X-Ray Diffraction:
Method and Experiments

Outline

- Introduction and Motivation
- History
- How Diffraction Works
  - Demonstration
  - Analyzing Diffraction Patterns
- Solving DNA
- Applications
- Summary and Conclusions

Introduction

Motivation:

- X-ray diffraction is used to obtain structural information about crystalline solids.
- Useful in biochemistry to solve the 3D structures of complex biomolecules.
- Bridge the gaps between physics, chemistry, and biology.

X-ray diffraction is important for:

- Solid-state physics
- Biophysics
- Medical physics
- Chemistry and Biochemistry

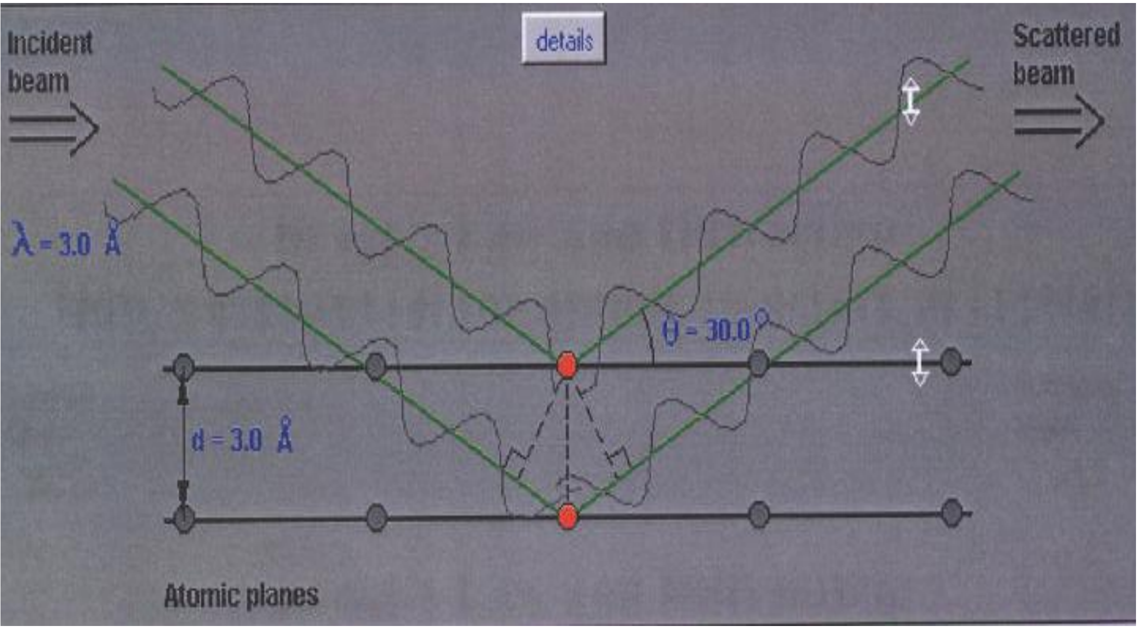
History of X-Ray Diffraction

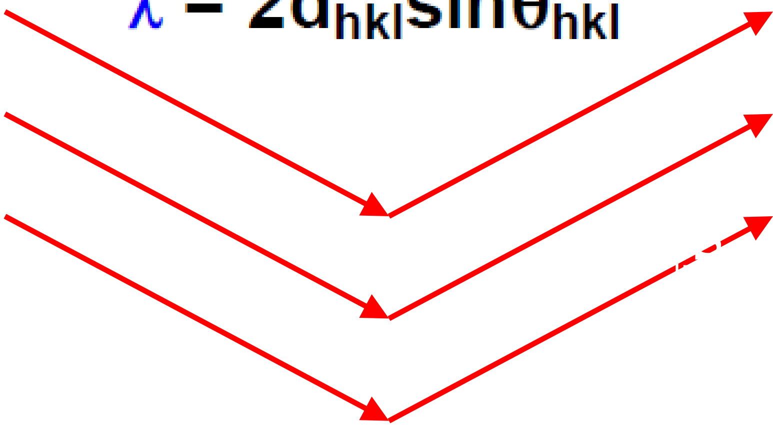
1895	X-rays discovered by Roentgen 
1914	First diffraction pattern of a crystal made by Knipping and von Laue 
1915	Theory to determine crystal structure from diffraction pattern developed by Bragg. 
1953	DNA structure solved by Watson and Crick 
Now	Diffraction improved by computer technology; methods used to determine atomic structures and in medical applications

How Diffraction Works

- Wave Interacting with a Single Particle
  - Incident beams scattered uniformly in all directions
- Wave Interacting with a Solid
  - Scattered beams interfere constructively in some directions, producing diffracted beams
  - Random arrangements cause beams to randomly interfere and no distinctive pattern is produced
- Crystalline Material
  - Regular pattern of crystalline atoms produces regular diffraction pattern.
  - Diffraction pattern gives information on crystal structure

How Diffraction Works: Bragg’s Law





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

- Constructive and destructive interference patterns depend on lattice spacing (d) and wavelength of radiation (λ)
- By varying wavelength and observing diffraction patterns, information about lattice spacing is obtained
  - In some diffractometers, the X-ray wavelength λ is fixed.
  - Consequently, a family of planes produces a diffraction peak only at a specific angle θ

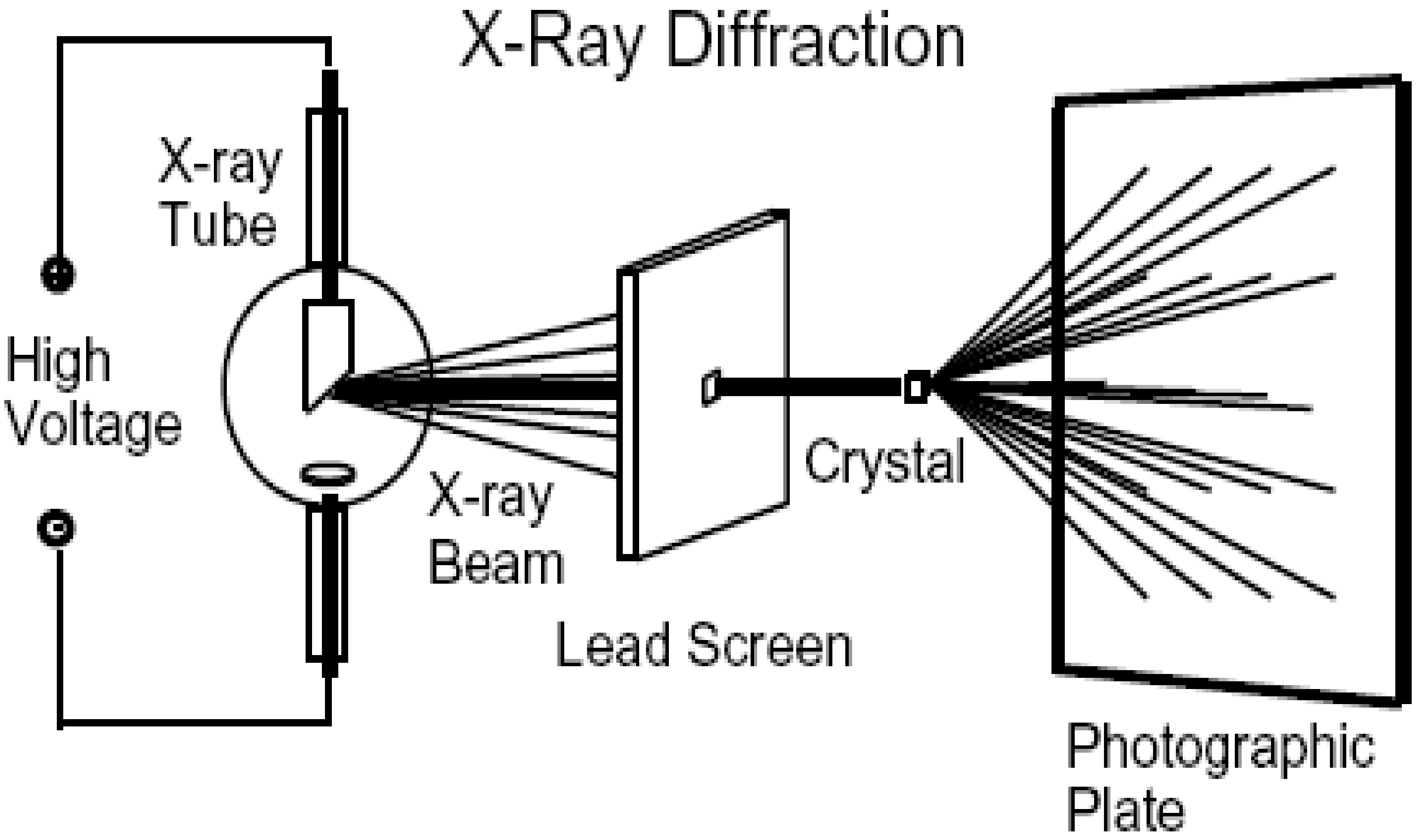
  Additionally, the plane normal must be parallel to the diffraction vector

    Plane normal: the direction perpendicular to a plane of atoms

    Diffraction vector: the vector that bisects the angle between the incident and diffracted beam

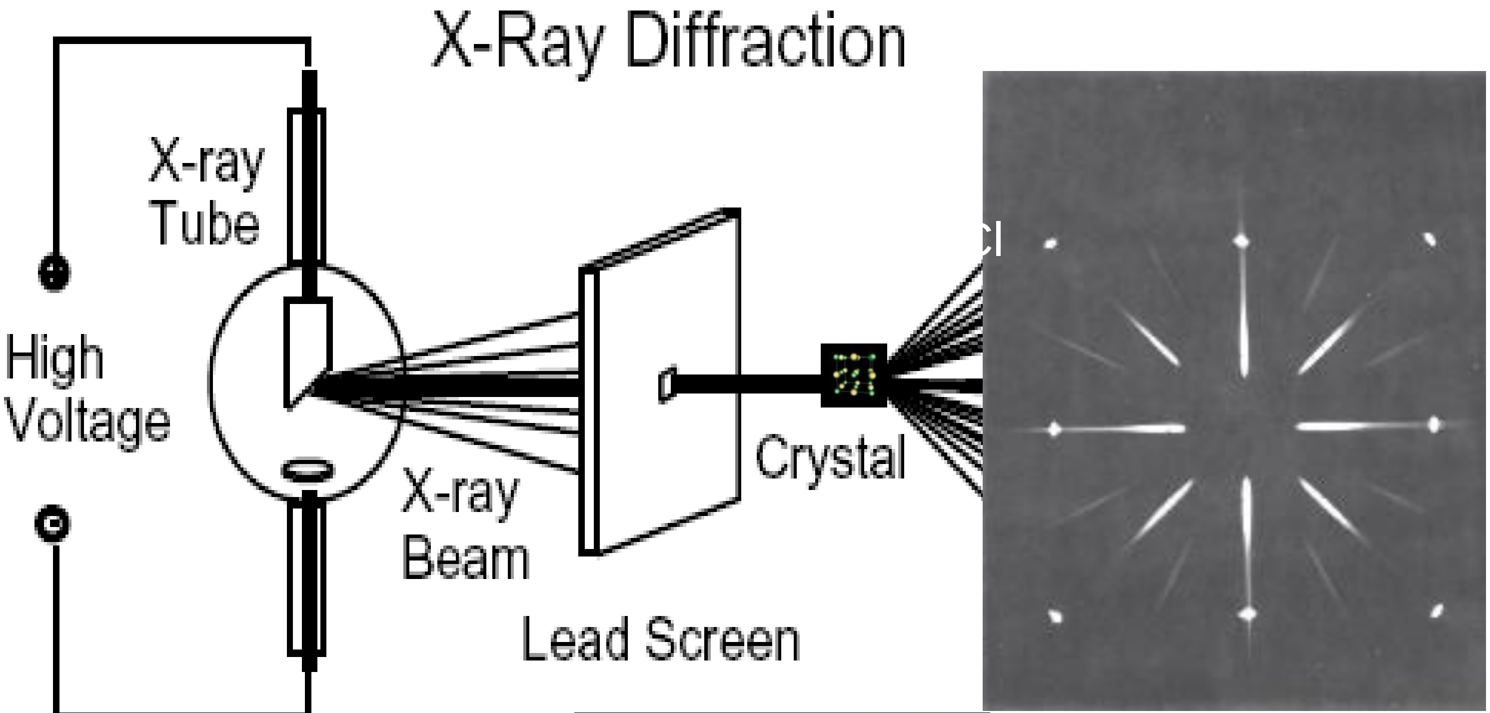
The space between diffracting planes of atoms determines peak positions.
The peak intensity is determined by what atoms are in the diffracting plane.

How Diffraction Works: Schematic

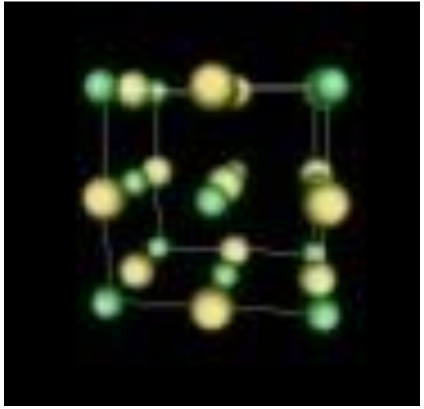


A schematic of X-ray diffraction.

How Diffraction Works: Schematic



A schematic of X-ray diffraction.



Demonstration

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

Array A versus Array B

- Dots in A are closer together than in B
- Diffraction pattern A has spots farther apart than pattern B

Array E

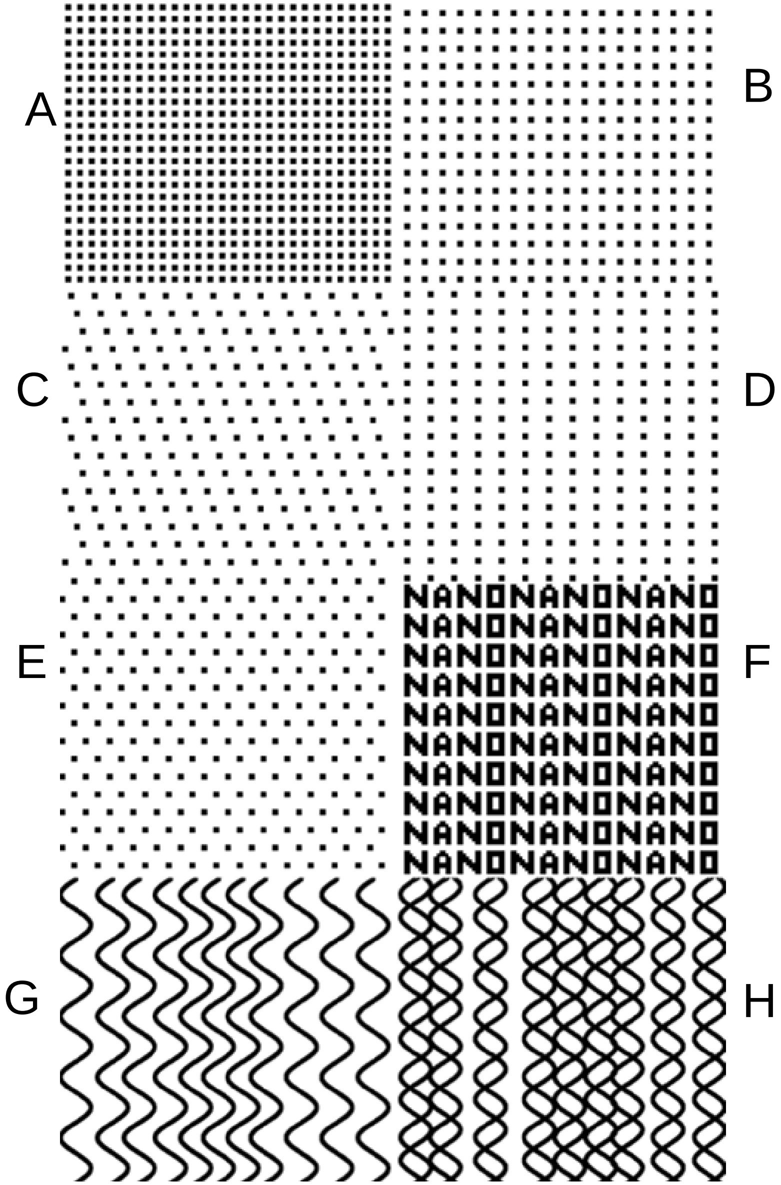
- Hexagonal arrangement

Array F

- Pattern created from the word “NANO” written repeatedly
- Any repeating arrangement produces a characteristic diffraction pattern

Array G versus Array H

- G represents one line of the chains of atoms of DNA (a single helix)
- H represents a double helix
- Distinct patterns for single and double helices

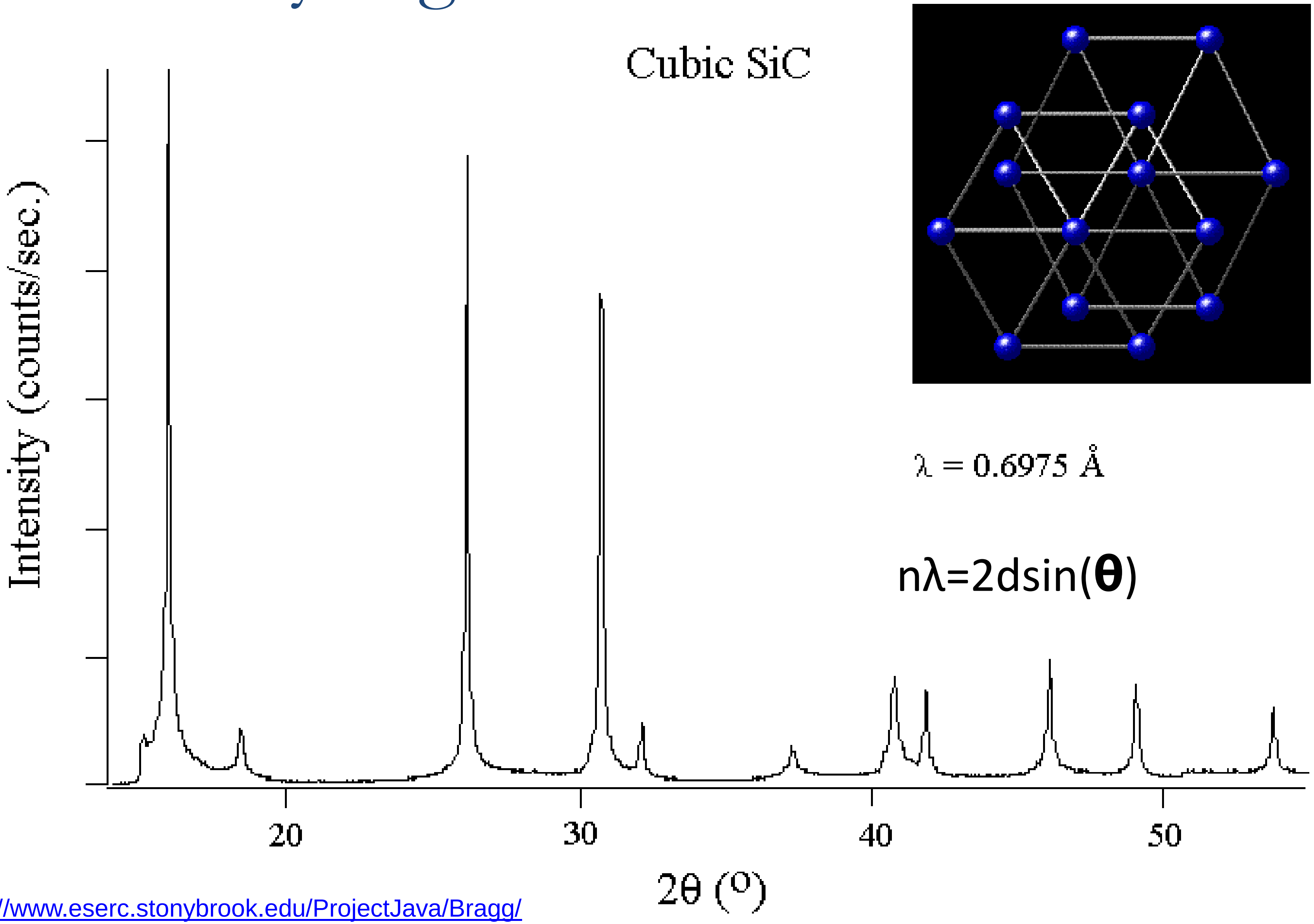


Credit: Exploring the Nanoworld

Analyzing Diffraction Patterns

- Data is taken from a full range of angles
- For simple crystal structures, diffraction patterns are easily recognizable
- Phase Problem
  - Only intensities of diffracted beams are measured
  - Phase info is lost and must be inferred from data
- For complicated structures, diffraction patterns at each angle can be used to produce a 3-D electron density map

Analyzing Diffraction Patterns



$\lambda = 0.6975$ Å

$n\lambda = 2d\sin(\boldsymbol{\theta})$

http://www.eserc.stonybrook.edu/ProjectJava/Bragg/

Solving the Structure of DNA: History

- Rosalind Franklin- physical chemist and x-ray crystallographer who first crystallized and photographed DNA
- Maurice Wilkins- collaborator of Franklin
- Watson & Crick- chemists who combined the information from Photo 51 with molecular modeling to solve the structure of DNA in 1953

Solving the Structure of DNA

- Photo 51 Analysis
  - “X” pattern characteristic of helix
  - Diamond shapes indicate long, extended molecules
  - Smear spacing reveals distance between repeating structures
  - Missing smears indicate interference from second helix

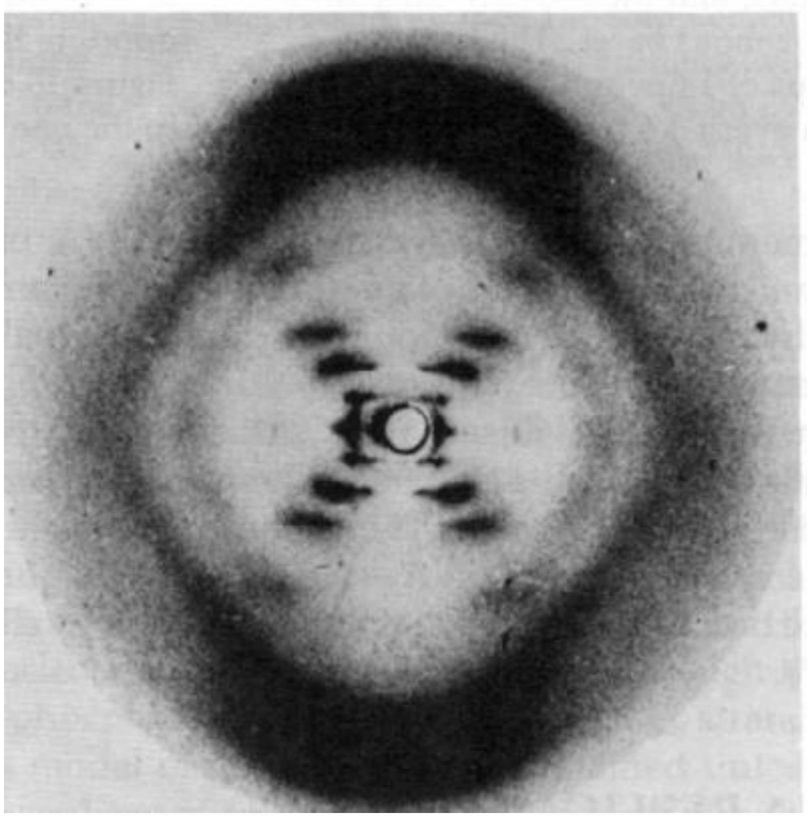


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

www.pbs.org/wgbh/nova/photo51

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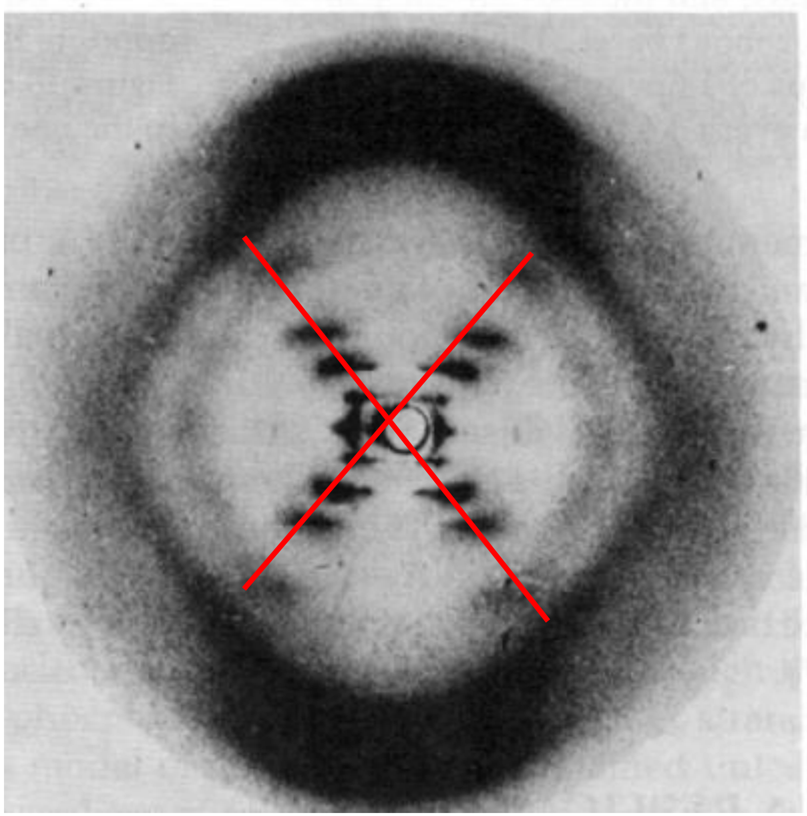

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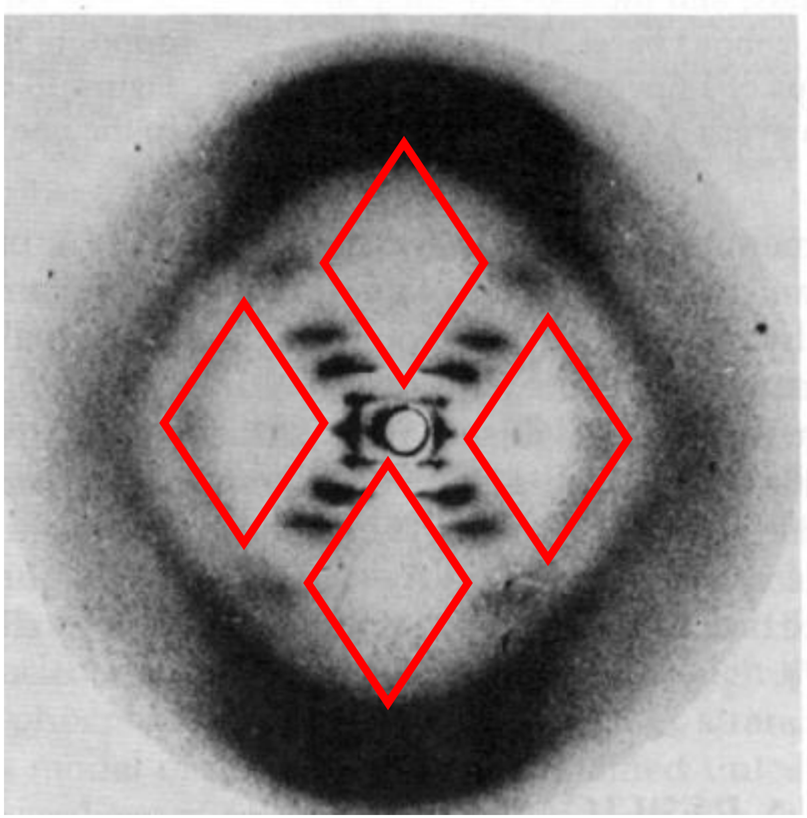

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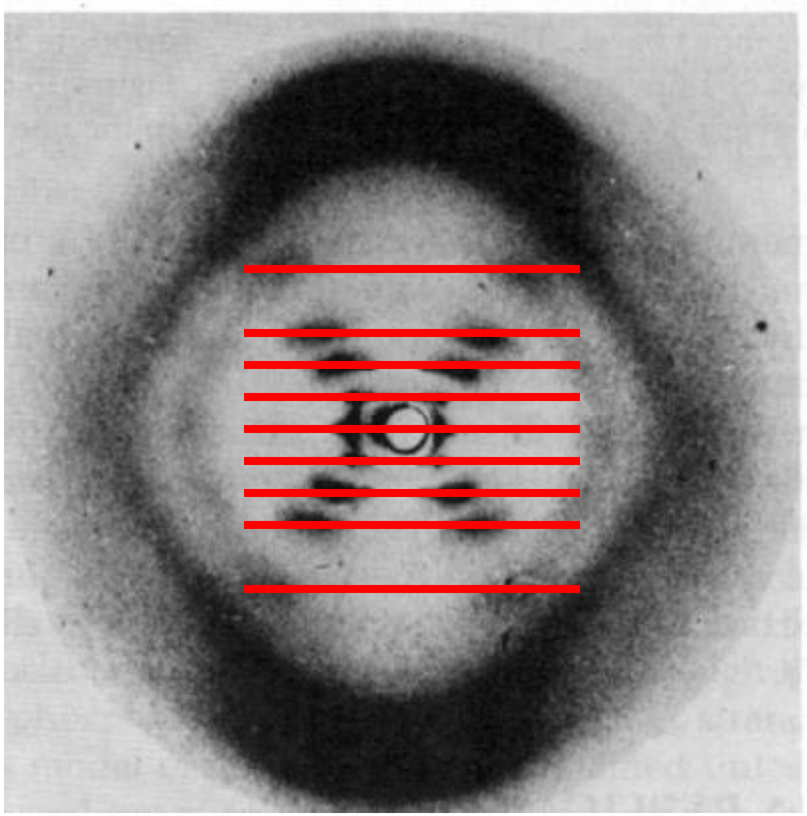

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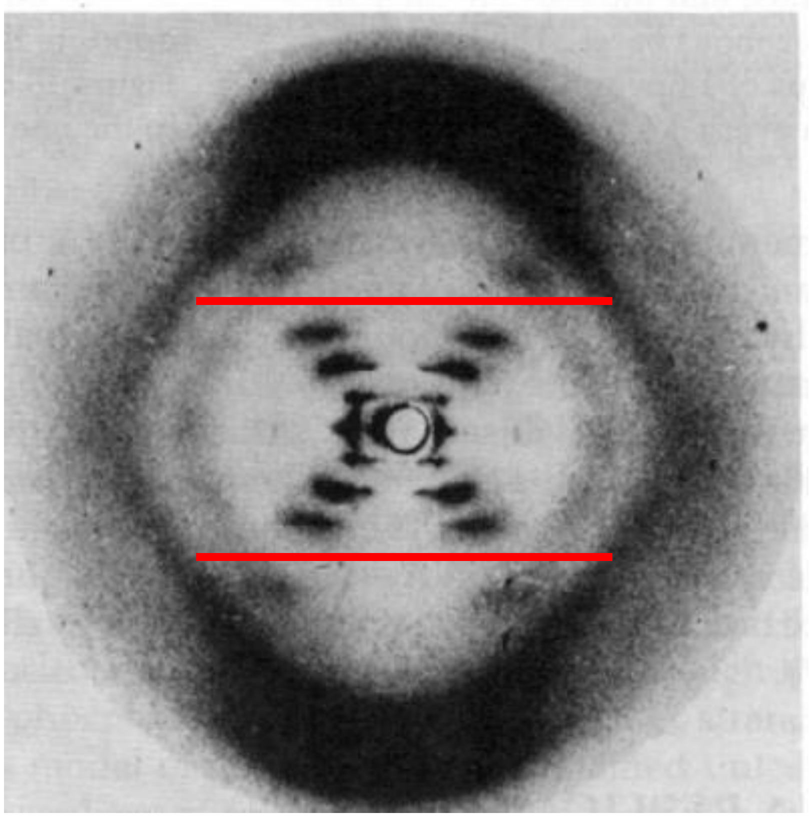


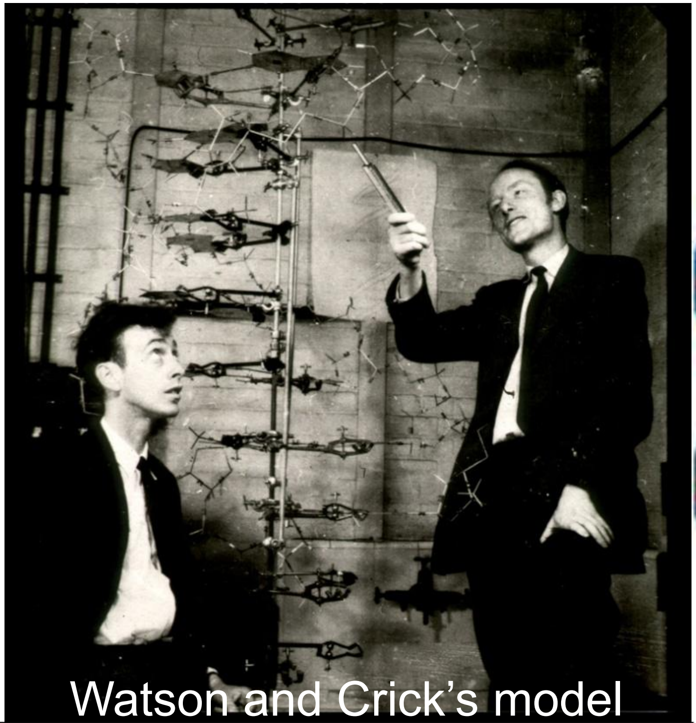
Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

www.pbs.org/wgbh/nova/photo51

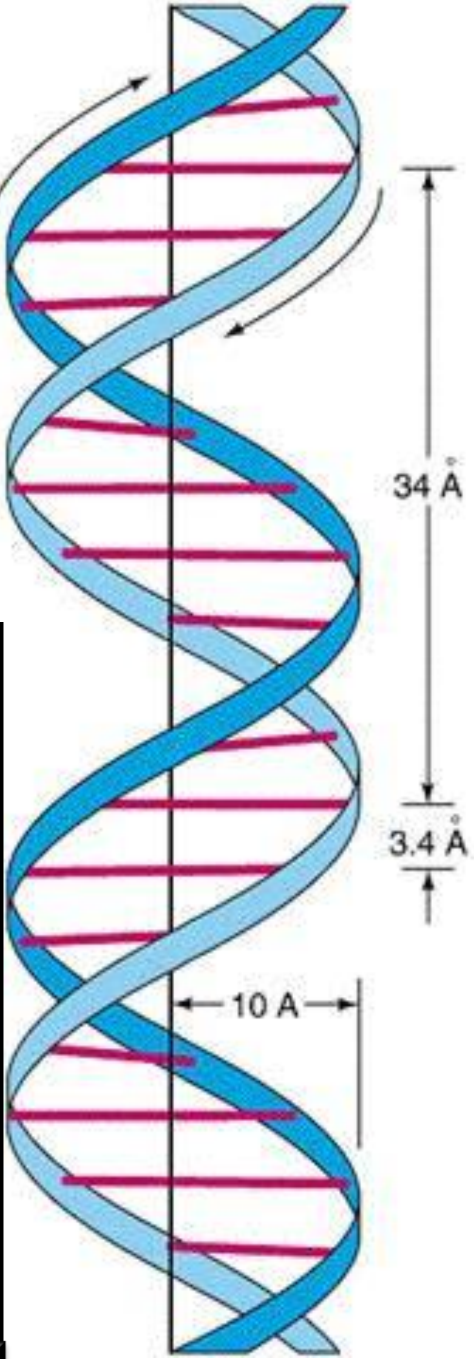
Solving the Structure of DNA

- Information Gained from Photo 51
  - Double Helix
  - Radius: 10 angstroms
  - Distance between bases: 3.4 angstroms
  - Distance per turn: 34 angstroms
- Combining Data with Other Information
  - DNA made from:
    - sugar
    - phosphates
    - 4 nucleotides (A,C,G,T)
  - Chargaff's Rules
    - %A=%T
    - %G=%C

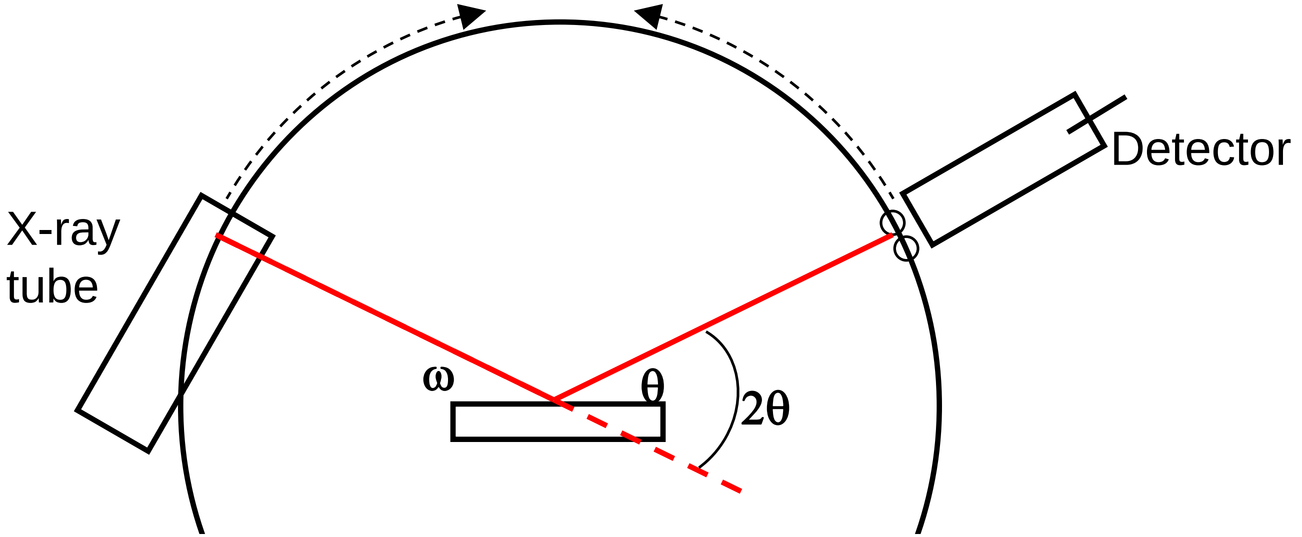
Adenine, Guanine, Cytosine, Thymine, Uracil



Watson and Crick's model

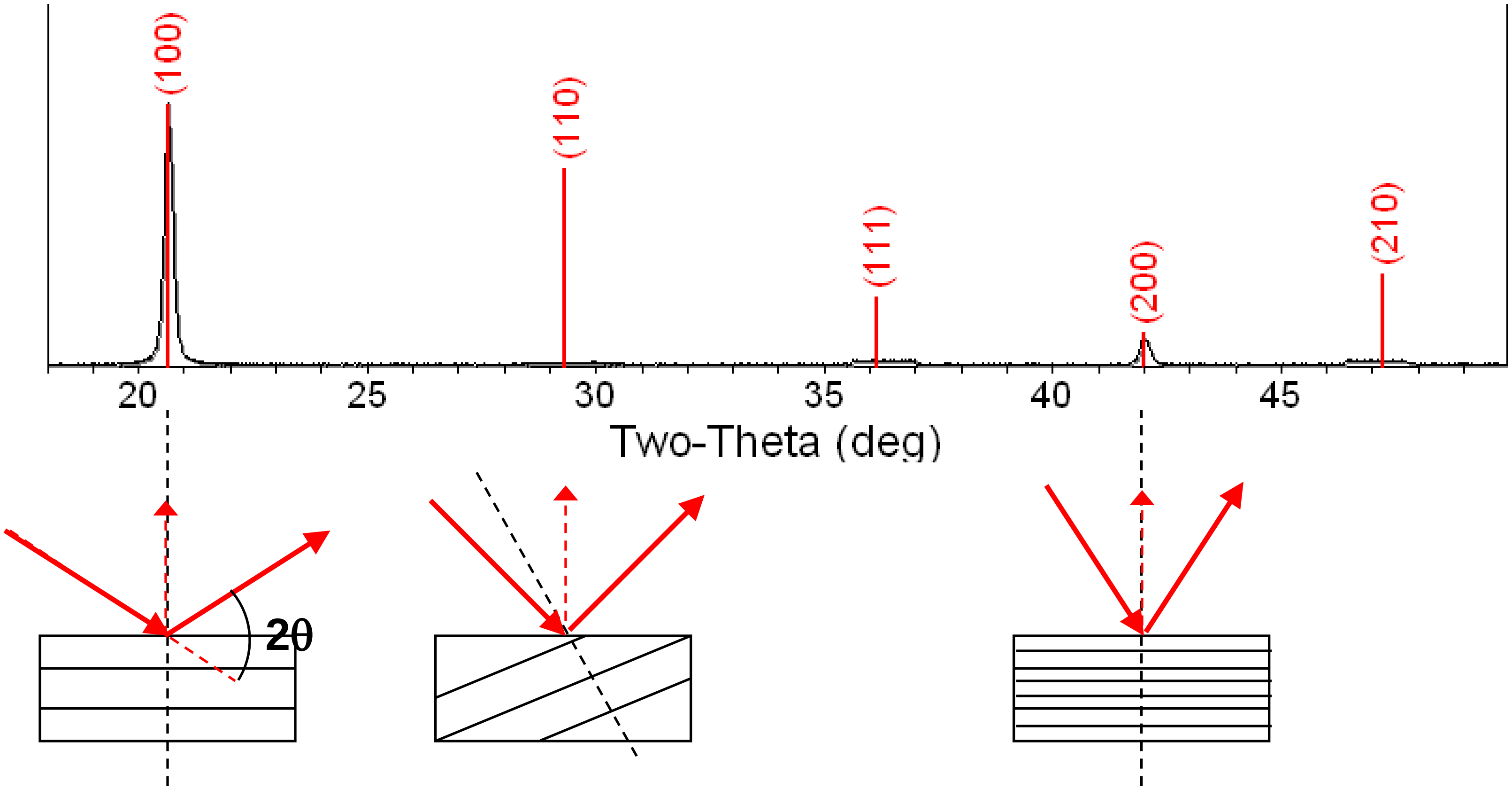


Powder diffractometers typically use the Bragg-Brentano geometry.



- The incident angle, ω, is defined between the X-ray source and the sample.
- The diffracted angle, 2θ, is defined between the incident beam and the detector angle.
- The incident angle ω is always ½ of the detector angle 2θ .
- In a θ:2θ instrument (e.g. Rigaku RU300), 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.

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



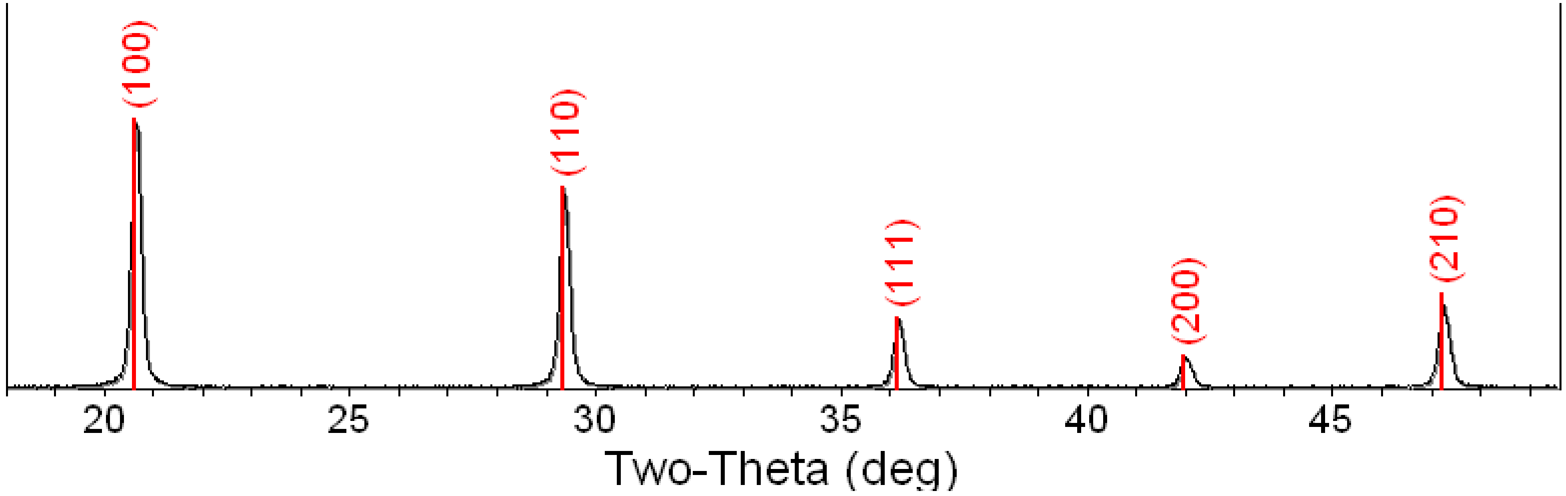
At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

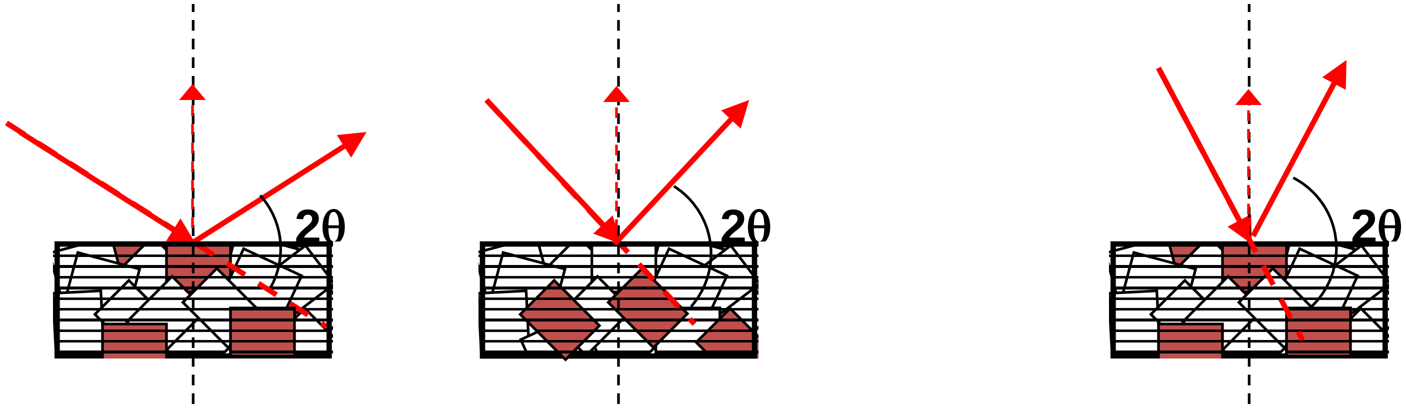
The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

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 41.2 °2θ.

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

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 …
- If the crystallites are randomly oriented, and there are enough of them, then they will produce a continuous Debye cone.
- In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point; thus giving the appearance of a discrete diffraction peak.

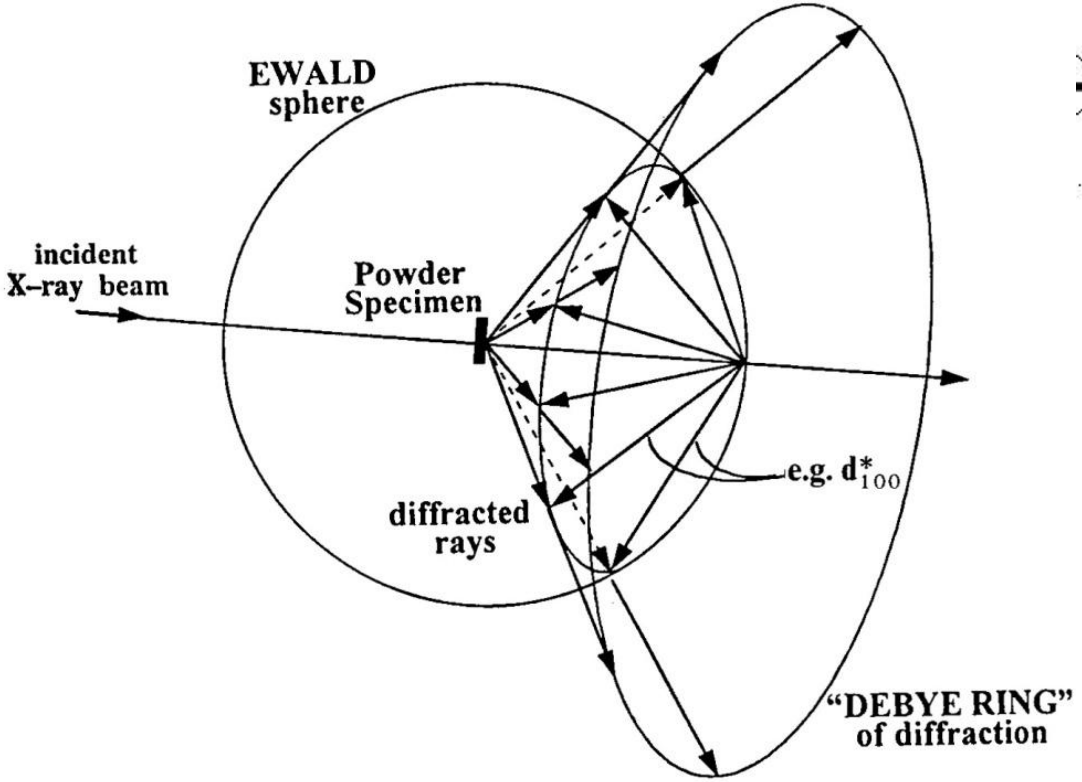
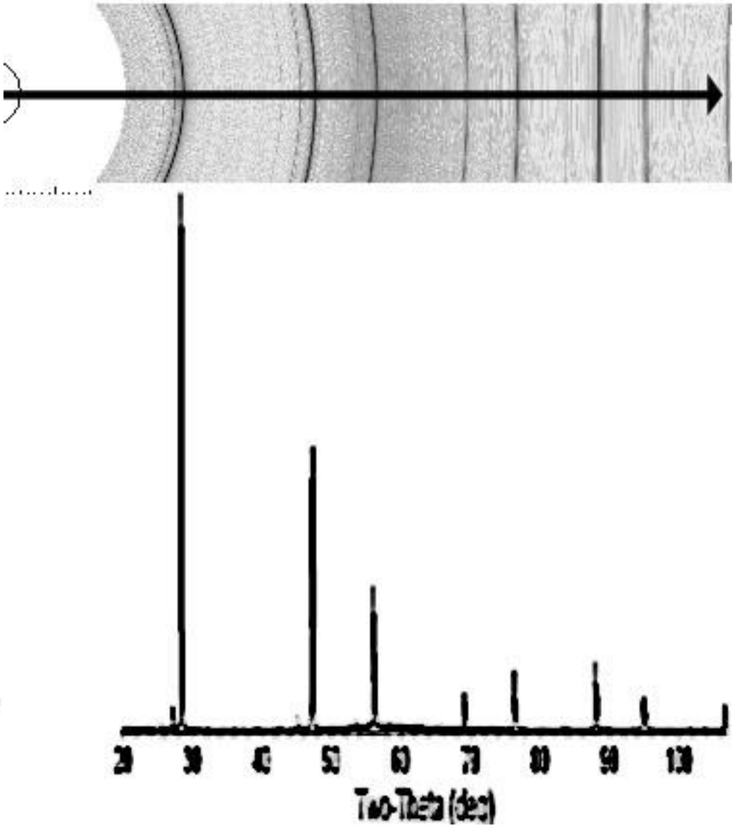
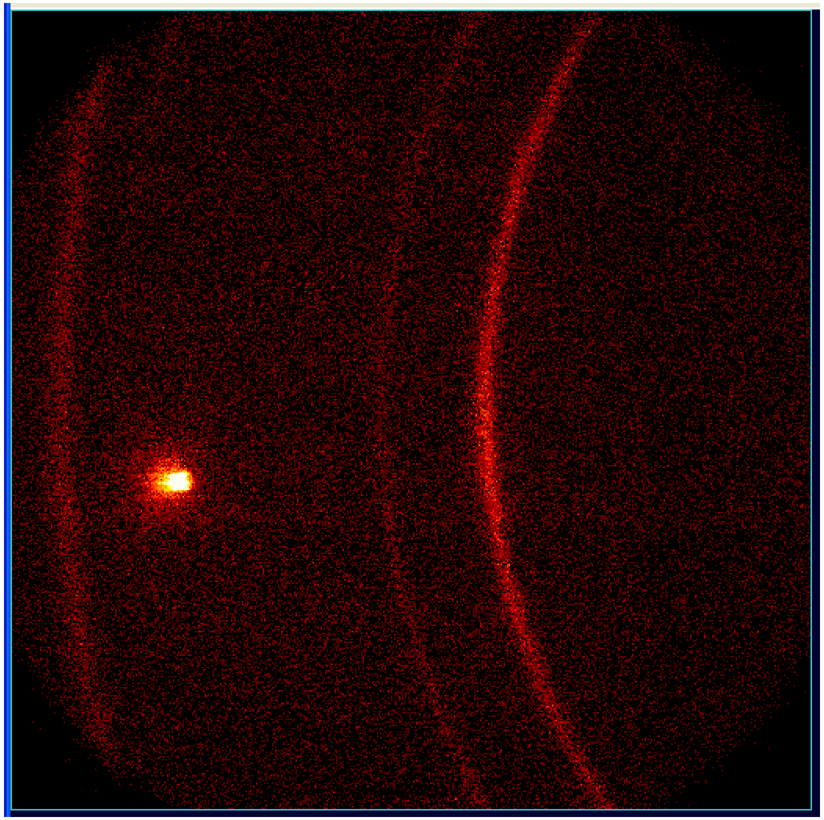


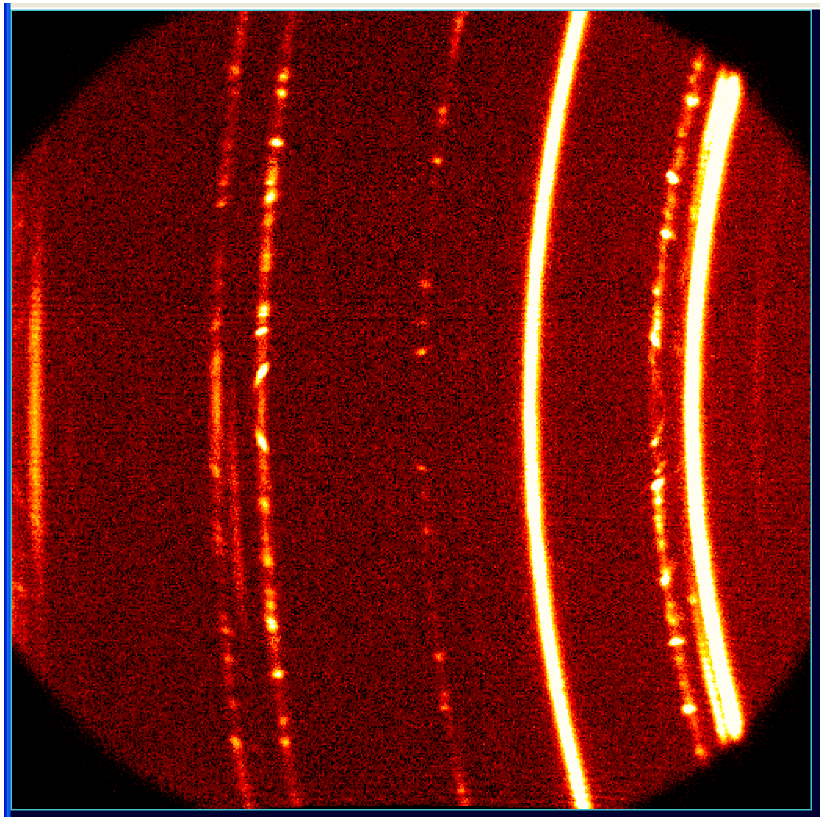
Figure 3.9. The intersection of $\mathbf{d}^*_{100}$ vectors from a powder with the Ewald sphere.



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



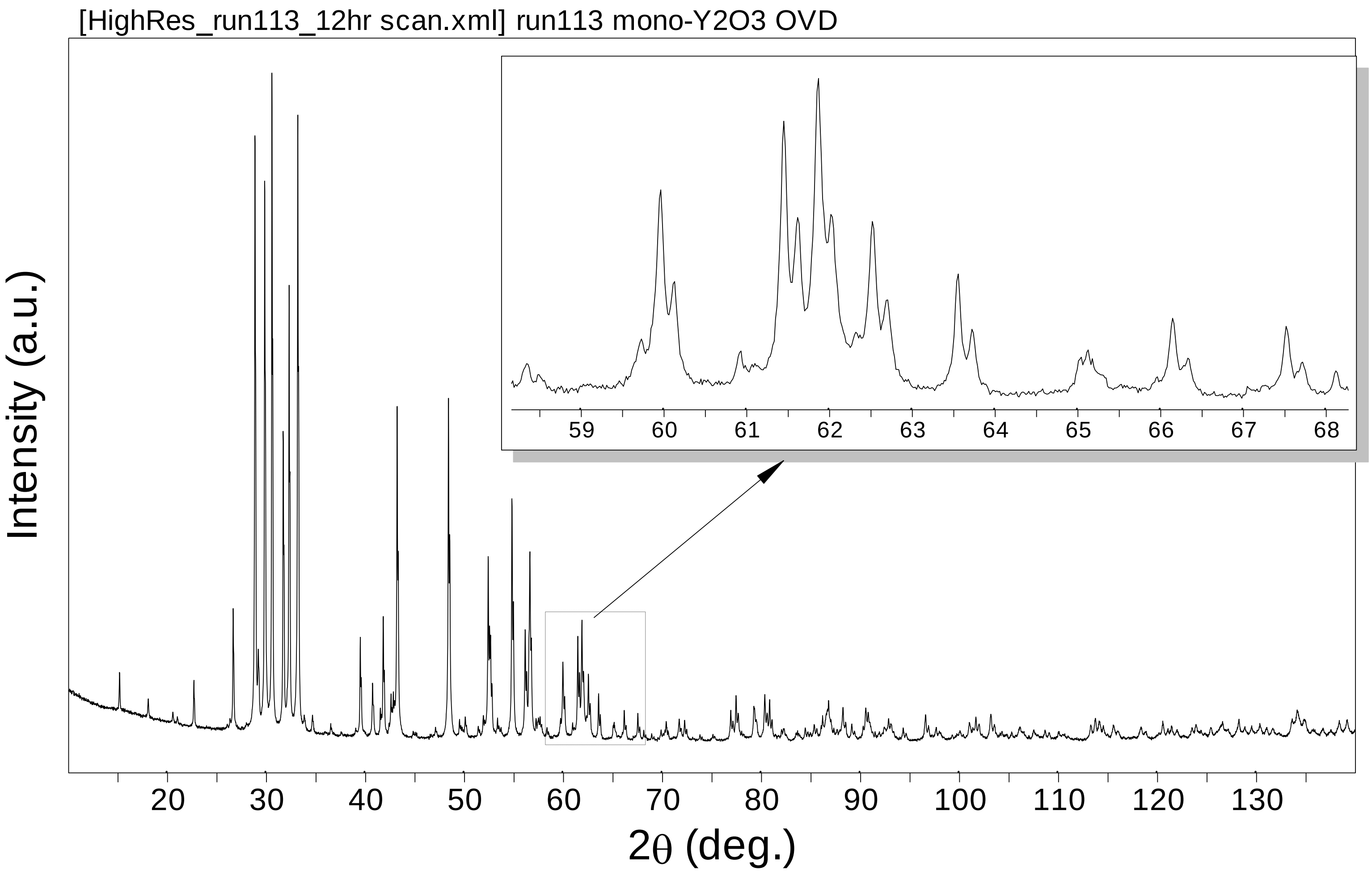
Polycrystalline thin film on a single crystal substrate



Mixture of fine and coarse grains in a metallic alloy

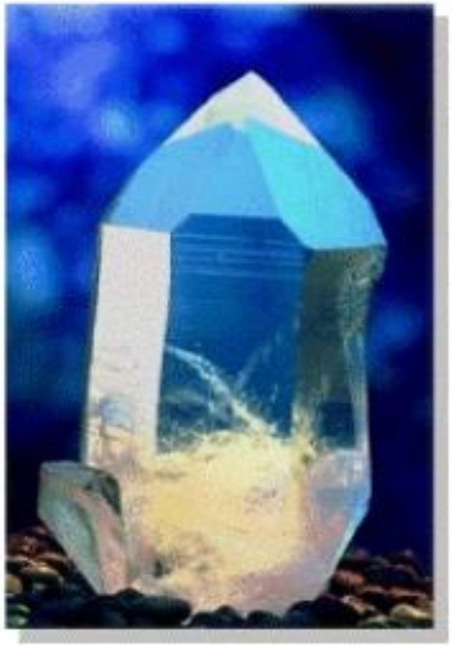
Conventional linear diffraction patterns would miss information about single crystal or coarse grained materials

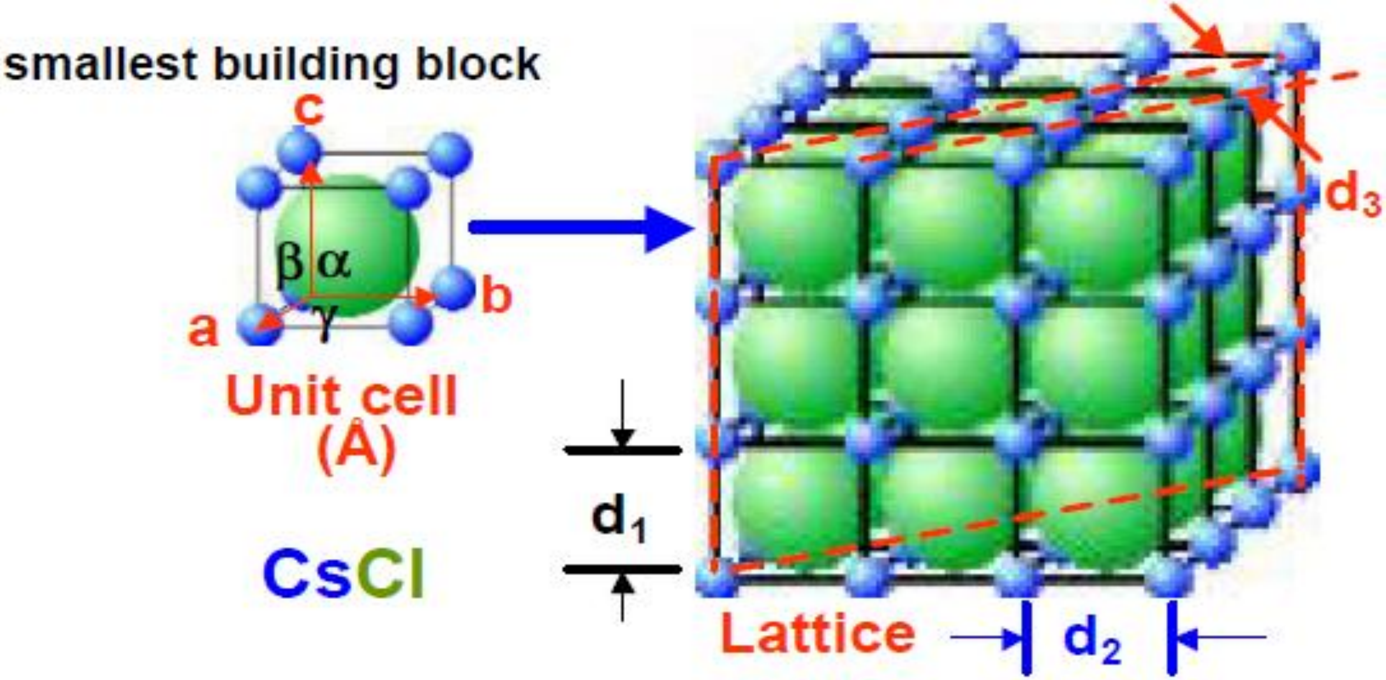
Linear (1D) Diffraction Scans have better resolution and less noise



Diffraction patterns are best reported using d_{hkl} and relative intensity rather than 2θ and absolute intensity.

- The peak position as 2θ 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.



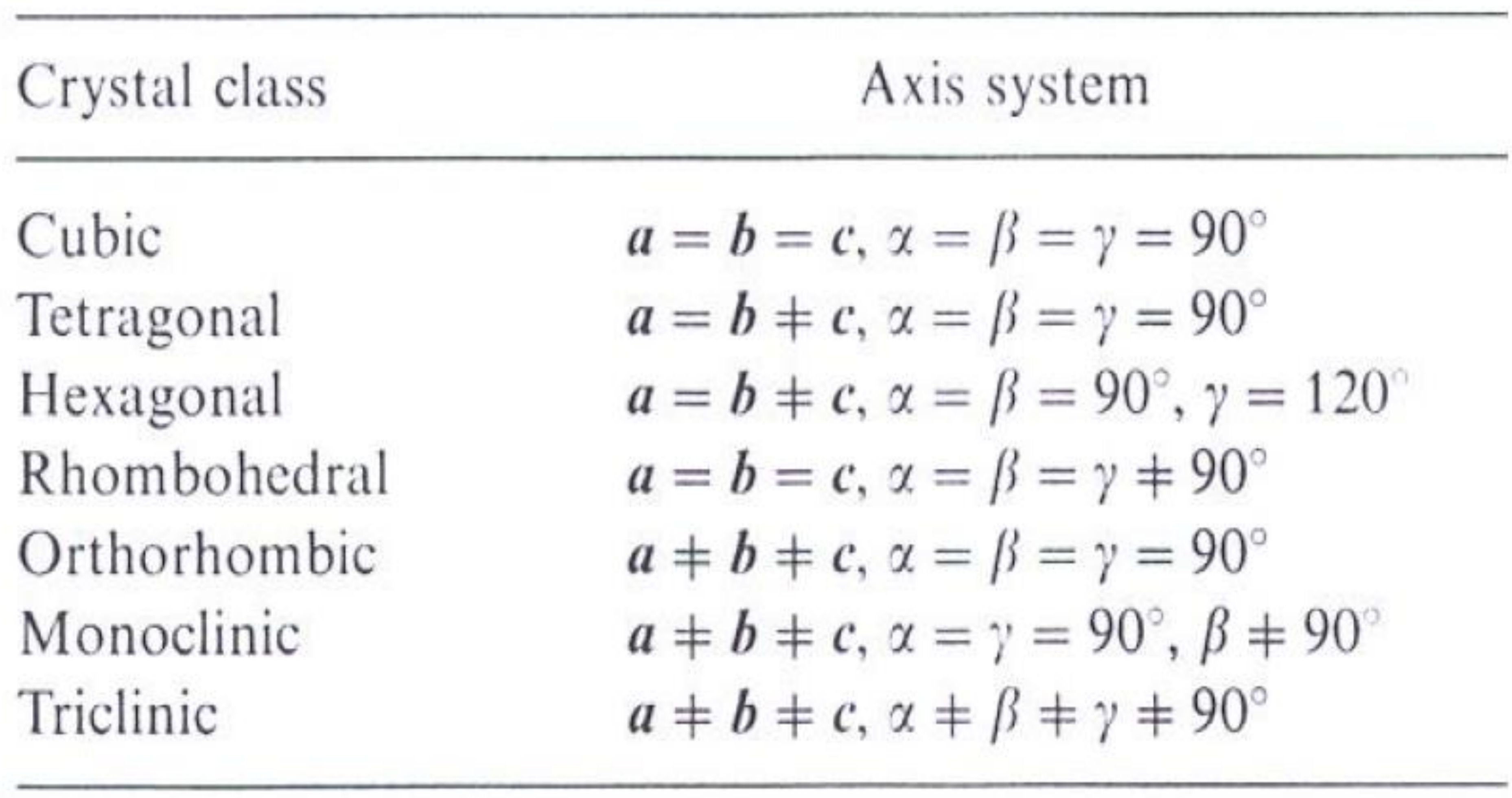


A crystal consists of a periodic arrangement of the unit cell into a lattice. The unit cell can contain a single atom or atoms in a fixed arrangement.

Crystals consist of planes of atoms that are spaced a distance d apart, but can be resolved into many atomic planes, each with a different d-spacing.

a,b and c (length) and α, β and γ angles between a,b and c are lattice constants or parameters which can be determined by XRD.

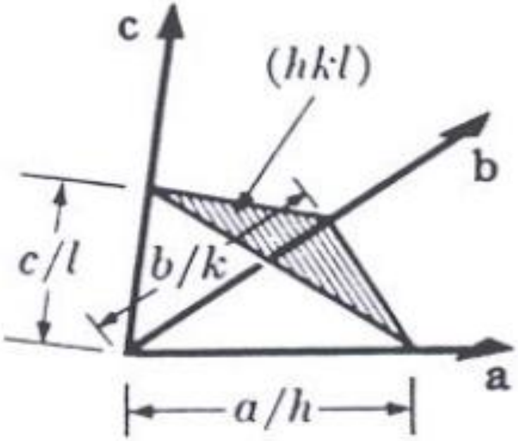
The Seven Crystal Systems

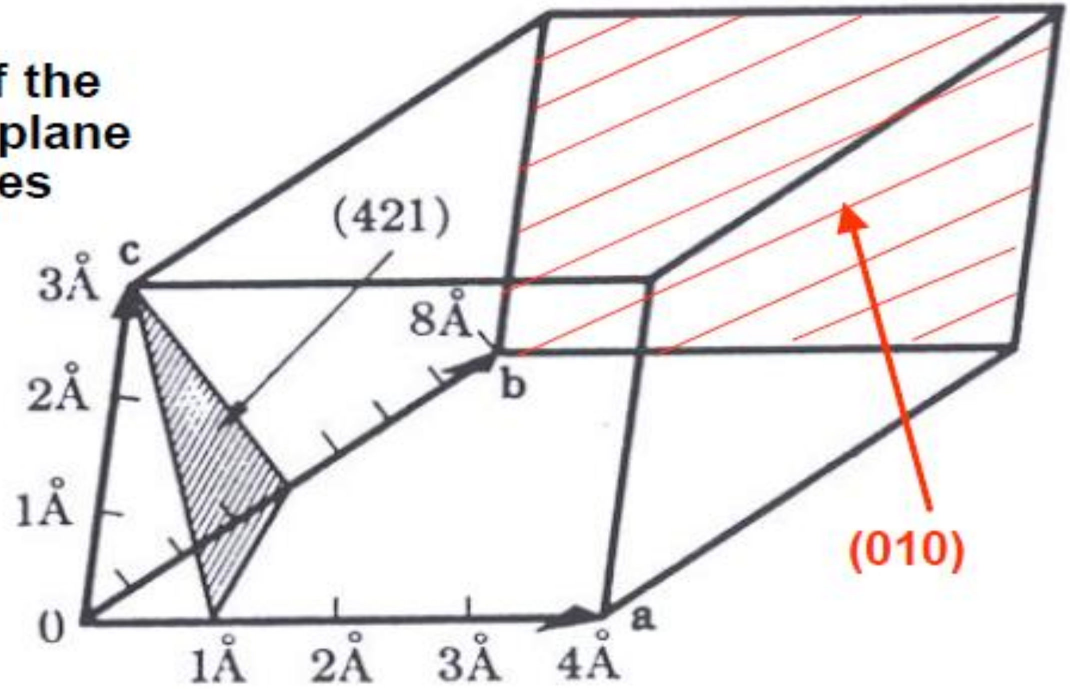


Crystal class	Axis system
Cubic	$a = b = c,\ \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c,\ \alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c,\ \alpha = \beta = 90^\circ,\ \gamma = 120^\circ$
Rhombohedral	$a = b = c,\ \alpha = \beta = \gamma \neq 90^\circ$
Orthorhombic	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c,\ \alpha = \gamma = 90^\circ,\ \beta \neq 90^\circ$
Triclinic	$a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90^\circ$

Miller Indices *hkl*

Miller indices-the reciprocals of the fractional intercepts which the plane makes with crystallographic axes



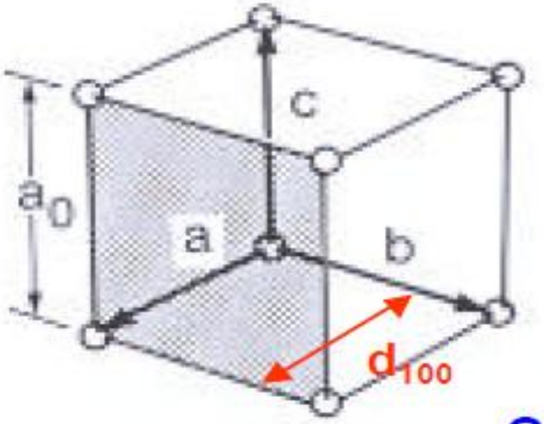


	a	b	c	a	b	c
Axial length	4Å	8Å	3Å	4Å	8Å	3Å
Intercept lengths	1Å	4Å	3Å	∞	8Å	∞
Fractional intercepts	¼	½	1	∞	1	∞
Miller indices	4	2	1	0	1	0
	h	k	l	h	k	l

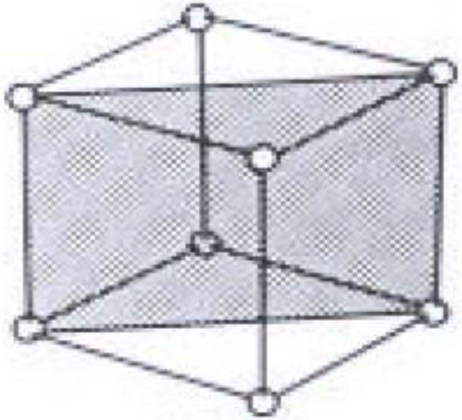
4/ ∞ =0

Atomic planes: d-spacings in a simple cube

a	b	c
1	0	0
1	0	0



(100)

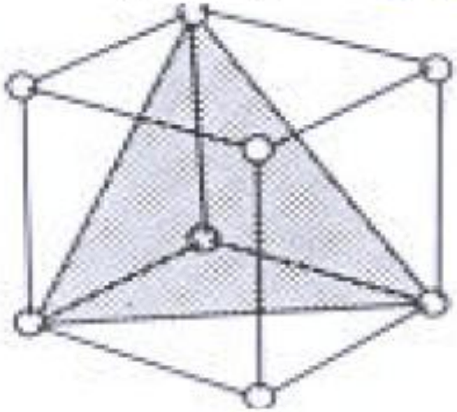


(110)

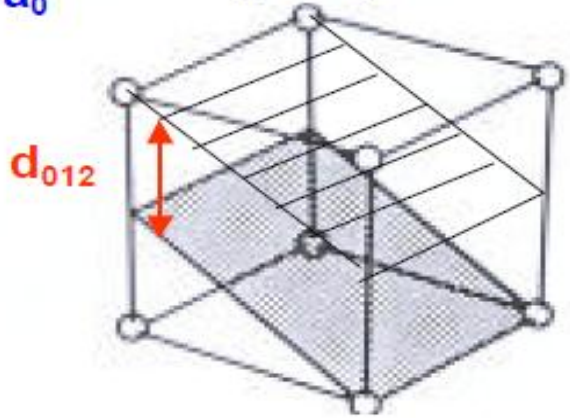
a	b	c
1	1	0
1	1	0

Cubic
$a=b=c=a_0$

a	b	c
1	1	1
1	1	1



(111)

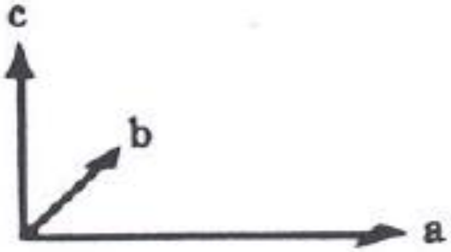


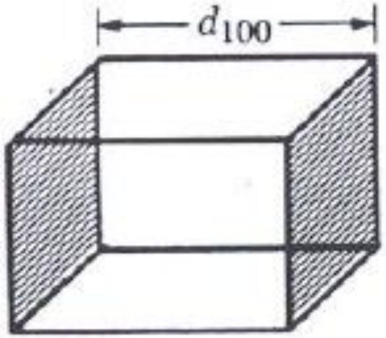
(012)

a	b	c
0	1	½
0	1	2

Black numbers-fractional intercepts, Blue numbers-Miller indices

Planes and Spacings





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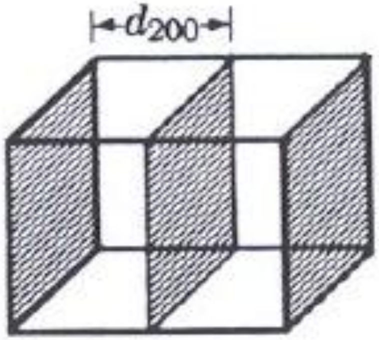
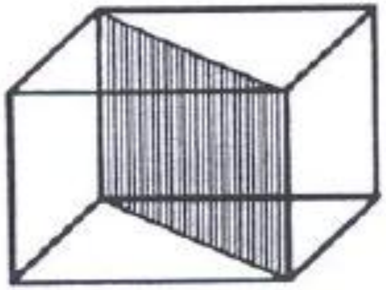
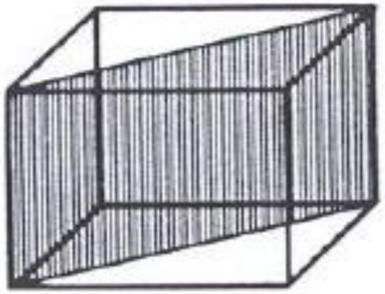


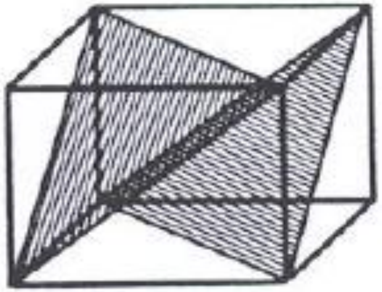
(200)



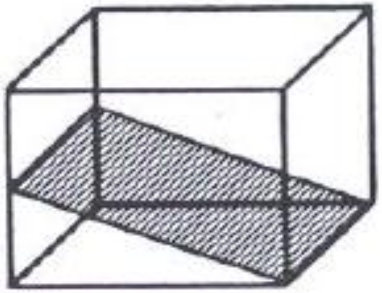
(110)



$(\bar{1}10)$

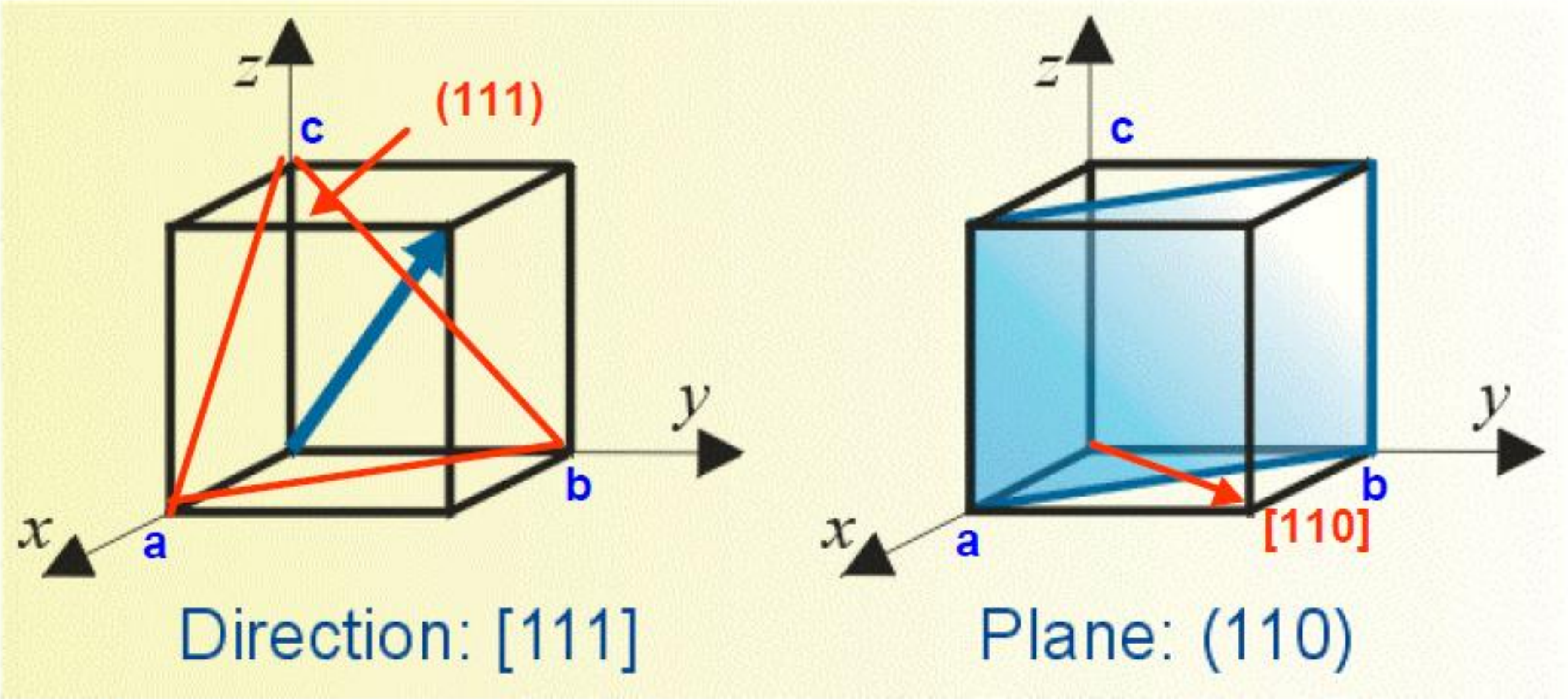


$(11\bar{1})$



(102)

Indexing of planes and directions



Direction: [111]

Plane: (110)

a direction: [uvw]
<uvw>: a set of equivalent directions

a plane: (hkl)
{hkl}: a set of equivalent planes

d-spacings and lattice parameters

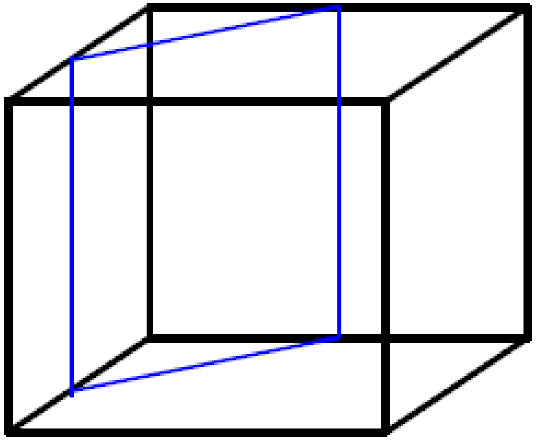
$$\lambda = 2d_{hkl}\sin\theta_{hkl}$$

Fix λ (Cu kα) = 1.54Å $\quad d_{hkl} = 1.54\text{Å}/2\sin\theta_{hkl}$

(Most accurate d-spacings are those calculated from high-angle peaks)

For a simple cubic ($a = b = c = a_0$)

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

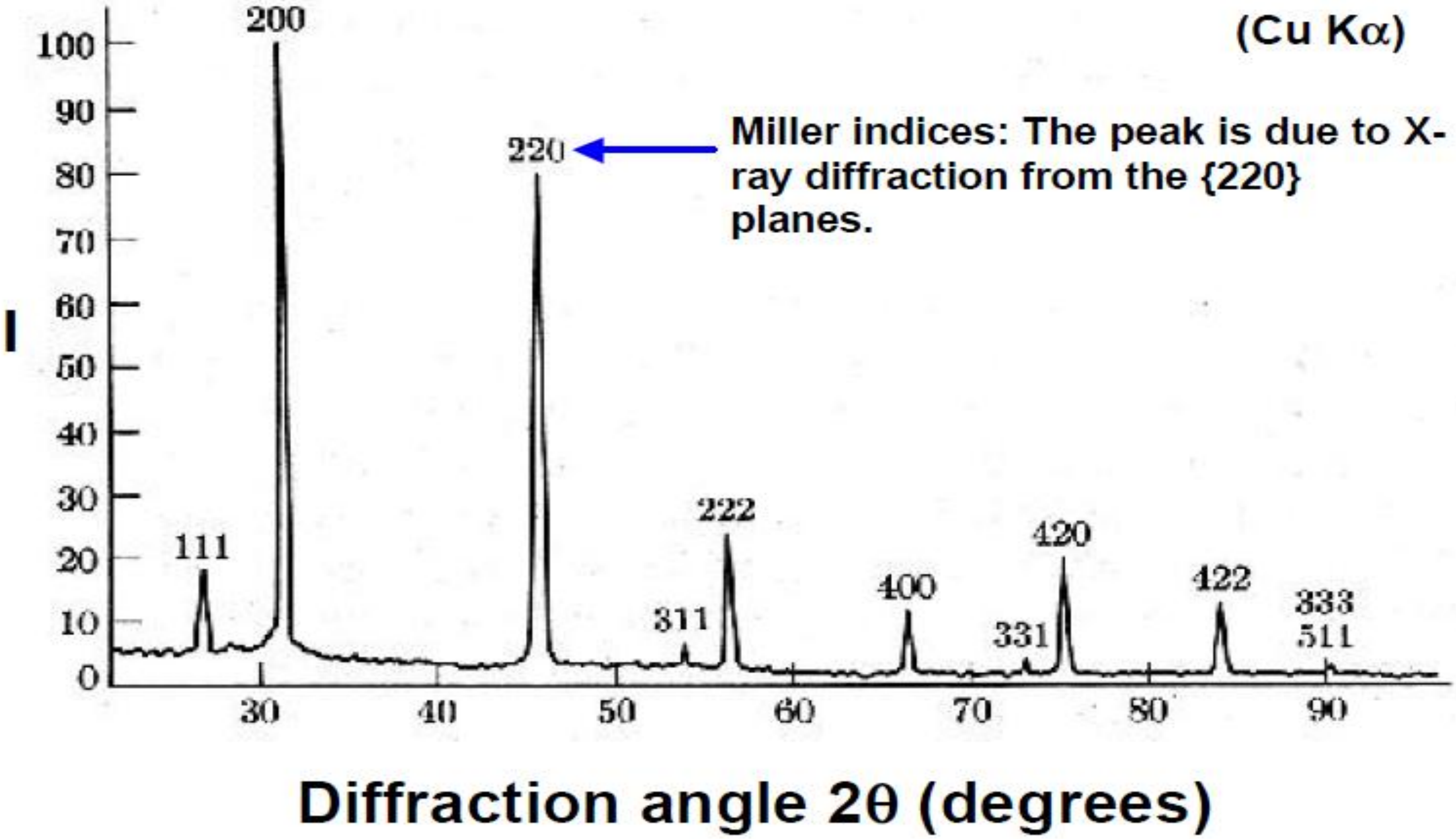


→ $a_0 = d_{hkl} / (h^2+k^2+l^2)^{½}$

e.g., for NaCl, $2\theta_{220}$=46°, θ_{220}=23°,

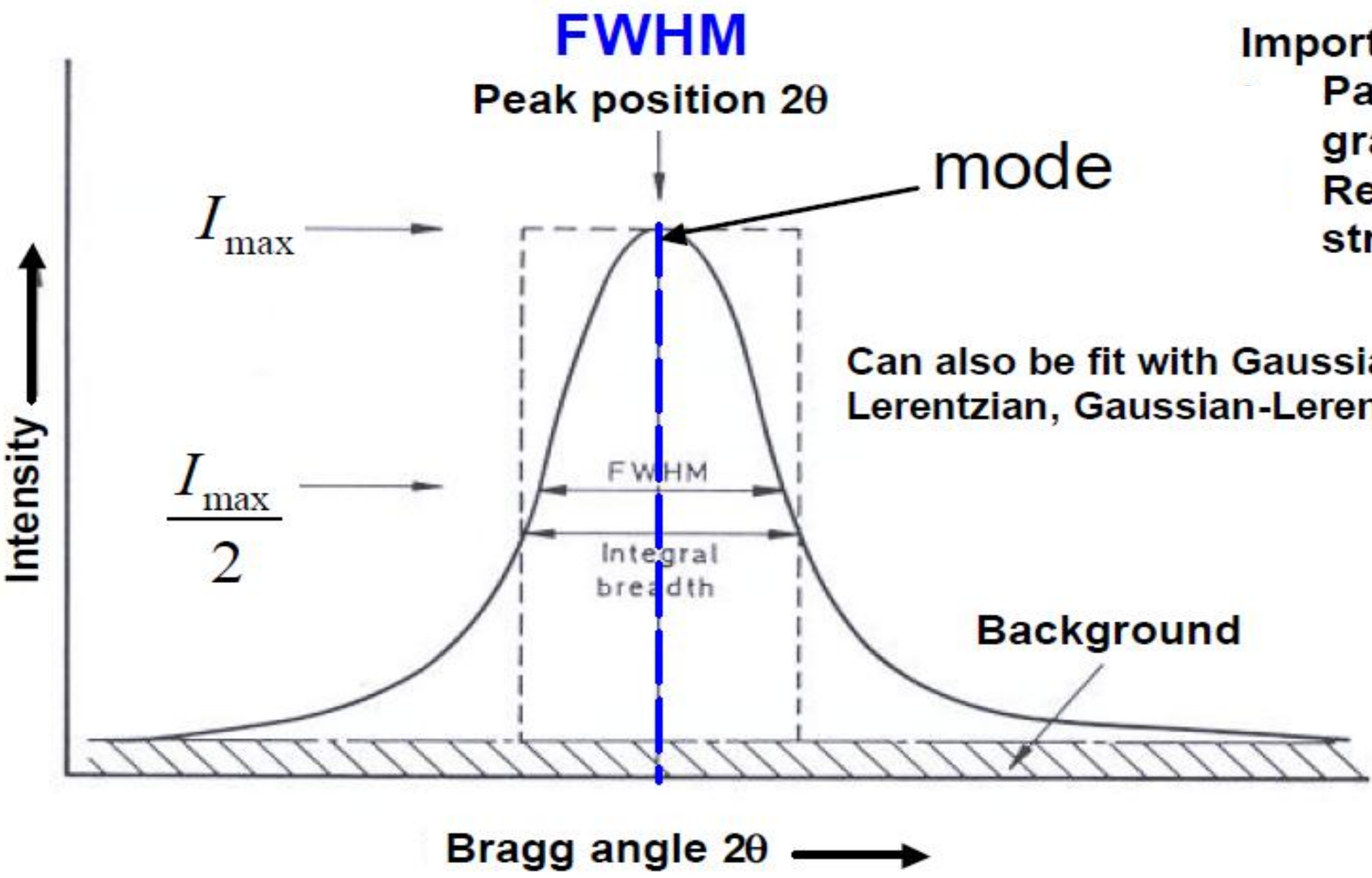
d_{220} =1.9707Å, a_0=5.5739Å

XRD pattern of NaCl powder



Miller indices: The peak is due to X-ray diffraction from the {220} planes.

Significance of Peaks: peak position, peak width and peak Intensity



Important for:
- **Particle or grain size**
- **Residual strain**

Can also be fit with Gaussian, Lerentzian, Gaussian-Lerentzian etc.

Effect of Lattice Strain on Diffraction Peak Position and Width

No Strain

Uniform Strain

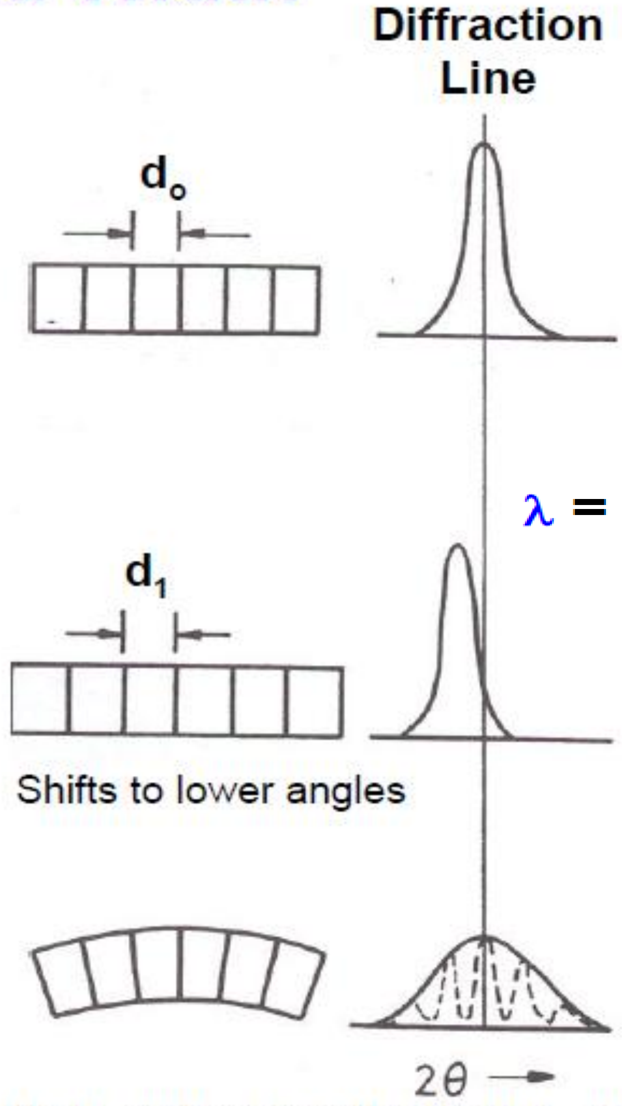
$(d_1 - d_o)/d_o$

Peak moves, no shape changes

Non-uniform Strain

$d_1 \neq \text{constant}$

Peak broadens



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

Shifts to lower angles

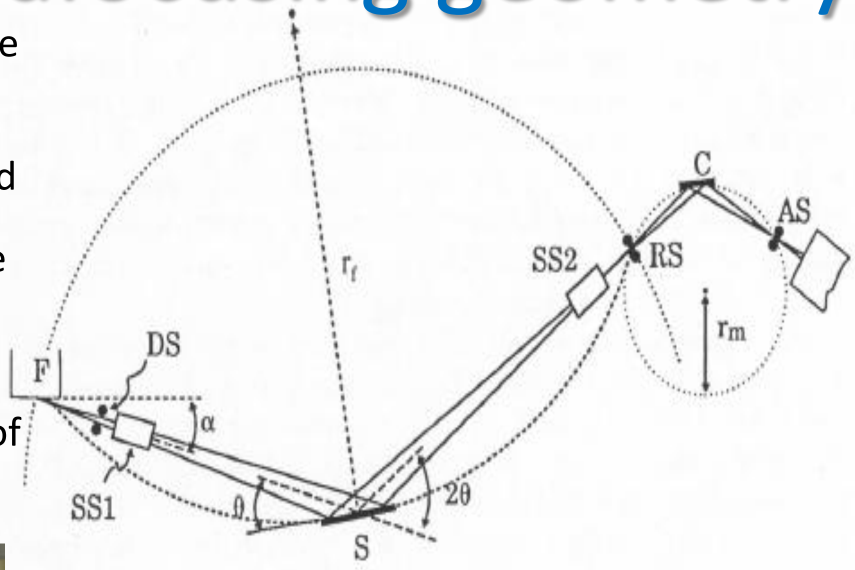
Exceeds d_0 on top, smaller than d_0 on the bottom

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

Powder diffractometers use Bragg-Brentano parafocusing geometry

- A point detector and sample are moved so that the detector is always at 2θ and the sample surface is always at θ to the incident X-ray beam.
- In the parafocusing arrangement, the incident- and diffracted-beam slits move on a circle that is centered on the sample. Divergent X rays from the source hit the sample at different points on its surface. During the diffraction process the X rays are refocused at the detector slit.
- This arrangement provides the best combination of intensity, peak shape, and angular resolution for the widest number of samples.



Goniometer Circle Radius

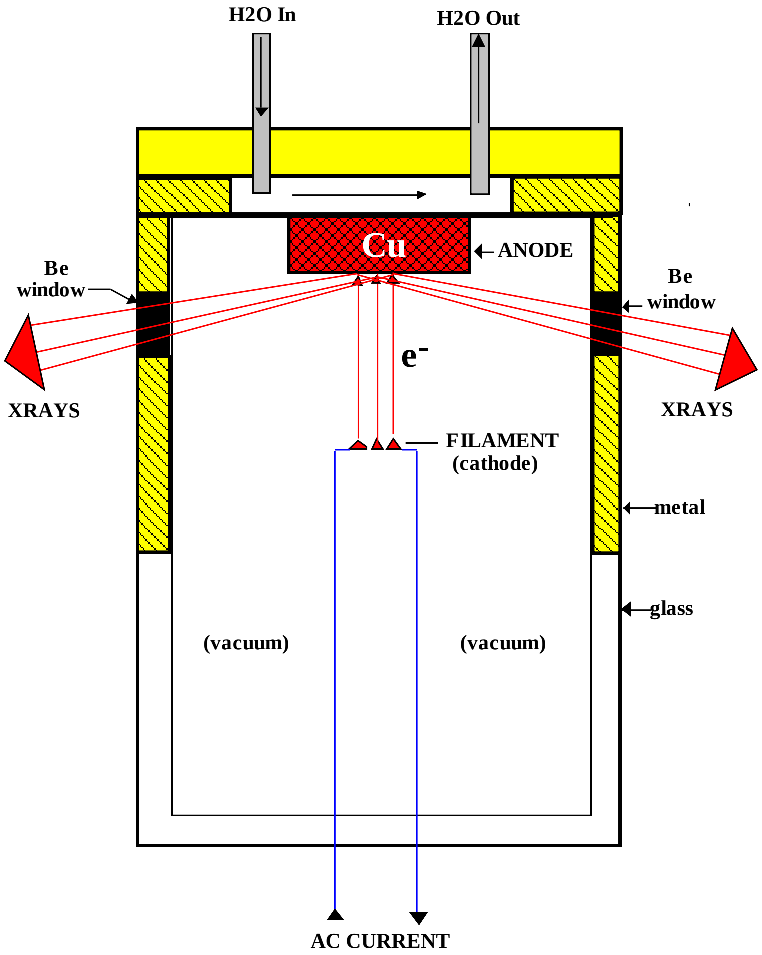
$$R = F \rightarrow S = S \rightarrow RS$$

Figure 7.7. Geometric arrangement of the Bragg–Brentano diffractometer.

F: the X-ray source
DS: the incident-beam divergence-limiting slit
SS: the Soller slit assembly
S: the sample
RS: the diffracted-beam receiving slit
C: the monochromator crystal
AS: the anti-scatter slit

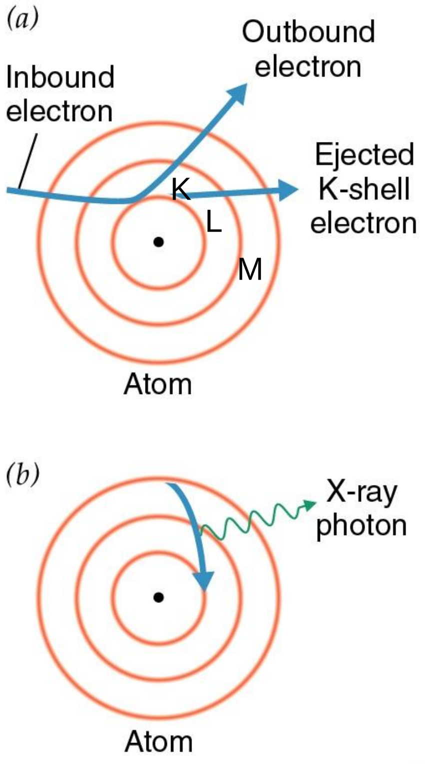
X-ray is produced by a sealed tube or rotating anode

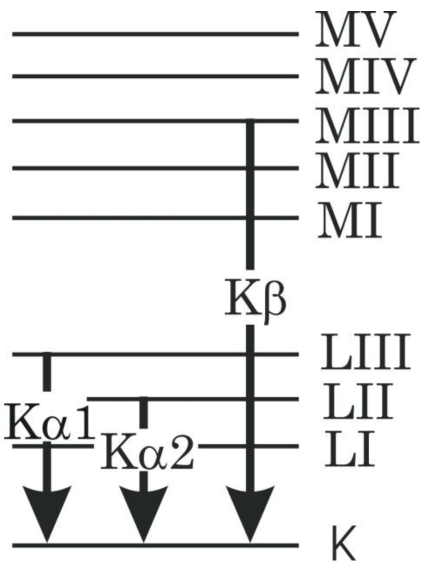
- Sealed X-ray tubes tend to operate at 1.8 to 3 kW.
- Rotating anode X-ray tubes produce much more flux because they operate at 9 to 18 kW.
  - A rotating anode spins the anode at 6000 rpm, helping to distribute heat over a larger area and therefore allowing the tube to be run at higher power without 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.

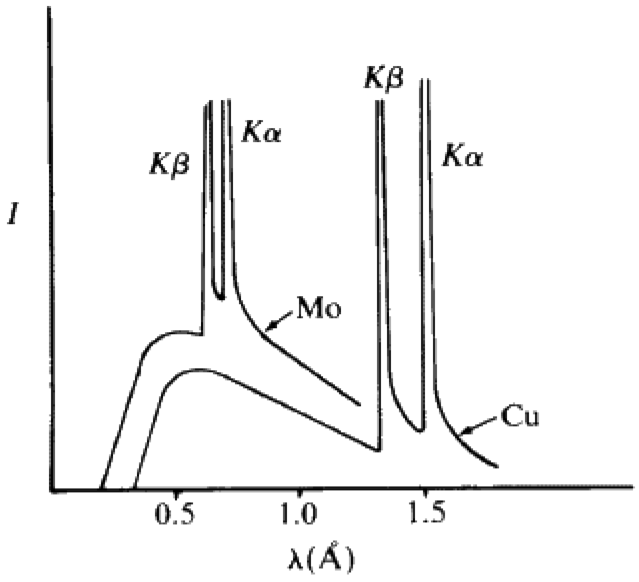


The wavelength of X rays is determined by the anode of the X-ray source

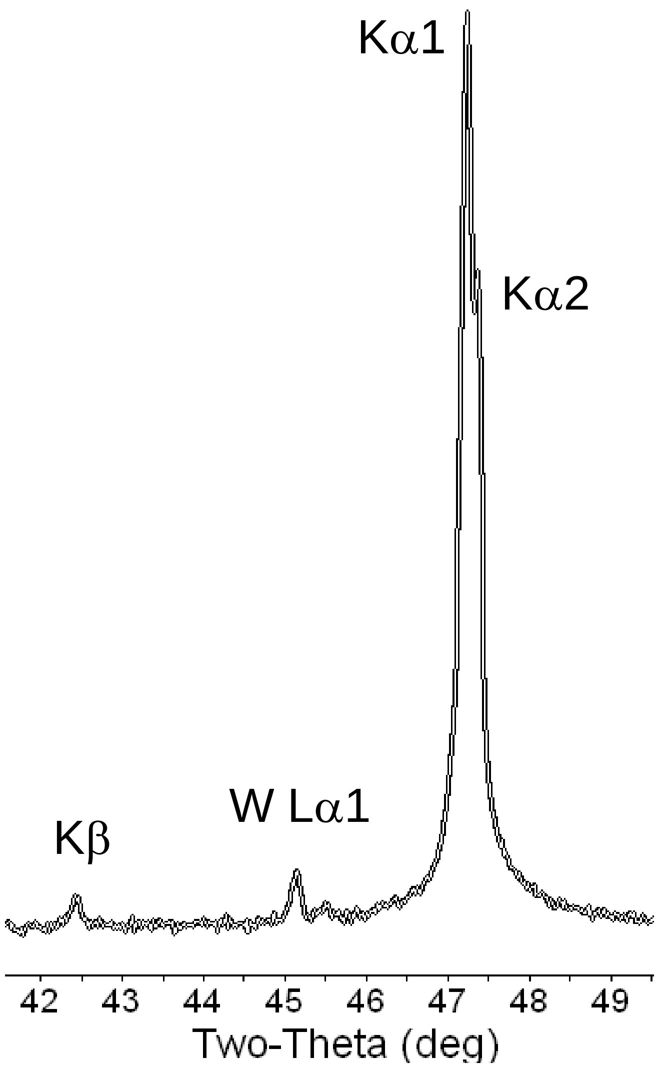
- Electrons from the filament strike the target anode, producing characteristic radiation via the photoelectric effect.
- The anode material determines the wavelengths of characteristic radiation.
- While we would prefer a monochromatic source, the X-ray beam actually consists of several characteristic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

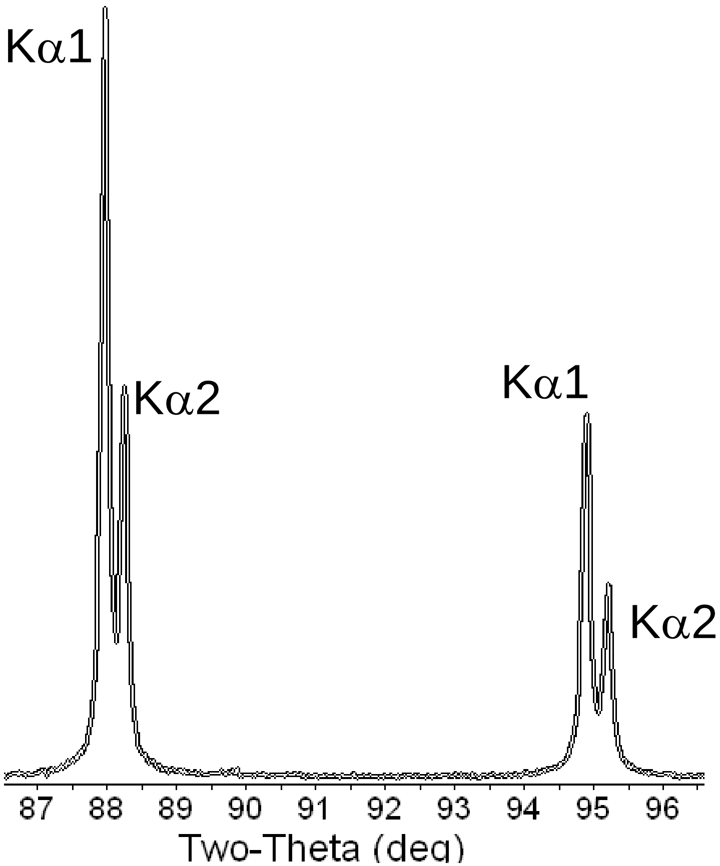






Spectral Contamination in Diffraction Patterns





- 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

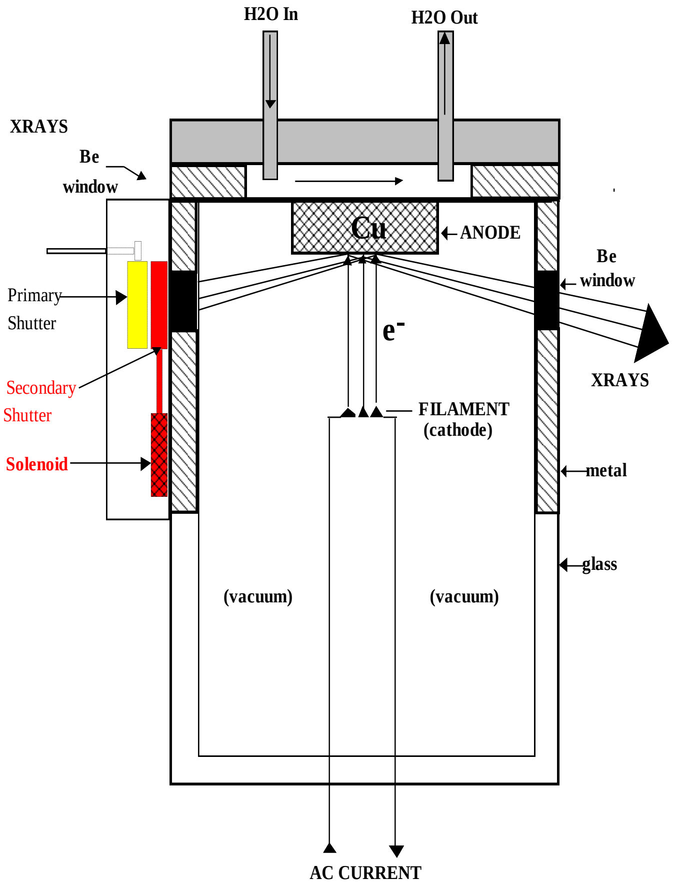
Wavelengths for X-Radiation are sometimes Updated

Copper Anodes	Bearden (1967)	Holzer et al. (1997)		Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu Kα1	1.54056Å	1.540598 Å		Co Kα1	1.788965Å	1.789010 Å
Cu Kα2	1.54439Å	1.544426 Å		Co Kα2	1.792850Å	1.792900 Å
Cu Kβ	1.39220Å	1.392250 Å		Co Kβ	1.62079Å	1.620830 Å
Molybdenum Anodes				Chromium Anodes		
Mo Kα1	0.709300Å	0.709319 Å		Cr Kα1	2.28970Å	2.289760 Å
Mo Kα2	0.713590Å	0.713609 Å		Cr Kα2	2.293606Å	2.293663 Å
Mo Kβ	0.632288Å	0.632305 Å		Cr Kβ	2.08487Å	2.084920 Å

- Often quoted values from Cullity (1956) and Bearden, *Rev. Mod. Phys.* **39** (1967) are incorrect.
  - Values from Bearden (1967) are reprinted in *international Tables for X-Ray Crystallography* and most XRD textbooks.
- Most recent values are from Hölzer et al. *Phys. Rev. A* **56** (1997)

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.



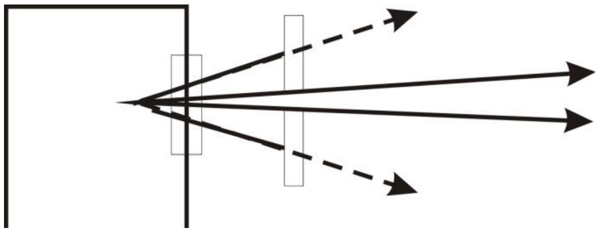
The X-ray beam produced by the X-ray tube is divergent. Incident-beam optics are used to limit this divergence

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

- X Rays from an X-ray tube are:
  - divergent
  - contain multiple characteristic wavelengths as well as Bremmsstrahlung radiation
- neither of these conditions suit our ability to use X rays for analysis
  - the divergence means that instead of a single incident angle q, 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

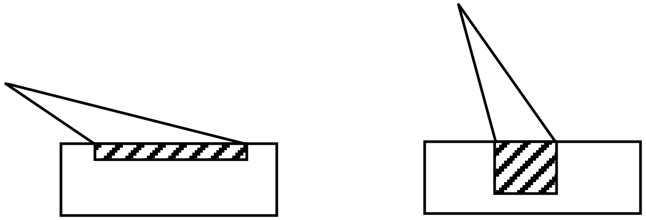
Divergence slits are used to limit the divergence of the incident X-ray beam

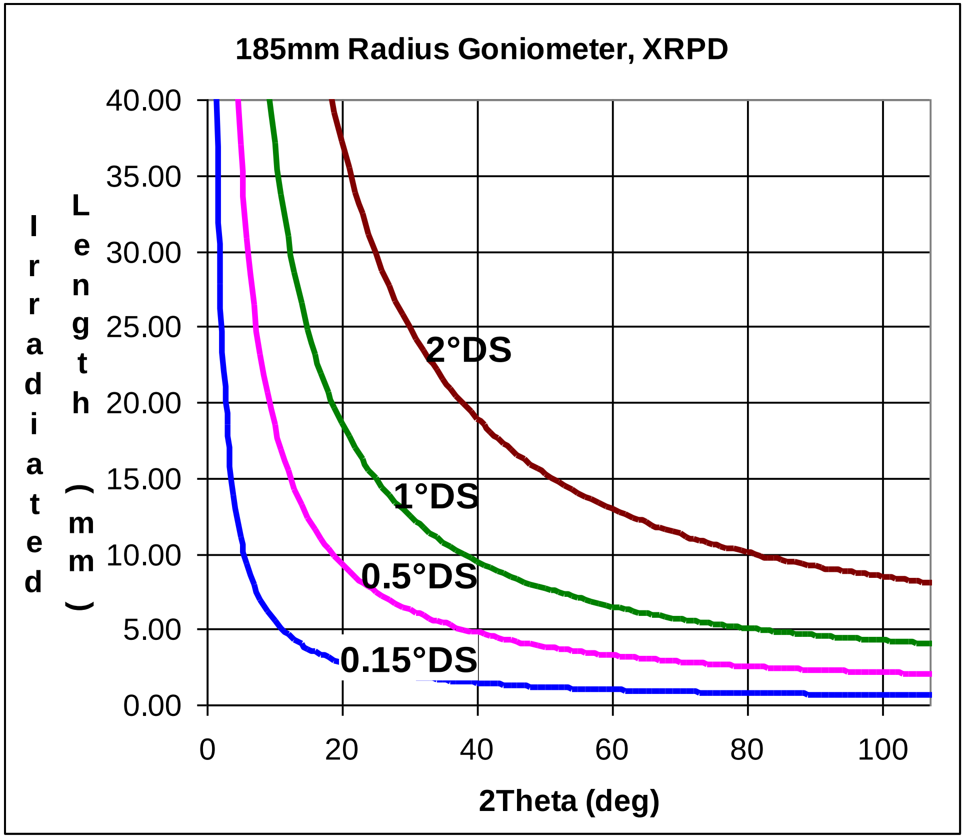
- The slits block X-rays that have too great divergence.
- The size of the divergence slit influences peak intensity and peak shapes.
- Narrow divergence slits:
  - reduce the intensity of the X-ray beam
  - reduce the length of the X-ray beam hitting the sample
  - produce sharper peaks
    - the instrumental 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.

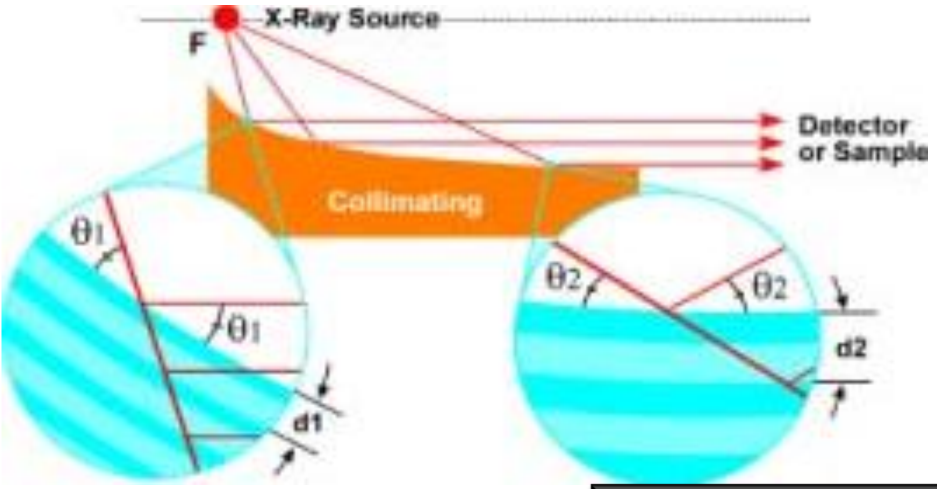
- The length of the incident beam is determined by the divergence slit, goniometer radius, and incident angle.
- This should be considered when choosing a divergence slits size:
  - if the divergence slit is too large, the beam may be significantly longer than your sample at low angles
  - if the slit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

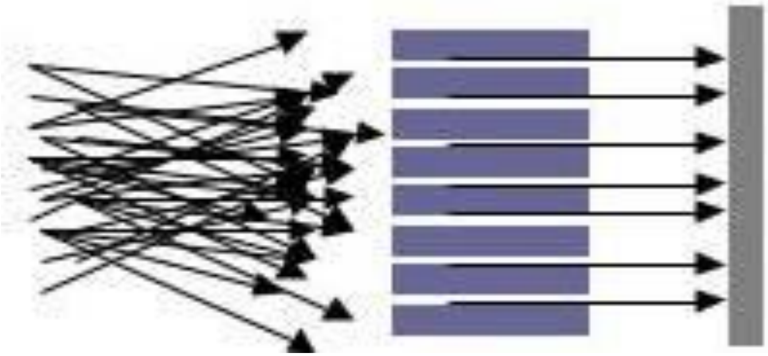




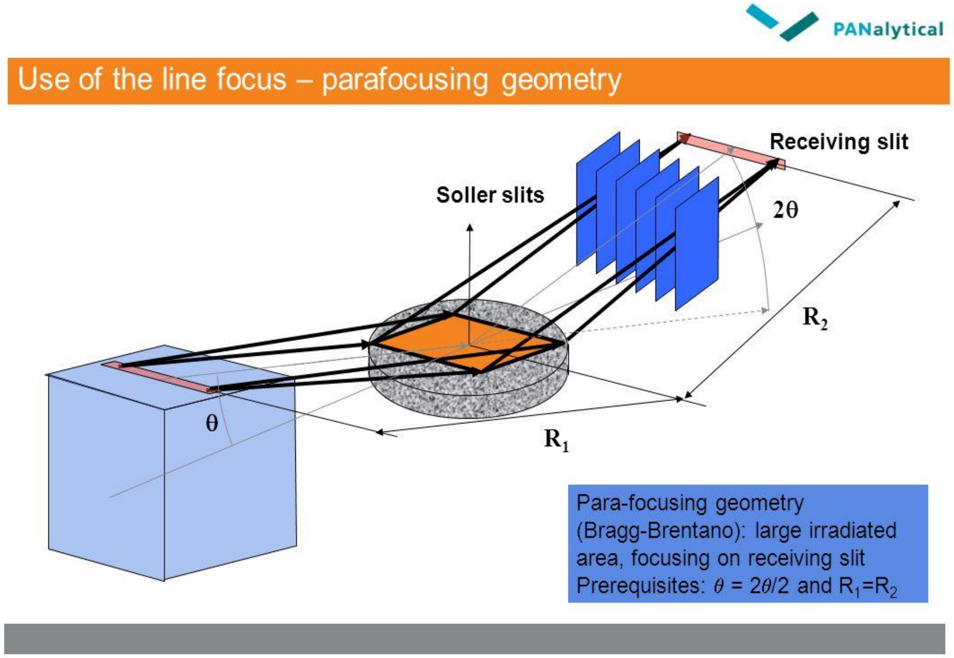
Other optics:

- 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
  - Kβ filters





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



Use of the line focus – parafocusing geometry

Para-focusing geometry (Bragg-Brentano): large irradiated area, focusing on receiving slit
Prerequisites: $\theta = 2\theta/2$ and $R_1 = R_2$

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

- Diffraction from a crystal monochromator can be used to select one wavelength of radiation and provide energy discrimination.
- An incident-beam monochromator might be used to select only Kα1 radiation for the tube source.
- A diffracted-beam monochromator, such as on the Rigaku RU300, may be used to remove fluoresced photons, Kβ, or W-contimination photons from reaching the detector.
  - Without the RSM slit, the monochromator removes ~75% of unwanted wavelengths of radiation.
  - When the RSM slit is used, over 99% of the unwanted wavelengths of radiation can be removed from the beam.

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
  - gas proportional (gas on wire; microgap anodes)
    - limited resolution, issues with deadtime and saturation
  - CCD
    - limited in size, expensive
  - solid state real-time multiple semiconductor strips
    - high speed with high resolution, robust

Applications include:

- XRD is a nondestructive technique
- To identify crystalline phases and orientation
- To determine structural properties:

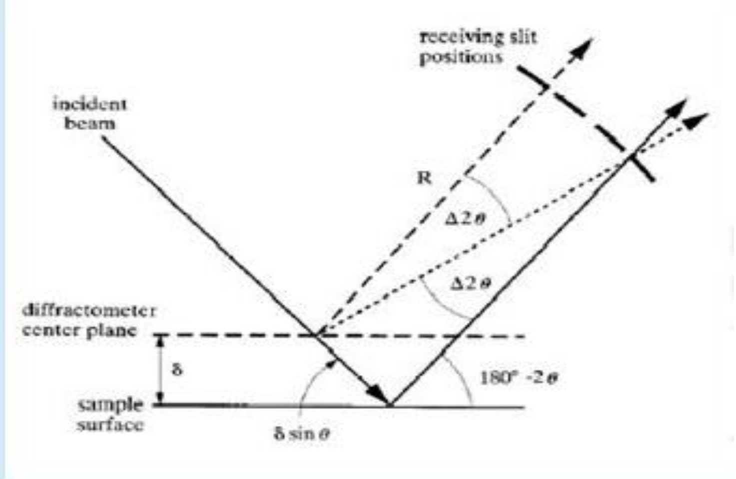
  Lattice parameters (10^{-4}Å), strain, grain size, expitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion
- To measure thickness of thin films and multi-layers*
- To determine atomic arrangement
- Detection limits: ~3% in a two phase mixture; can be ~0.1% with synchrotron radiation

  Spatial resolution: normally none

Instrumental Sources of Errors

- Sample Displacement
  - occurs when the sample is not on the focusing circle (or in the center of the goniometer circle)
  - The greatest source of error in most data
  - A systematic error:

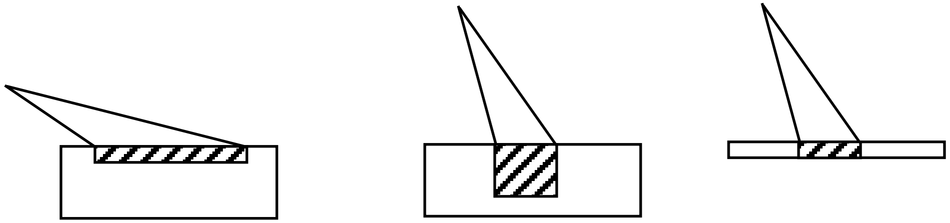
$$\Delta 2\theta = -\frac{2\delta\cos\theta}{R}(inradians)$$



    - δ is the amount of displacement, R is the goniometer radius.
    - at 28.4° 2theta, δ =0.006” will result in a peak shift of 0.08°
  - Can be minimized by using a zero background sample holder
  - Can be corrected by using an internal calibration standard
  - Can be analyzed and compensated for with many data analysis algorithms
    - For sample ID, simply remember that your peak positions may be shifted a little bit
  - Can be eliminated by using parallel-beam optics

Sample Transparency Error

- X Rays penetrate into your sample
  - the depth of penetration depends on:
    - the mass absorption coefficient of your sample
    - the incident angle of the X-ray beam
- This produces errors because not all X rays are diffracting from the same location
  - Angular errors and peak asymmetry
  - Greatest for organic and low absorbing (low atomic number) samples
- Can be eliminated by using parallel-beam optics or reduced by using a thin sample

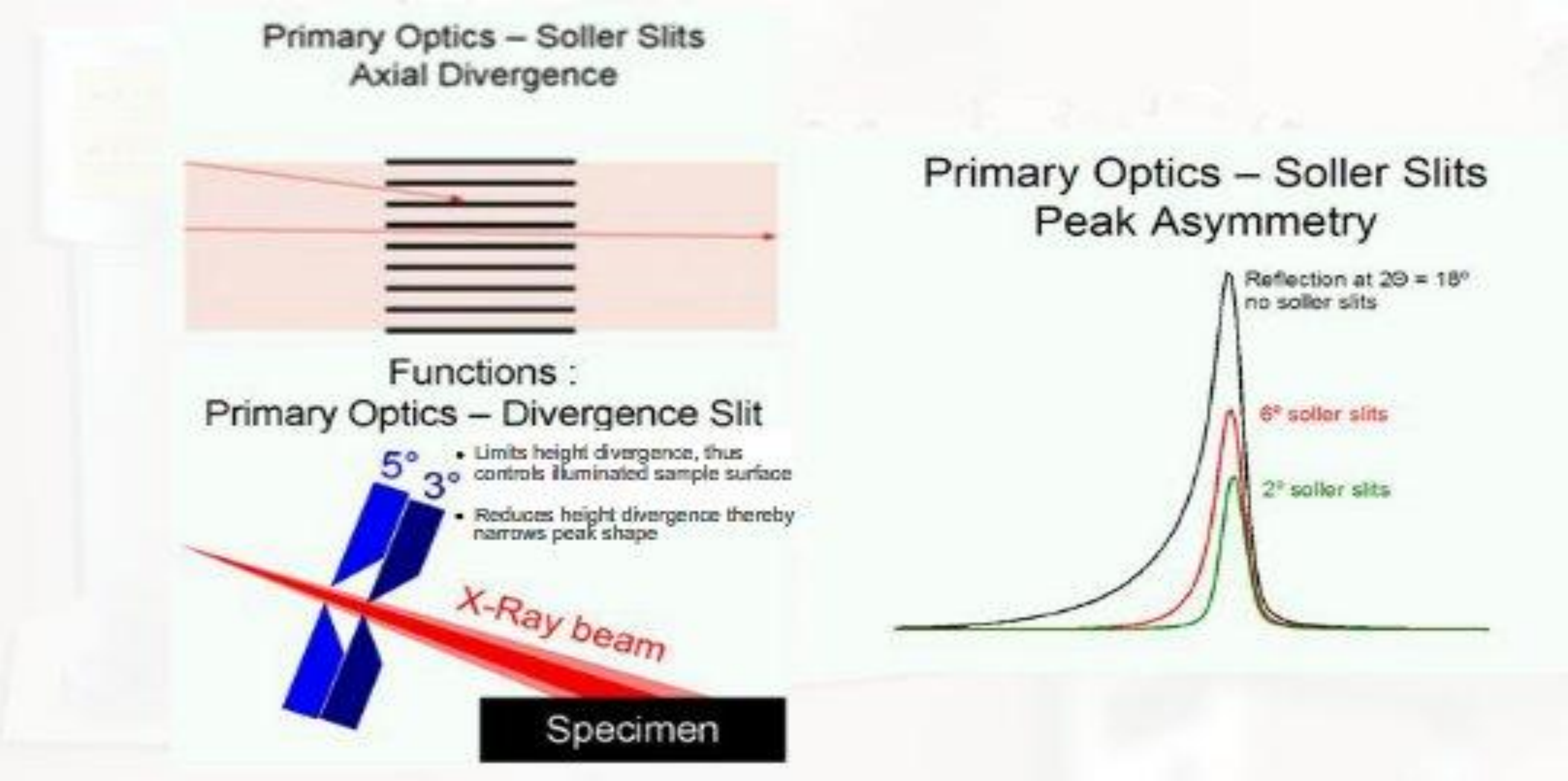


$$\Delta 2\theta = \frac{\sin 2\theta}{2\mu R}$$

μ is the linear mass absorption coefficient for a specific sample

Other sources of error

- **Axial divergence**
  - Due to divergence of the X-ray beam in plane with the sample
  - creates asymmetric broadening of the peak toward low 2theta angles
  - Creates peak shift: negative below 90° 2theta and positive above 90°
  - Reduced by Soller slits and/or capillary lenses



Primary Optics – Soller Slits
Axial Divergence

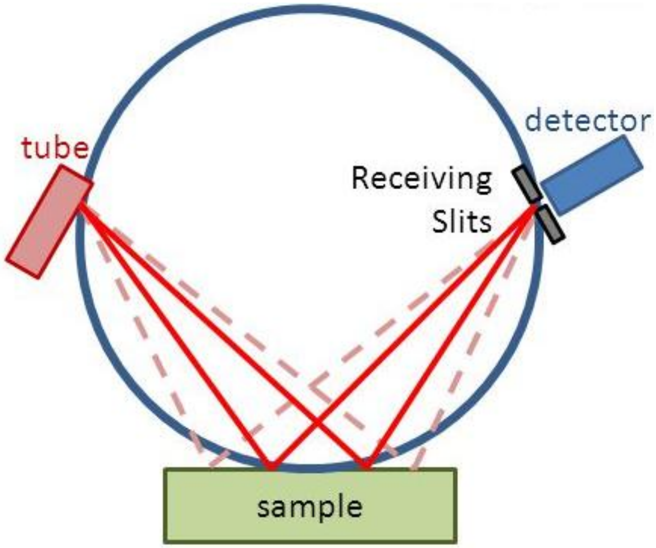
Functions :
Primary Optics – Divergence Slit

- Limits height divergence, thus controls illuminated sample surface
- Reduces height divergence thereby narrows peak shape

Primary Optics – Soller Slits
Peak Asymmetry

Other sources of error

- Flat specimen error
  - The entire surface of a flat specimen cannot lie on the focusing circle
  - Creates asymmetric broadening toward low 2theta angles
  - Reduced by small divergence slits; eliminated by parallel-beam optics
- Poor counting statistics
  - The sample is not made up of thousands of randomly oriented crystallites, as assumed by most analysis techniques
  - The sample might be textured or have preferred orientation
    - Creates a systematic error in peak intensities
    - Some peaks might be entirely absent
  - The sample might have large grain sizes
    - Produces ‘random’ peak intensities and/or spotty diffraction peaks



Techniques in the XRD SEF

- X-ray Powder Diffraction (XRPD)
- Single Crystal Diffraction (SCD)
- Back-reflection Laue Diffraction
- Grazing Incidence Angle Diffraction (GIXD)
- X-ray Reflectivity (XRR)
- Small Angle X-ray Scattering (SAXS)

X-Ray Powder Diffraction (XRPD)

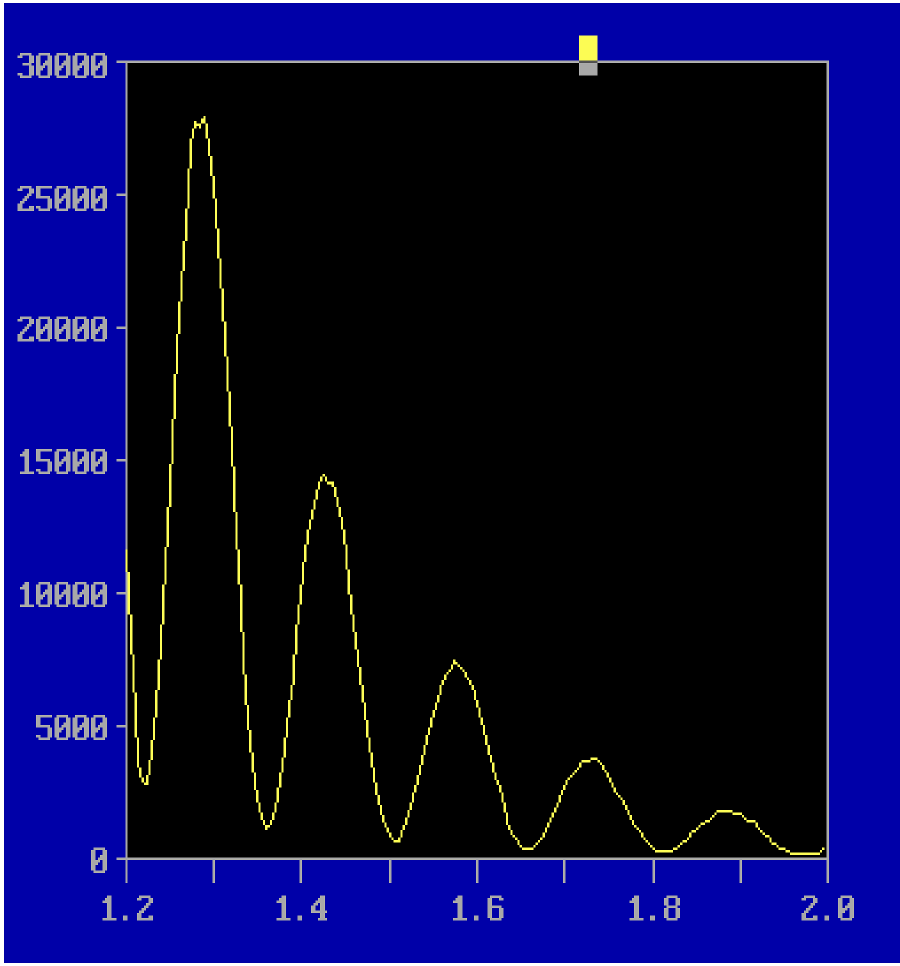
- More appropriately called polycrystalline X-ray diffraction, because it can also be used for sintered samples, metal foils, coatings and films, finished parts, etc.
- Used to determine:
  - phase composition (commonly called phase ID)- what phases are present?
  - quantitative phase analysis- how much of each phase is present?
  - unit cell lattice parameters
  - crystal structure
  - average crystallite size of nanocrystalline samples
  - crystallite microstrain
  - texture
  - residual stress (really residual strain)
  - in-situ diffraction (from 11 K to 1200C in air, vacuum, or inert gas)

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

X-Ray Reflectivity (XRR)

- A glancing, but varying, incident angle, combined with a matching detector angle collects the X rays reflected from the samples surface
- Interference fringes in the reflected signal can be used to determine:
  - thickness of thin film layers
  - density and composition of thin film layers
  - roughness of films and interfaces



Back Reflection Laue

- Used to determine crystal orientation
- The beam is illuminated with ‘white’ radiation
  - Use filters to remove the characteristic radiation wavelengths from the X-ray source
  - The Bremmsstrahlung radiation is left
    - Weak radiation spread over a range of wavelengths
- The single crystal sample diffracts according to Bragg’s Law
  - Instead of scanning the angle theta to make multiple crystallographic planes diffract, we are effectively ‘scanning’ the wavelength
  - Different planes diffract different wavelengths in the X-ray beam, producing a series of diffraction spots

Small Angle X-ray Scattering (SAXS)

- Highly collimated beam, combined with a long distance between the sample and the detector, allow sensitive measurements of the X-rays that are just barely scattered by the sample (scattering angle <6°)
- The length scale of d (Å) is inversely proportional to the scattering angle: therefore, small angles represented larger features in the samples
- Can resolve features of a size as large as 200 nm
  - Resolve microstructural features, as well as crystallographic
- Used to determine:
  - crystallinity of polymers, organic molecules (proteins, etc.) in solution,
  - structural information on the nanometer to submicrometer length scale
  - ordering on the meso- and nano- length scales of self-assembled molecules and/or pores
  - dispersion of crystallites in a matrix

Single Crystal Diffraction (SCD)

- Used to determine:
  - crystal structure
  - orientation
  - degree of crystalline perfection/imperfections
- Sample is illuminated with monochromatic radiation
  - The sample axis, phi, and the goniometer axes omega and 2theta are rotated to capture diffraction spots from at least one hemisphere
  - Easier to index and solve the crystal structure because it diffraction peak is uniquely resolved

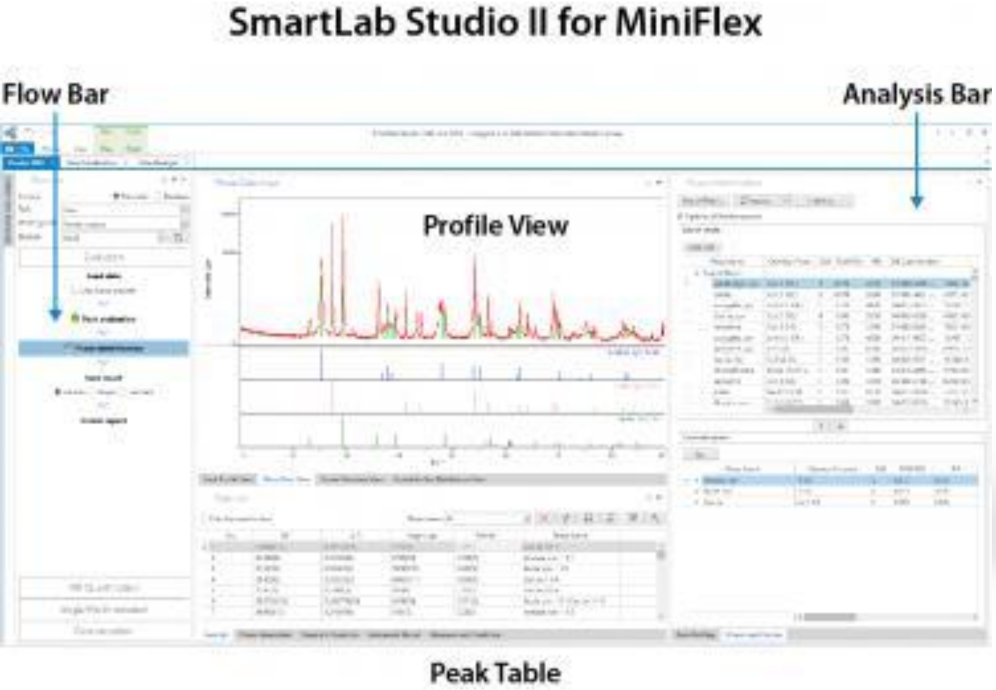
Instruments in the XRD SEF

- Rigaku RU300 Powder Diffractometers
- Bruker D8 with GADDS
- Bede D3
- PANalytical X'Pert Pro
- Back-reflection Laue (polaroid)
- SAXS
- Bruker Smart APEX

Rigaku RU300 Powder Diffractometer

Qualitative and quantitative phase analysis of poly-crystalline material

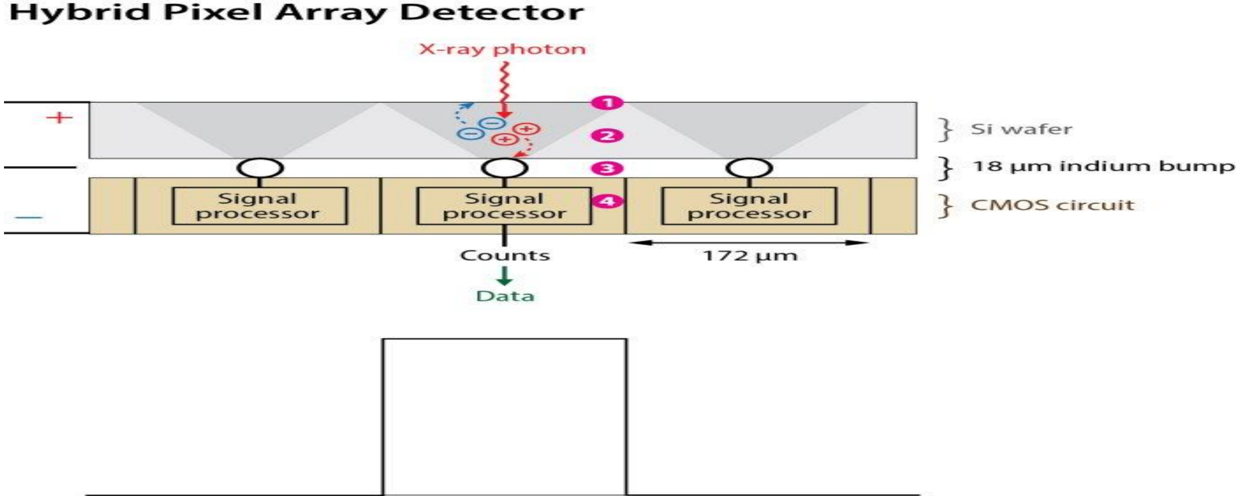
- Fast, precision XRPD using theta/2theta motion
- High-power (18kW) rotating anode source supplies high X ray flux
- Two horizontal-circle powder diffractometers
  - Horizontal circle facilitates precision movement of goniometer
  - Disadvantage: sample sits vertical, can easily fall out of sample holder
  - The 185mm Bragg-Brentano diffractometer is optimized for high intensity for fast data collection.
  - The 250mm Bragg-Brentano diffractometer is optimized for high resolution at slightly slower data collection speeds.
- Sample size is generally 20mm x 10mm x 0.3mm, though we have a variety of sample holders and mounting procedures to accommodate varied sample geometries.
- Special accessories include:
  - Attachment for GIXD of thin films
  - Inert atmosphere sample chamber for air/moisture sensitive samples
  - Zero background sample holders for high accuracy measurements from small quantities of powder
- Requires special considerations if your sample is a single crystal or a thin film on a single crystal substrate



MiniFlex

- can determine: crystalline phase identification (phase ID) and quantification, percent (%) crystallinity, crystallite size and strain, lattice parameter refinement, Rietveld refinement, and molecular structure.
- delivers speed and sensitivity through innovative technology advances, including the HyPix-400 MF 2D hybrid pixel array detector (HPAD) together with an available 600 W X-ray source and new 8-position automatic sample changer.

- **Hybrid pixel array detector HPAD:**
  - direct photon counting detector enables high-speed, low-noise data collection and may be operated in 0D and 1D modes for conventional XRD analysis and 2D mode for samples with coarse grain size and/or preferred orientation.
- **Advanced SmartLab Studio II powder diffraction software:**
  - Each MiniFlex comes standard with the latest version of SmartLab Studio II, Rigaku's full-function powder diffraction analysis package. The latest version of SmartLab Studio II offers important new functionality; including a fundamental parameter method (FP) for more accurate peak calculation, phase identification using the Crystallography Open Database (COD), and a wizard for *ab inito* crystal structure analysis.



Bruker D8 Diffractometer with GADDS

- Ideal for texture (pole figure) and stress measurements, as well as traditional XRPD and limited SCD and GIXD.
- Two-dimensional area detector (GADDS) permits simultaneous collection of diffraction data over a 2theta and chi (tilt) range as large as 30°
- Eularian cradle facilitates large range of tilts and rotations of the sample
- A selectable collimator, which conditions the X-ray beam to a spot 0.5mm to 0.05mm diameter, combined with a motorized xy stage, permits microdiffraction for multiple select areas of a sample or mapping across a sample's surface.
- Samples can include thin films on wafers or dense pieces up to 6" in diameter (maximum thickness of 3 mm), powders in top-loaded sample holders or in capillaries, dense pieces up to 60mm x 50mm x 15mm (and maybe even larger).
- Accessories include a furnace for heating a sample up to 900°C in air, vacuum, or inert gas (maximum sample size of 20mm x 20mm x 1mm)

- Dynamic Beam Optimization (DBO) provides best in class powder diffraction data by setting new benchmarks in terms of counting statistics and peak-to-background ratio, all without the need for manual instrument reconfiguration.

-The high-speed energy-dispersive LYNXEYE XE-T detector uniquely combines fast data collection with unprecedented filtering of fluorescence and Kβ radiation. Its proprietary Variable Active Detector Window and the Motorized Anti-Scatter Screen (MASS) enable data collection from lowest 2Th angles without parasitic low-angle background scattering, in particular air scattering. The fully automated MASS retraction avoids beam cropping, even in combination with continuously variable slits that provide superb counting statistics over the whole angular range.

Bruker D8 Triple Axis Diffractometer

- For GIXD and for analysis of rocking curves, lattice mismatch, and reciprocal space maps of thin films and semiconductors
  - This instrument is typically used to measure the perfection or imperfection of the crystal lattice in thin films (i.e. rocking curves), the misalignment between film and substrate in epitaxial films, and reciprocal space mapping.
- High precision Bruker D8 triple axis goniometer
- Beam-conditioning analyzer crystals remove Kα2 radiation and provide extremely high resolution.

Bruker Small Angle Diffractometer

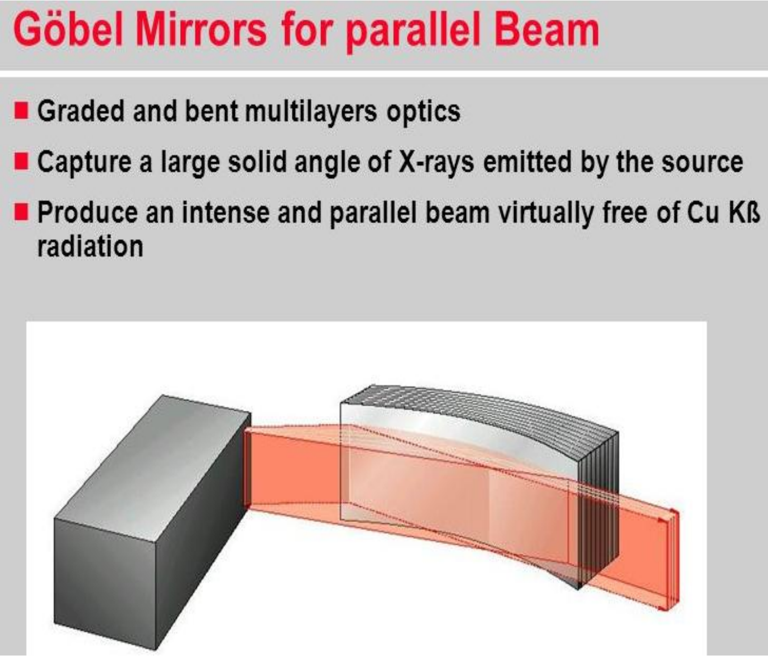
- Used for SAXS
- high-power rotating anode X-ray source
- two-dimensional detector for real-time data collection
- A long X-ray beam path allows this instrument to measure X-rays that are only slightly scattered away from the incident beam. The two-dimensional detector allows entire Debye rings to be collected and observed in real time. The current beam path length of 60.4 cm allows the resolution of crystallographic and structural features on a length scale from 1.8nm to 40nm (1.8nm is near the maximum resolvable length scale for XRPD in our other systems).
- A heater is available to heat the sample up to 200°C.

Bruker Single Crystal Diffractometer

- Designed primarily to determine the crystal structure of single crystals
  - can also be used for determining crystal orientation
- This diffractometer uses a two-dimensional CCD detector for fast, high precision transmission diffraction through small single crystals.
- A variety of goniometer heads fit on the fix chi stage
- A cryostat is available to cool samples down to 100 K in air, which permits more precise determination of atom positions in large organic crystals.

PANalytical X'Pert Pro Multipurpose Diffractometer

- Prefix optics allow the configuration to be quickly changed to accommodate a wide variety of data collection strategies.
- This diffractometer can be used to collect XRPD, GIXD, XRR, residual stress, and texture data.
- A vertical-circle theta-theta goniometer is used so that the sample always lies flat and does not move.
  - Sample sizes may be as large as 60mm diameter by 3-12mm thick, though a more typical sample size is 10-20mm diameter.
- Data collection modes can be changed between:
  - high-speed high-resolution divergent beam diffraction
    - Programmable divergence slits can maintain a constant irradiated area on sample surface
  - parallel beam diffraction using incident Gobel mirror and receiving-side parallel plate collimator
    - eliminates errors due to irregular sample surfaces, sample displacement, and defocusing during glancing angle measurements

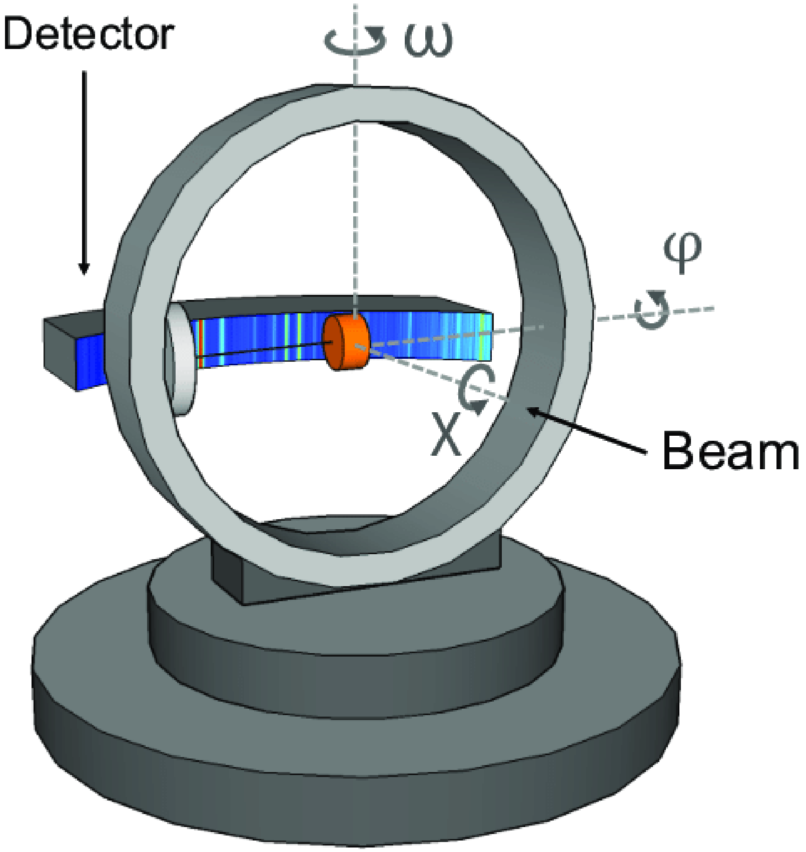


Göbel Mirrors for parallel Beam

- Graded and bent multilayers optics
- Capture a large solid angle of X-rays emitted by the source
- Produce an intense and parallel beam virtually free of Cu Kß radiation

PANalytical X'Pert Pro Multipurpose Diffractometer

- A variety of sample stages include:
  - 15 specimen automatic sample changer
  - open Eulerian cradle with automated z-translation as well as phi and psi rotation for texture, reflectivity, and residual stress measurements
  - furnace for heating a sample to 1200°C in air, vacuum, or controlled atmosphere
  - a cryostat for cooling a sample to 11 K in vacuum



Available Software

- MDI Jade
  - phase ID
  - indexing and unit cell refinement
  - RIR quantitative phase analysis
  - residual stress
  - nanocrystallite size and strain
  - calculated diffraction patterns

Available Software

- PANalytical HighScore Plus
  - whole pattern fitting for
    - unit cell refinement
    - nanocrystallite size and strain
    - quantitative phase analysis
  - indexing
  - Rietveld refinement of crystal structures
  - cluster analysis

Available Software

- PANalytical Stress- residual stress analysis
- PANalytical Texture- pole figure mapping of texture
- PANalytical Reflectivity- reflectivity from multilayer thin films
- Bruker Multex Area- pole figure mapping of texture

Available Free Software

- GSAS- Rietveld refinement of crystal structures
- FullProf- Rietveld refinement of crystal structures
- Rietan- Rietveld refinement of crystal structures

- PowderCell- crystal visualization and simulated diffraction patterns
- JCryst- stereograms

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