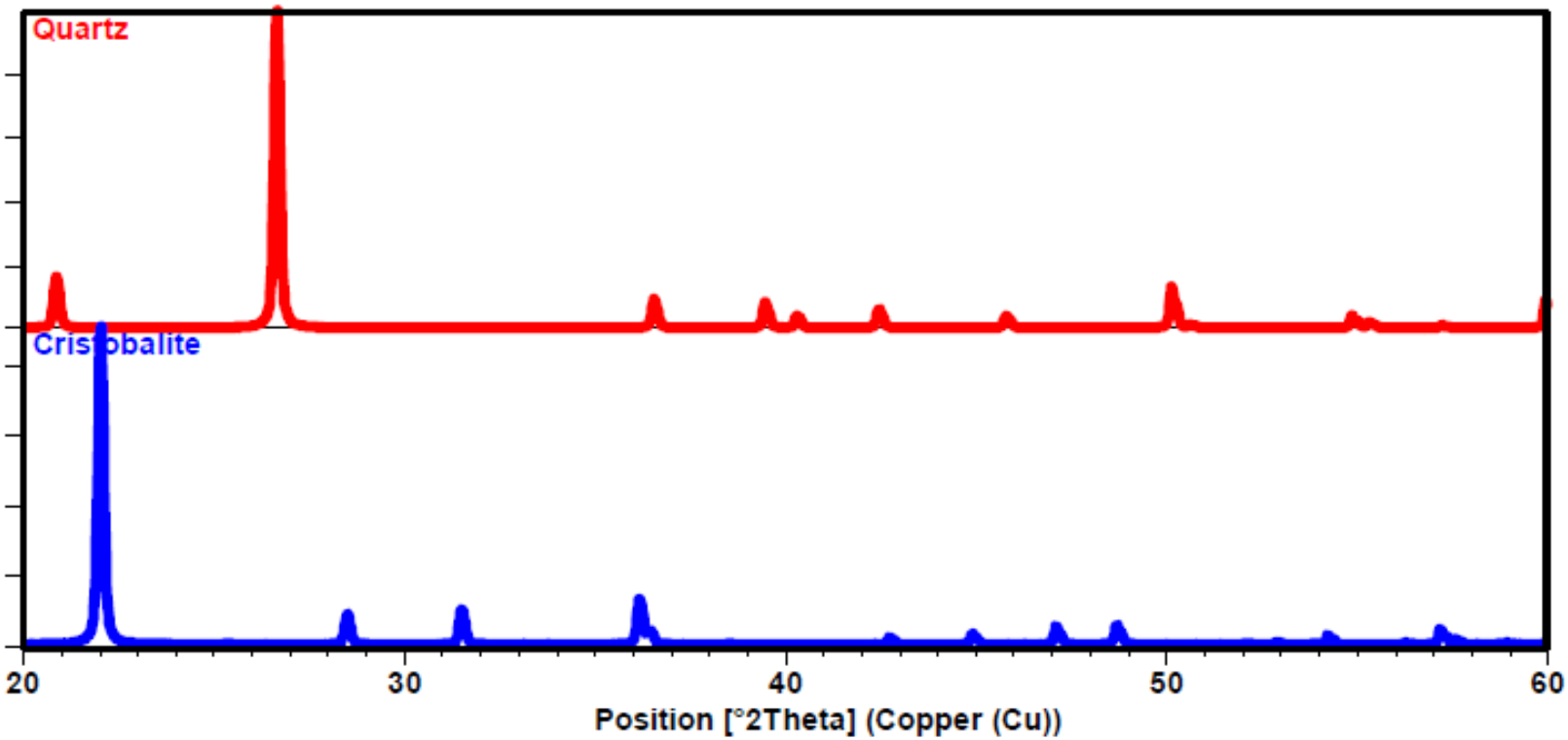
Crystalline materials are characterized by the long-range orderly periodic arrangements of atoms.

- The unit cell is the basic repeating unit that defines the crystal structure.
  - –The unit cell contains the symmetry elements required to uniquely define the crystal structure.
  - –The unit cell might contain more than one molecule:
    - for example, the quartz unit cell contains 3 complete molecules of SiO_2.
  - –The crystal system describes the shape of the unit cell
  - –The lattice parameters describe the size of the unit cell

- The unit cell repeats in all dimensions to fill space and produce the macroscopic grains or crystals of the material

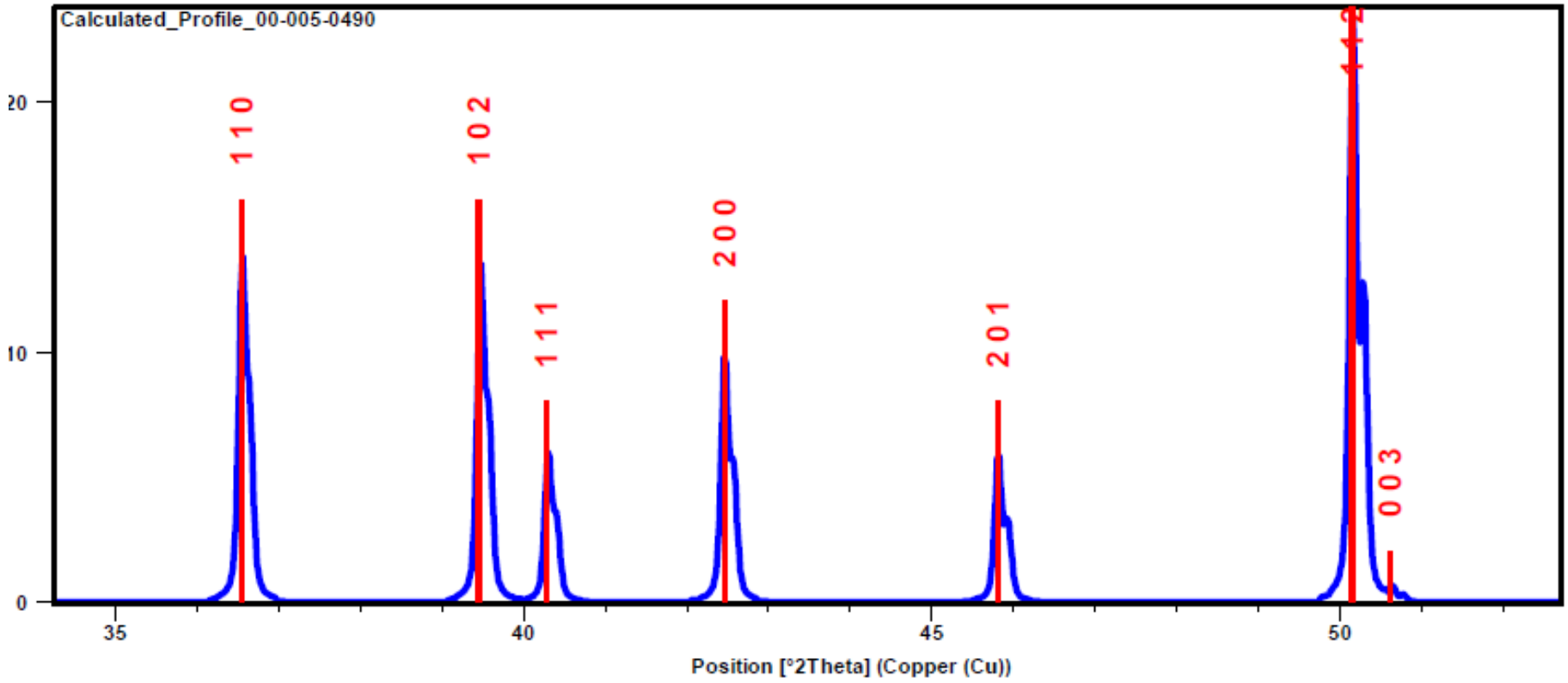


The diffraction pattern is a product of the unique crystal structure of a material



- The crystal structure describes the atomic arrangement of a material.
- The crystal structure determines the position and intensity of the diffraction peaks in an X-ray scattering pattern.
  - –Interatomic distances determine the positions of the diffraction peaks.
  - –The atom types and positions determine the diffraction peak intensities.
- Diffraction peak widths and shapes are mostly a function of instrument and microstructural parameters.

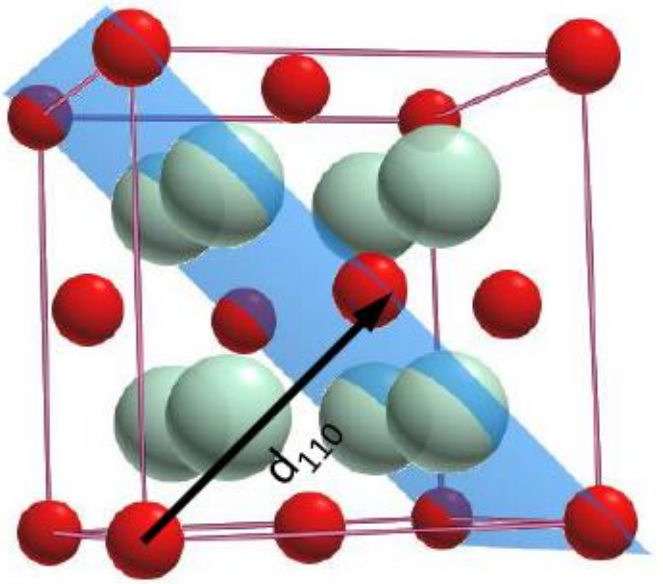
Diffraction pattern calculations treat a crystal as a collection of planes of atoms

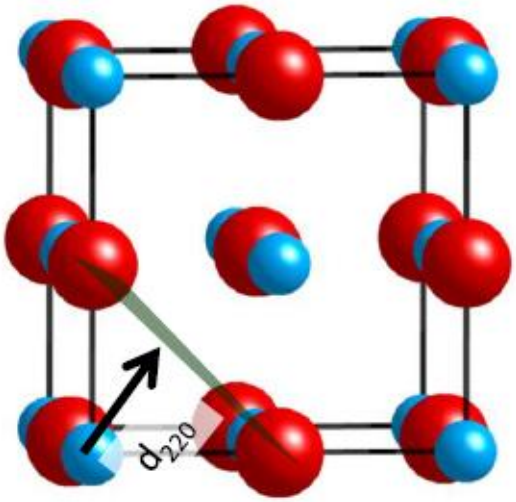


- Each diffraction peak is attributed to the scattering from a specific set of parallel planes of atoms.
- Miller indices (hkl) are used to identify the different planes of atoms
- Observed diffraction peaks can be related to planes of atoms to assist in analyzing the atomic structure and microstructure of a sample

A Brief Introduction to Miller Indices

- The Miller indices (hkl) define the reciprocal axial intercepts of a plane of atoms with the unit cell
  - –The (hkl) plane of atoms intercepts the unit cell at a/h, b/k, and c/l
  - –The (220) plane drawn to the right intercepts the unit cell at ½a, ½b, and does not intercept the c-axis.
- When a plane is parallel to an axis, it is assumed to intercept at ∞; therefore its reciprocal is 0
- The vector d_{hkl} is drawn from the origin of the unit cell to intersect the crystallographic plane (hkl) at a 90° angle.
  - –The direction of d_{hkl} is the crystallographic direction.
  - –The crystallographic direction is expressed using [] brackets, such as [220]

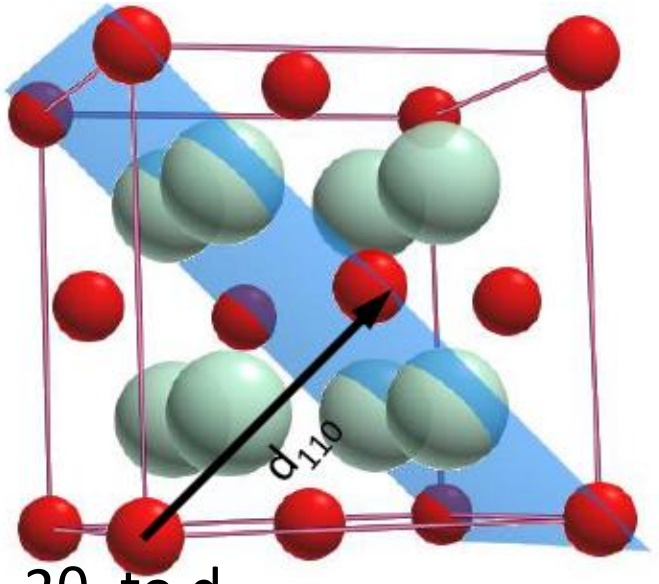




The diffraction peak position is a product of interplanar spacing, as calculated by Bragg's law

Bragg's Law

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



- Bragg's law relates the diffraction angle, 2θ, to d_{hkl}
  - In most diffractometers, the X-ray wavelength λ is fixed.
  - Consequently, a family of planes produces a diffraction peak only at a specific angle 2θ.
- d_{hkl} is a geometric function of the size and shape of the unit cell
  - d_{hkl} is the vector drawn from the origin to the plane (hkl) at a 90° angle.
  - *d_{hkl}, the vector magnitude, is the distance between parallel planes of atoms in the family (hkl)*
  - Therefore, we often consider that the position of the diffraction peaks are determined by the distance between parallel planes of atoms.

The diffraction peak intensity is determined by the arrangement of atoms in the entire crystal

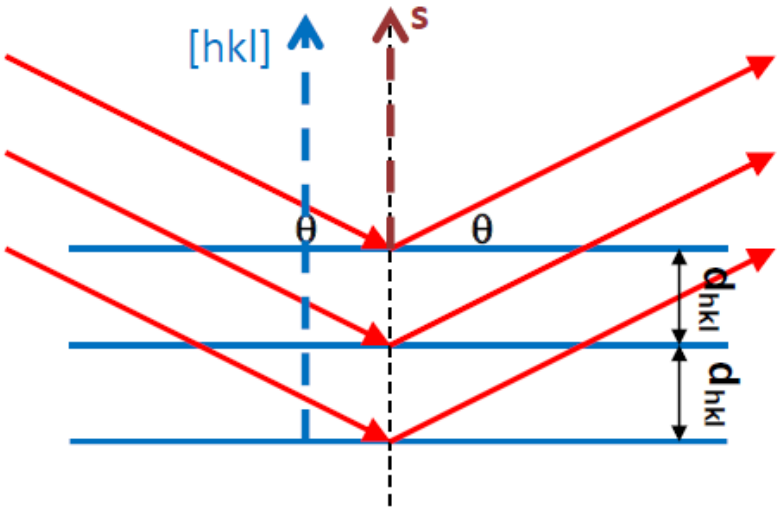
$$I_{hkl} \propto |F_{hkl}|^2$$

$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

- The structure factor F_{hkl} sums the result of scattering from all of the atoms in the unit cell to form a diffraction peak from the (hkl) planes of atoms.
- The amplitude of scattered light is determined by:
  - where the atoms are on the atomic planes
    - this is expressed by the fractional coordinates x_j y_j z_j
  - what atoms are on the atomic planes
    - the scattering factor f_j quantifies the efficiency of X-ray scattering at any angle by the group of electrons in each atom
      - The scattering factor is equal to the number of electrons around the atom at 0° θ, the drops off as θ increases
    - N_j is the fraction of every equivalent position that is occupied by atom j

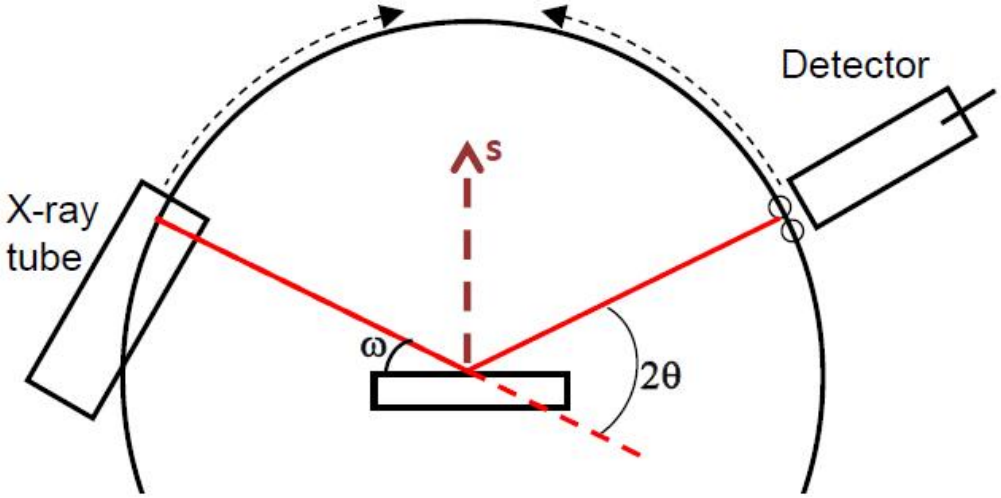
Bragg's law provides a simplistic model to understand what conditions are required for diffraction.

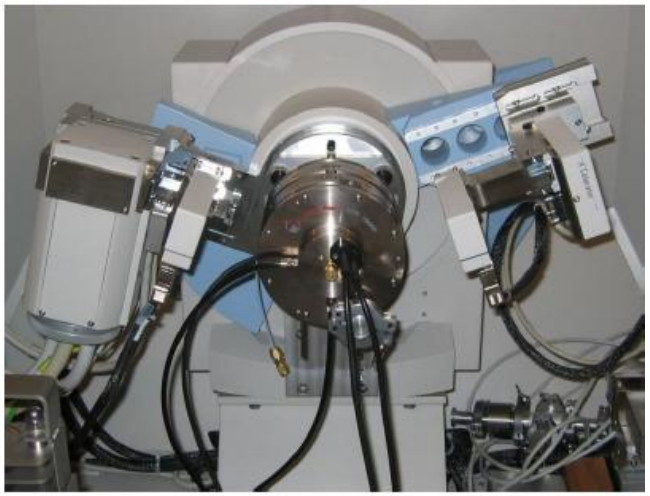
$$\lambda = 2d_{hkl}\sin\theta$$



- For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied.
  - In our diffractometers, the X-ray wavelength λ is fixed.
  - A family of planes produces a diffraction peak only at a specific angle 2θ.
- **Additionally, the plane normal [hkl] must be parallel to the diffraction vector s**
  - Plane normal [hkl]: the direction perpendicular to a plane of atoms
  - Diffraction vector **s: the vector that bisects the angle between the incident and** diffracted beam

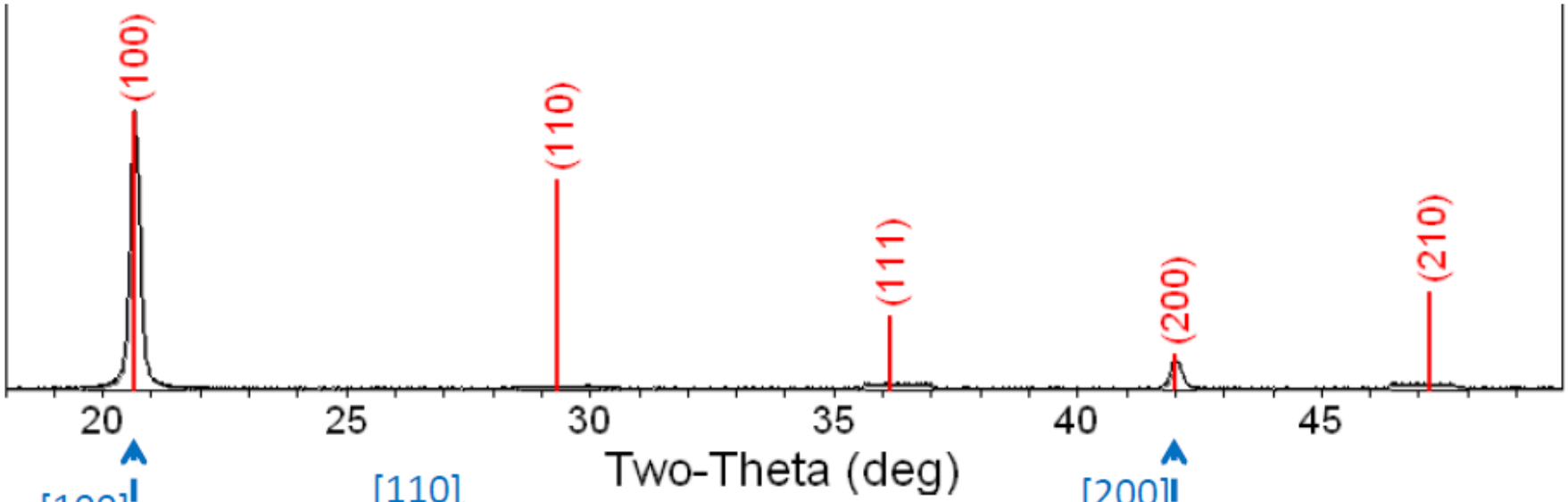
Many powder diffractometers use the Bragg-Brentano parafocusing geometry.

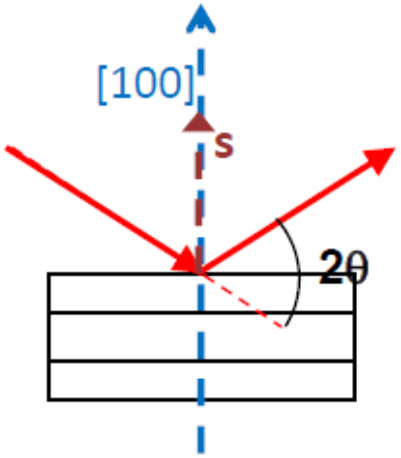




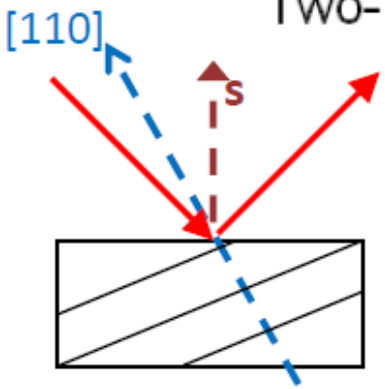
- The incident angle, ω, is defined between the X-ray source and the sample.
- The diffraction angle, 2θ, is defined between the incident beam and the detector.
- The incident angle ω is always ½ of the detector angle 2θ .
  - In a θ:2θ instrument (e.g. Rigaku H3R), the tube is fixed, the sample rotates at θ °/min and the detector rotates at 2θ °/min.
  - In a θ:θ instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate -θ °/min and the detector rotates at a rate of θ °/min.
- **In the Bragg-Brentano geometry, the diffraction vector (s) is always normal to the surface of the sample.**
  - **The diffraction vector is the vector that bisects the angle between the incident and scattered beam**

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

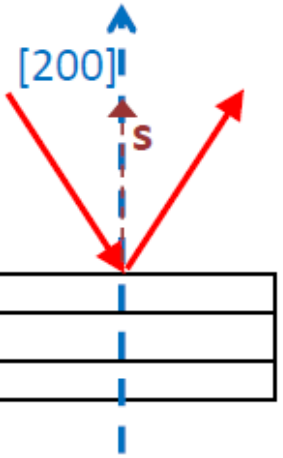




At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

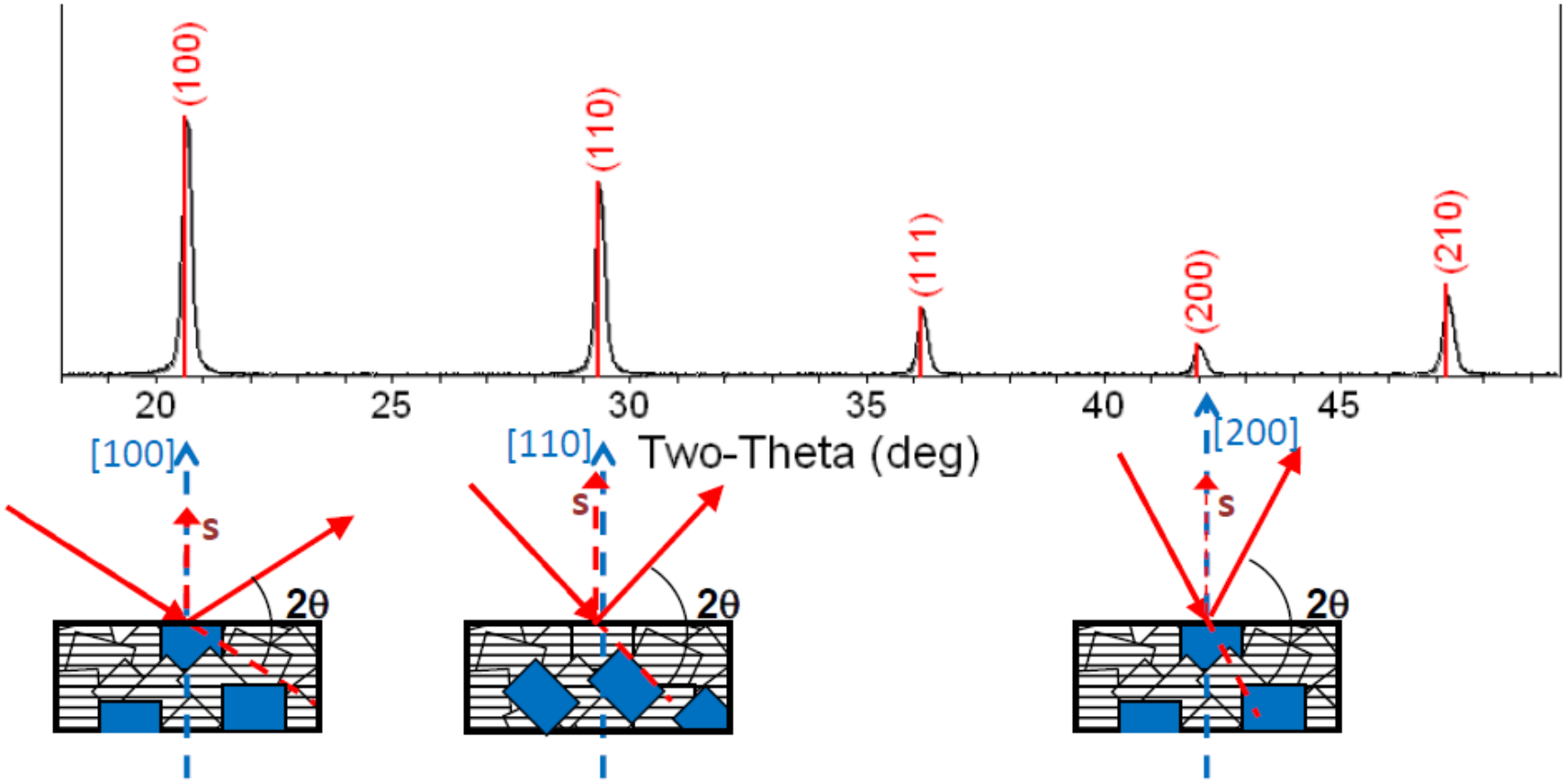


The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.



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

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



•For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).

•Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

Powder diffraction is more aptly named polycrystalline diffraction

- Samples can be powder, sintered pellets, coatings on substrates, engine blocks...

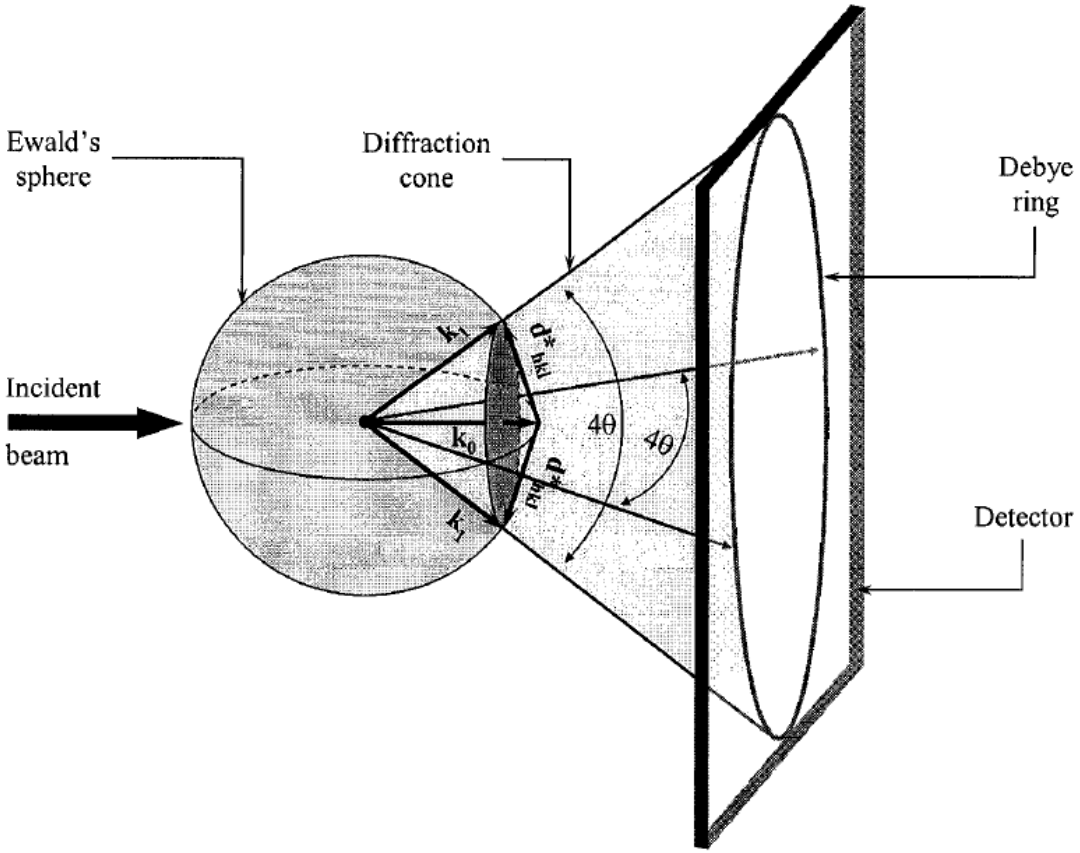
- The ideal “powder” sample contains tens of thousands of randomly oriented crystallites
  - Every diffraction peak is the product of X-rays scattering from an equal number of crystallites
  - Only a small fraction of the crystallites in the specimen actually contribute to the measured diffraction pattern

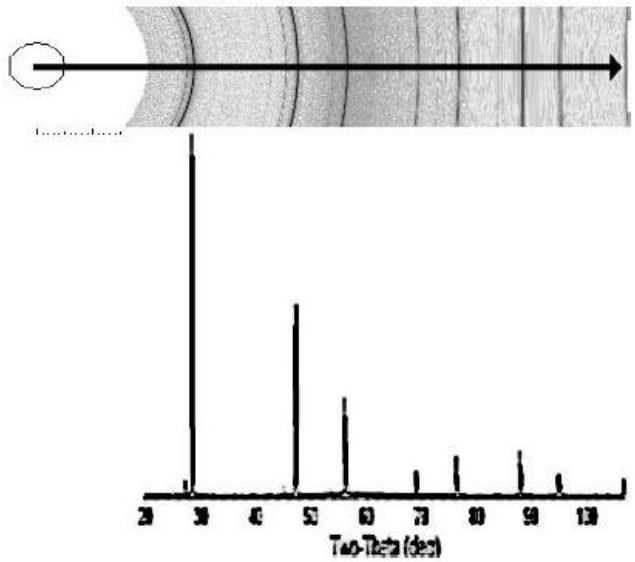
- XRPD is a somewhat inefficient measurement technique

- Irradiating a larger volume of material can help ensure that a statistically relevant number of grains contribute to the diffraction pattern
  - Small sample quantities pose a problem because the sample size limits the number of crystallites that can contribute to the measurement

X-rays are scattered in a sphere around the sample

- Each diffraction peak is actually a Debye diffraction cone produced by the tens of thousands of randomly oriented crystallites in an ideal sample.
  - –A cone along the sphere corresponds to a single Bragg angle 2theta
- The linear diffraction pattern is formed as the detector scans along an arc that intersects each Debye cone at a single point
- Only a small fraction of scattered X-rays are observed by the detector.





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

Diffraction patterns are collected as absolute intensity vs 2θ, but are best reported as relative intensity vs d_{hkl}.

- The peak position as 2theta depends on instrumental characteristics such as wavelength.
  - The peak position as d_{hkl} is an intrinsic, instrument-independent, material property.
    - Bragg's Law is used to convert observed 2θ positions to d_{hkl}.

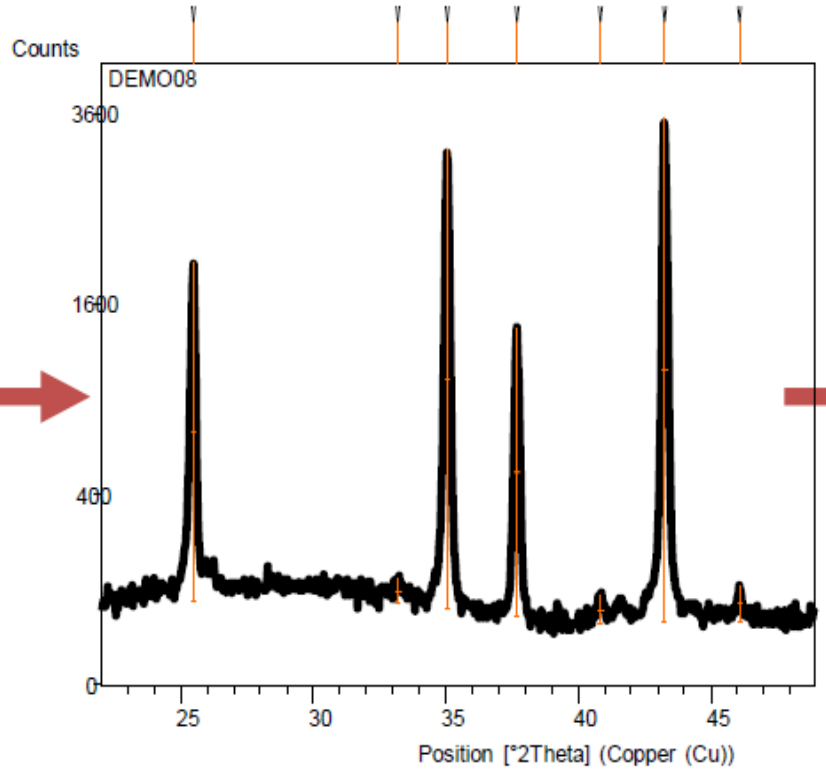
- The absolute intensity, i.e. the number of X rays observed in a given peak, can vary due to instrumental and experimental parameters.
  - The relative intensities of the diffraction peaks should be instrument independent.
    - To calculate relative intensity, divide the absolute intensity of every peak by the absolute intensity of the most intense peak, and then convert to a percentage. The most intense peak of a phase is therefore always called the "100% peak".
  - Peak areas are much more reliable than peak heights as a measure of intensity.

Powder diffraction data consists of a record of photon intensity versus detector angle 2θ.

- Diffraction data can be reduced to a list of peak positions and intensities
  - Each d_{hkl} corresponds to a **family of atomic planes {hkl}**
  - individual planes cannot be resolved- this is a limitation of powder diffraction versus single crystal diffraction

Raw Data

Position [°2θ]	Intensity [cts]
25.2000	372.0000
25.2400	460.0000
25.2800	576.0000
25.3200	752.0000
25.3600	1088.0000
25.4000	1488.0000
25.4400	1892.0000
25.4800	2104.0000
25.5200	1720.0000
25.5600	1216.0000
25.6000	732.0000
25.6400	456.0000
25.6800	380.0000
25.7200	328.0000



Reduced dI list

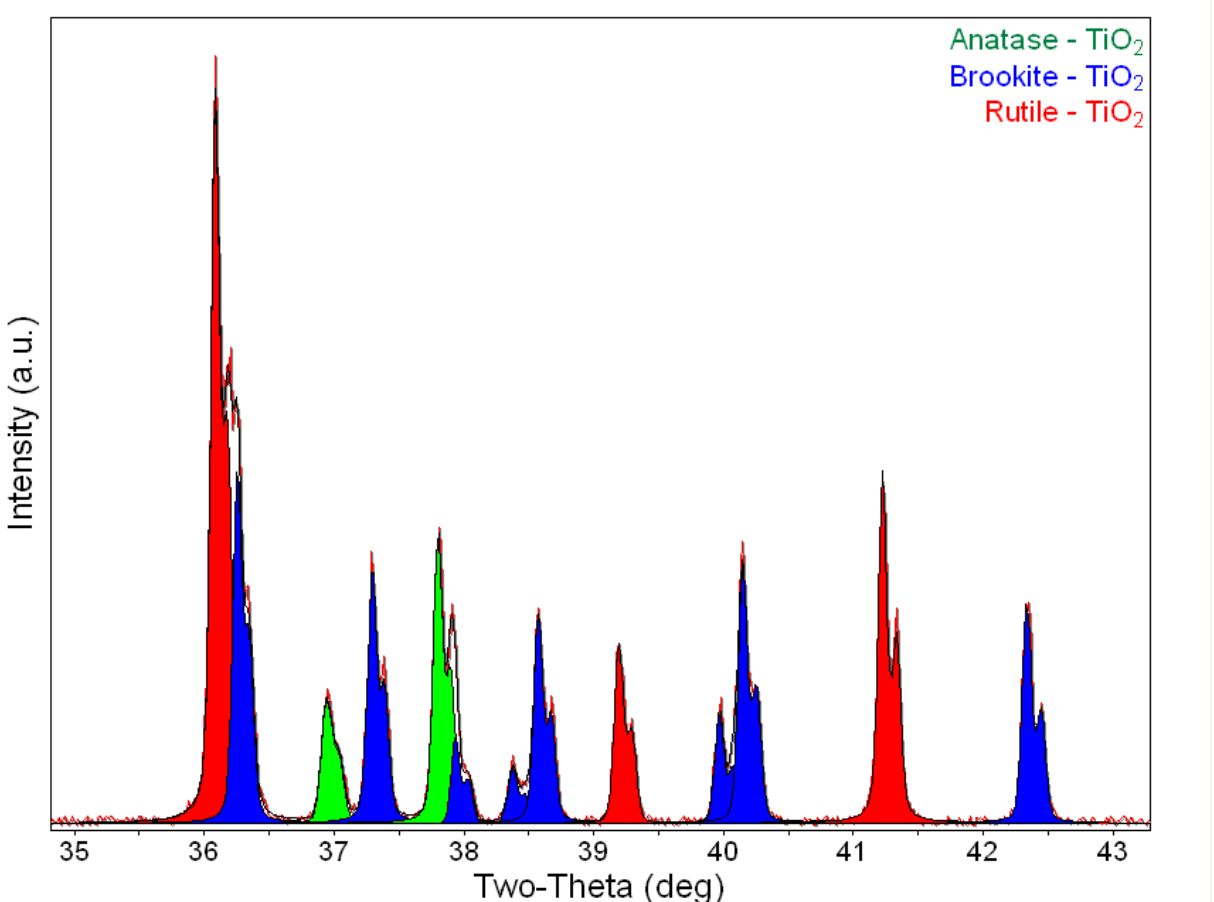
hkl	d_{hkl} (Å)	Relative Intensity (%)
{012}	3.4935	49.8
{104}	2.5583	85.8
{110}	2.3852	36.1
{006}	2.1701	1.9
{113}	2.0903	100.0
{202}	1.9680	1.4

You can use XRD to determine

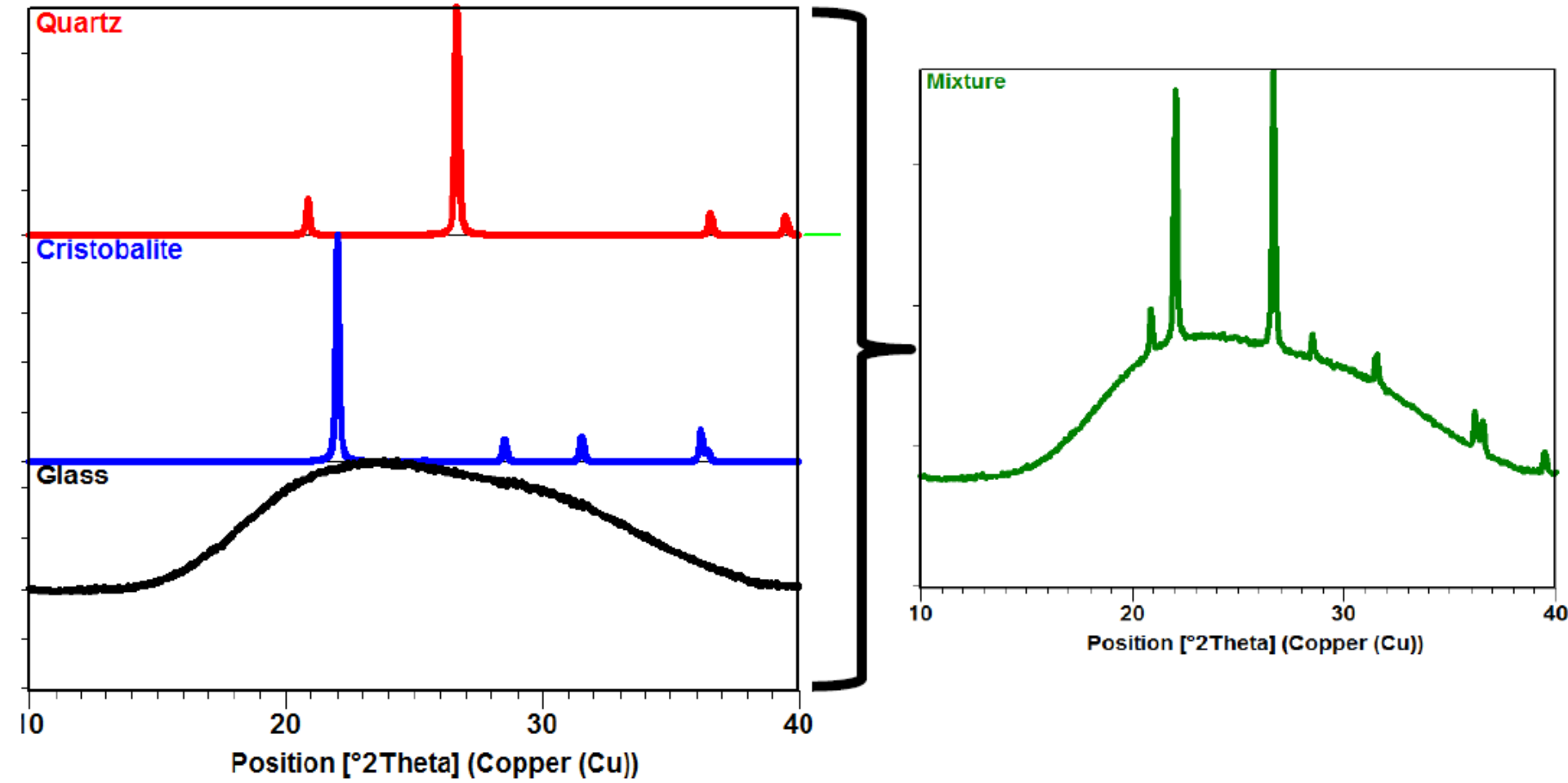
- Phase Composition of a Sample
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Residual Strain (macrostrain)
- Crystal Structure
  - By Rietveld refinement of the entire diffraction pattern
- Epitaxy/Texture/Orientation
- Crystallite Size and Microstrain
  - Indicated by peak broadening
  - Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width

Phase Identification

- The diffraction pattern for every phase is as unique as your fingerprint
  - Phases with the same chemical composition can have drastically different diffraction patterns.
  - Use the position and relative intensity of a series of peaks to match experimental data to the reference patterns in the database

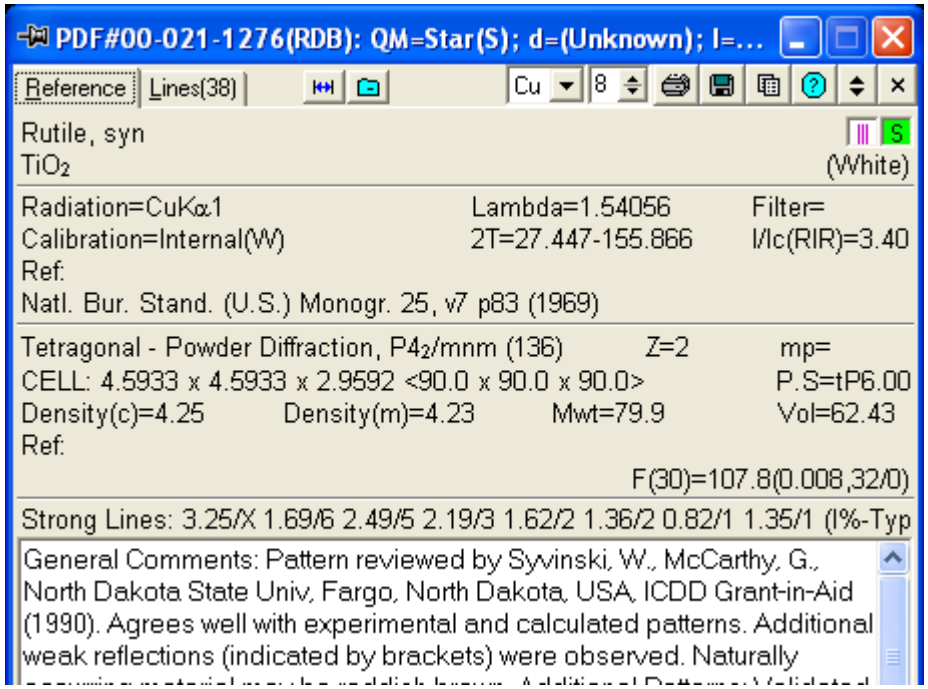


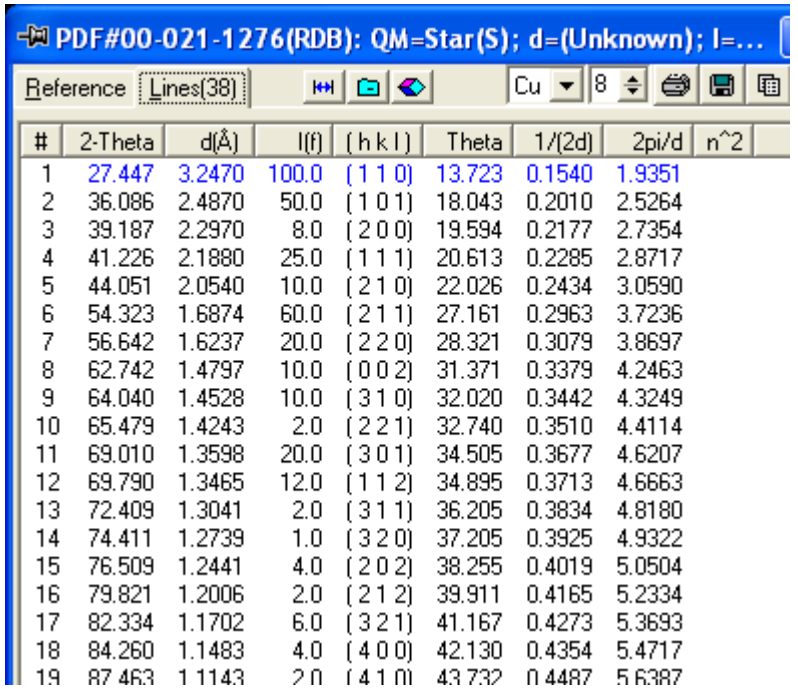
The diffraction pattern of a mixture is a simple sum of the scattering from each component phase



Databases such as the Powder Diffraction File (PDF) contain dI lists for thousands of crystalline phases.

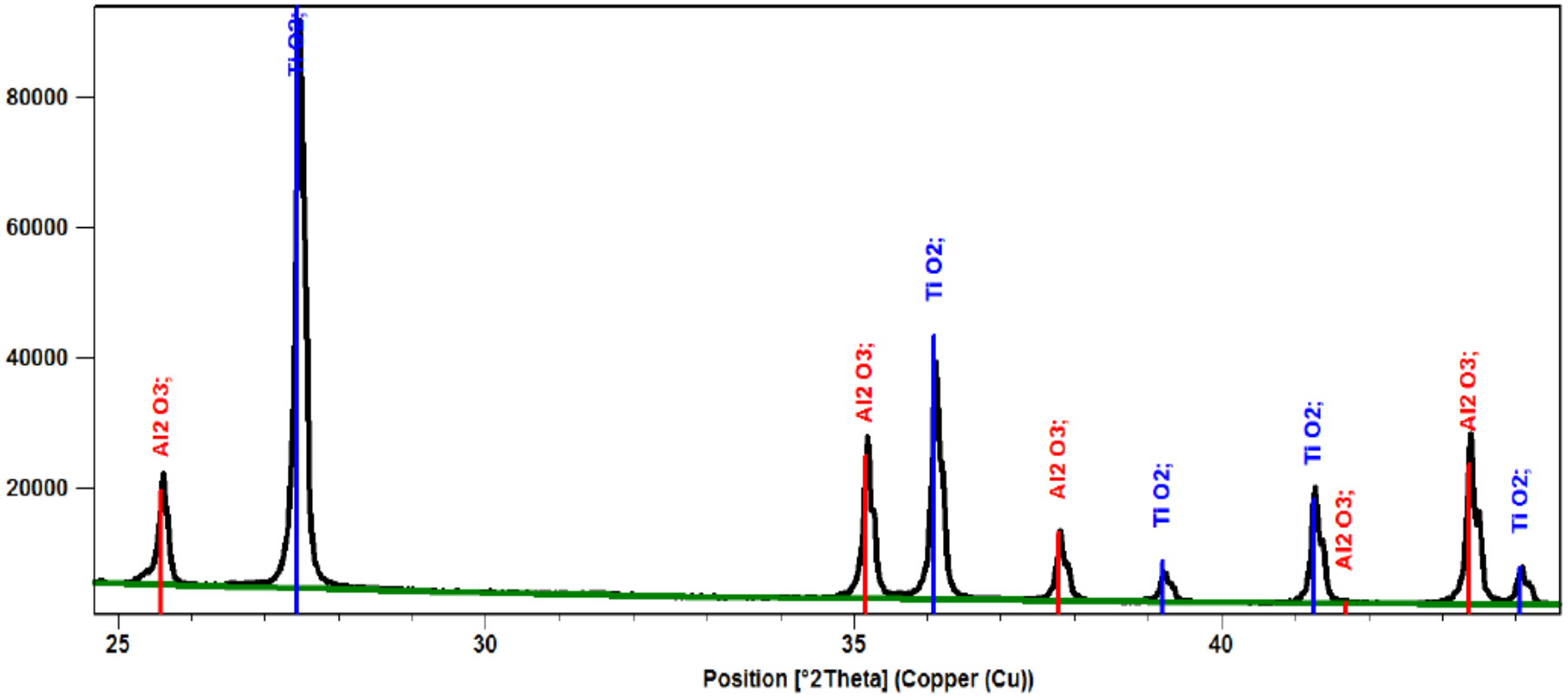
- The PDF contains over 200,000 diffraction patterns.
- Modern computer programs can help you determine what phases are present in your sample by quickly comparing your diffraction data to all of the patterns in the database.
- The PDF card for an entry contains a lot of useful information, including literature references.





#	2-Theta	d(Å)	I(f)	(h k l)	Theta	1/(2d)	2pi/d	n^2
1	27.447	3.2470	100.0	(1 1 0)	13.723	0.1540	1.9351	
2	36.086	2.4870	50.0	(1 0 1)	18.043	0.2010	2.5264	
3	39.187	2.2970	8.0	(2 0 0)	19.594	0.2177	2.7354	
4	41.226	2.1880	25.0	(1 1 1)	20.613	0.2285	2.8717	
5	44.051	2.0540	10.0	(2 1 0)	22.026	0.2434	3.0590	
6	54.323	1.6874	60.0	(2 1 1)	27.161	0.2963	3.7236	
7	56.642	1.6237	20.0	(2 2 0)	28.321	0.3079	3.8697	
8	62.742	1.4797	10.0	(0 0 2)	31.371	0.3379	4.2463	
9	64.040	1.4528	10.0	(3 1 0)	32.020	0.3442	4.3249	
10	65.479	1.4243	2.0	(2 2 1)	32.740	0.3510	4.4114	
11	69.010	1.3598	20.0	(3 0 1)	34.505	0.3677	4.6207	
12	69.790	1.3465	12.0	(1 1 2)	34.895	0.3713	4.6663	
13	72.409	1.3041	2.0	(3 1 1)	36.205	0.3834	4.8180	
14	74.411	1.2739	1.0	(3 2 0)	37.205	0.3925	4.9322	
15	76.509	1.2441	4.0	(2 0 2)	38.255	0.4019	5.0504	
16	79.821	1.2006	2.0	(2 1 2)	39.911	0.4165	5.2334	
17	82.334	1.1702	6.0	(3 2 1)	41.167	0.4273	5.3693	
18	84.260	1.1483	4.0	(4 0 0)	42.130	0.4354	5.4717	
19	87.463	1.1143	2.0	(4 1 0)	43.732	0.4487	5.6387	

You cannot guess the relative amounts of phases based only on the relative intensities of the diffraction peaks



- The pattern shown above contains equal amounts of TiO_2 and Al_2O_3
- The TiO_2 pattern is more intense because TiO_2 diffracts X-rays more efficiently

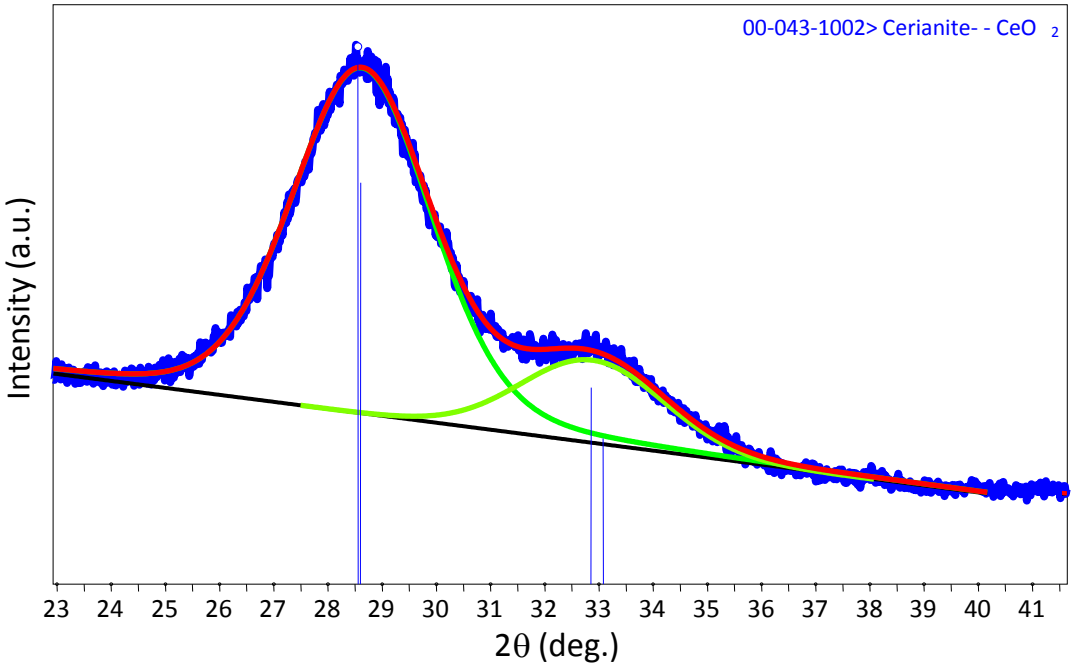
With proper calibration, you can calculate the amount of each phase present in the sample

Unit Cell Lattice Parameter Refinement

- By accurately measuring peak positions over a long range of 2theta, you can determine the unit cell lattice parameters of the phases in your sample
  - alloying, substitutional doping, temperature and pressure, etc can create changes in lattice parameters that you may want to quantify
  - use many peaks over a long range of 2theta so that you can identify and correct for systematic errors such as specimen displacement and zero shift
  - measure peak positions with a peak search algorithm or profile fitting
    - profile fitting is more accurate but more time consuming
  - then numerically refine the lattice parameters

Crystallite Size and Microstrain

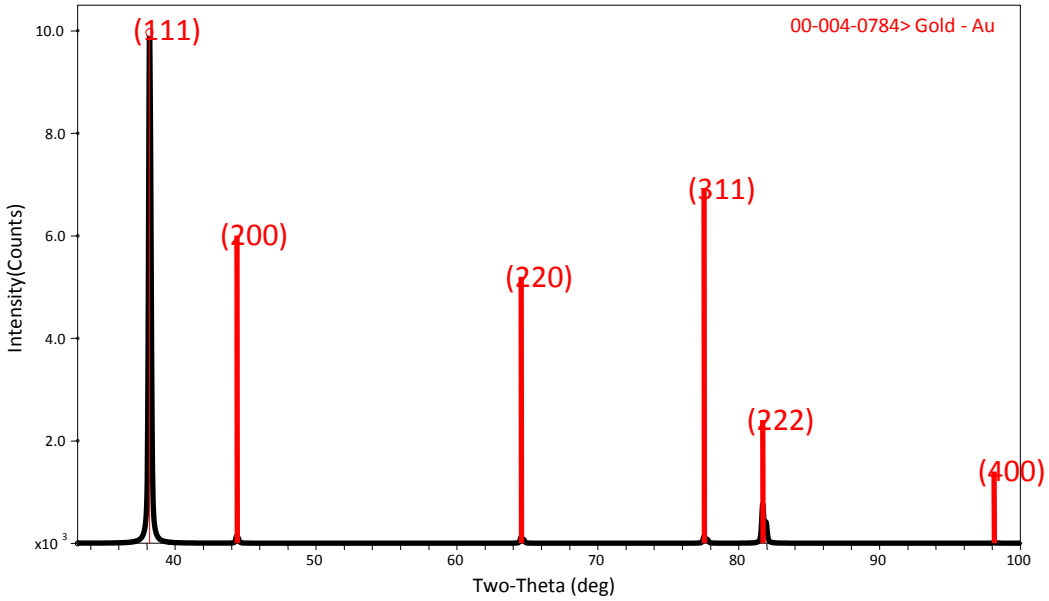
- Crystallites smaller than ~120nm create broadening of diffraction peaks
  - this peak broadening can be used to quantify the average crystallite size of nanoparticles using the Scherrer equation
  - must know the contribution of peak width from the instrument by using a calibration curve
- microstrain may also create peak broadening
  - analyzing the peak widths over a long range of 2theta using a Williamson-Hull plot can let you separate microstrain and crystallite size

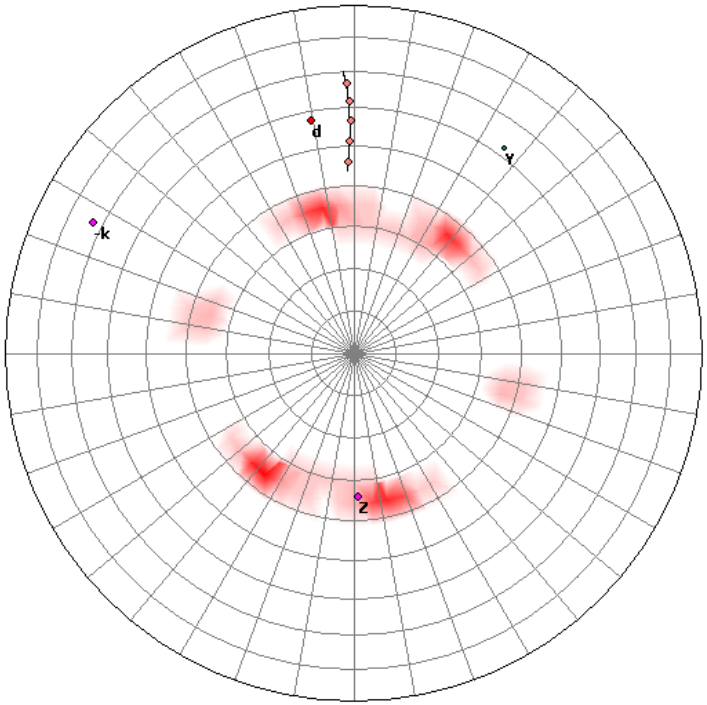


$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

Preferred Orientation (texture)

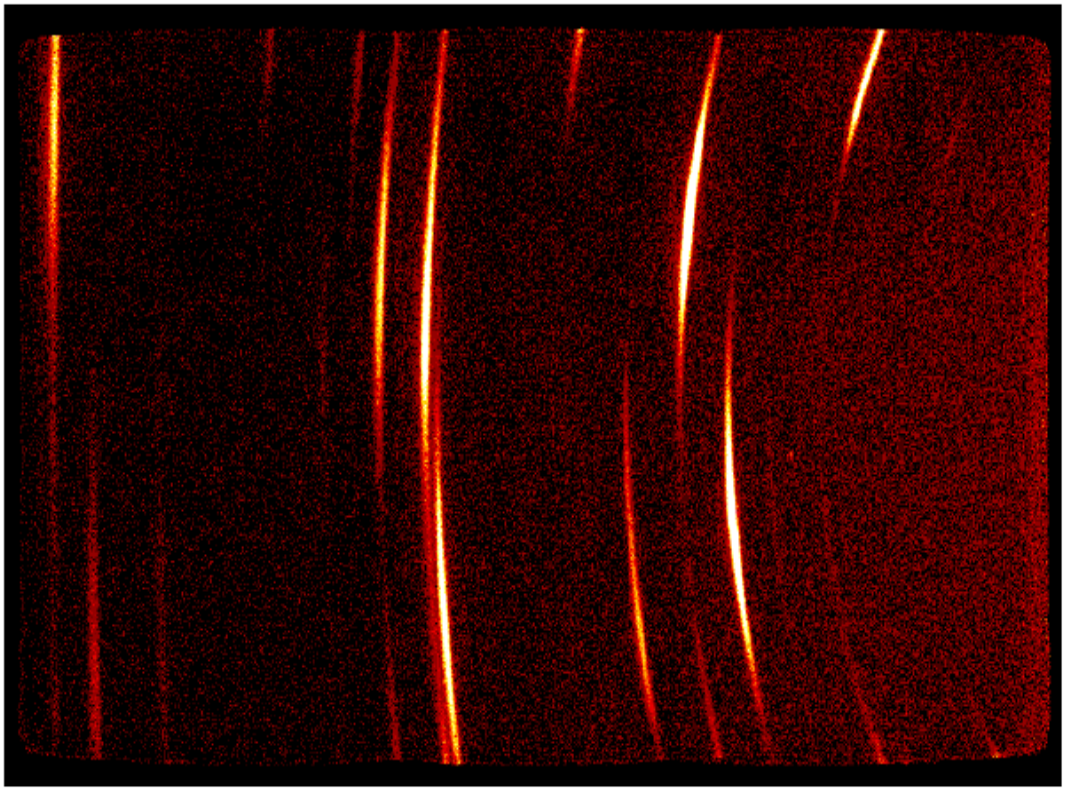
- Preferred orientation of crystallites can create a systematic variation in diffraction peak intensities
  - can qualitatively analyze using a 1D diffraction pattern
  - a pole figure maps the intensity of a single peak as a function of tilt and rotation of the sample
    - this can be used to quantify the texture

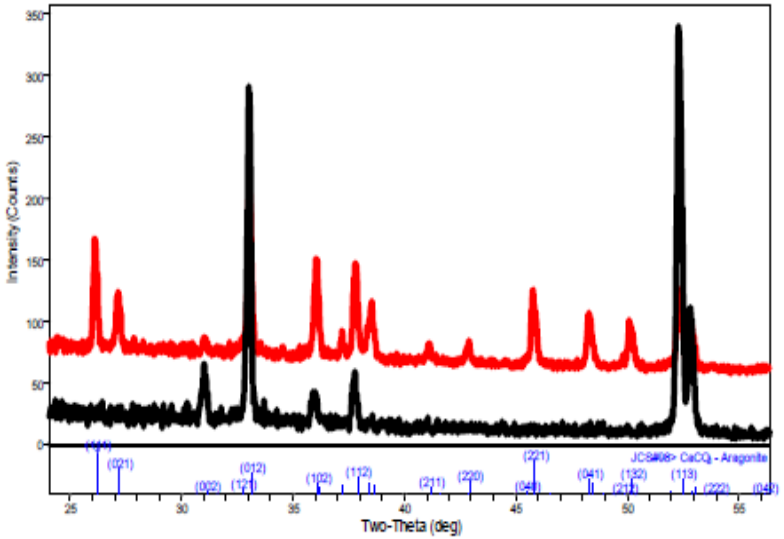




Non-ideal samples: Texture (i.e. preferred crystallographic orientation)

- 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.

Essential Parts of the Diffractometer

- X-ray Tube: the source of X Rays

- Incident-beam optics: condition the X-ray beam before it hits the sample

- The goniometer: the platform that holds and moves the sample, optics, detector, and/or tube

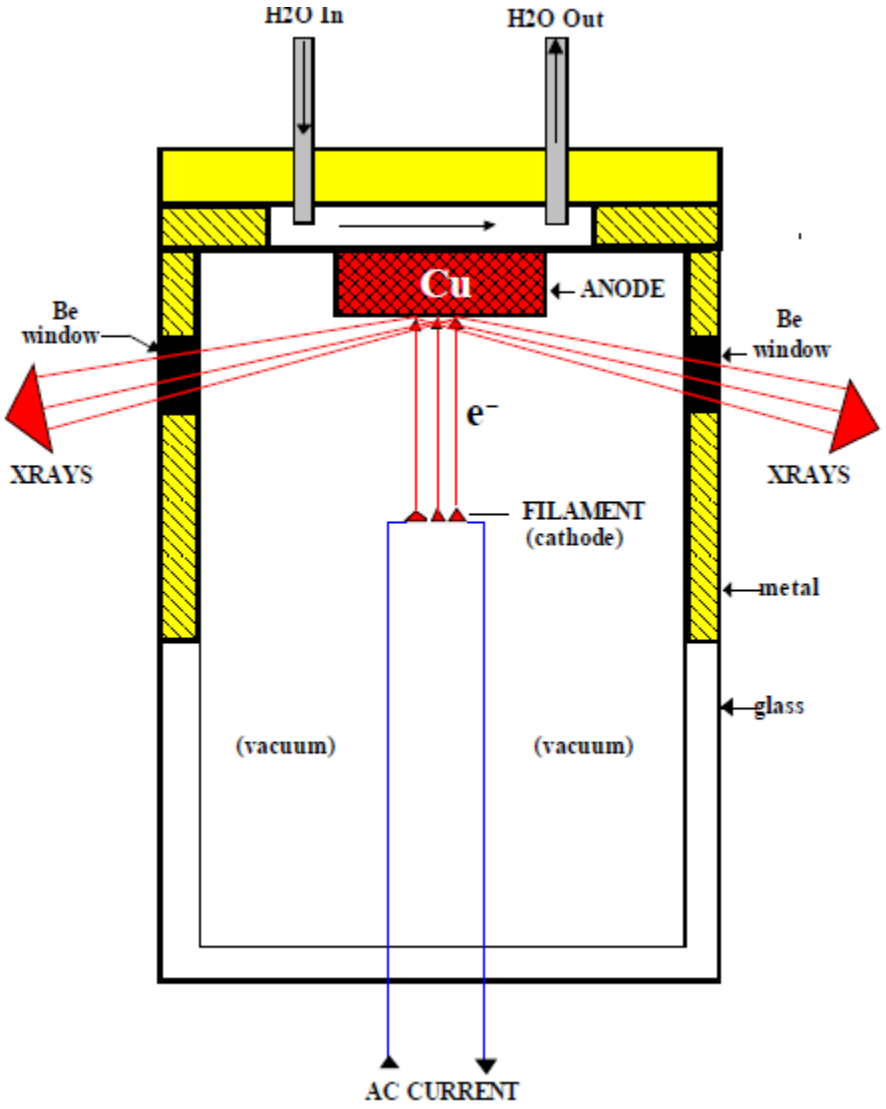
- The sample & sample holder

- Receiving-side optics: condition the X-ray beam after it has encountered the sample

- Detector: count the number of X Rays scattered by the sample

X-radiation for diffraction measurements is produced by a sealed tube or rotating anode.

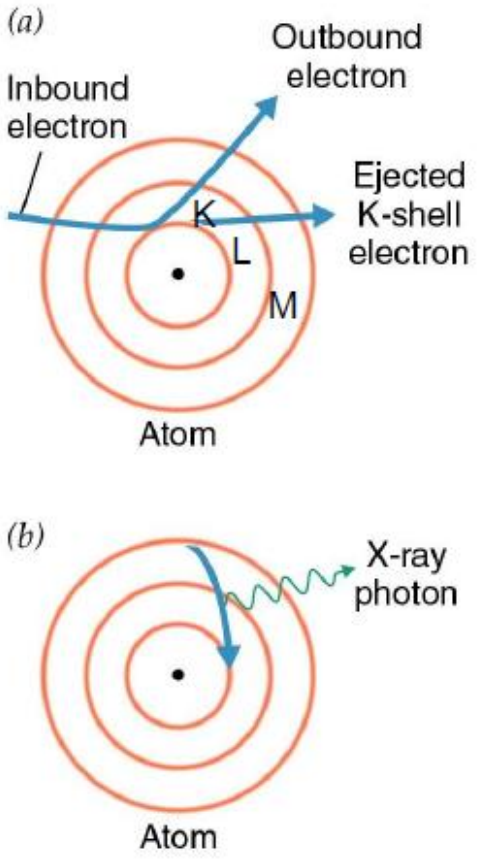
- Sealed X-ray tubes tend to operate at 1.8 to 3 kW.
- Rotating anode X-ray tubes produce much more flux because they operate at 9 to 18 kW.
  - A rotating anode spins the anode at 6000 rpm, helping to distribute heat over a larger area and therefore allowing the tube to be run at higher power without melting the target.
- **Both sources generate X rays by striking the anode target with an electron beam from a tungsten filament.**
  - The target must be water cooled.
  - The target and filament must be contained in a vacuum

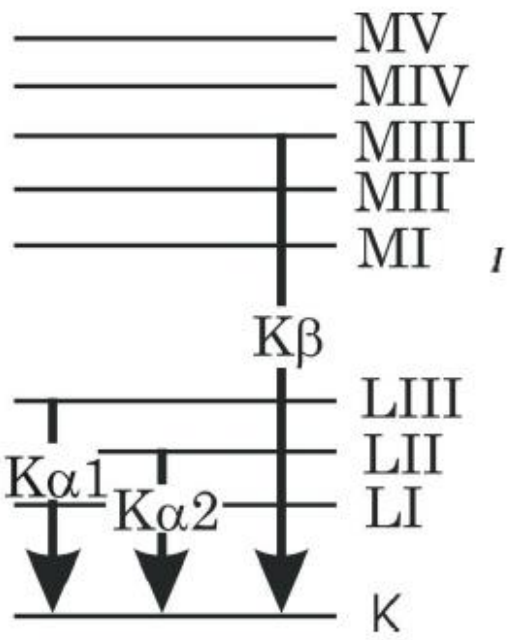


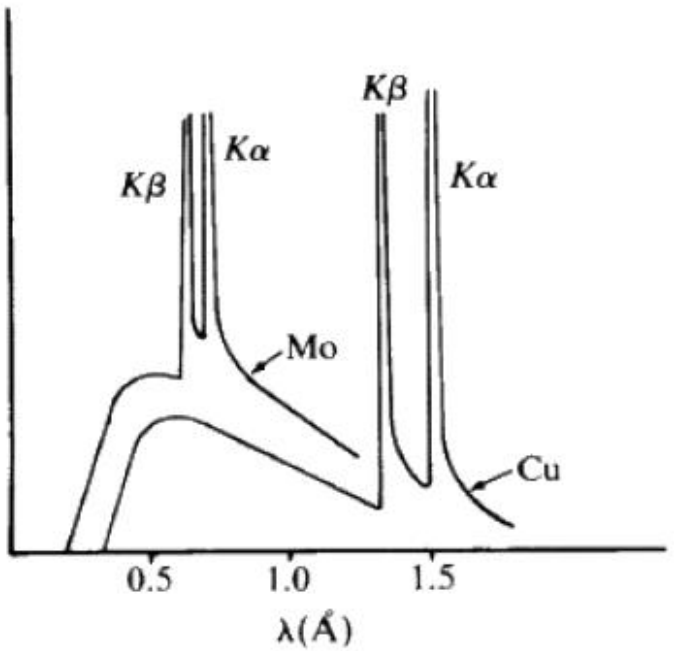
Be is transparent to x-rays, so it's used in the windows of x-ray tubes, which need to be strong enough to hold a perfect vacuum, yet thin enough to let the delicate x-rays out.

The wavelength of X rays is determined by the anode of the X-ray source

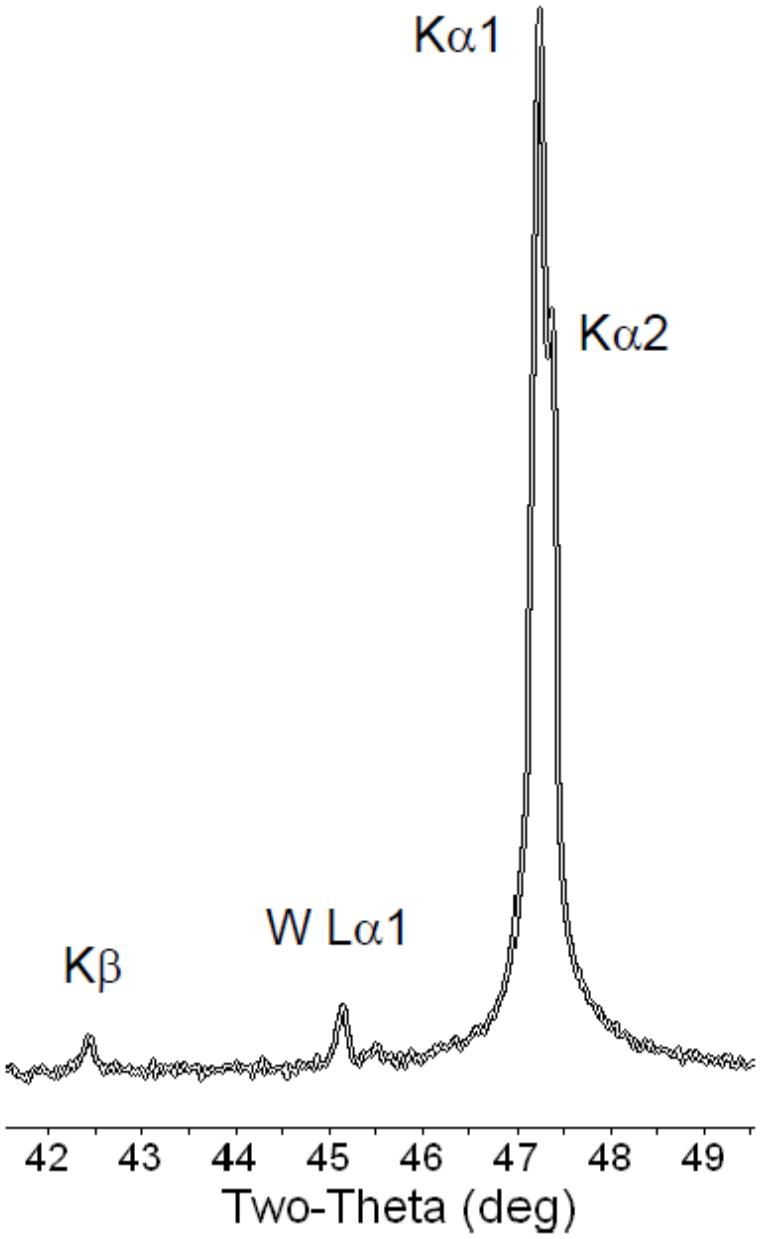
- Electrons from the filament strike the target anode, producing characteristic radiation via the photoelectric effect.
- The anode material determines the wavelengths of characteristic radiation.
- While we would prefer a monochromatic source, the X-ray beam actually consists of several characteristic wavelengths of X rays.

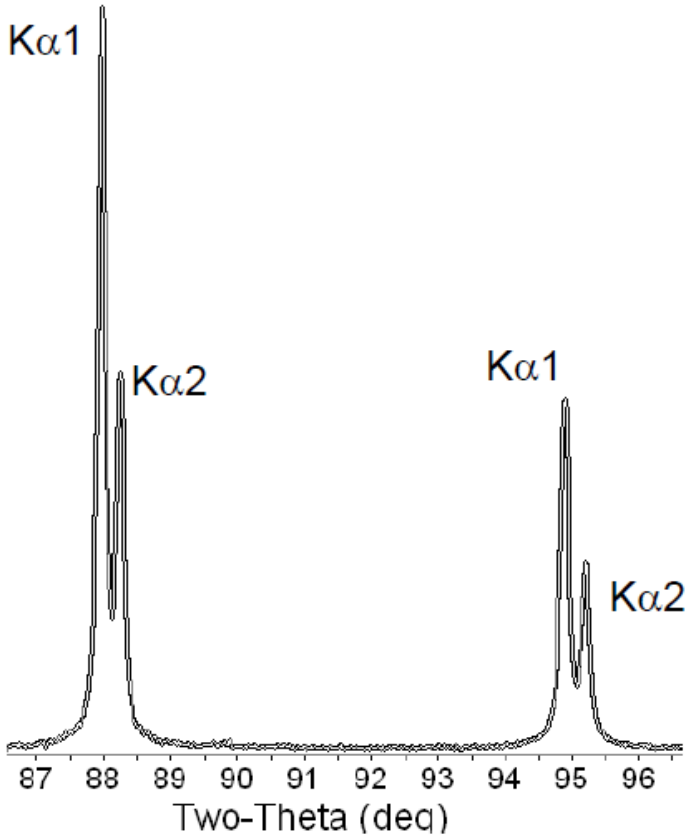






Spectral Contamination in Diffraction Patterns





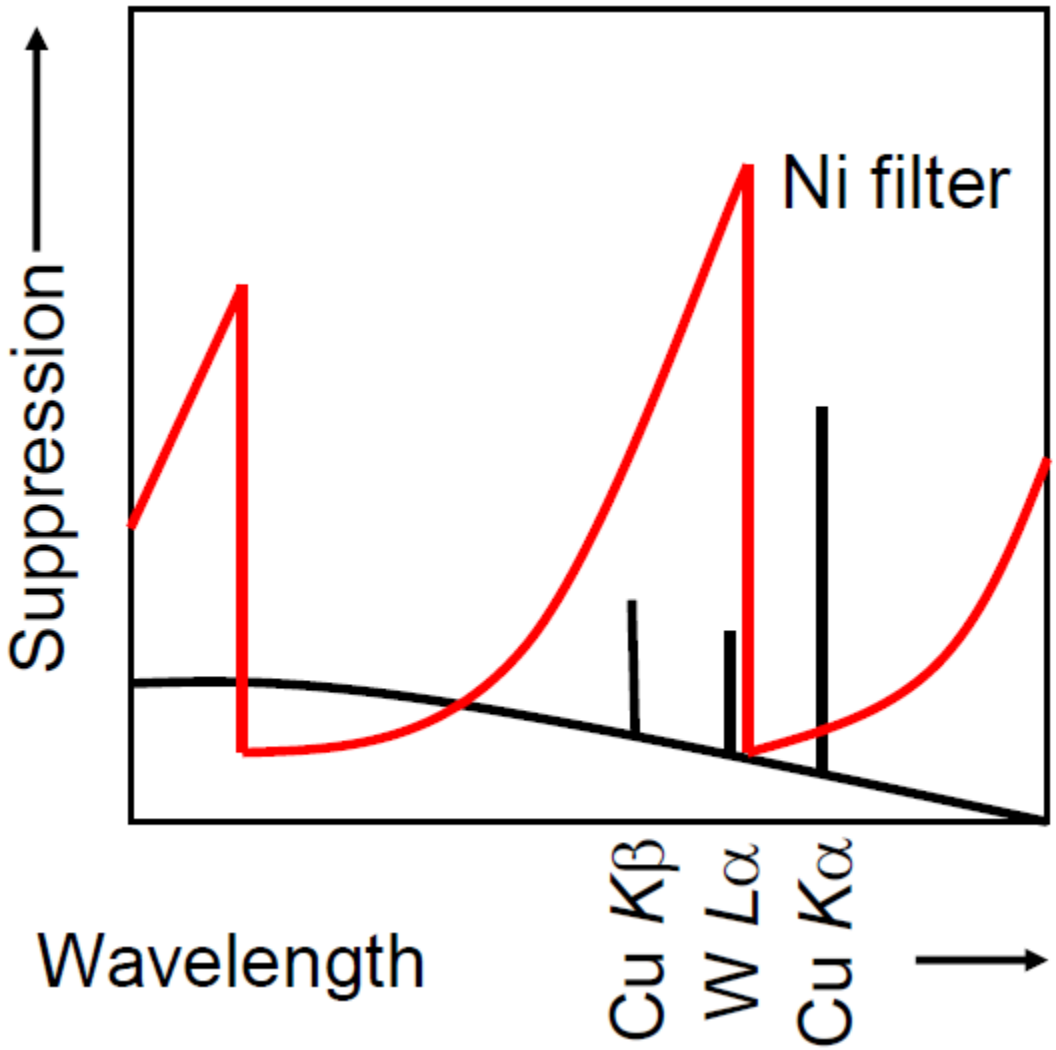
- **The Kα1 & Kα2 doublet will almost always be present**
  - **Very expensive optics can remove the Kα2 line**
  - **Kα1 & Kα2 overlap heavily at low angles and are more separated at high angles**
- **W lines form as the tube ages: the W filament contaminates the target anode and becomes a new X-ray source**
- **W and Kβ lines can be removed with optics**

Monochromators remove unwanted wavelengths of radiation from the incident or diffracted X-ray beam.

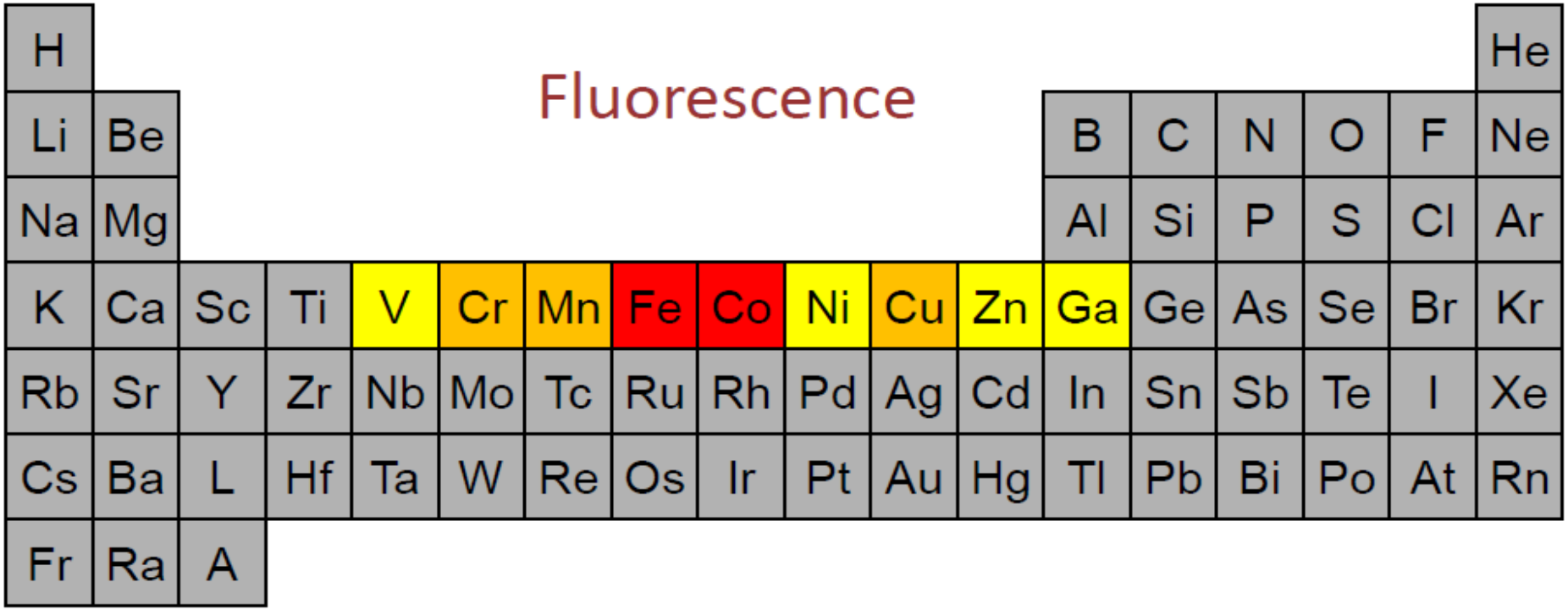
- Diffraction from a monochromator crystal can be used to select one wavelength of radiation and provide energy discrimination.
- Most powder diffractometer monochromators only remove K-beta, W-contamination, and Brehmstralung radiation
  - –Only HRXRD monochromators or specialized powder monochromators remove K-alpha2 radiation as well.
- A monochromator can be mounted between the tube and sample (incident-beam) or between the sample and detector (diffracted-beam)
  - –An incident-beam monochromator only filters out unwanted wavelengths of radiation from the X-ray source
  - –A diffracted-beam monochromator will also remove fluoresced photons.
  - –A monochromator may eliminate 99% of K-beta and similar unwanted wavelengths of radiation.
  - –A diffracted-beam monochromator will provide the best signal-to-noise ratio, but data collection will take a longer time

Beta filters can also be used to reduce the intensity of K-beta and W wavelength radiation

- 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
  - The Ni absorption of Cu radiation is:
- 50% of Cu K-alpha
- 99% of Cu K-beta



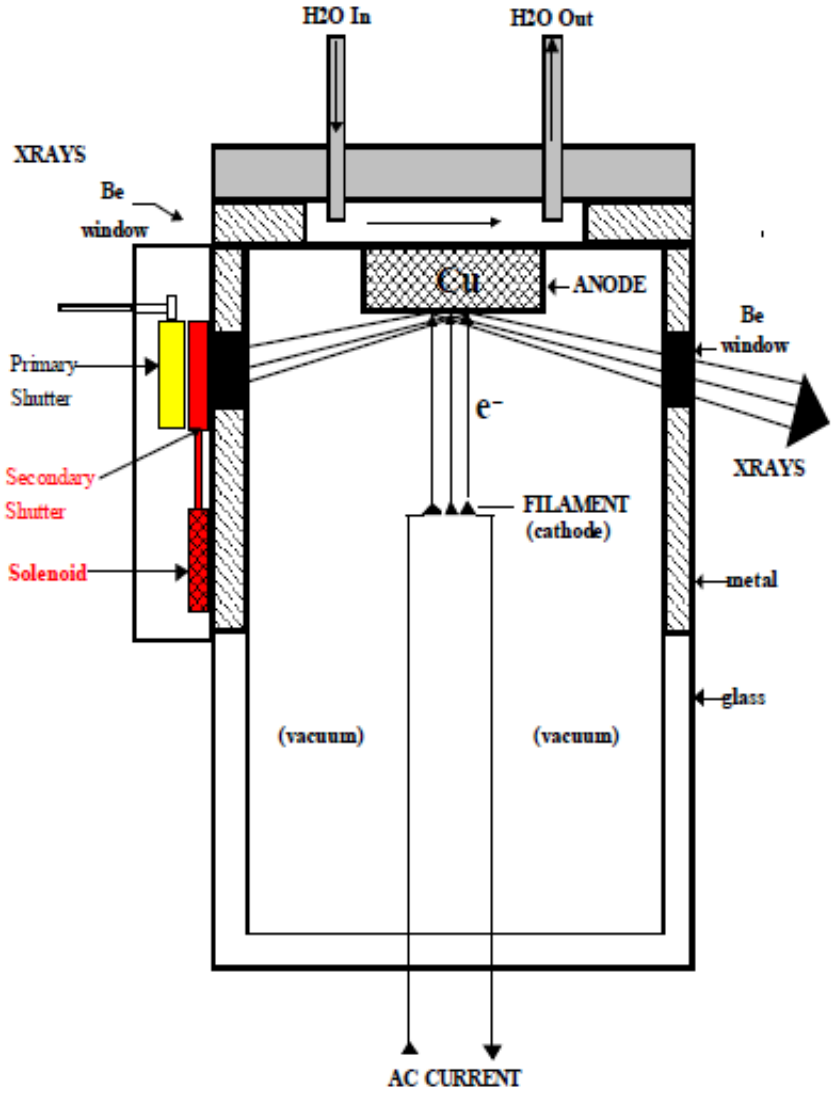
Fluorescence



- 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 Shutter is the most important safety device on a diffractometer

- X-rays exit the tube through X-ray transparent Be windows.
- X-Ray safety shutters contain the beam so that you may work in the diffractometer without being exposed to the X-rays.
- Being aware of the status of the shutters is the most important factor in working safely with X rays.



Detectors

- point detectors
  - –observe one point of space at a time
    - slow, but compatible with most/all optics
  - –scintillation and gas proportional detectors count all photons, within an energy window, that hit them
  - –Si(Li) detectors can electronically analyze or filter wavelengths
- position sensitive detectors
  - –linear PSDs observe all photons scattered along a line from 2 to 10° long
  - –2D area detectors observe all photons scattered along a conic section

Preparing a powder specimen

- An ideal powder sample should have many crystallites in random orientations
  - the distribution of orientations should be smooth and equally distributed amongst all orientations

- Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation
  - the measured diffraction pattern will not agree with that expected from an ideal powder
  - the measured diffraction pattern will not agree with reference patterns in the Powder Diffraction File (PDF) database

- If the crystallites in a sample are very large, there will not be a smooth distribution of crystal orientations. You will not get a powder average diffraction pattern.
  - crystallites should be <10mm in size to get good powder statistics

Grazing Incident Angle Diffraction (GIXD)

- Also called Glancing Angle X-Ray Diffaction

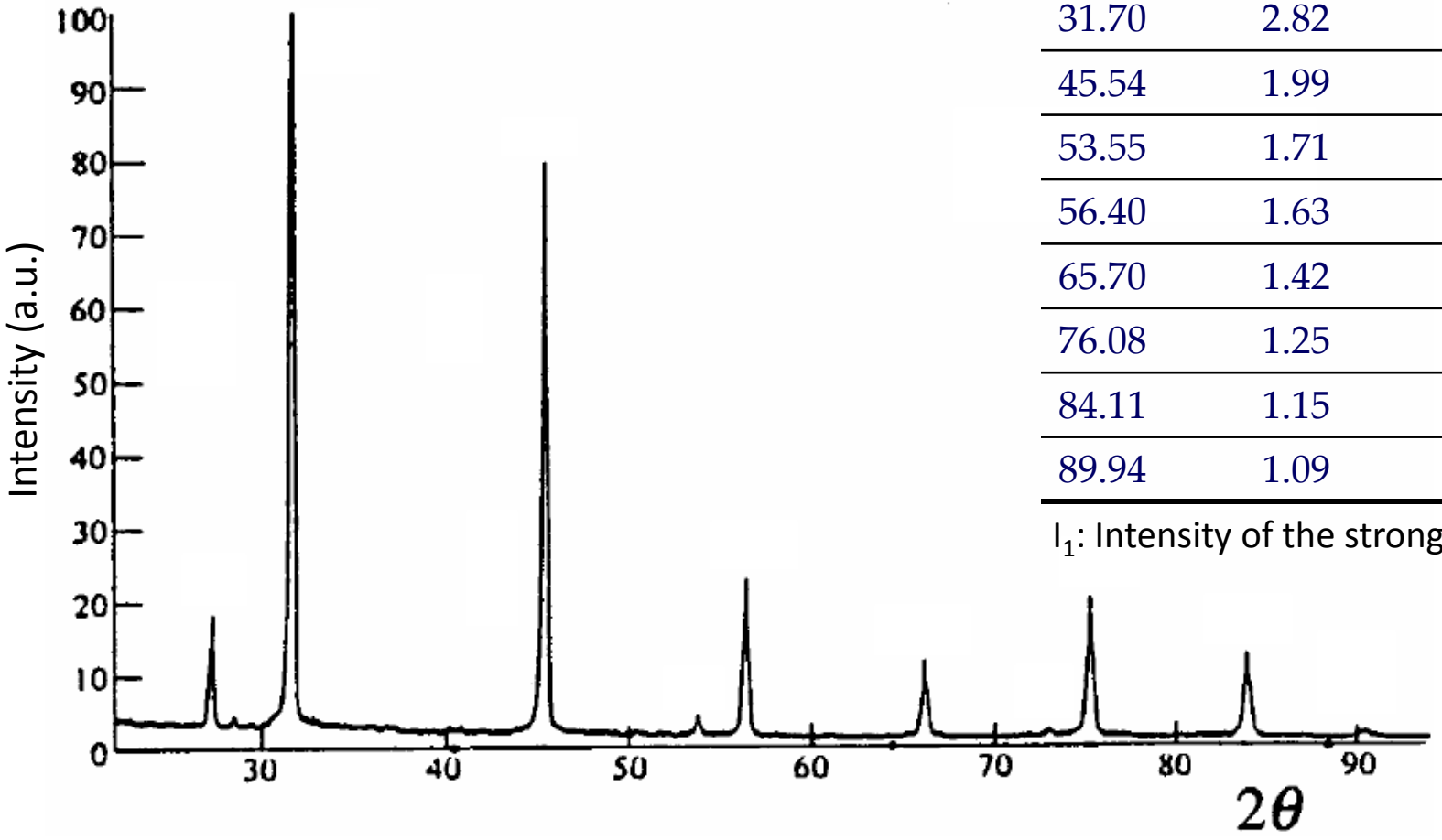
- The incident angle is fixed at a very small angle (<5°) so that X-rays are focused in only the top-most surface of the sample.

- GIXD can perform many of analyses possible with XRPD with the added ability to resolve information as a function of depth (depth-profiling) by collecting successive diffraction patterns with varying incident angles
  - orientation of thin film with respect to substrate
  - lattice mismatch between film and substrate
  - epitaxy/texture
  - macro- and microstrains
  - reciprocal space map

Information in a Diffraction Pattern

- Phase Identification
- Crystal Size
- Crystal Quality
- Texture (to some extent)
- Crystal Structure

Analysis of Single Phase



2θ(°)	d (Å)	$(I/I_1)*100$
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_1: 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……Hurrah**

Specimen and Intensities	Substance	ıber
$2.82_9\ 1.99_9\ 2.26_x\ 1.61_9\ 1.51_9\ 1.49_9\ 3.57_8\ 2.66_8$	$(ErSe)_2Q$	
$2.82_x\ 1.99_6\ 1.63_2\ 3.26_1\ 1.26_1\ 1.15_1\ 1.41_1\ 0.89_1$	NaCl	5-628
$2.82_4\ 1.99_4\ 1.54_x\ 1.20_4\ 1.19_4\ 2.44_3\ 5.62_2\ 4.89_2$	$(NH_4)_2WO_2Cl_4$	22-65
$2.82_x\ 1.99_8\ 1.26_3\ 1.63_2\ 1.15_2\ 0.94_1\ 0.89_1\ 1.41_1$	(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

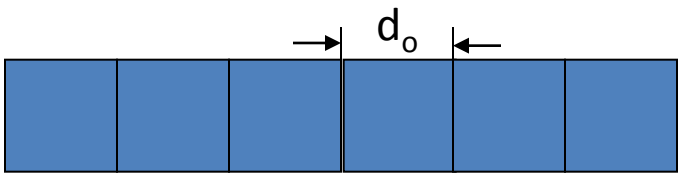
- More Complex
- Several permutations combinations
- e.g. d_1; d_2; and d_3, the first three str… c… several alternatives
- Then take any of the two lines toget…
- It turns out that 1st and 3rd stronges… and then all other peaks for Cu can…
- Now separate the remaining lines a… intensities
- Look for first three lines and it turns… phase is Cu_2O
- If more phases, more pain to solve

Pattern of Cu_2O	
d (Å)	I/I_1
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

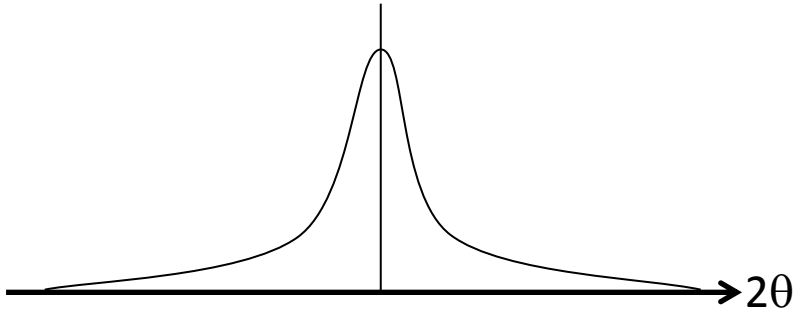
Remaining Lines		
d (Å)	I/I_1	
	Observed	Normalized
3.01	5	7
2.47	72	100
2.13	28	39
1.50	20	28
1.29	9	13
1.22	4	6
0.98	5	7

d (Å)	I/I_1
0.8083	8
0.81 *	10

Lattice Strain

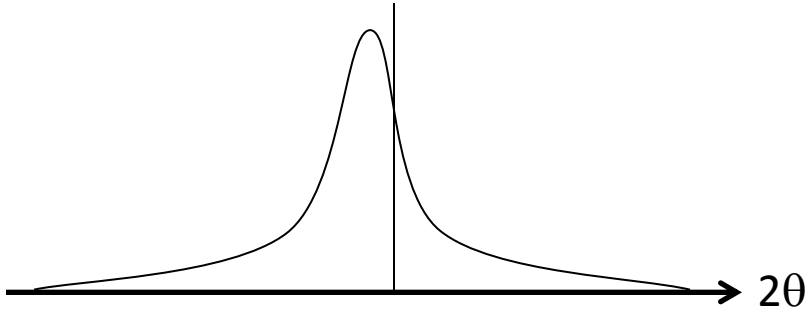


No Strain

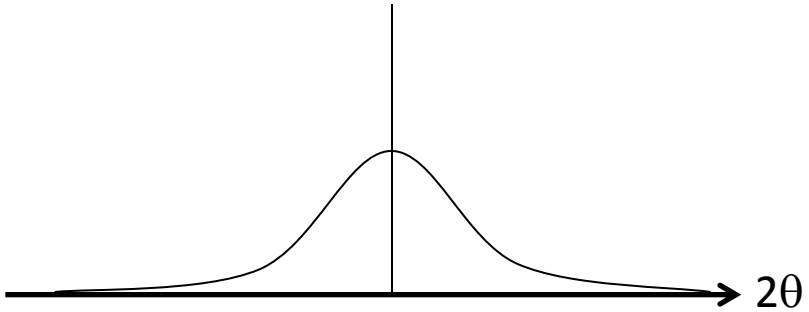


Uniform Strain

$\Delta\theta \propto \Delta d \propto$ strain



Non-uniform Strain



$$\text{Broadeing} \quad b = \Delta 2\theta = -2\frac{\Delta d}{d}\tan\theta$$

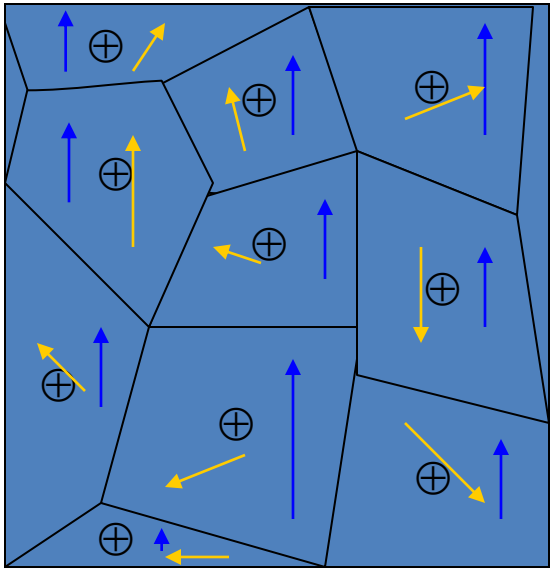
Texture in Materials

- Grains with in a polycrystalline are not completely randomly distributed
- Clustering of grains about some particular orientation(s) to a certain degree
- Examples:
  - Present in cold-rolled brass or steel sheets
  - Cold worked materials tend to exhibit some texture after recrystallization
- Affects the properties due to anisotropic nature

Texture

- Fiber Texture
  - A particular direction [uvw] for all grains is more or less parallel to the wire or fiber axis
    - e.g. [111] fiber texture in Al cold drawn wire
  - Double axis is also possible
    - Example: [111] and [100] fiber textures in Cu wire
- Sheet Texture
  - Most of the grains are oriented with a certain crystallographic plane (hkl) roughly parallel to the sheet surface and certain direction [uvw] parallel to the rolling direction
  - Notation: (hkl)[uvw]

Texture in materials

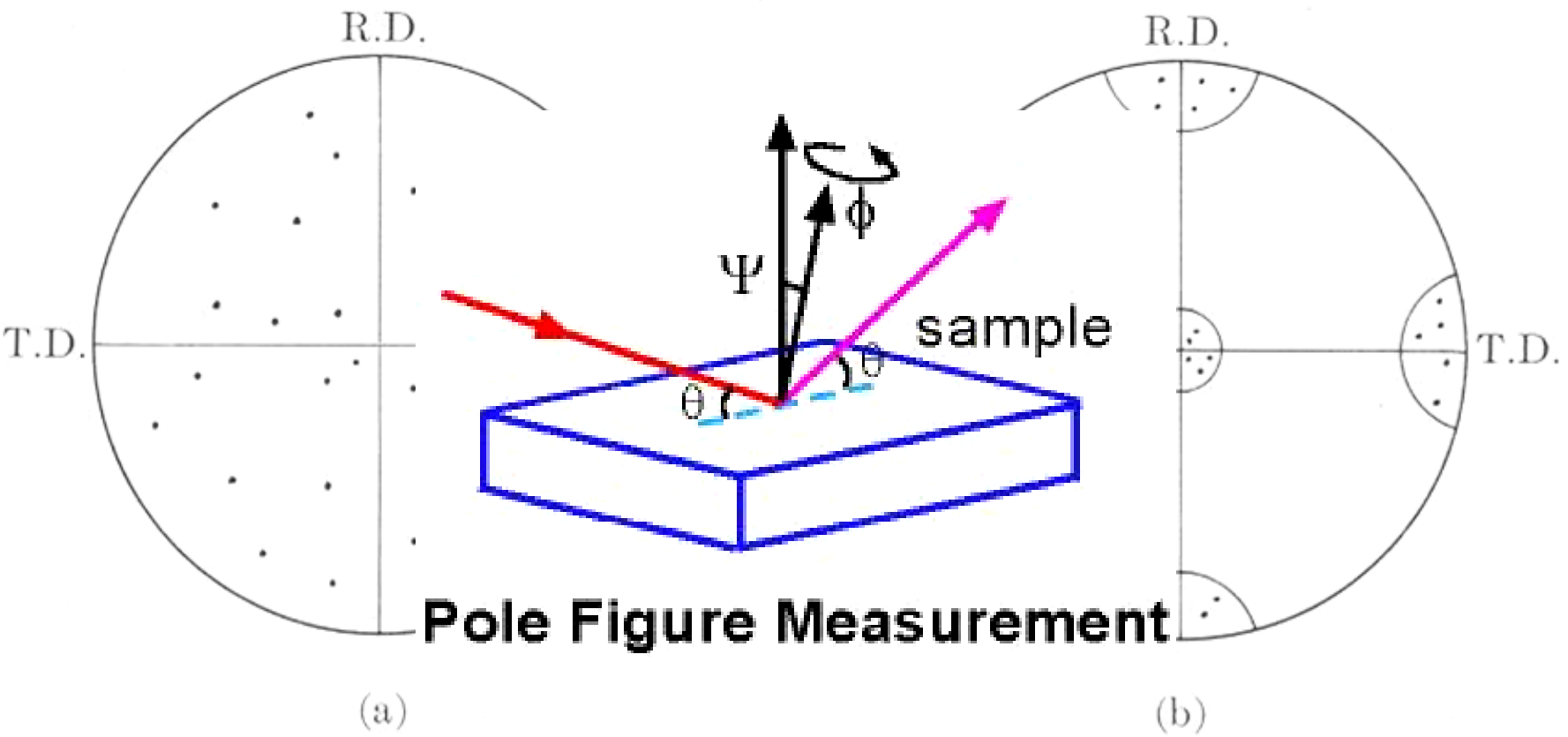


⊕ [uvw] i.e. perpendicular to the surface of all grains is parallel to a direction [uvw]

Also, if the direction $[u_1v_1w_1]$ is parallel for all regions, the structure is like a single crystal

However, the direction $[u_1v_1w_1]$ is not aligned for all regions, the structure is like a mosaic structure, also called as **Mosaic Texture**

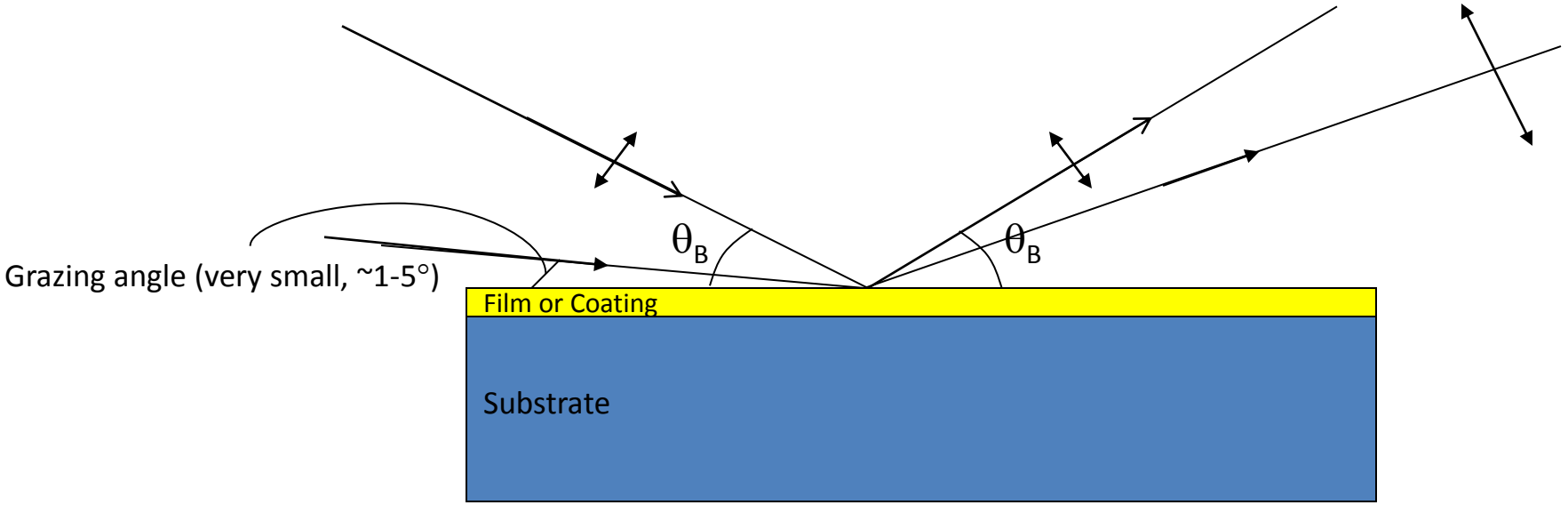
Pole Figures



(100) pole figures for a sheet material

(a) Random orientation (b) Preferred orientation

Thin Film Specimen



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

Thin Film XRD

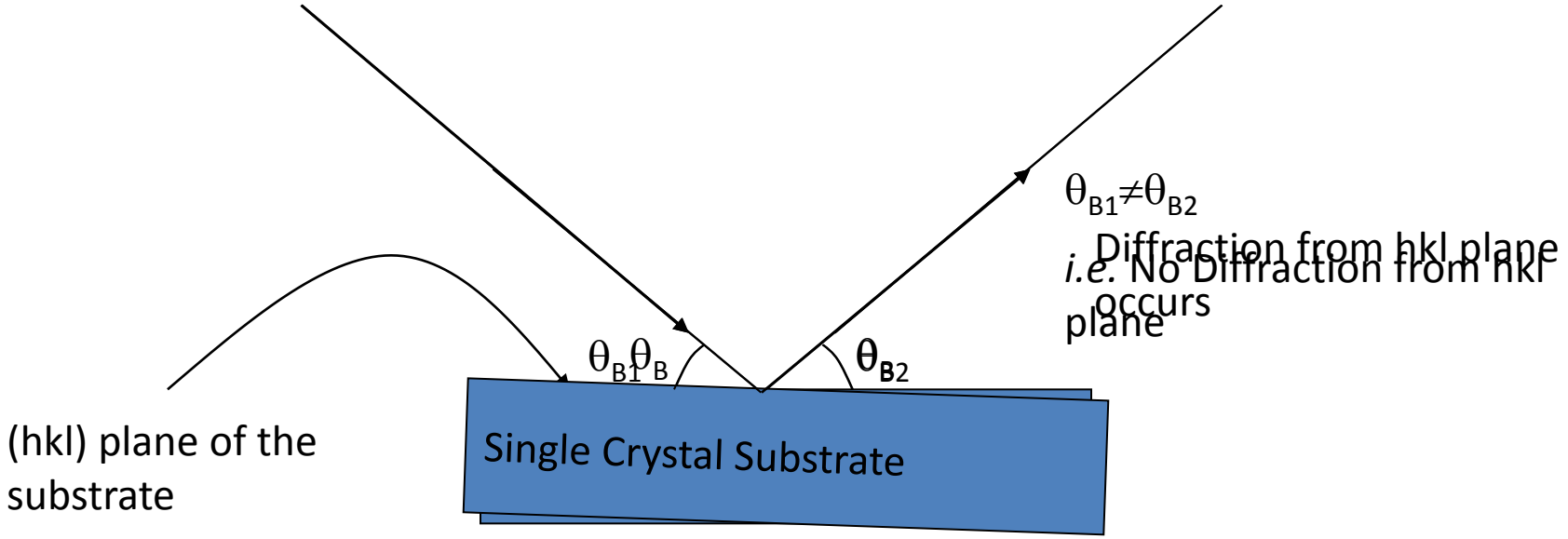
- Precise lattice constants measurements derived from 2θ-θ scans, which provide information about lattice mismatch between the film and the substrate and therefore is indicative of strain & stress

- Rocking curve measurements made by doing a q scan at a fixed $2\ \theta$ angle, the width of which is inversely proportionally to the dislocation density in the film and is therefore used as a gauge of the quality of the film.

- Superlattice measurements in multilayered heteroepitaxial structures, which manifest as satellite peaks surrounding the main diffraction peak from the film. Film thickness and quality can be deduced from the data.

- Glancing incidence x-ray reflectivity measurements, which can determine the thickness, roughness, and density of the film. This technique does not require crystalline film and works even with amorphous materials.

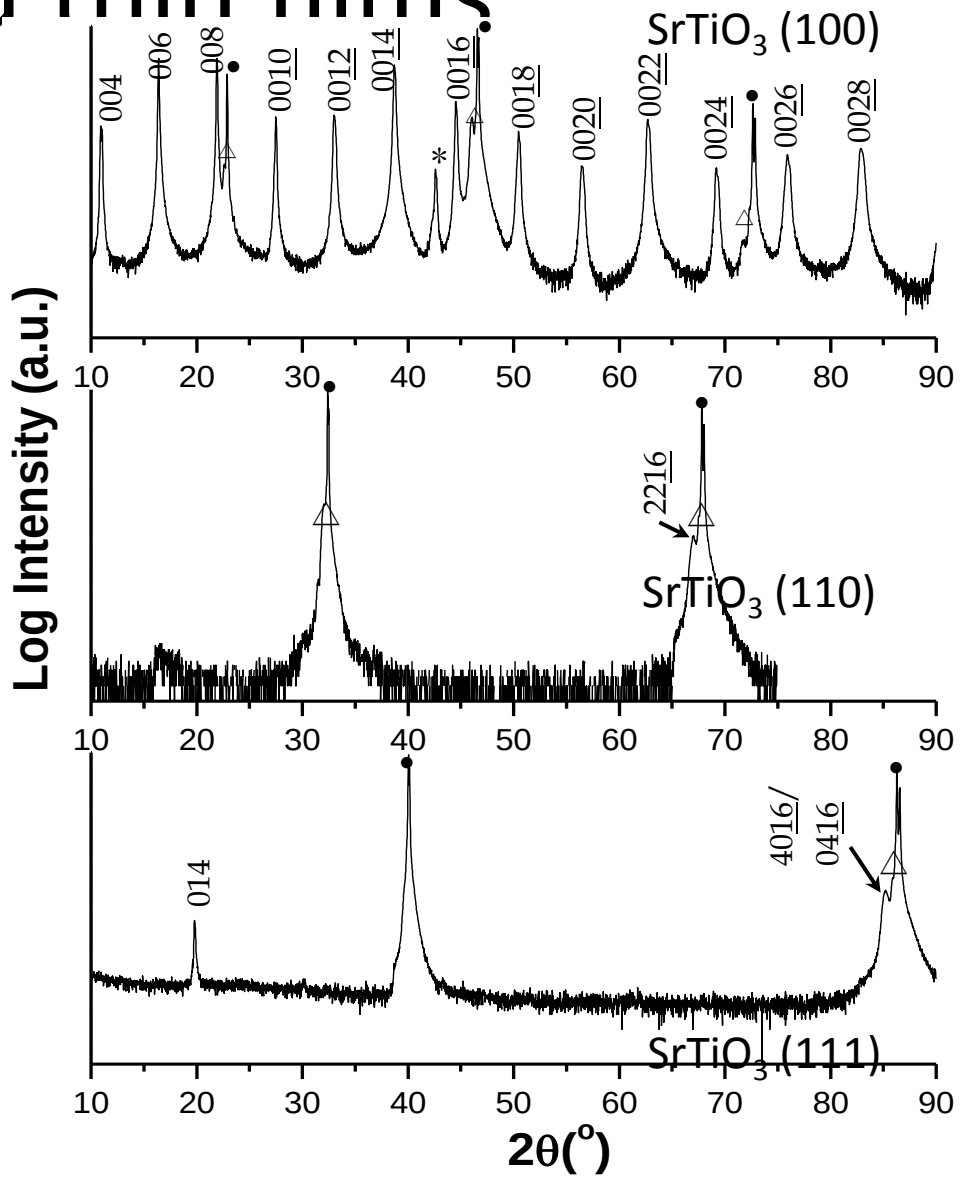
Thin Films Specimens



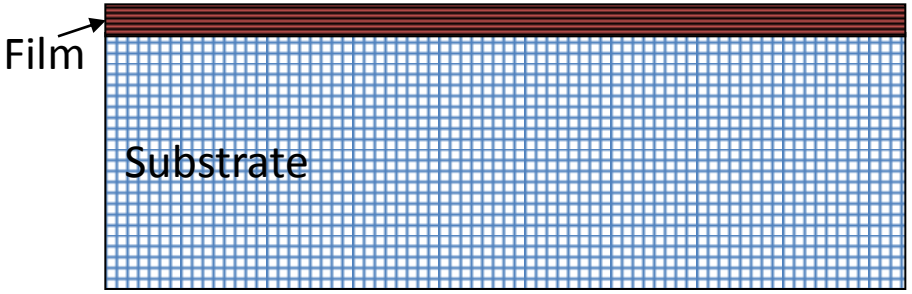
- If the sample and substrate is polycrystalline, then problems are less
- But if even if one of them is oriented, problems arise
- In such situations substrate alignment is necessary

Oriented thin films

- Bismuth Titanate thin films on oriented $SrTiO_3$ substrates
- Only one type of peaks
- It apparent that films are highly oriented



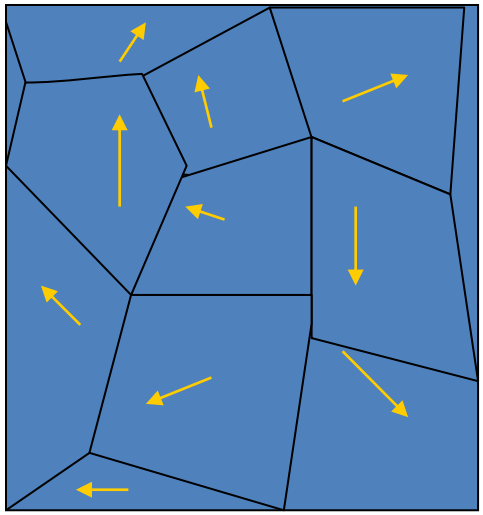
Degree of orientation



[uvw] corresponding to planes parallel to the surface

Side view

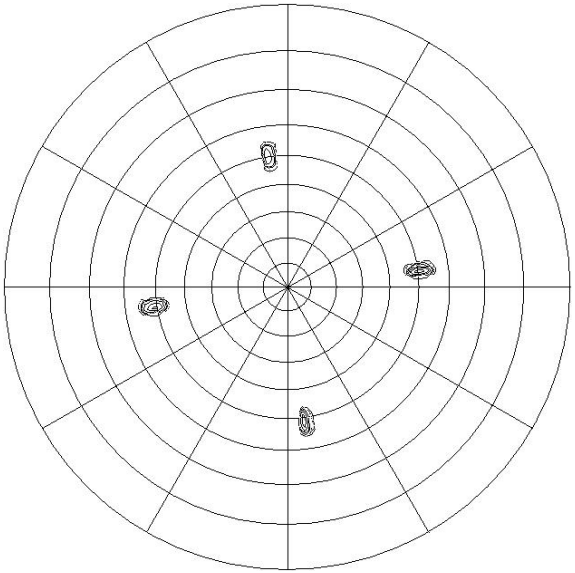
But what if the planes when looked from top have random orientation?



Top view

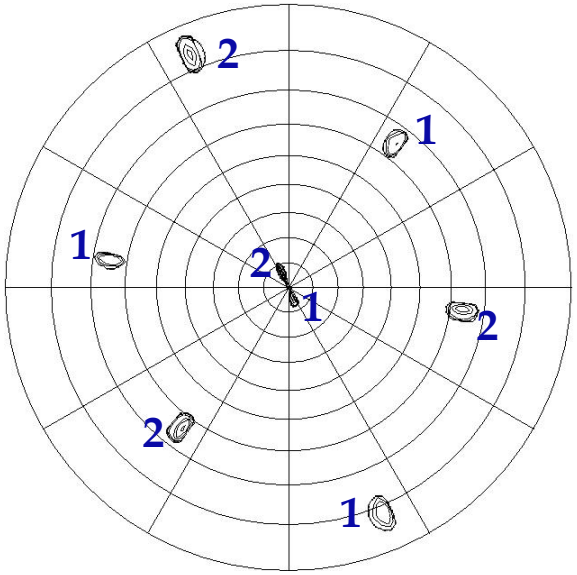
Pole Figure

$SrTiO_3$ (100)



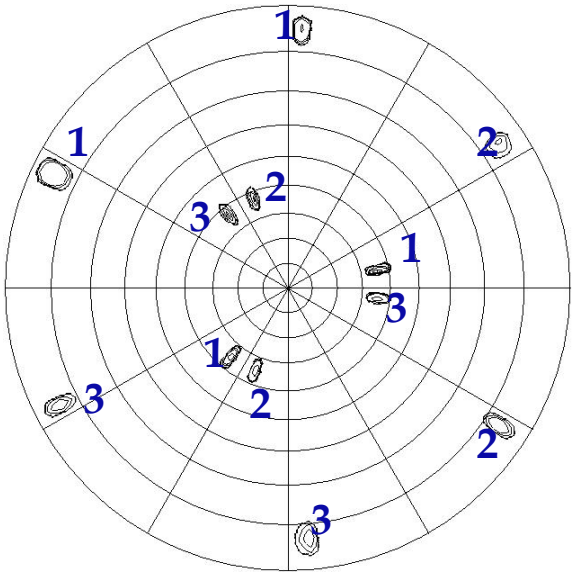
- 4 Peaks at ~50°
- Excellent in-plane orientation

$SrTiO_3$ (110)



- 2 sets of peaks at ~ 5, 65 and 85°
- Indicating a doublet or opposite twin growth

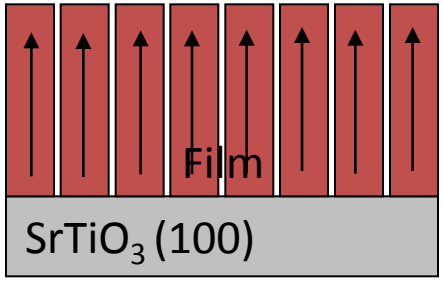
$SrTiO_3$ (111)

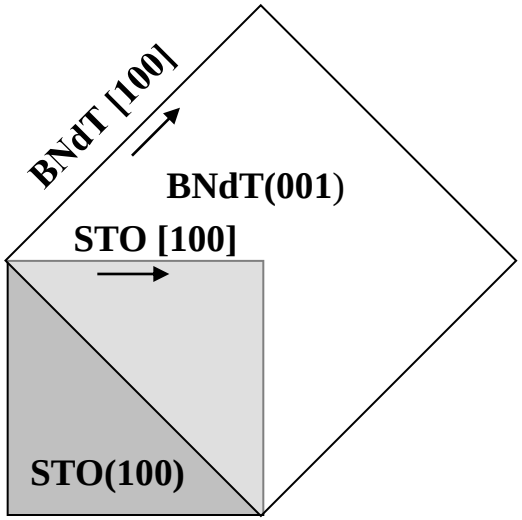


- 3 sets of peaks at ~ 35 and 85°
- indicating a triplet or triple twin growth

(117) Pole Figures for Bismuth Titanate Films

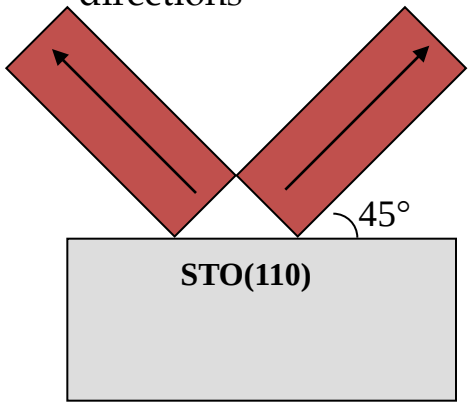
Texture Evolution





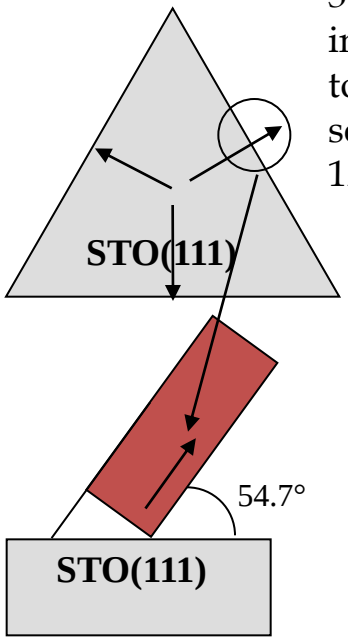
BNdT/SrTiO3 (100)

Two (100) planes inclined at 45° to (110) plane in opposite directions



$BNdT/SrTiO_3$ (110)

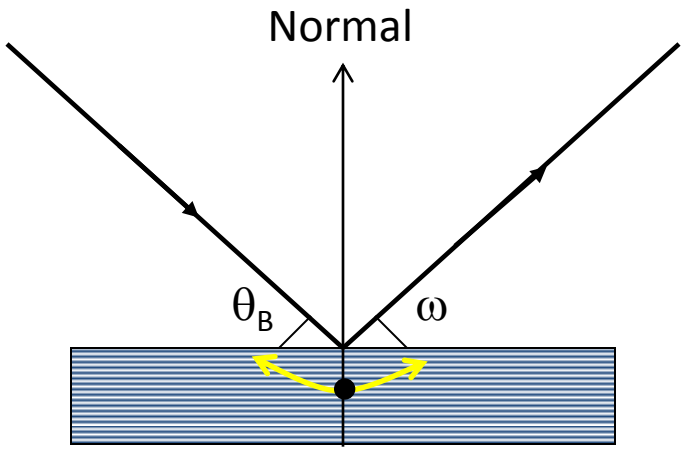
3 (100) planes inclined at 54.7° to (110) plane, separated by 120°

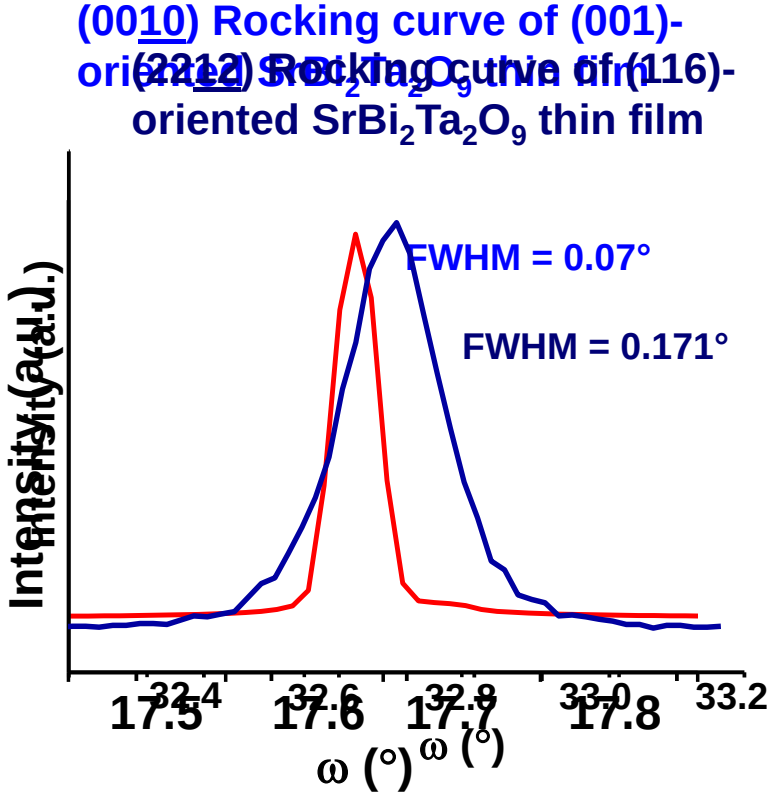


$BNdT/SrTiO_3$ (111)

Rocking Curve

- An useful method for evaluating the quality of oriented samples such as epitaxial films
- ω is changed by rocking the sample but θ_B is held constant
- Width of Rocking curve is a direct measure of the range of orientation present in the irradiated area of the crystal





Today **X-ray diffraction** supplemented by **electron** and **neutron** diffraction

Energies **X-ray**, **electrons** and **neutrons** wave-particle

X-ray:

$$E = h\upsilon = \frac{hc}{\lambda} \quad \Longleftrightarrow \quad \lambda = \frac{hc}{E}$$

$$\lambda \approx 1\,\text{Å} \rightarrow E \approx 12\ \text{k eV}$$

Electrons:

$$p = \hbar k = \frac{h}{\lambda} \quad \Longleftrightarrow \quad \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

$$\lambda \approx 1\,\text{Å} \qquad m_e = 9.1\ 10^{-31}\ \text{kg}$$

$$E \approx 150\ \text{eV}$$

Neutrons:

$$\lambda \approx 1\,\text{Å}$$

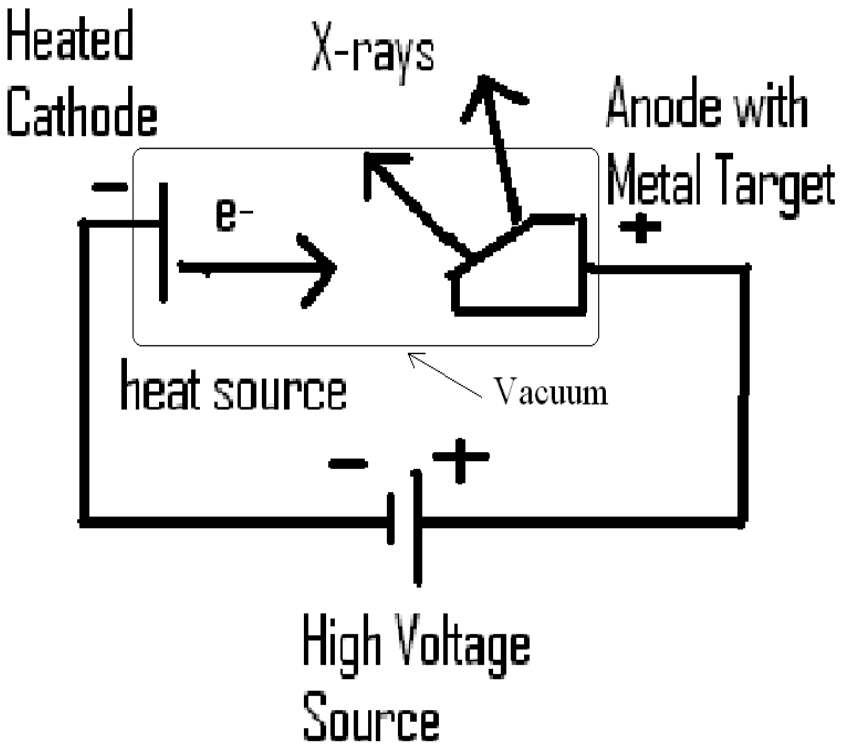
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

$$m_n = 1.6749\ 10^{-27}\ \text{kg}$$

$$E \approx 0.08\ \text{eV}$$

How do we get X-rays?

- The cathode is heated by a heat source to create an electron beam.
- The beam of electrons is then accelerated by the high voltage source, allowing them to collide with the metal target (usually Tungsten)
- X-rays are produced when the electrons are suddenly decelerated upon collision with the metal target (Brehmsstrahlung)
- If the bombarding electrons have sufficient energy, they can knock an electron out of an inner shell of the target metal atoms. Then electrons from higher states drop down to fill the vacancy, emitting x-ray photons (characteristic x-rays)



X-ray production Spectrum

- The characteristic x-rays, shown as two sharp peaks in the illustration occur when vacancies are produced in the n=1 or K-shell of the atom
- The x-rays produced by transitions from the n=2 to n=1 levels are called K-alpha x-rays
- The x-rays produced in the transition from n=3 → n=1 are called K-beta x-rays.