Introduction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions

X-ray diffraction is important for:

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

X-ray Diffractometer

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

The first X-ray

X-Ray Powder Diffraction (XRPD)

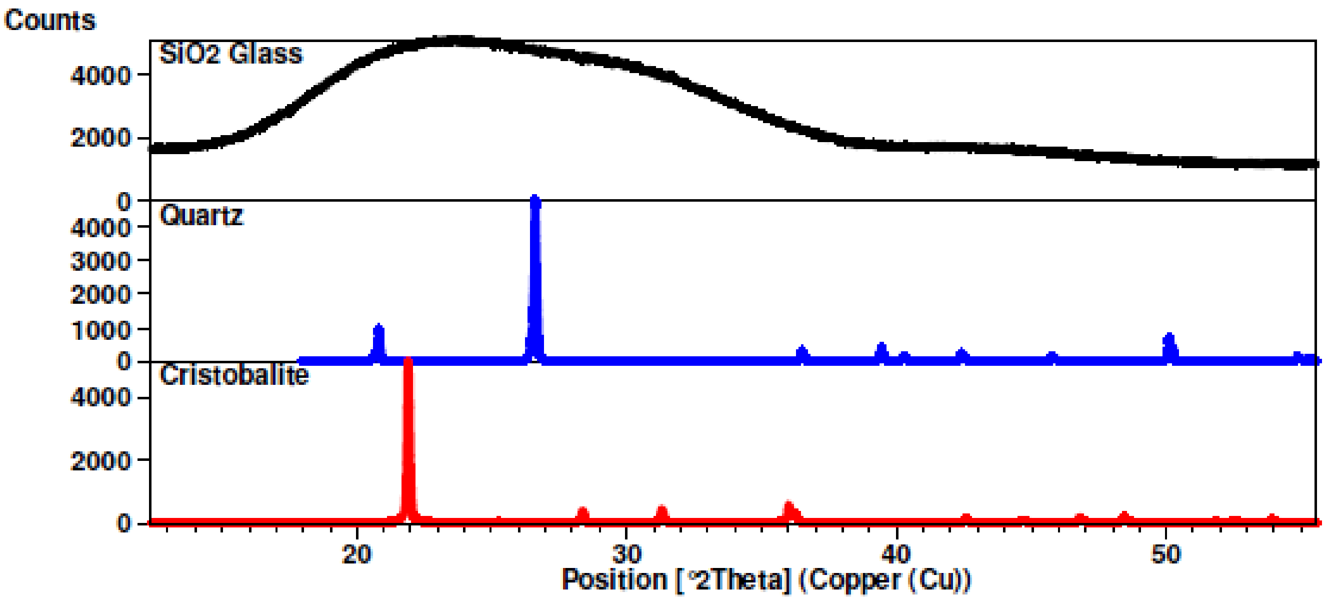
- More appropriately called polycrystalline X-ray diffraction, because it can also be used for sintered samples, metal foils, coatings and films, finished parts, etc.
- Used to determine:
  - phase composition (commonly called phase ID)- what phases are present?
  - quantitative phase analysis- how much of each phase is present?
  - unit cell lattice parameters
  - crystal structure
  - average crystallite size of nanocrystalline samples
  - crystallite microstrain

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

- The electrons in an 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 and thus can diffract light.
- The wavelength of X rays are similar to the distance between atoms.
- **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

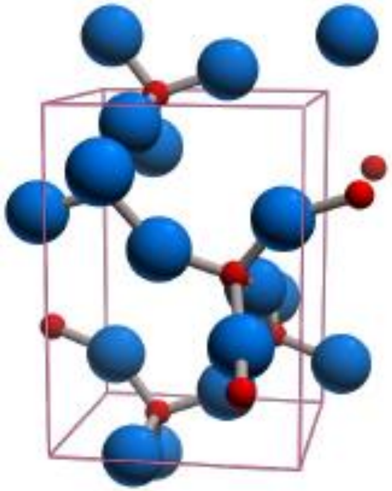
The figure below compares the X-ray diffraction patterns from 3 different forms of SiO_2



- These three phases of SiO_2 are chemically identical
- Quartz and cristobalite have two different crystal structures
  - The Si and O atoms are arranged differently, but both have structures with 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 peaks

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

Quartz



Cristobalite

- The crystal structure describes the atomic arrangement of a material.

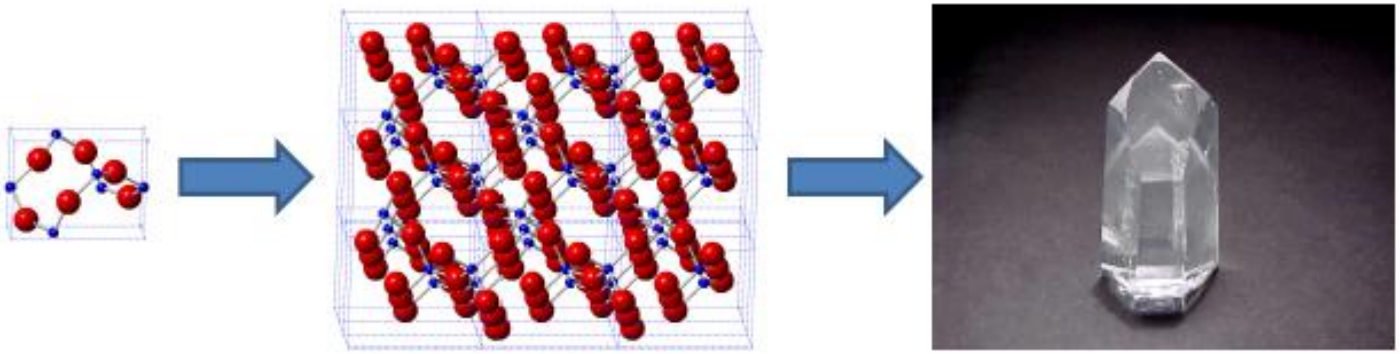
- When the atoms are arranged differently, a different diffraction pattern is produced (ie quartz vs cristobalite)

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

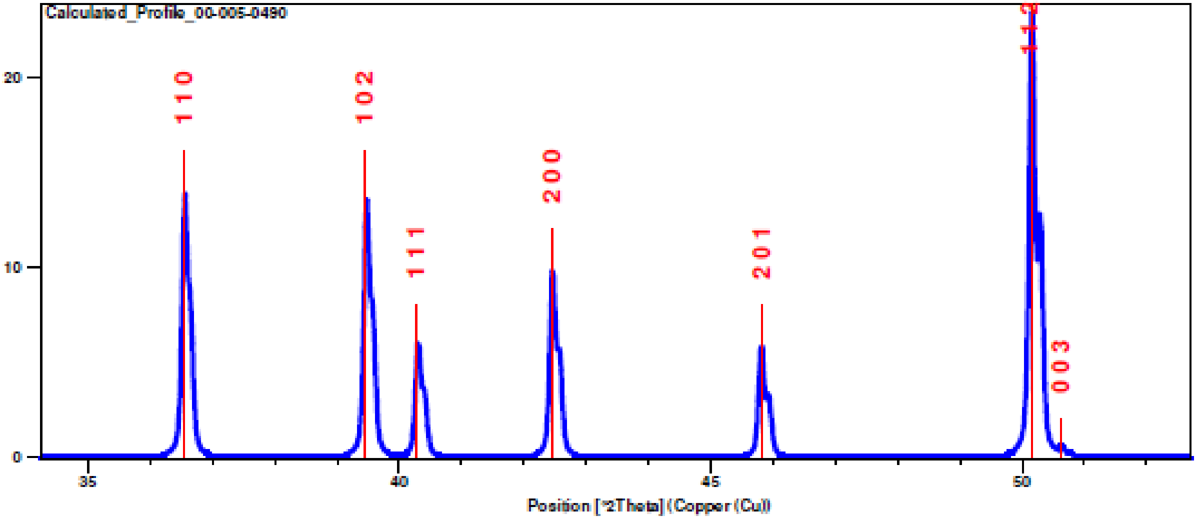
- The unit cell is the basic repeating unit that defines the crystal structure.
  - The unit cell contains the maximum symmetry that uniquely defines the crystal structure.
  - The unit cell might contain more than one molecule:
    - for example, the quartz unit cell contains 3 complete molecules of 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

Crystal System: hexagonal
Lattice Parameters:
4.9134 x 4.9134 x 5.4052 Å
(90 x 90 x 120°)

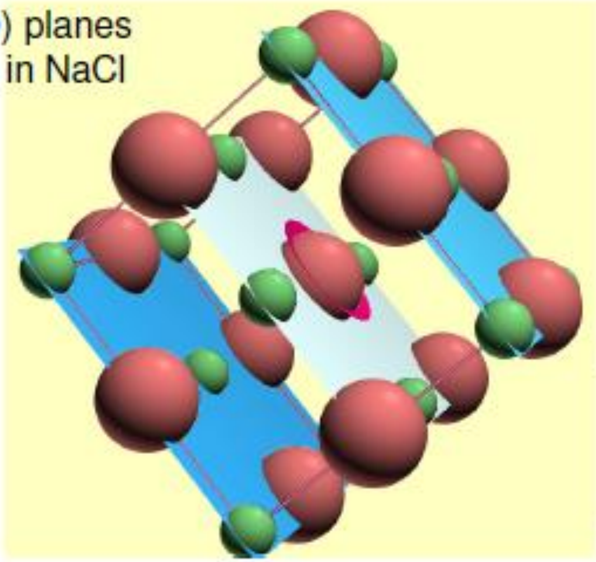


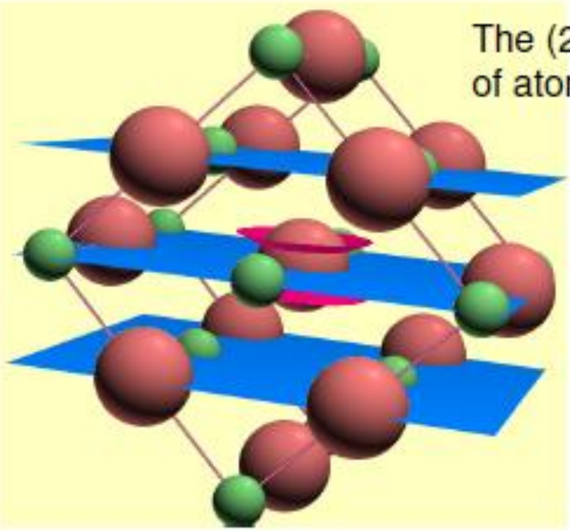
Diffraction peaks are associated with planes of atoms



- Miller indices (hkl) are used to identify 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

Parallel **planes of atoms** intersecting the unit cell define directions and distances in the crystal.


The (200) planes of atoms in NaCl


The (220) planes of atoms in NaCl

- Some planes may be equivalent because of symmetry
  - In a cubic crystal, (100) (010) and (001) are equivalent
  - They are the family of planes {100}

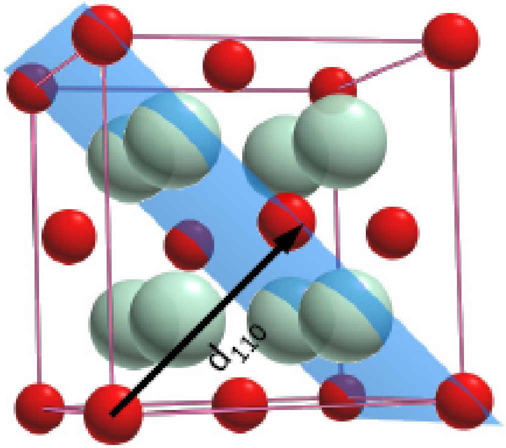
The intensity of the diffraction peaks are determined by the arrangement of atoms in the entire crystal

- 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 position of the diffraction peaks are determined by the distance between parallel planes of atoms.

Bragg's Law

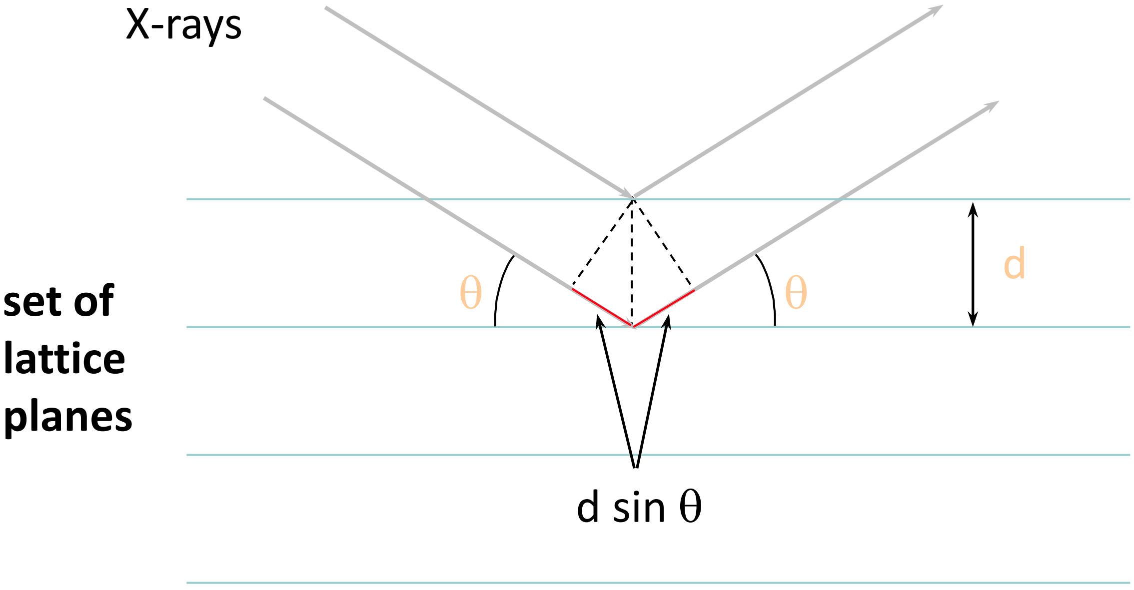
$$\lambda = 2d_{hkl} \sin\theta$$



- Bragg's law calculates the angle where constructive interference from X-rays scattered by parallel planes of atoms will produce a diffraction peak.
  - 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.

Braggs' law

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

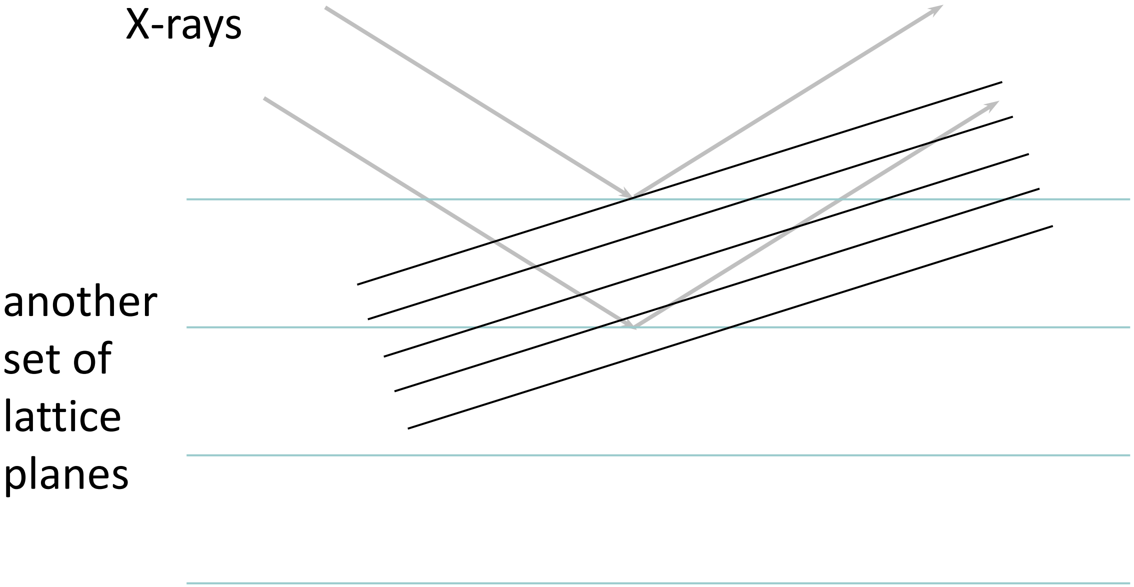


set of lattice planes

From this set of planes, only get reflection at one angle - θ

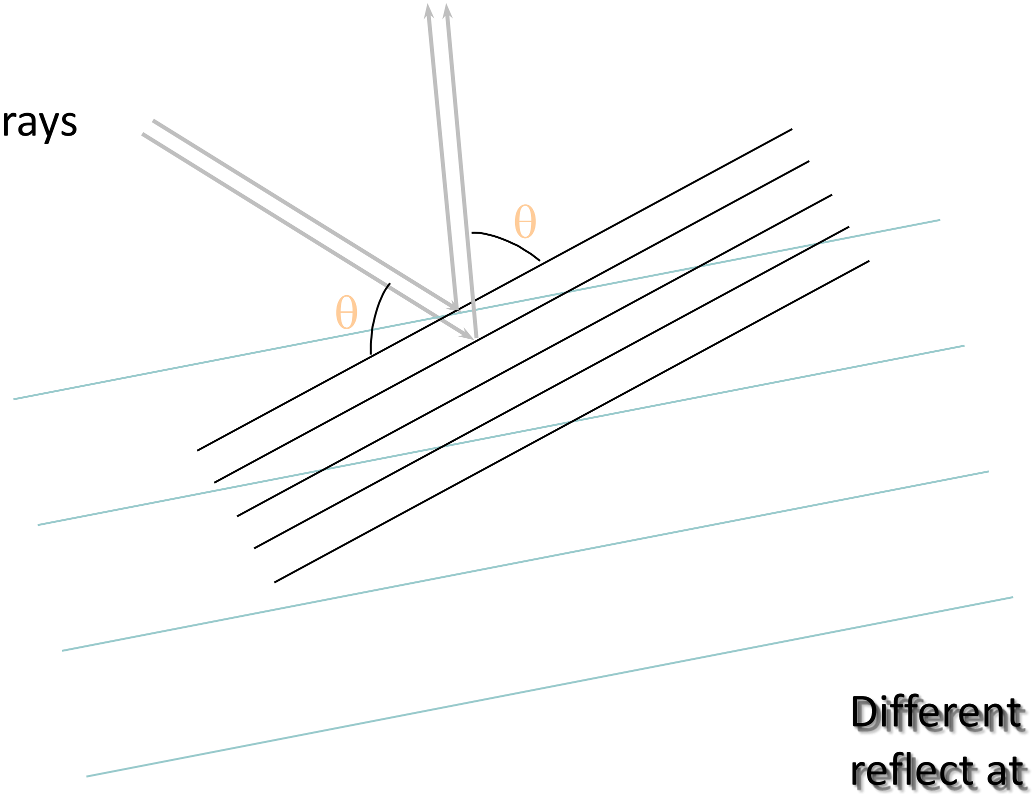
Braggs' law

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



Braggs' law

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



X-rays

another
set of
lattice
planes

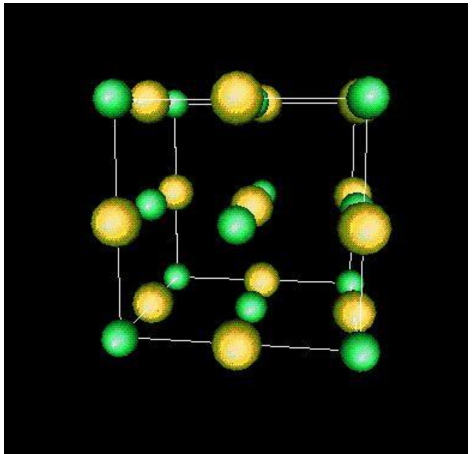
Different sets of planes
reflect at different θ angles

As d —> small,
θ —> large (λ is constant)

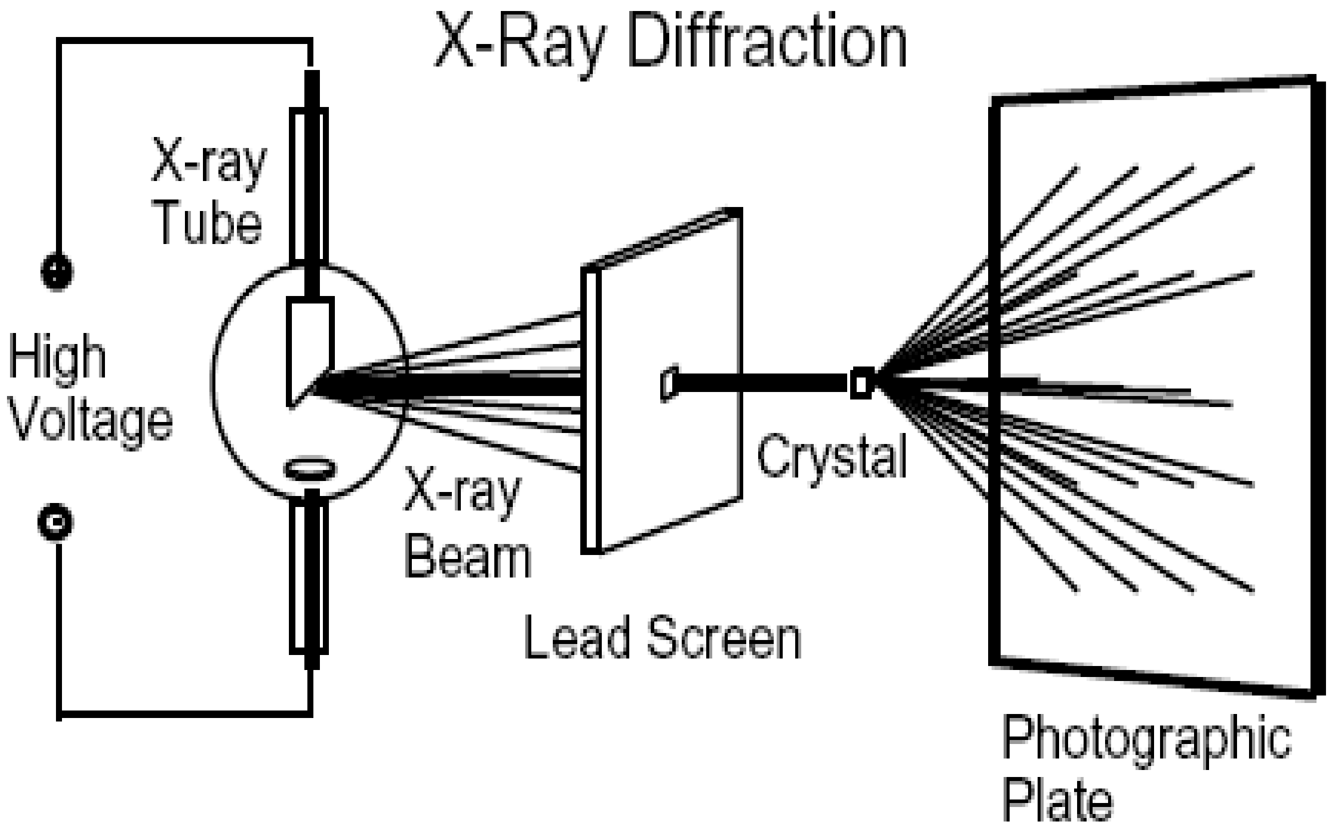
How Diffraction Works

- 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

NaCl



How Diffraction Works: Schematic



X-rays are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated. Electrons are usually used for this purpose, the radiation being produced in an x-ray tube which contains a source of electrons and two metal electrodes. The high voltage maintained across these electrodes, some tens of thousands of volts, rapidly draws the electrons to the anode, or target, which they strike with very high velocity. X-rays are produced at the point of impact and radiate in all directions

How Diffraction Works: Schematic

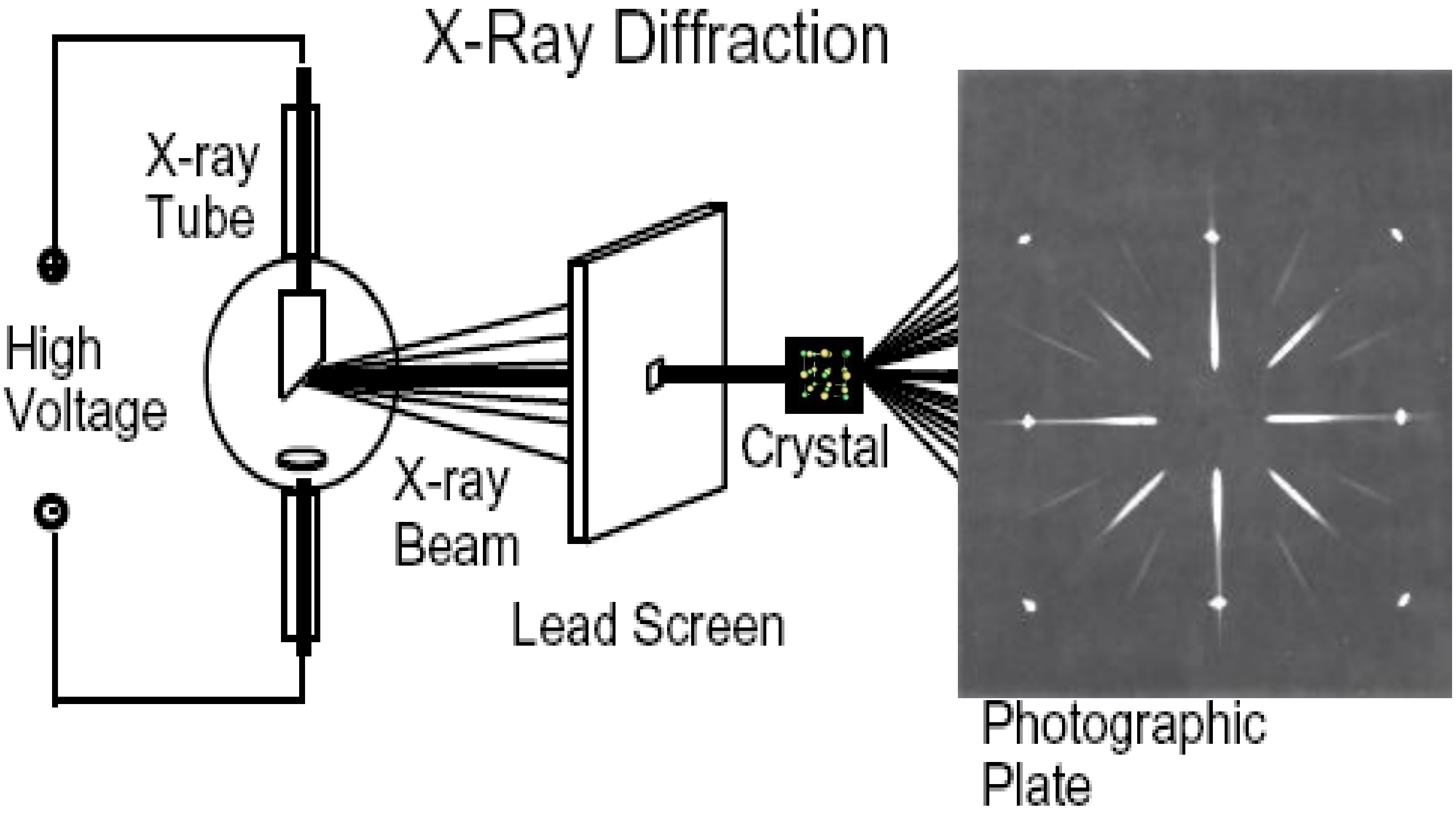
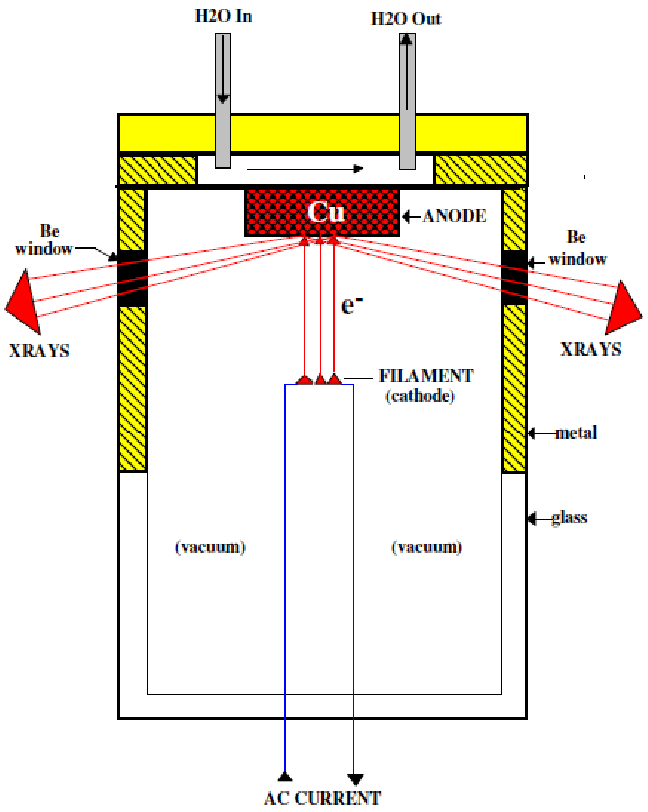


Figure 2. A schematic of X-ray diffraction.

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

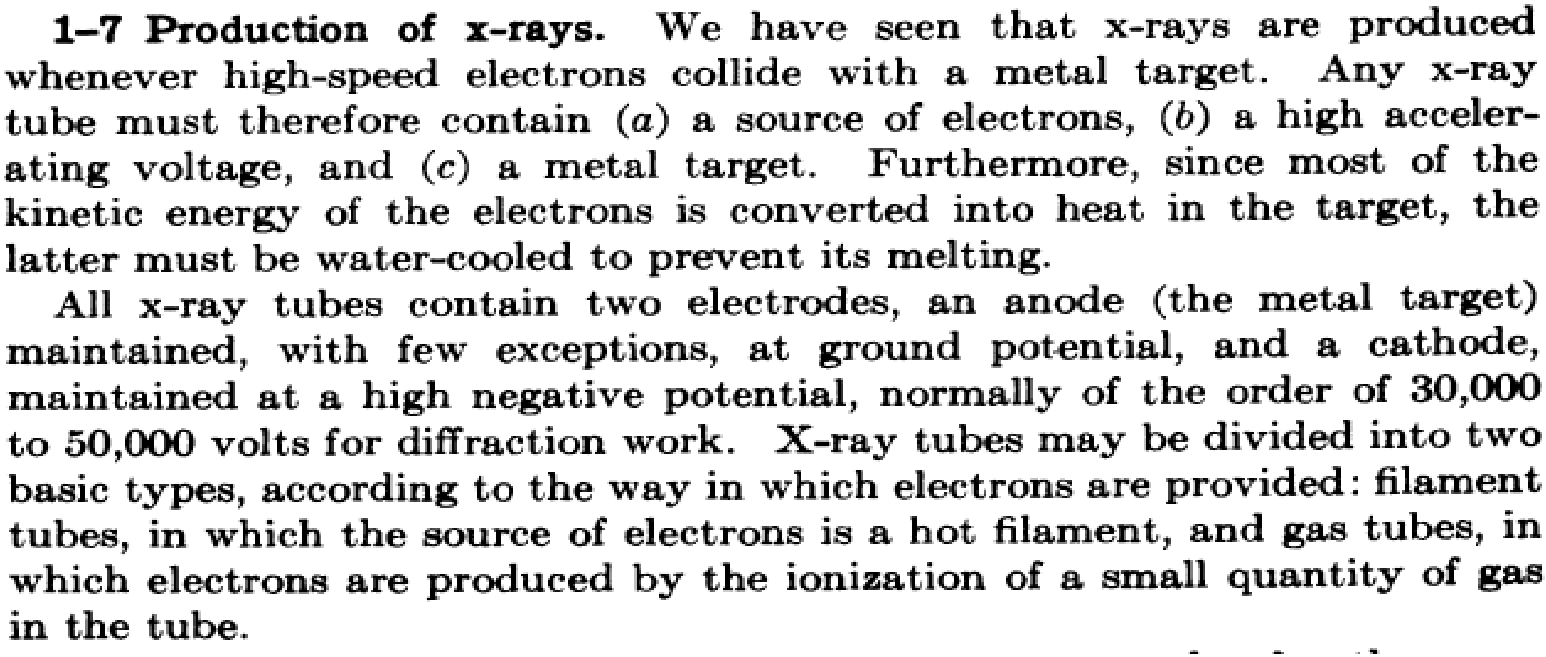
- Sealed X-ray tubes tend to operate at 1.8 to 3 kW.
- Rotating anode X-ray tubes produce much more flux because they operate at 9 to 18 kW.
  - A rotating anode spins the anode at 6000 rpm, helping to distribute heat over a larger area and therefore allowing the tube to be run at higher power without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



- Electrons from the filament strike the target anode, producing characteristic radiation via the photoelectric effect.

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



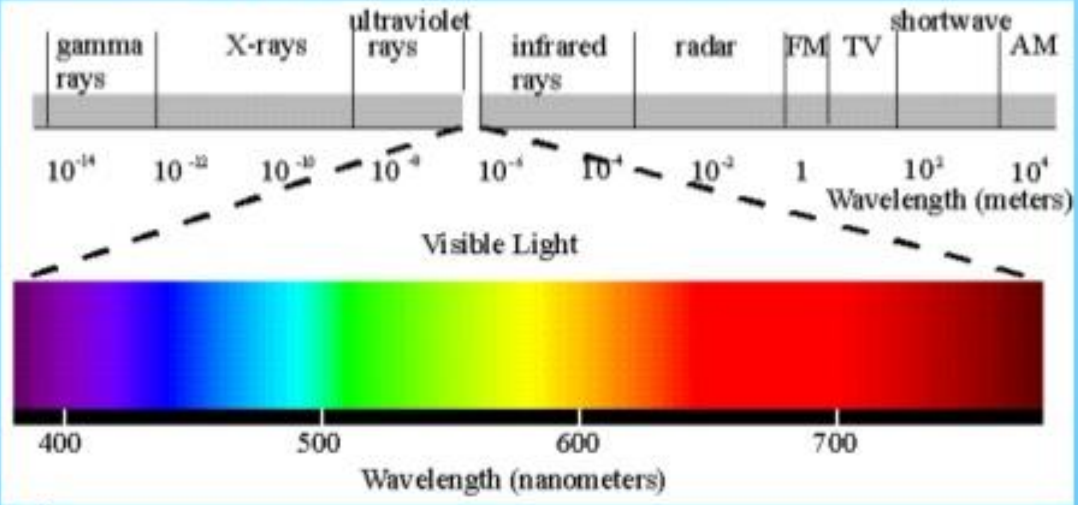
1–7 Production of x-rays. We have seen that x-rays are produced whenever high-speed electrons collide with a metal target. Any x-ray tube must therefore contain (*a*) a source of electrons, (*b*) a high accelerating voltage, and (*c*) a metal target. Furthermore, since most of the kinetic energy of the electrons is converted into heat in the target, the latter must be water-cooled to prevent its melting.

All x-ray tubes contain two electrodes, an anode (the metal target) maintained, with few exceptions, at ground potential, and a cathode, maintained at a high negative potential, normally of the order of 30,000 to 50,000 volts for diffraction work. X-ray tubes may be divided into two basic types, according to the way in which electrons are provided: filament tubes, in which the source of electrons is a hot filament, and gas tubes, in which electrons are produced by the ionization of a small quantity of gas in the tube.

To sum up, diffraction is essentially a scattering phenomenon in which a large number of atoms cooperate. Since the atoms are arranged periodically on a lattice, the rays scattered by them have definite phase relations between them; these phase relations are such that destructive interference occurs in most directions of scattering, but in a few directions constructive interference takes place and diffracted beams are formed. The two essentials are a wave motion capable of interference (x-rays) and a set of periodically arranged scattering centers (the atoms of a crystal).

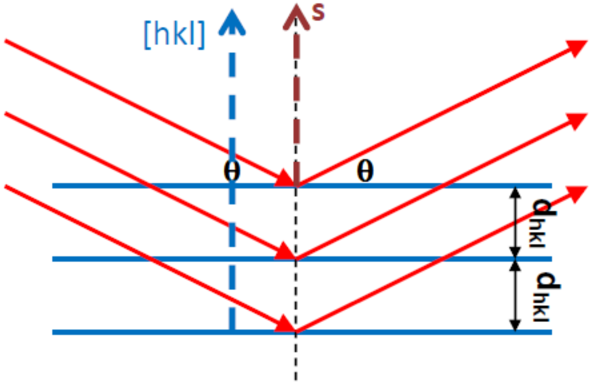
X-RAY PROPERTIES

- X ray, invisible, highly penetrating electromagnetic radiation of much shorter wavelength (higher frequency) than visible light. The wavelength range for X rays is from about 10^{-8} m to about 10^{-11} m, the corresponding frequency range is from about 3×10^{16} Hz to about 3×10^{19} Hz.



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.
  - Consequently, 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

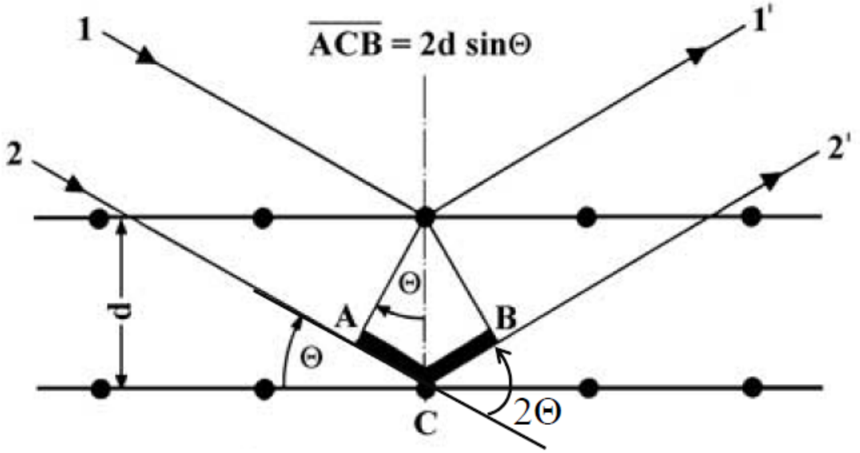
BRAGG'S LAW OF DIFFRACTION

When a collimated beam of X-rays strikes pair of parallel lattice planes in a crystal, each atom acts as a scattering center and emits a secondary wave.
→ All of the secondary waves interfere with each other to produce the diffracted beam

Bragg provided a simple, intuitive approach to diffraction:

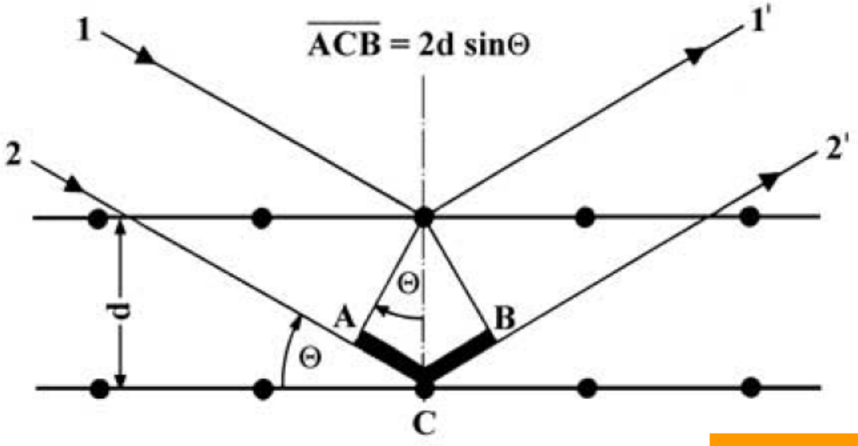
- Regard crystal as parallel planes of atoms separated by distance *d*
- Assume specular reflection of X-rays from any given plane

→ Peaks in the intensity of scattered radiation will occur when rays from successive planes interfere constructively



BRAGG'S LAW OF DIFFRACTION

No peak is observed unless the condition for constructive interference ($\delta = n\lambda$, with n an integer) is precisely met:



$$\overline{AC} = d \sin\theta$$

$$\overline{ACB} = 2d \sin\theta$$

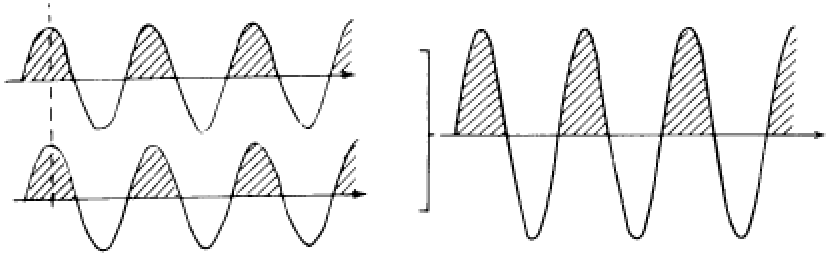
$$n\lambda = \overline{ACB}$$

Bragg's Law: $\boxed{n\lambda = 2d \sin\theta}$

When Bragg's Law is satisfied, "reflected" beams are in phase and interfere constructively. Specular "reflections" can occur only at these angles.

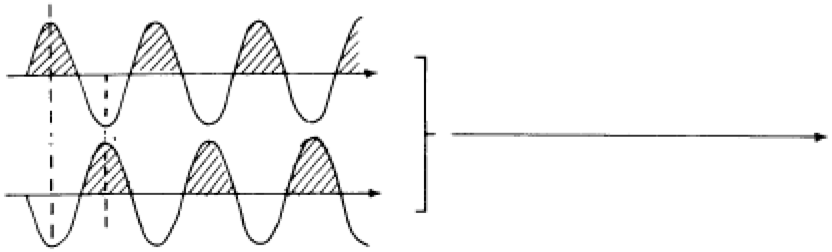
Interference between waves

(a)



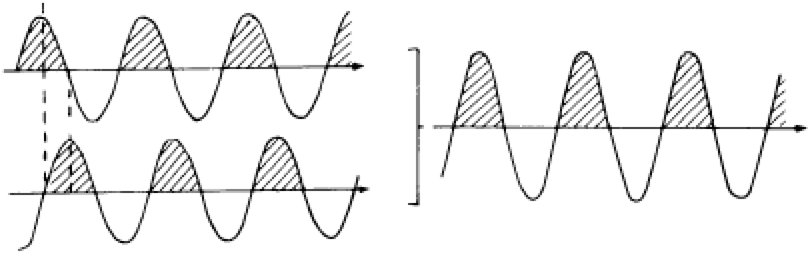
in phase
(constructive
interference)

(b)



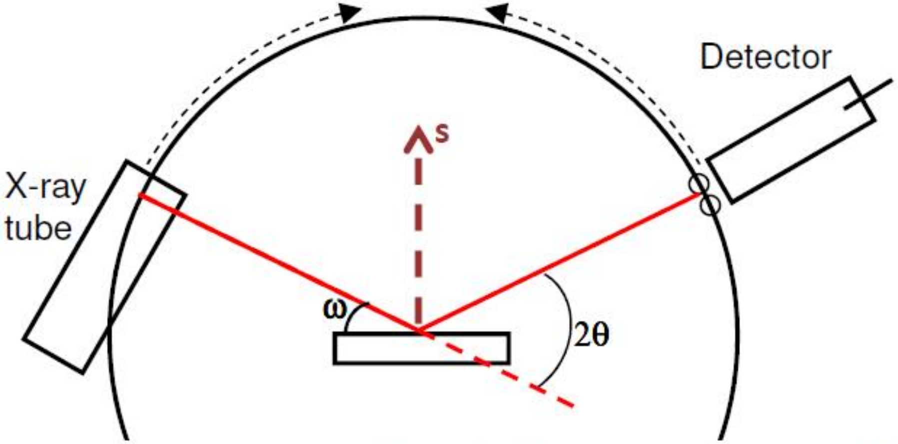
out of phase
(destructive
interference)

(c)



partially out of phase

Our powder diffractometers typically use the Bragg-Brentano geometry.



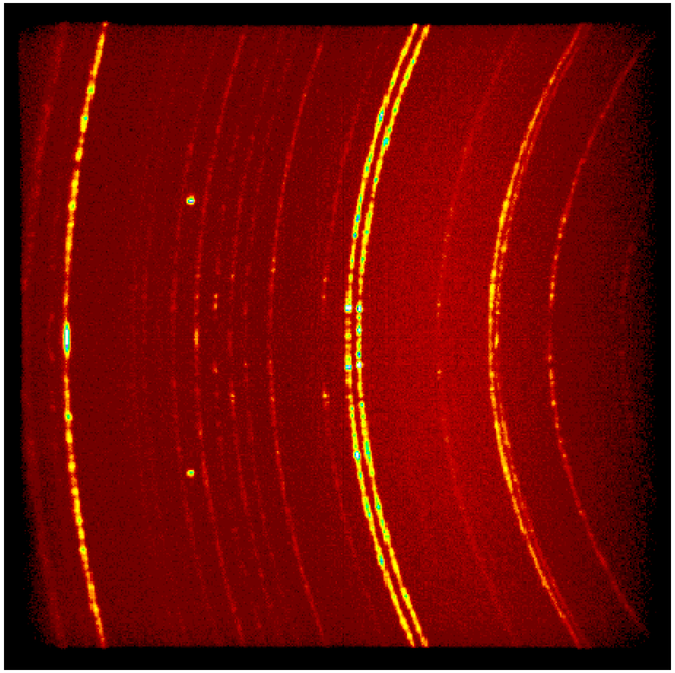
- The incident angle, ω, is defined between the X-ray source and the sample.
- The diffraction angle, 2θ, is defined between the incident beam and the detector.
- The incident angle ω is always ½ of the detector angle 2θ .

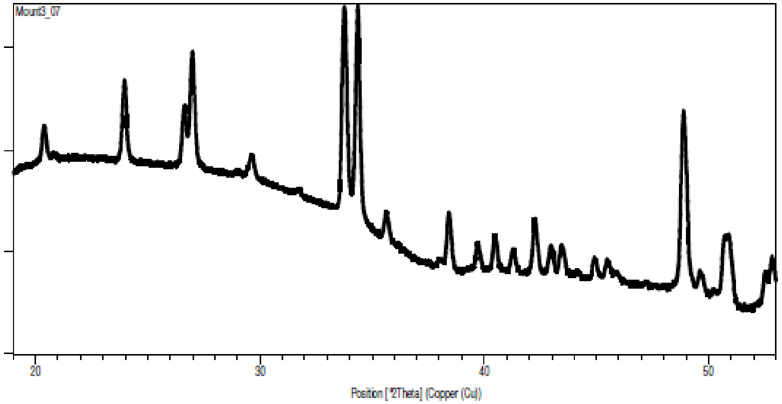
X-Ray Powder Diffraction (XRPD) is a somewhat inefficient measurement technique

- 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

Non-Ideal Samples: a “spotty” diffraction pattern

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

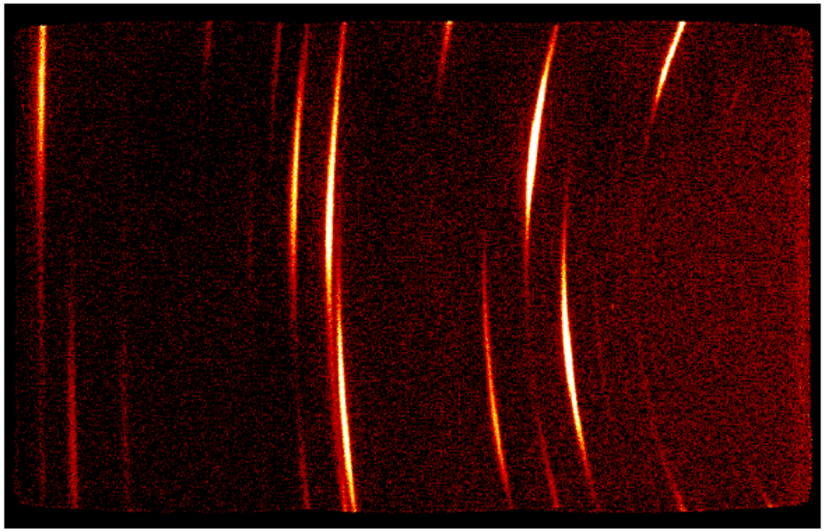


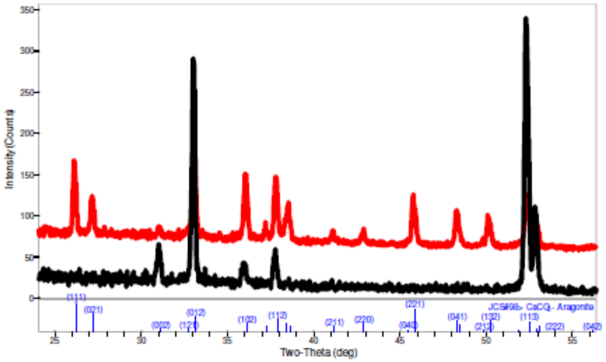


The poor particle statistics cause random error in the observed diffraction peak intensities.

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

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





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

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

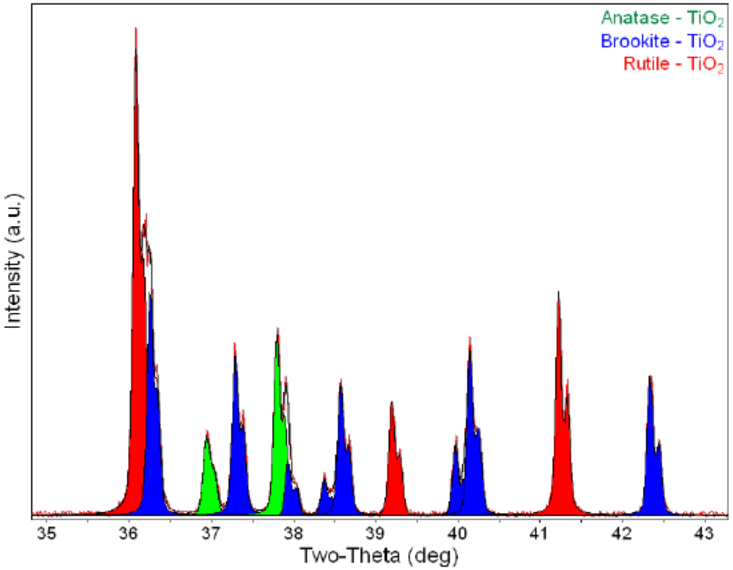
Application of XRD

You can use XRD to determine

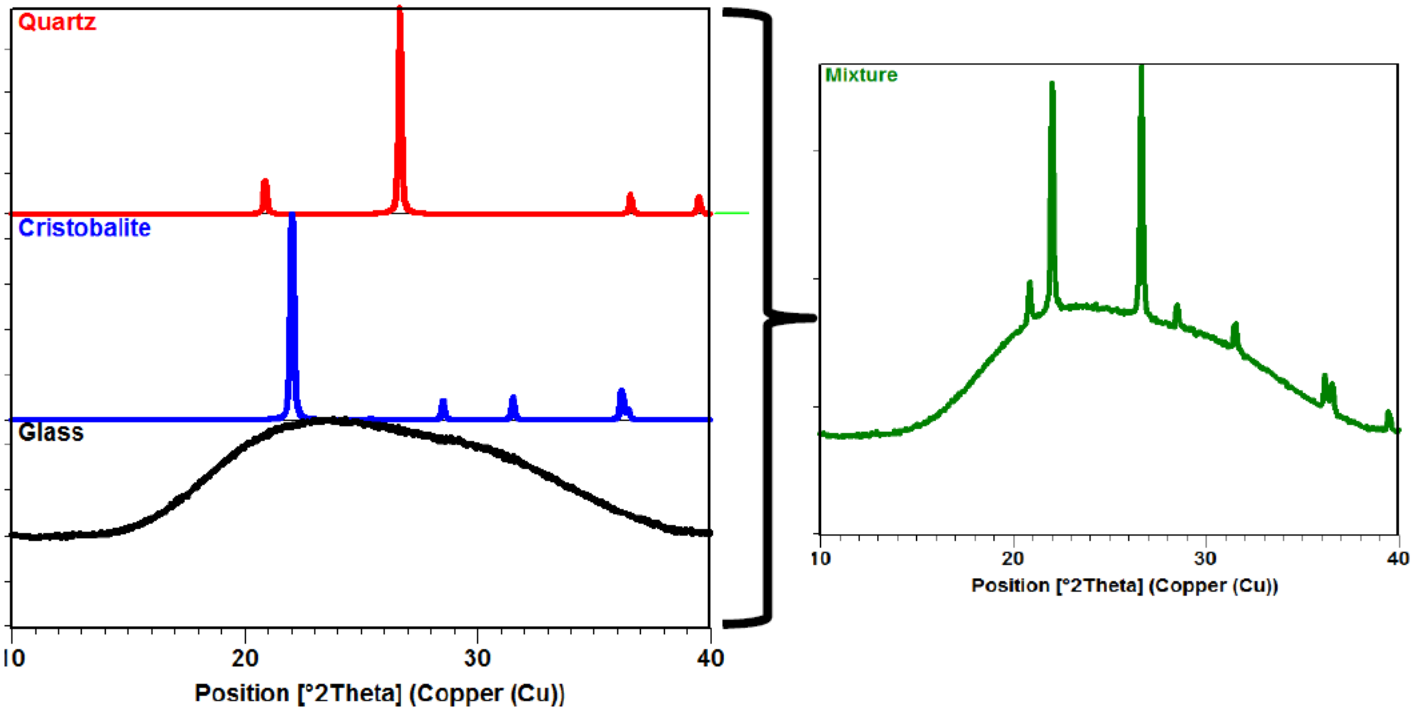
- Phase Composition of a Sample
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and 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

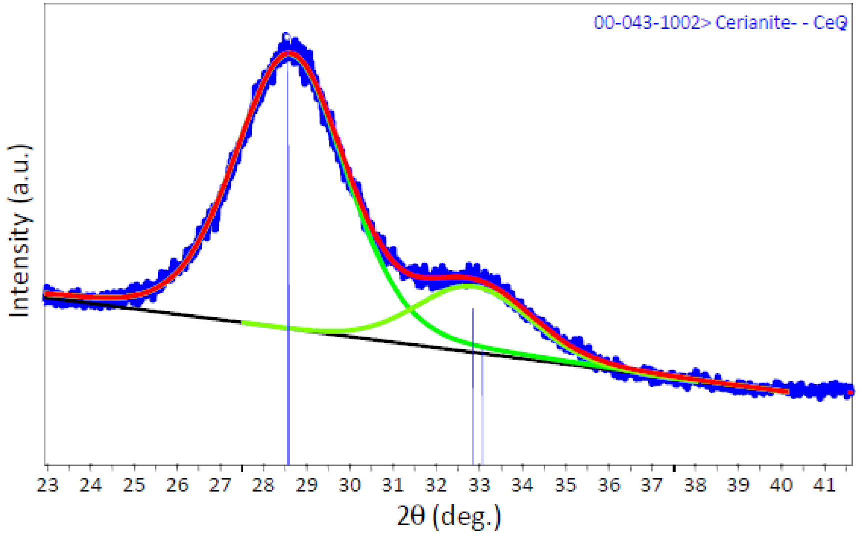


The diffraction pattern of a mixture is a simple sum of the scattering from each component phase



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



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

Crystallite: Crystallites are also referred to as grains. The areas where crystallites meet are known as grain boundaries. Polycrystalline or multicrystalline materials or polycrystals are solids that are composed of many crystallites of varying size and orientation.

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 smaple 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

Sample Preparation

Important characteristics of samples for XRPD

- a flat plate sample for XRPD should have a smooth flat surface
  - if the surface is not smooth and flat, X-ray absorption may reduce the intensity of low angle peaks
  - parallel-beam optics can be used to analyze samples with odd shapes or rought surfaces
- Densely packed
- Randomly oriented grains/crystallites
- Grain size less than 10 microns
  - So that there are tens of thousands of grains irradiated by the X-ray beam
- ‘Infinitely’ thick
- homogeneous

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 <10μm in size to get good powder statistics

Preferred orientation

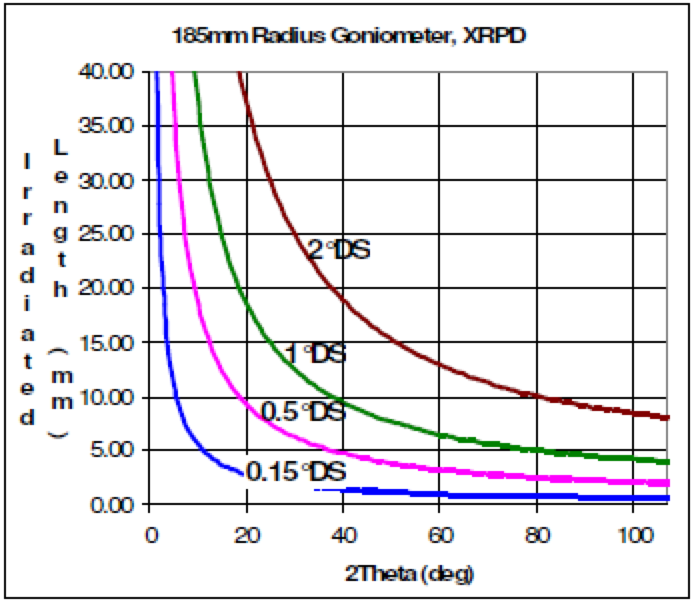
- If the crystallites in a powder sample have plate or needle like shapes it can be very difficult to get them to adopt random orientations
  - top-loading, where you press the powder into a holder, can cause problems with preferred orientation
- in samples such as metal sheets or wires there is almost always preferred orientation due to the manufacturing process
- for samples with systematic orientation, XRD can be used to quantify the texture in the specimen

Ways to prepare a powder sample

- Top-loading a bulk powder into a well
  - deposit powder in a shallow well of a sample holder. Use a slightly rough flat surface to press down on the powder, packing it into the well.
    - using a slightly rough surface to pack the powder can help minimize preferred orientation
    - mixing the sample with a filler such as flour or glass powder may also help minimize preferred orientation
    - powder may need to be mixed with a binder to prevent it from falling out of the sample holder
      - alternatively, the well of the sample holder can be coated with a thin layer of vaseline
- Dispersing a thin powder layer on a smooth surface
  - a smooth surface such as a glass slide or a zero background holder (ZBH) may be used to hold a thin layer of powder
    - glass will contribute an amorphous hump to the diffraction pattern
    - the ZBH avoids this problem by using an off-axis cut single crystal
  - dispersing the powder with alcohol onto the sample holder and then allowing the alcohol to evaporate, often provides a nice, even coating of powder that will adhere to the sample holder
  - powder may be gently sprinkled onto a piece of double-sided tape or a thin layer of vaseline to adhere it to the sample holder
    - the double-sided tape will contribute to the diffraction pattern
  - these methods are necessary for mounting small amounts of powder
  - these methods help alleviate problems with preferred orientation

Varying Irradiated area of the sample

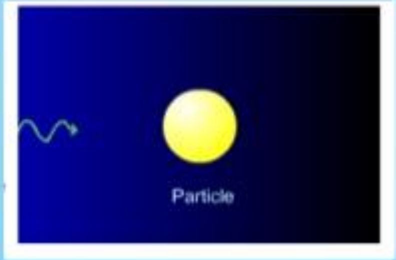
- the area of your sample that is illuminated by the X-ray beam varies as a function of:
  - incident angle of X rays
  - divergence angle of the X rays
- at low angles, the beam might be wider than your sample
  - “beam spill-off”
- This will cause problems if you sample is not homogeneous



Diffraction from a particle and solid

Single particle

- To understand diffraction we also have to consider what happens when a wave interacts with a single particle**.** The particle scatters the incident beam uniformly in **all** directions

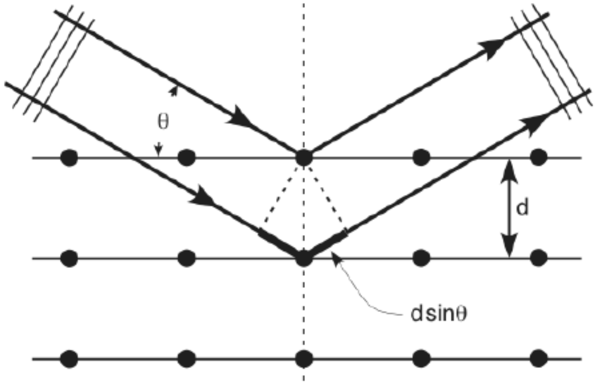


Solid material

- What happens if the beam is incident on solid material? If we consider a crystalline material, the scattered beams may add together in a few directions and reinforce each other to give **diffracted** beams

POWDER DIFFRACTOGRAMS

In powder XRD, a finely powdered sample is probed with monochromatic X-rays of a known wavelength in order to evaluate the *d*-spacings according to Bragg's Law.



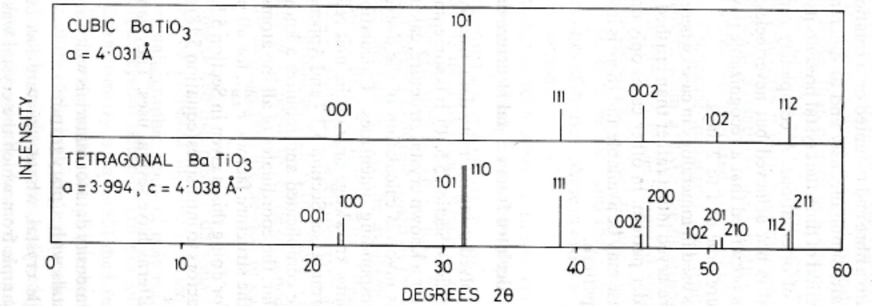
BRAGG LAW

$$2d(\sin\theta) = \lambda_o$$

where:

d = lattice interplanar spacing of the crystal
θ = x-ray incidence angle (Bragg angle)
λ = wavelength of the characteristic x-rays

Cu Kα radiation: λ = 1.54 Å



increasing θ, **decreasing** *d*

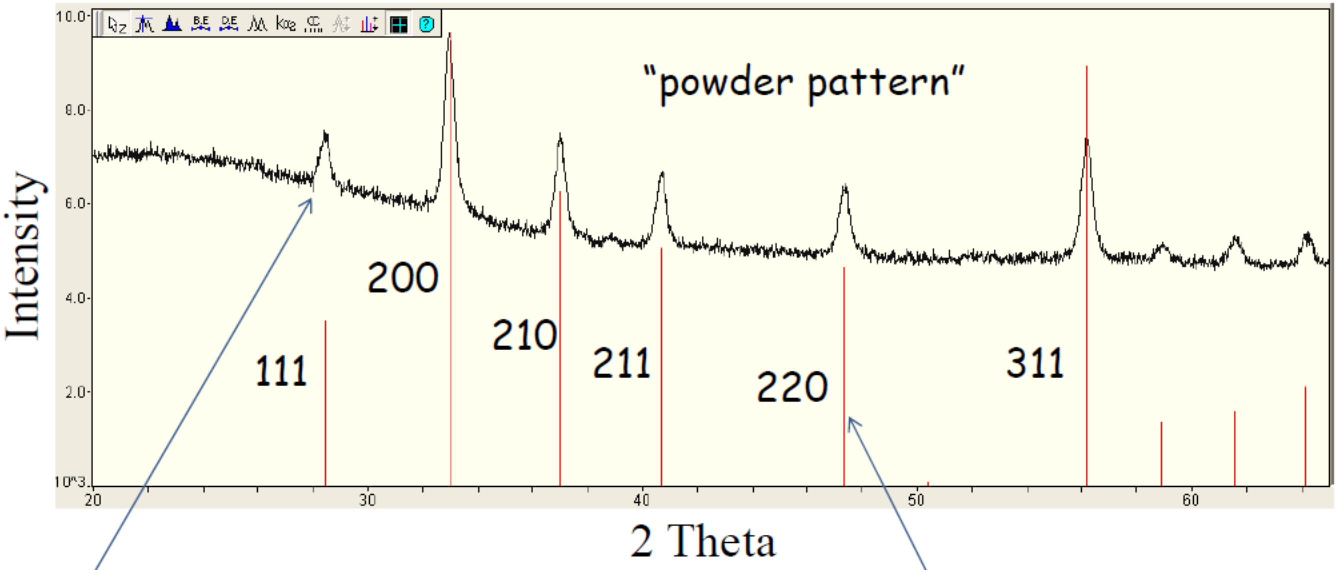
peak positions depend on:

- *d*-spacings of {hkl}

EXAMPLE

FeS_2 - cubic (a = 5.43 Å)
Random crystal orientations

Cu $K\alpha$ = 1.54 Å



$$2\theta = 28.3° \rightarrow d = 1.54/[2\sin(14.15)] = 3.13 \text{ Å} = d_{111}$$

reference pattern from ICDD
(384,000+ datasets)

POWDER DIFFRACTION

Peak positions determined by size and shape of unit cell

Peak intensities determined by the atomic number and position of the various atoms within the unit cell

Peak widths determined by instrument parameters, temperature, and crystal size, strain, and imperfections

Other factors that affect intensity:

- scattering angle
- multiplicities
- temperature factor
- absorption factor
- preferred orientation

SCHERRER FORMULA

A more rigorous treatment includes a unitless shape factor:

Scherrer Formula (1918)

$$T = \frac{K\lambda}{B\cos\theta_B}$$

T = crystallite thickness
λ (X-ray wavelength, Å)
K (shape factor) ~ 0.9
B, θ_B in radians

Accurate size analysis requires correction for instrument broadening:

$$B^2 = B_M^2 - B_R^2$$

B_M: Measured FWHM (in radians)
B_R: Corresponding FWHM of bulk reference (large grain size, > 200 nm)

Readily applied for crystal size of 2-100 nm.
Up to 500 nm if synchrotron is used.

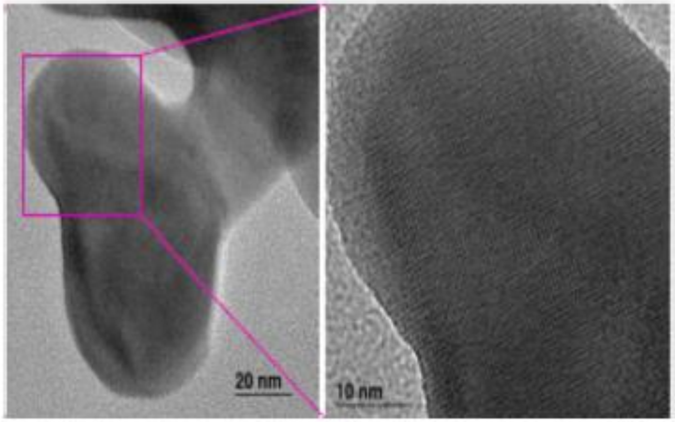
SCHERRER CONSTANT

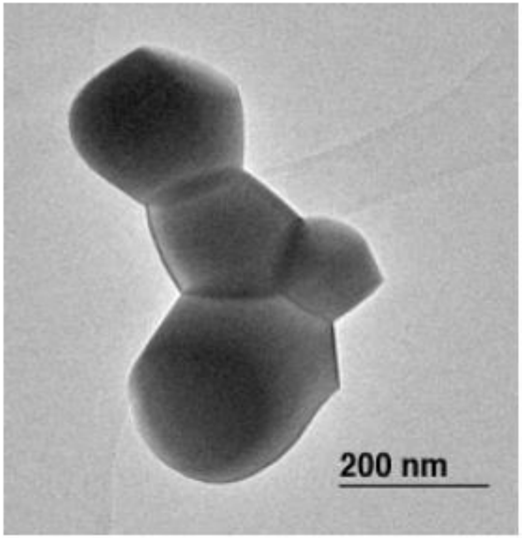
$$T = \frac{K\lambda}{B\cos\theta_B} \quad \Rightarrow \quad T = \frac{0.94\lambda}{B\cos\theta_B}$$

- The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution
  - the most common values for K are:
    - 0.94 for FWHM of spherical crystals with cubic symmetry
    - 0.89 for integral breadth of spherical crystals w/ cubic symmetry
    - 1, because 0.94 and 0.89 both round up to 1
  - K actually varies from 0.62 to 2.08

What do we mean by crystallite size?

- A particle may be made up of several different crystallites (also called grains)
- The crystallites, not the particles, are the coherent scattering units





CRYSTALLITE SHAPE

- Though the shape of crystallites is usually irregular, we can often approximate them as:
  - sphere, cube, tetrahedra, or octahedra
  - parallelepipeds such as needles or plates
  - prisms or cylinders

- Most applications of Scherrer analysis assume spherical crystallite shapes

- If we know the average crystallite shape from another analysis, we can select the proper value for the Scherrer constant K

STRAIN EFFECTS

Strain: $\varepsilon = \dfrac{\Delta L}{L}$

No Strain

Uniform Strain

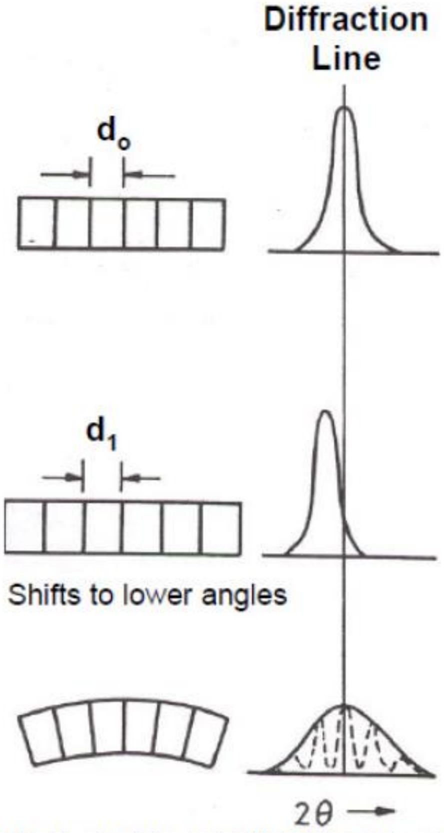
$(d_1-d_o)/d_o$

Peak moves, no shape changes

Non-uniform Strain

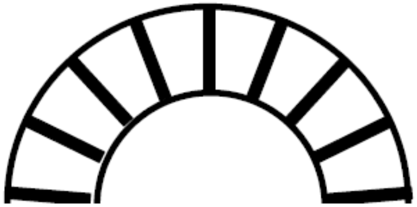
$d_1 \neq$constant

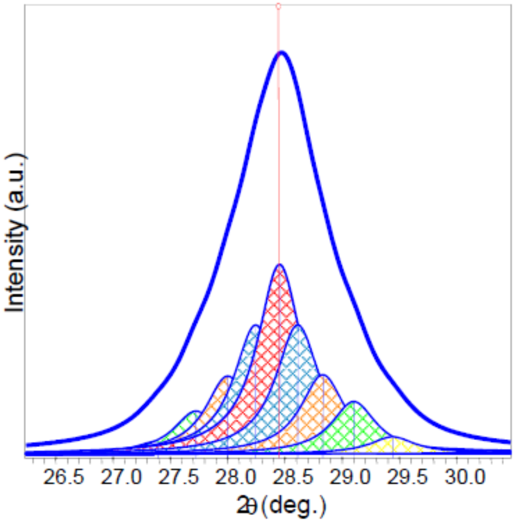
Peak broadens



Non-Uniform Lattice Distortions

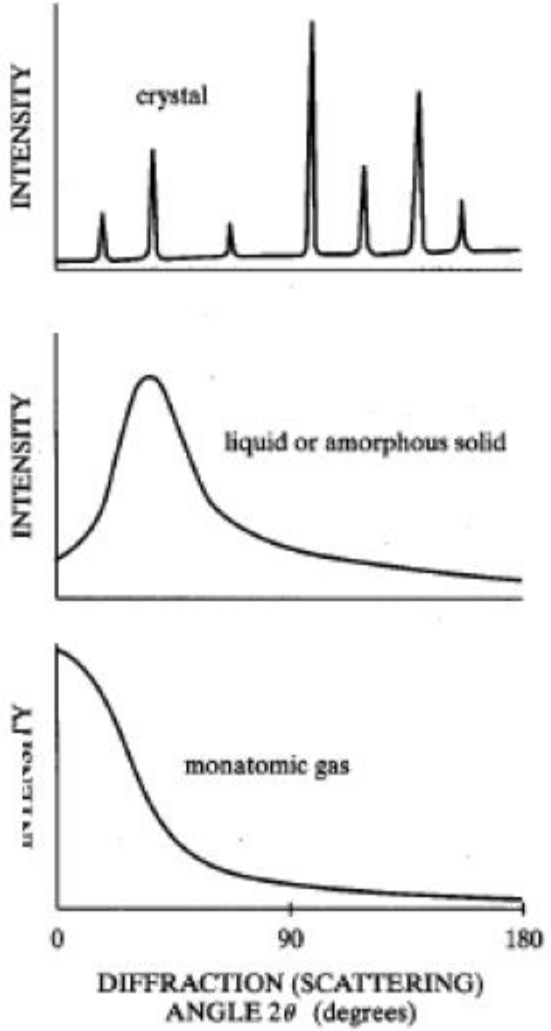
- Rather than a single *d*-spacing, the crystallographic plane has a distribution of *d*-spacings
- This produces a broader observed diffraction peak
- Such distortions can be introduced by:
  - mechanical force
  - surface tension of nanocrystals
  - morphology of crystal shape, such as nanotubes
  - interstitial impurities





Scattering patterns for different substances

All materials scatter x-rays, even if they are not crystalline. Deviations from perfect periodicity spread the scattering out through reciprocal space, but there is still information about interatomic distances



- Diffraction is large or small angle depending on the size of the "particle"

Production of X-rays

- X-rays are produced in the laboratory by bombarding a metal target with high energy electrons
- The high energy electrons knock electrons out of the core orbitals in target metal
- These empty core orbitals are refilled by atomic transitions that lie in the x-ray region

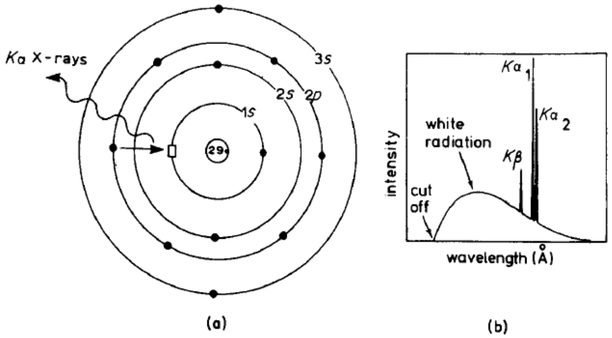


Fig. 3.1 (a) Generation of Cu *Kα* X-rays. A 1*s* electron is ionized; a 2*p* electron falls into the empty 1*s* level (□) and the excess energy is released as X-rays. (b) X-ray emission spectrum of Cu

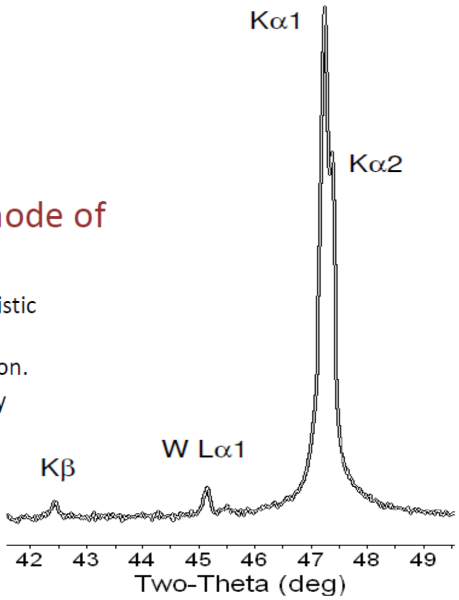
The wavelength of X rays is determined by the anode of the X-ray source.

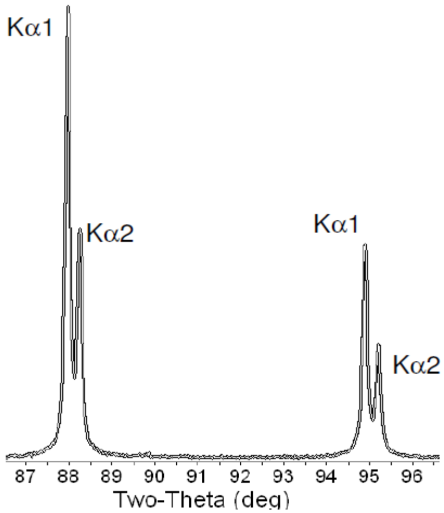
- Electrons from the filament strike the target anode, producing characteristic radiation via the photoelectric effect.
- The anode material determines the wavelengths of characteristic radiation.
- While we would prefer a monochromatic source, the X-ray beam actually consists of several characteristic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

◆ The wavelength of x-rays produced depends on the element the target is made from

Target	$k\alpha_1$	$k\alpha_2$	$k\alpha$	Filter
Cr	2.2896	2.2935	2.2909	V
Fe	1.936	1.9399	1.9373	Mn
Cu	1.5405	1.5443	1.5418	Ni
Mo	0.7093	0.7135	0.7107	Nb
Ag	0.5594	0.5638	0.5608	Pd

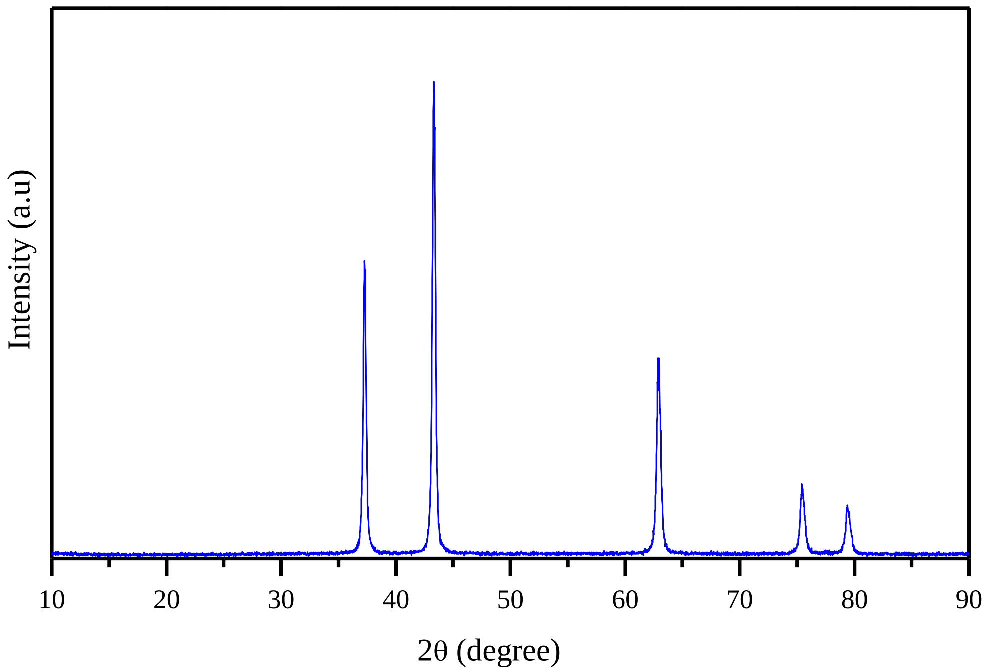
Copper K-α is an x-ray energy frequently used on labscale x-ray instruments. The energy is 8.04 keV, which corresponds to an x-ray wavelength of 1.5406 Å.





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



Name and formula

Reference code:	00-004-0835
Mineral name:	Bunsenite, syn
PDF index name:	Nickel Oxide
Empirical formula:	NiO
Chemical formula:	NiO

Crystallographic parameters

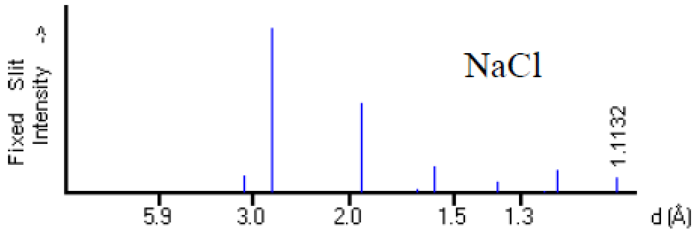
Crystal system:	Cubic
Space group:	Fm-3m
Space group number:	225
a (Å):	4.1769
b (Å):	4.1769
c (Å):	4.1769
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Calculated density (g/cm^3):	6.81
Measured density (g/cm^3):	6.90
Volume of cell (10^6 pm^3):	72.87

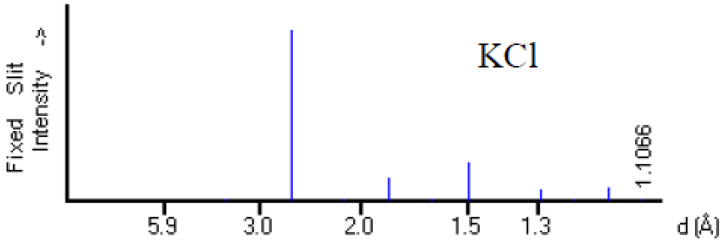
Peak list

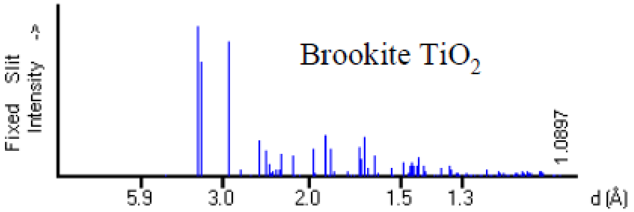
No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	2.41000	37.281	91.0
2	2	0	0	2.08800	43.298	100.0
3	2	2	0	1.47600	62.917	57.0
4	3	1	1	1.25900	75.445	16.0
5	2	2	2	1.20600	79.393	13.0
6	4	0	0	1.04410	95.083	8.0
7	3	3	1	0.95820	107.009	7.0
8	4	2	0	0.93380	111.159	21.0
9	4	2	2	0.85270	129.208	17.0
10	5	1	1	0.80400	146.705	7.0

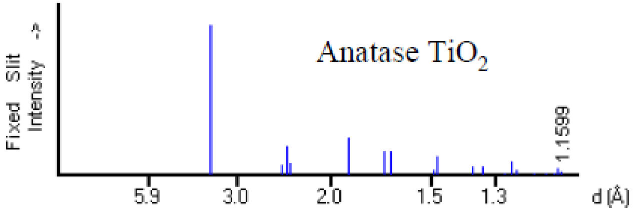
Powder patterns for different substances

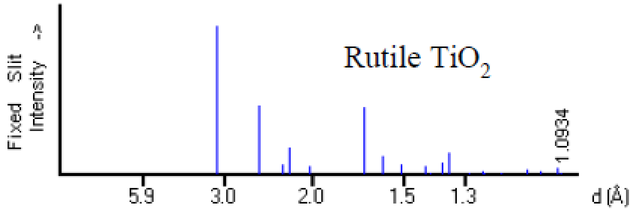
- Can distinguish between the same compound with different structures and different compounds with the same structure











Phase identification

usually done by comparing the measured pattern against the ICDD/JCPDS powder diffraction file data base. This contains powder patterns for a very large number of compounds.

Name and formula

Reference code: 00-021-1272

Mineral name: Anatase, syn
PDF index name: Titanium Oxide

Empirical formula: O_2Ti
Chemical formula: TiO_2

Crystallographic parameters

Crystal system: Tetragonal
Space group: I41/amd
Space group number: 141

a (Å): 3.7852
b (Å): 3.7852
c (Å): 9.5139
Alpha (°): 90.0000
Beta (°): 90.0000
Gamma (°): 90.0000

Calculated density (g/cm^3): 3.89
Volume of cell (10^6 pm^3): 136.31
Z: 4.00

RIR: 3.30

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	0	1	3.52000	25.281	100.0
2	1	0	3	2.43100	36.947	10.0
3	0	0	4	2.37800	37.801	20.0
4	1	1	2	2.33200	38.576	10.0
5	2	0	0	1.89200	48.050	35.0
6	1	0	5	1.69990	53.891	20.0
7	2	1	1	1.66650	55.062	20.0
8	2	1	3	1.49300	62.121	4.0
9	2	0	4	1.48080	62.690	14.0
10	1	1	6	1.36410	68.762	6.0
11	2	2	0	1.33780	70.311	6.0
12	1	0	7	1.27950	74.031	2.0
13	2	1	5	1.26490	75.032	10.0
14	3	0	1	1.25090	76.020	4.0
15	0	0	8	1.18940	80.727	2.0
16	3	0	3	1.17250	82.139	2.0
17	2	2	4	1.16640	82.662	6.0
18	3	1	2	1.16080	83.149	4.0
19	2	1	7	1.06000	93.221	2.0
20	3	0	5	1.05170	94.182	4.0
21	3	2	1	1.04360	95.143	4.0
22	1	0	9	1.01820	98.319	2.0
23	2	0	8	1.00700	99.804	2.0
24	3	2	3	0.99670	101.221	2.0
25	3	1	6	0.95550	107.448	4.0
26	4	0	0	0.94640	108.963	4.0
27	3	0	7	0.92460	112.841	2.0
28	3	2	5	0.91920	113.861	2.0
29	4	1	1	0.91380	114.909	2.0
30	2	1	9	0.89660	118.439	4.0
31	2	2	8	0.88900	120.104	2.0
32	4	1	3	0.88190	121.725	2.0
33	4	0	4	0.87930	122.336	2.0
34	4	2	0	0.84640	131.036	2.0
35	3	2	7	0.83080	135.998	2.0
36	4	1	5	0.82680	137.391	4.0
37	3	0	9	0.81020	143.888	2.0
38	4	2	4	0.79740	150.039	4.0
39	0	0	12	0.79280	152.634	2.0

Other diffraction methods

- Single crystal X-ray diffraction
  - routinely used to get crystal structures
- Electron diffraction
  - useful for very small particles of material
  - can give you unit cell and space group
- Neutron diffraction
  - good for looking at light atoms
  - sensitive to magnetic moments
  - good when sample “environment”is used

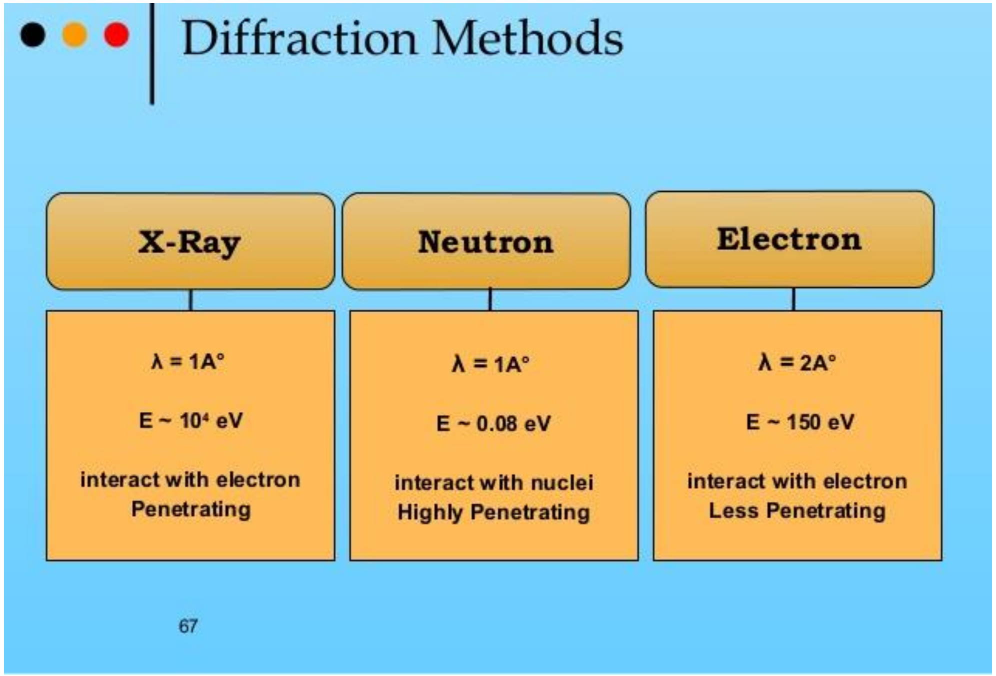
The physical basis for the diffraction of electron and neutron beams is the same as that for the diffraction of X rays, the only difference being in the mechanism of scattering.

Electron diffraction

- Very high energy electrons are employed to examine small crystals of materials
- Electrons interact strongly with matter
  - can only use thin samples to observe a diffraction pattern in transmission
- Not good for solving crystal structures due to multiple scattering

Neutron diffraction

- Neutrons are very expensive
  - from nuclear reactor or a "spallation" source
- They are uniquely suited to studying magnetic materials
- Very good for looking at weak X-ray scatterers like H, or O in the presence of heavy metals
- Good for crystal structure refinement from powder diffraction data



Diffraction Methods

X-Ray

$\lambda = 1A^{\circ}$

E ~ 10^4 eV

interact with electron
Penetrating

Neutron

$\lambda = 1A^{\circ}$

E ~ 0.08 eV

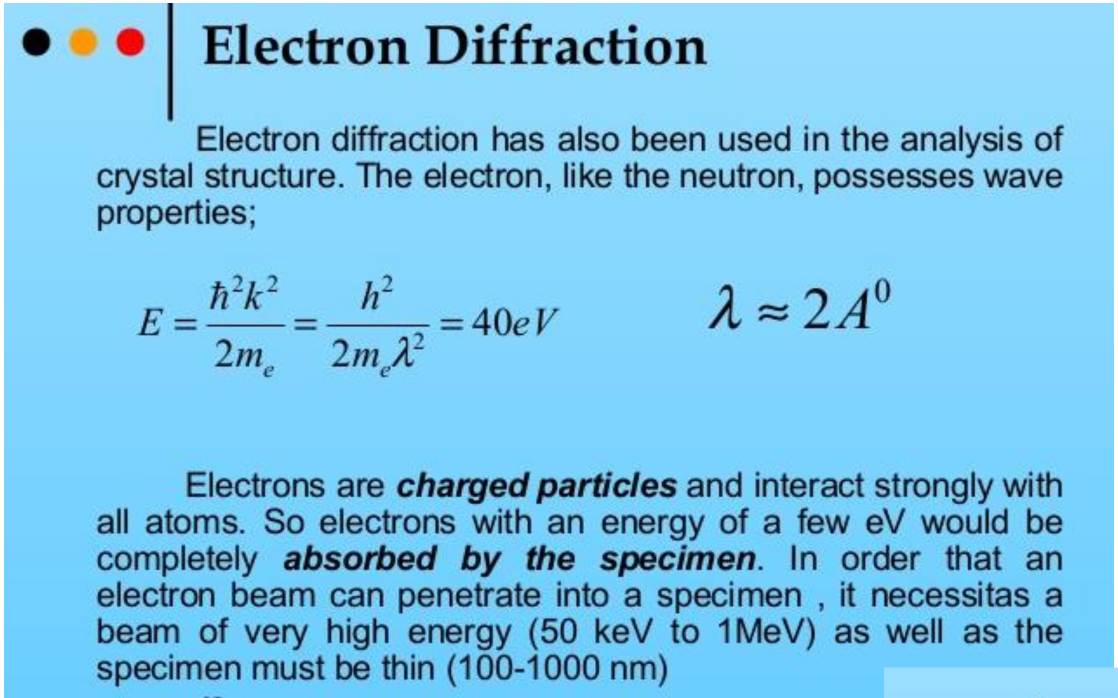
interact with nuclei
Highly Penetrating

Electron

$\lambda = 2A^{\circ}$

E ~ 150 eV

interact with electron
Less Penetrating



Electron Diffraction

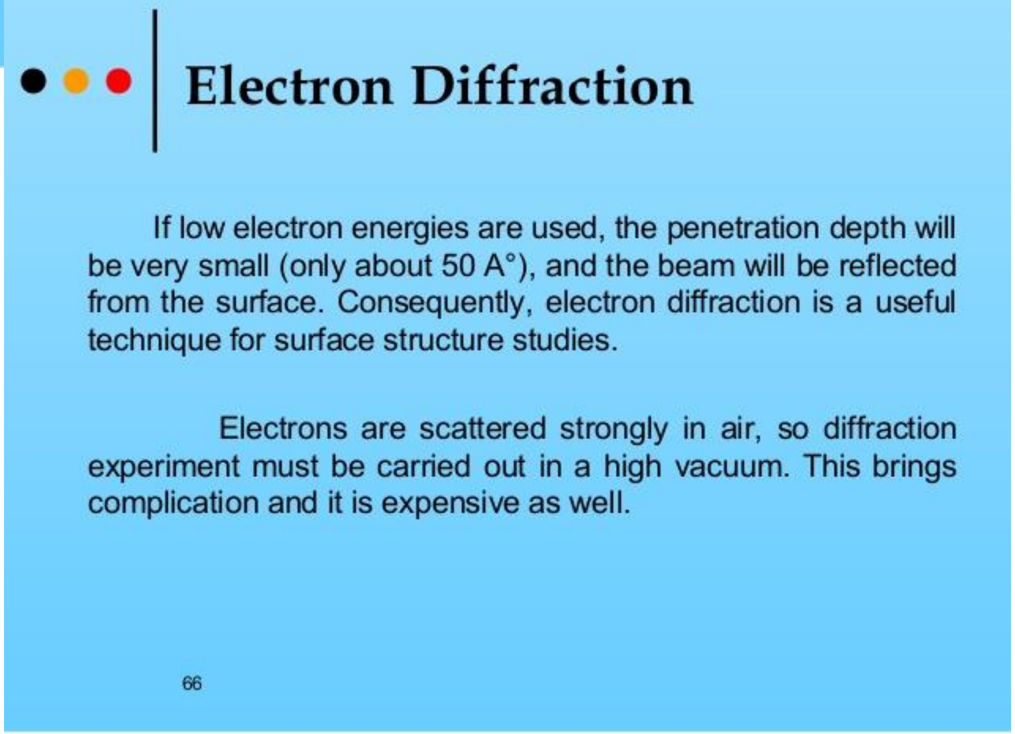
Electron diffraction has also been used in the analysis of crystal structure. The electron, like the neutron, possesses wave properties;

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{h^2}{2m_e \lambda^2} = 40eV \qquad \lambda \approx 2A^0$$

Electrons are ***charged particles*** and interact strongly with all atoms. So electrons with an energy of a few eV would be completely ***absorbed by the specimen***. In order that an electron beam can penetrate into a specimen , it necessitas a beam of very high energy (50 keV to 1MeV) as well as the specimen must be thin (100-1000 nm)

Electron diffraction is the phenomenon resulting from the interaction between electrons and crystalline materials, producing a pattern of rings or spots that characterize the sample

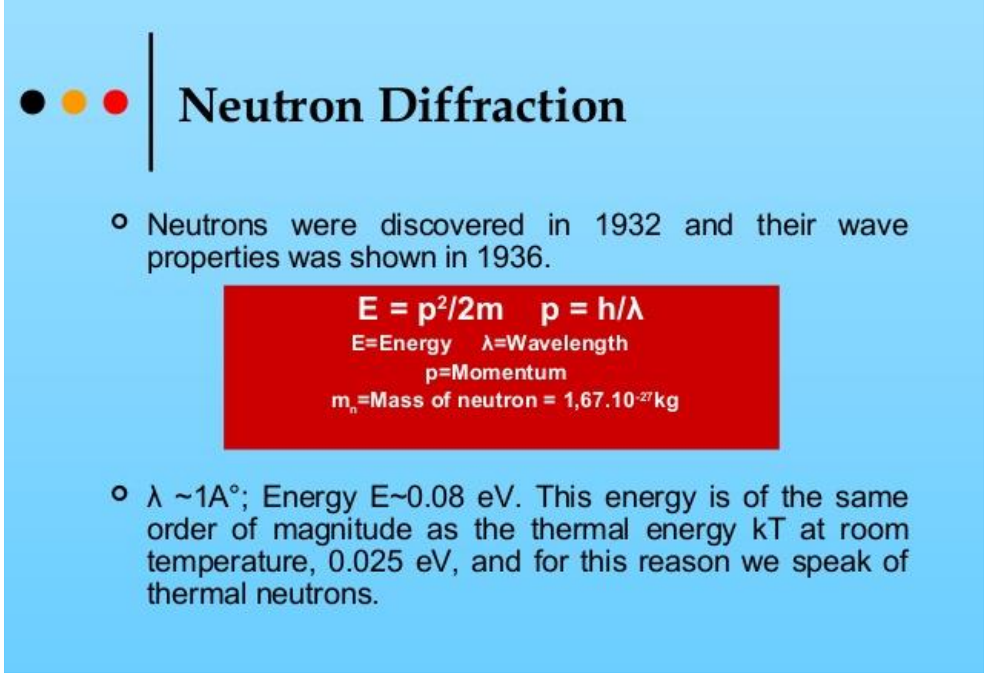
As the crystals **are** arranged at any angle, each crystal produces a **diffraction** pattern, and their **diffraction** patterns combine around 360° to **form rings**.



Electron Diffraction

If low electron energies are used, the penetration depth will be very small (only about 50 A°), and the beam will be reflected from the surface. Consequently, electron diffraction is a useful technique for surface structure studies.

Electrons are scattered strongly in air, so diffraction experiment must be carried out in a high vacuum. This brings complication and it is expensive as well.



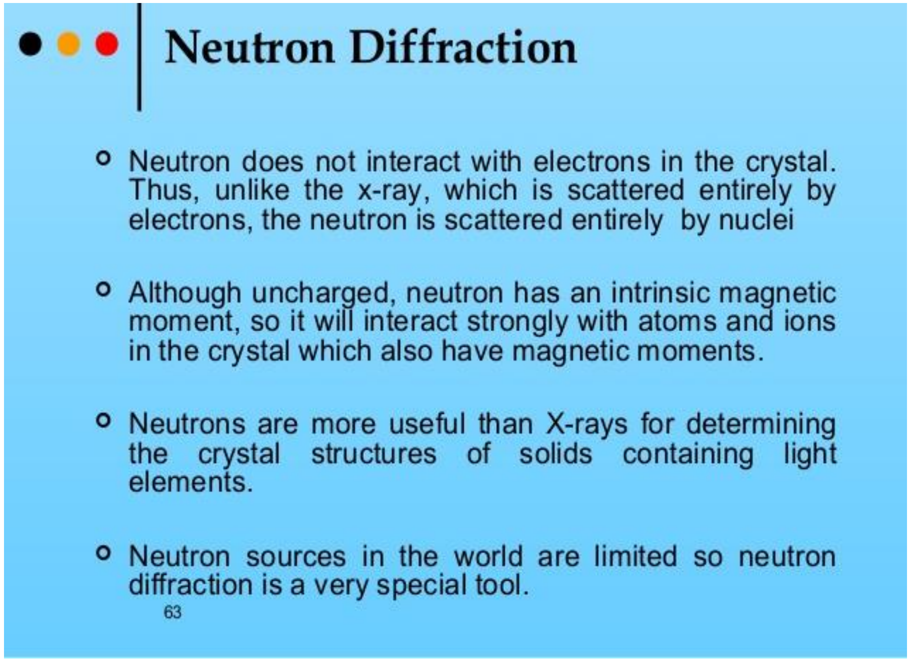
Neutron Diffraction

- Neutrons were discovered in 1932 and their wave properties was shown in 1936.

$E = p^2/2m \quad p = h/\lambda$

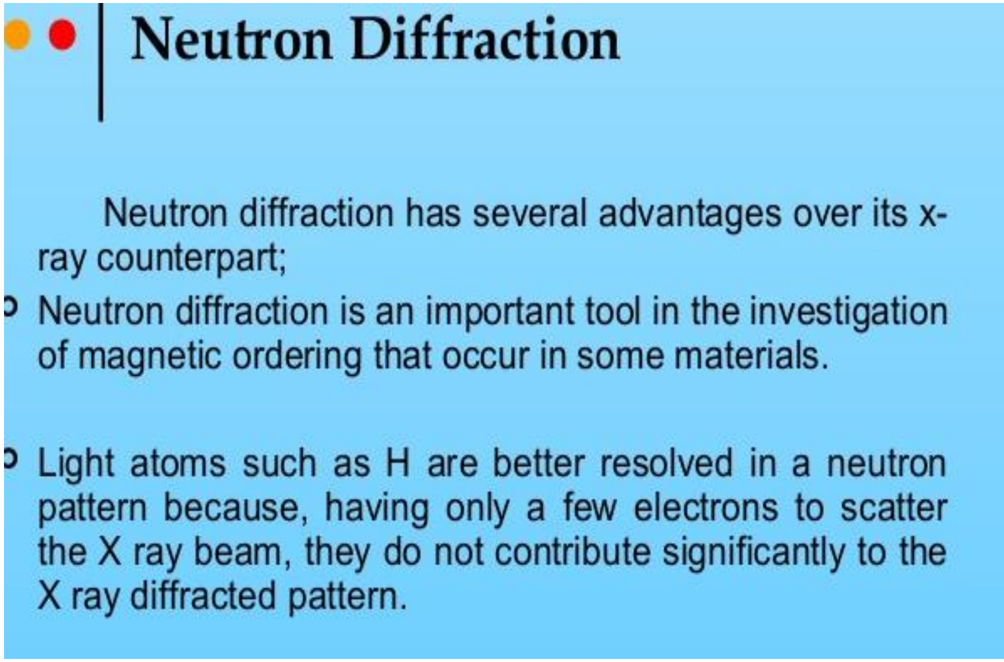
E=Energy λ=Wavelength
p=Momentum
m_n=Mass of neutron = $1,67.10^{-27}$kg

- λ ~1A°; Energy E~0.08 eV. This energy is of the same order of magnitude as the thermal energy kT at room temperature, 0.025 eV, and for this reason we speak of thermal neutrons.



Neutron Diffraction

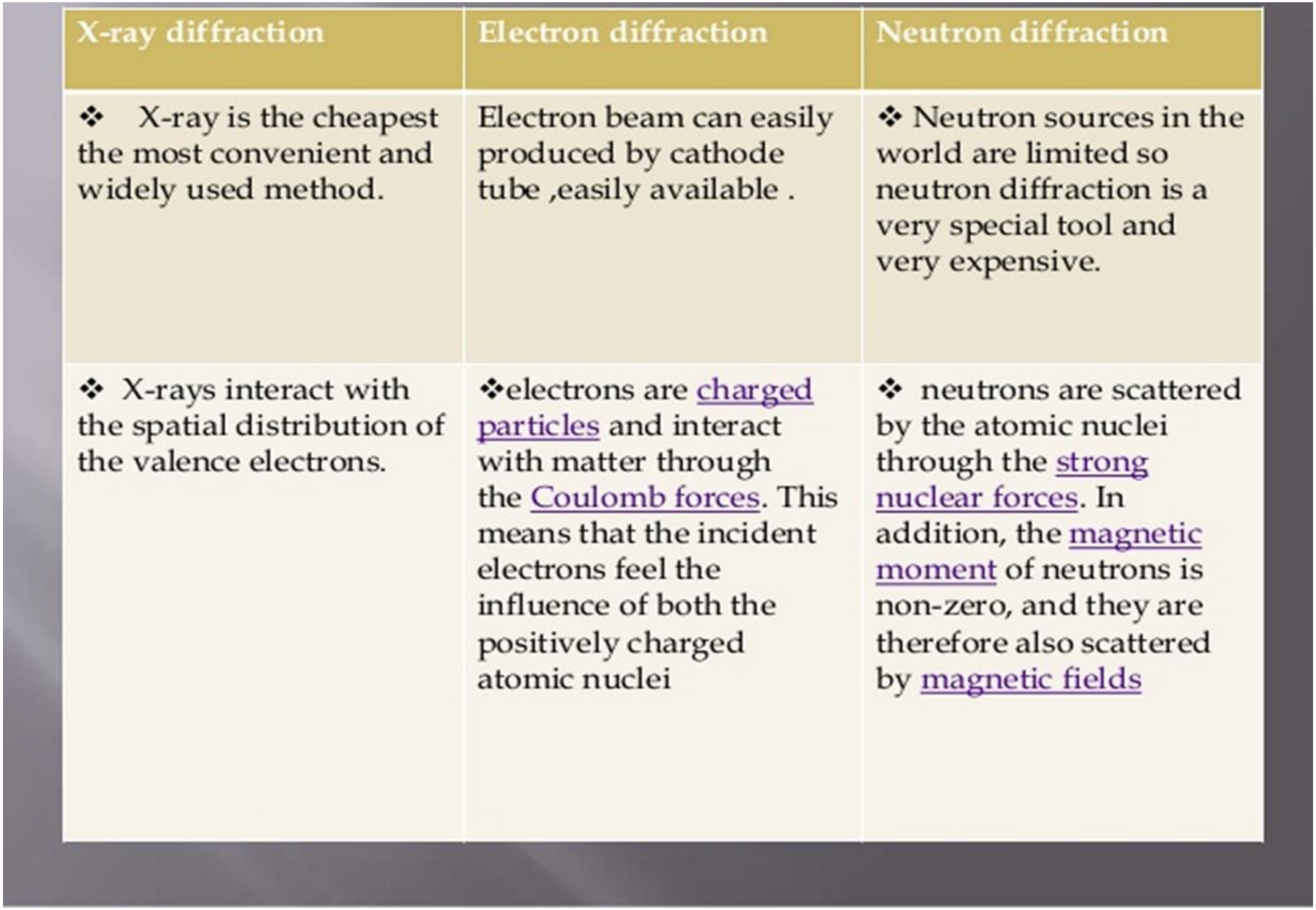
- Neutron does not interact with electrons in the crystal. Thus, unlike the x-ray, which is scattered entirely by electrons, the neutron is scattered entirely by nuclei
- Although uncharged, neutron has an intrinsic magnetic moment, so it will interact strongly with atoms and ions in the crystal which also have magnetic moments.
- Neutrons are more useful than X-rays for determining the crystal structures of solids containing light elements.
- Neutron sources in the world are limited so neutron diffraction is a very special tool.



Neutron Diffraction

Neutron diffraction has several advantages over its x-ray counterpart;

- Neutron diffraction is an important tool in the investigation of magnetic ordering that occur in some materials.
- Light atoms such as H are better resolved in a neutron pattern because, having only a few electrons to scatter the X ray beam, they do not contribute significantly to the X ray diffracted pattern.



X-ray diffraction	Electron diffraction	Neutron diffraction
❖ X-ray is the cheapest the most convenient and widely used method.	Electron beam can easily produced by cathode tube ,easily available .	❖ Neutron sources in the world are limited so neutron diffraction is a very special tool and very expensive.
❖ X-rays interact with the spatial distribution of the valence electrons.	❖electrons are charged particles and interact with matter through the Coulomb forces. This means that the incident electrons feel the influence of both the positively charged atomic nuclei	❖ neutrons are scattered by the atomic nuclei through the strong nuclear forces. In addition, the magnetic moment of neutrons is non-zero, and they are therefore also scattered by magnetic fields

Peak Position

d-spacings and lattice parameters

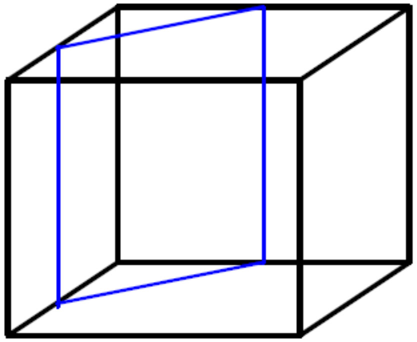
$$\lambda = 2d_{hkl}\sin\theta_{hkl}$$

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

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

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

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

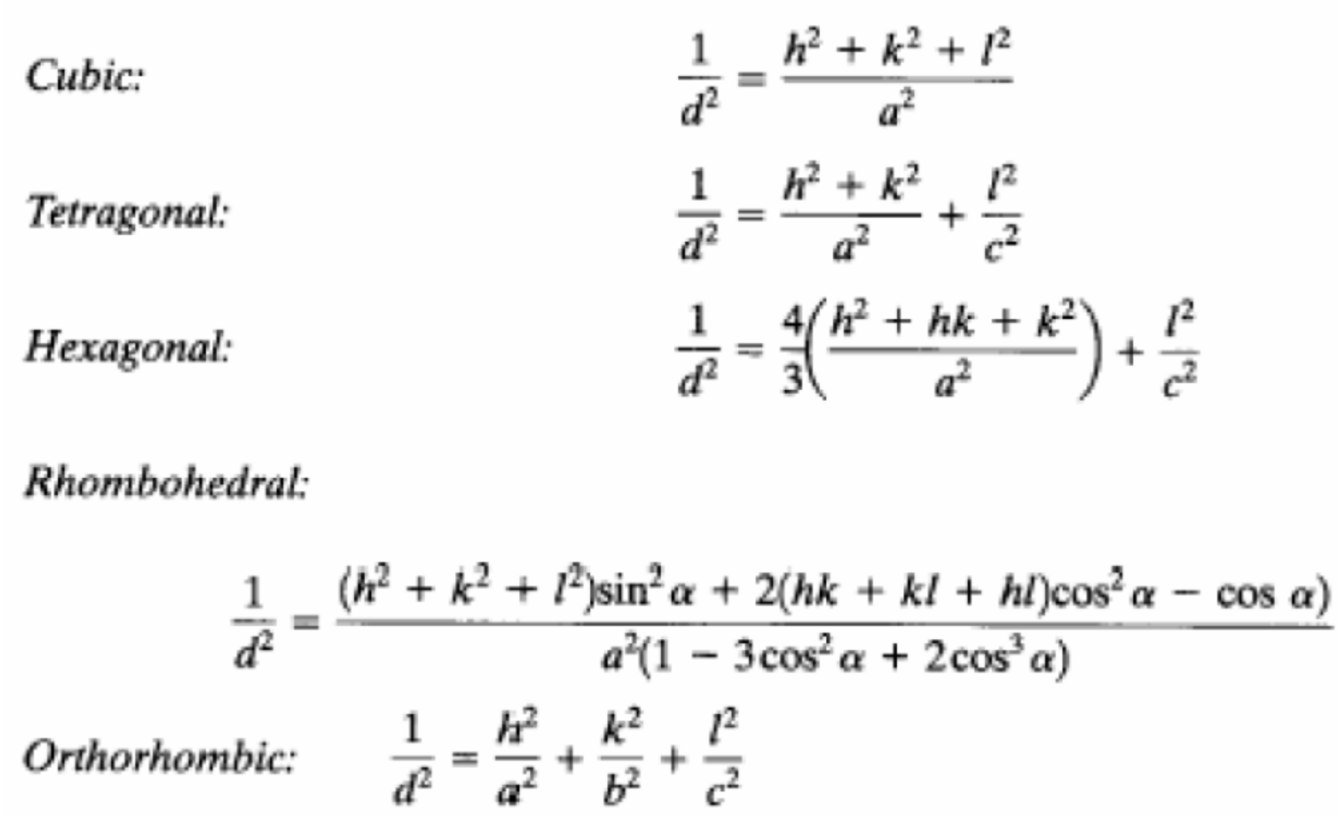


→ $a_0 = d_{hkl} / (h^2+k^2+l^2)^{1/2}$

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

$d_{220} = 1.9707$Å, $a_0 = 5.5739$Å

d-spacing



Cubic:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Orthorhombic: $$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Q. The crystal structure of $SrTiO_3$ is cubic, space group Pm3m with a unit cell edge a = 3.90 Å. Calculate the expected 2θ positions of the first three peaks in the diffraction pattern, if the radiation is Cu K_α (λ = 1.54 Å).

A.

1. Recognize the *hkl* values for the first few peaks:
   100, 110, 111, 200, 210, 211, 220, etc.
2. Calculate the interplanar spacing, *d*, for each peak:
   $1/d^2 = (h^2 + k^2 + l^2)/a^2$
3. Use Bragg's Law to determine the 2θ value:
   $\lambda = 2d_{hkl} \sin \theta_{hkl}$

   ***hkl* = 100**

   $1/d^2 = (1^2 + 0^2 + 0^2)/(3.90\ \text{Å})^2 \rightarrow d = 3.90\ \text{Å}$

   $\sin \theta_{100} = 1.54\ \text{Å}/\{2(3.90\ \text{Å})\} \rightarrow \theta = 11.4° \ (2\theta = 22.8°)$

   ***hkl* = 110**

   $1/d^2 = (1^2 + 1^2 + 0^2)/(3.90\ \text{Å})^2 \rightarrow d = 2.76\ \text{Å}$

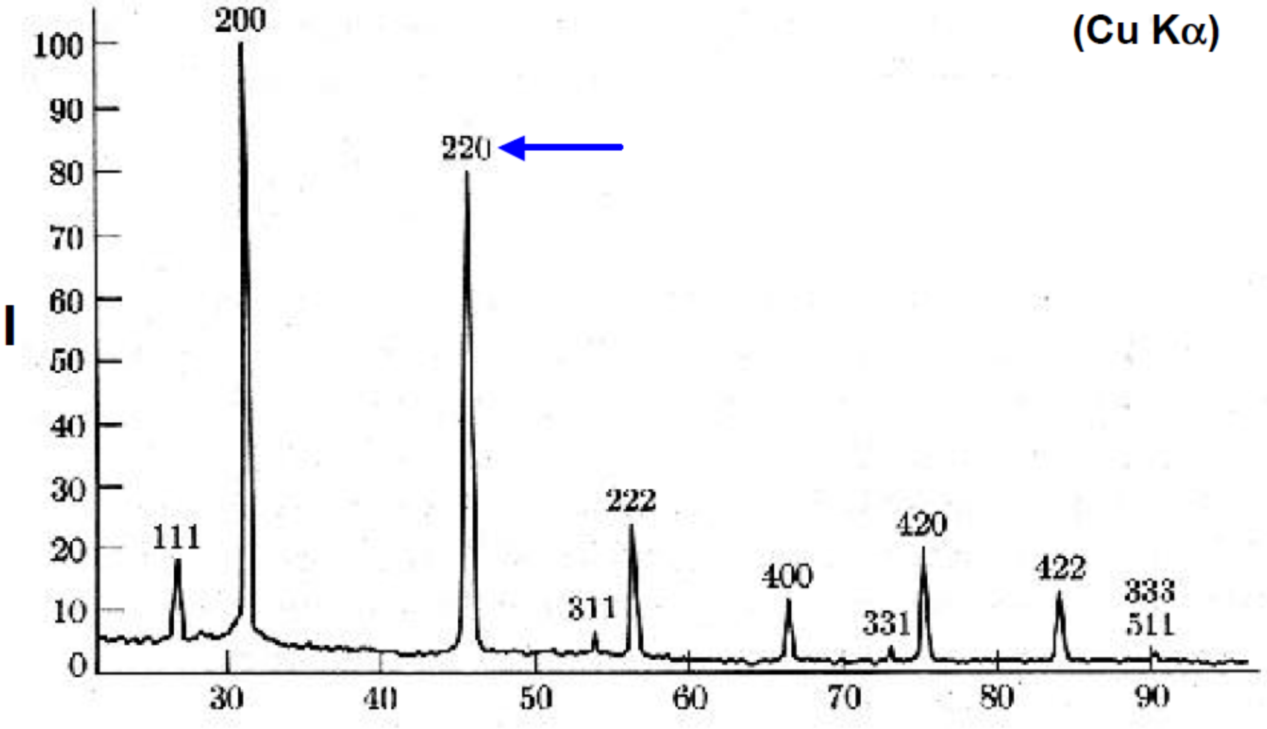
   $\sin\theta_{110} = 1.54\ \text{Å}/\{2(2.76\ \text{Å})\} \rightarrow \theta = 16.2° \ (2\theta = 32.4°)$

   ***hkl* = 111**

   $1/d^2 = (1^2 + 1^2 + 1^2)/(3.90\ \text{Å})^2 \rightarrow d = 2.25\ \text{Å}$

   $\sin \theta_{111} = 1.54\ \text{Å}/\{2(2.25\ \text{Å})\} \rightarrow \theta = 20.0° \ (2\theta = 40.0°)$

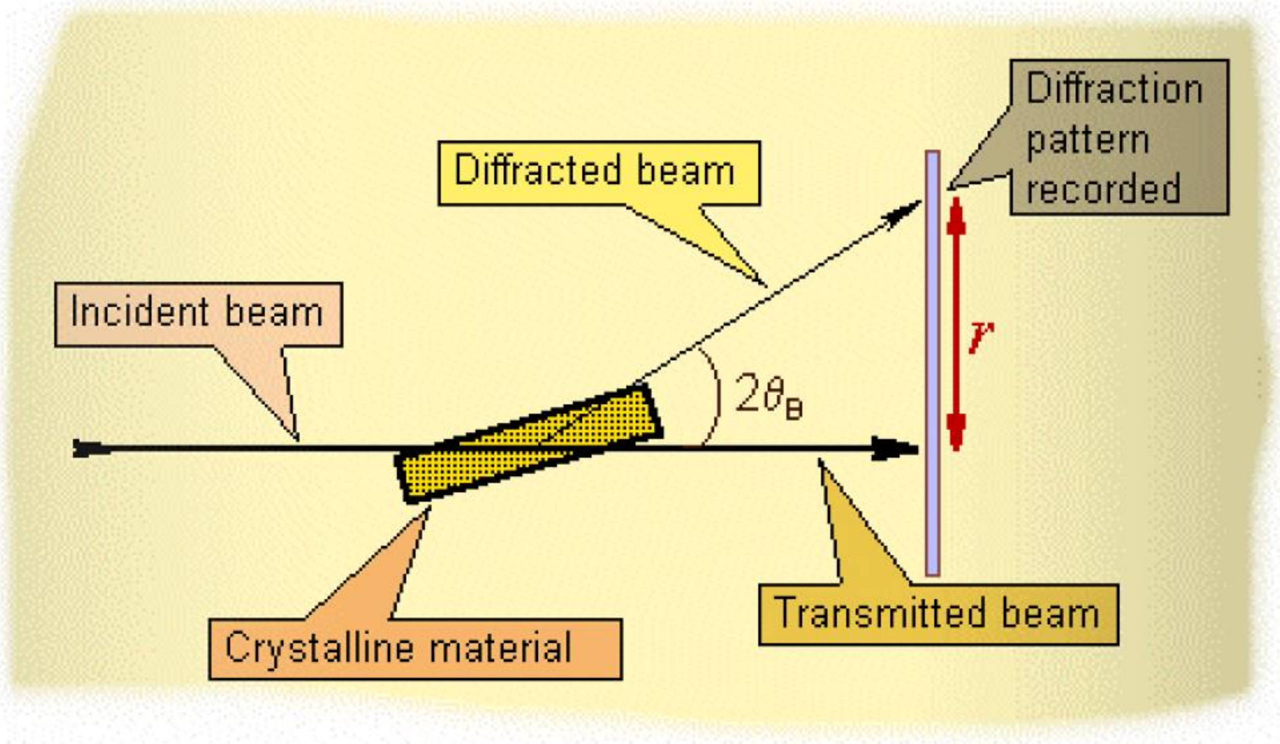
XRD Pattern of NaCl Powder



Diffraction angle 2θ (degrees)

1.0 What is X-ray Diffraction ?

I

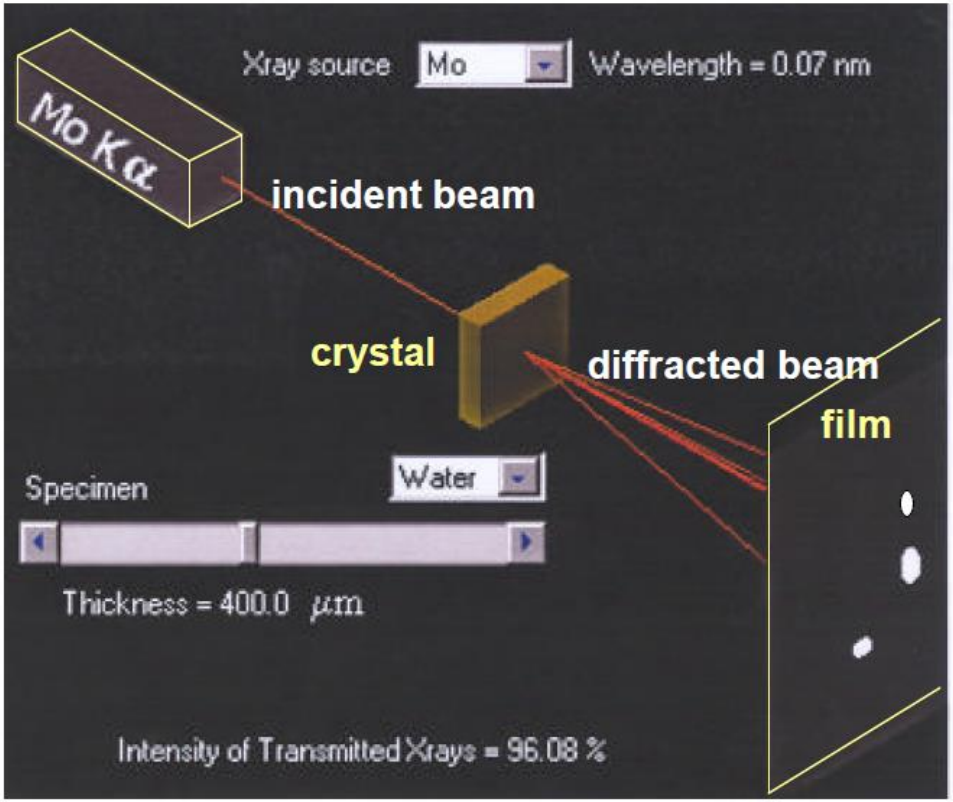


Why XRD?

- Measure the average spacings between layers or rows of atoms
- Determine the orientation of a single crystal or grain
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline regions

X-ray Diffraction (XRD)

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction.



Xray source Mo

Wavelength = 0.07 nm

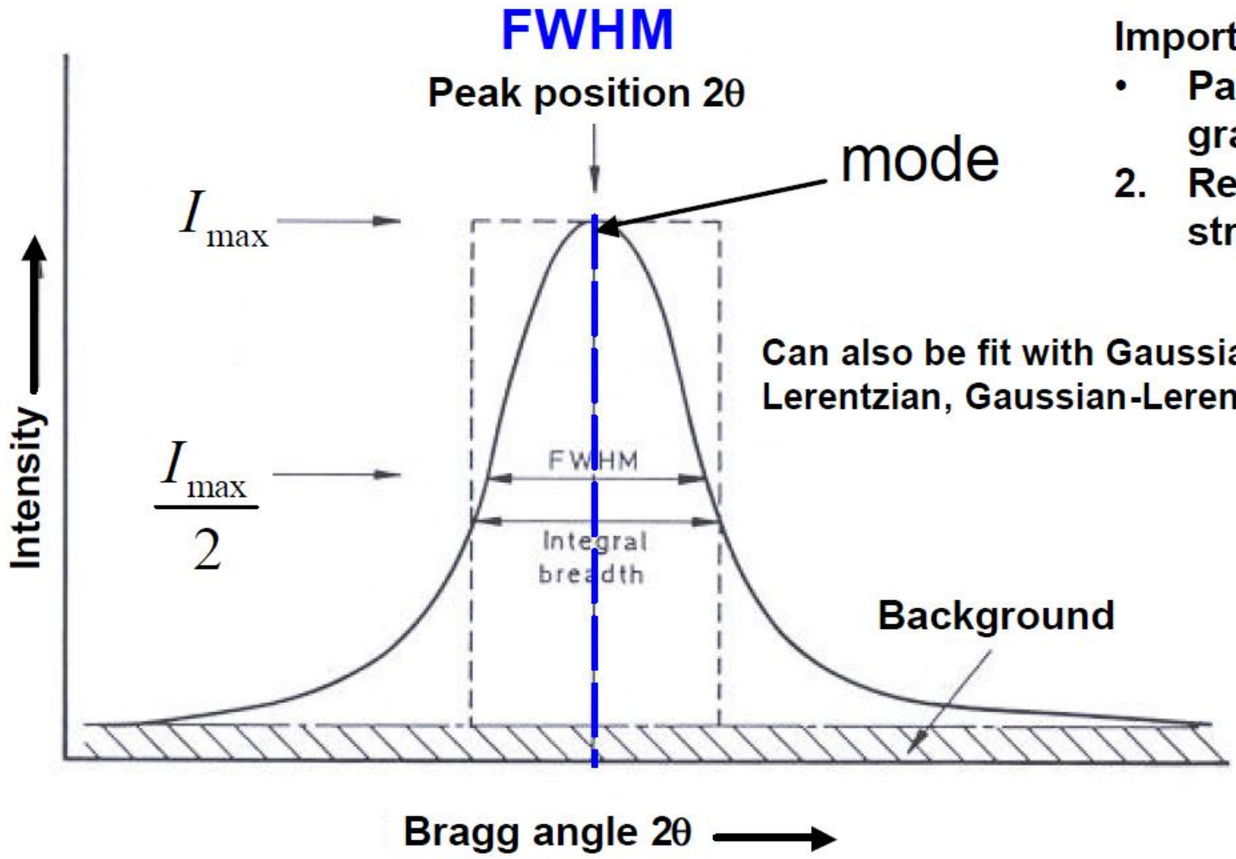
Specimen Water

Thickness = 400.0 μm

Intensity of Transmitted Xrays = 96.08 %

Effect of sample thickness on the absorption of X-rays

Peak Width-Full Width at Half Maximum



Important for:

- **Particle or grain size**

2. **Residual strain**

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

Bragg's Law tells us the location of a peak with indices *hkl*. θ_{hkl} is related to the interplanar spacing, *d*, as follows:

Braggs law can be rewritten as

$$\lambda^2 = 4d^2 \sin^2\theta \;\text{ OR }\; \sin^2\theta = \frac{\lambda^2}{4d^2}$$

Combining this relationship with the plane spacing equation gives us a new relationship:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4\sin^2\theta}{\lambda^2},$$

which can be rearranged to:

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2+k^2+l^2\right)$$

The term in parentheses $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any one pattern (because the X-ray wavelength λ and the lattice parameters a do not change). Thus $\sin^2\theta$ is proportional to $h^2+k^2+l^2$. This proportionality shows that planes with higher Miller indices will diffract at higher values of θ.

Since $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any pattern, we can write the following relationship for any two different planes:

$$\frac{\sin^2\theta_1}{\sin^2\theta_2}=\frac{\left(\frac{\lambda^2}{4a^2}\right)\left(h_1^2+k_1^2+l_1^2\right)}{\left(\frac{\lambda^2}{4a^2}\right)\left(h_2^2+k_2^2+l_2^2\right)} \text{ or } \frac{\sin^2\theta_1}{\sin^2\theta_2}=\frac{\left(h_1^2+k_1^2+l_1^2\right)}{\left(h_2^2+k_2^2+l_2^2\right)}.$$

Since h, k, and l are always integers, we can obtain $h^2+k^2+l^2$ values by dividing the $\sin^2\theta$ values for the different XRD peaks with the minimum one in the pattern (*i.e.*, the $\sin^2\theta$ value from the first XRD peak) and multiplying that ratio by the proper integer (either 1, 2 or 3). This should yield a list of integers that represent the various $h^2+k^2+l^2$ values. You can identify the correct Bravais lattice by recognizing the sequence of allowed reflections for cubic lattices (*i.e.*, the sequence of allowed peaks written in terms of the quadratic form of the Miller indices).

Primitive $h^2+k^2+l^2=1,2,3,4,5,6,8,9,10,11,12,13,14,16\ldots$
Body-centered $h^2+k^2+l^2=2,4,6,8,10,12,14,16\ldots$
Face-centered $h^2+k^2+l^2=3,4,8,11,12,16,19,20,24,27,32\ldots$

Conditions for allowed reflection for cubic lattices:

Primitive:

All possible *h*, *k* and *l* values

Body-centered:

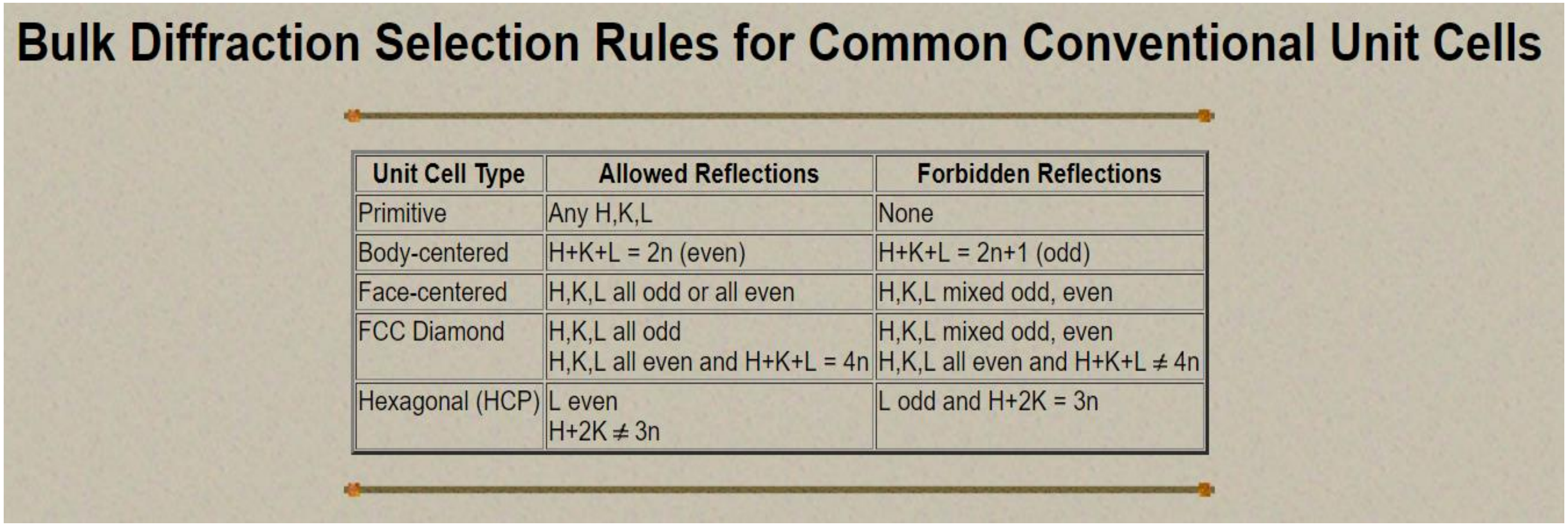
reflection is allowed when (*h* + *k* + *l*) is even

reflection is not allowed when (*h* + *k* + *l*) is odd

Face-centered:

reflection is allowed when *h*, *k* and *l* are either all even or all odd

no reflection when *h*, *k* and *l* are mixed i.e., even and odd

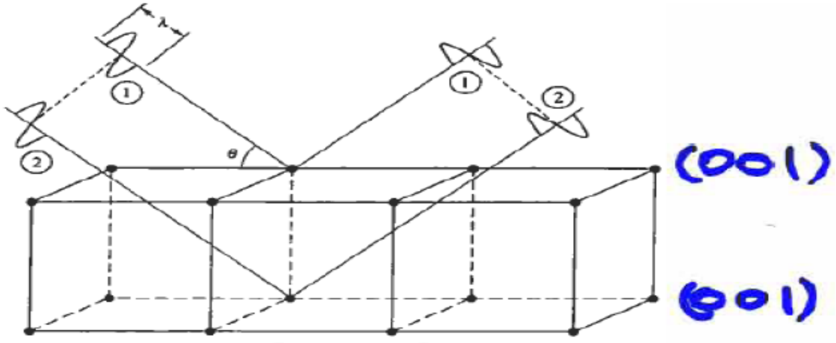


Bulk Diffraction Selection Rules for Common Conventional Unit Cells

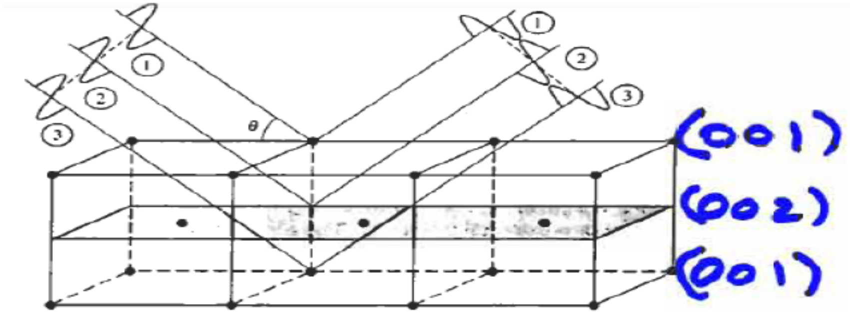
Unit Cell Type	Allowed Reflections	Forbidden Reflections
Primitive	Any H,K,L	None
Body-centered	H+K+L = 2n (even)	H+K+L = 2n+1 (odd)
Face-centered	H,K,L all odd or all even	H,K,L mixed odd, even
FCC Diamond	H,K,L all odd H,K,L all even and H+K+L = 4n	H,K,L mixed odd, even H,K,L all even and H+K+L ≠ 4n
Hexagonal (HCP)	L even H+2K ≠ 3n	L odd and H+2K = 3n

Hence,

- **Primitive $h^2 + k^2 + l^2 = 1,2,3,4,5,6,8,9,10,11,12,13,14,16\ldots$**
- **Body-centered $h^2 + k^2 + l^2 = 2,4,6,8,10,12,14,16\ldots$**
- **Face-centered $h^2 + k^2 + l^2 = 3,4,8,11,12,16,19,20,24,27,32\ldots$**



Pathlength ② – Pathlength ① = $N\lambda$



Pathlength ③ – Pathlength ① = $n\lambda$

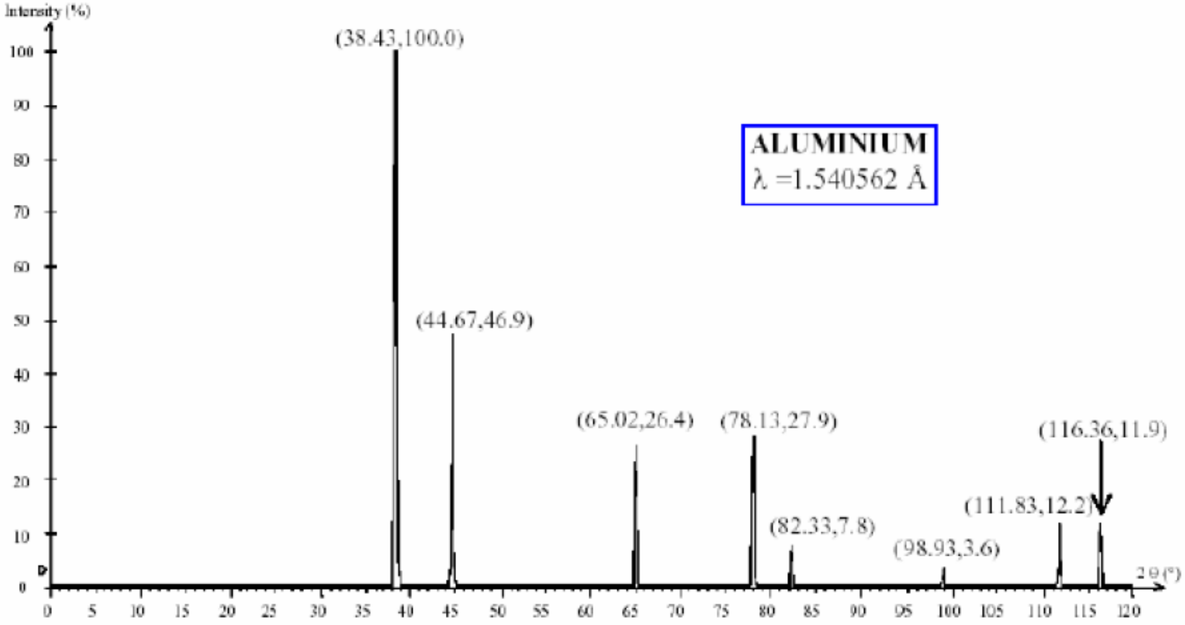
Pathlength ③ – Pathlength ② = Pathlength ② – Pathlength ① = $\left(\frac{2n-1}{2}\right)\lambda$

Two Methods of Indexing

1. **Mathematical**
2. **Analytical**

Worked Example

Consider the following XRD pattern for Aluminum, which was collected using CuKα radiation.



Index this pattern and determine the lattice parameters.

Worked Example cont…

Steps:

(1) Identify the peaks.

(2) Determine $\sin^2\theta$

(3) Calculate the ratio $\sin^2\theta / \sin^2\theta_{min}$ and multiply by the appropriate integers.

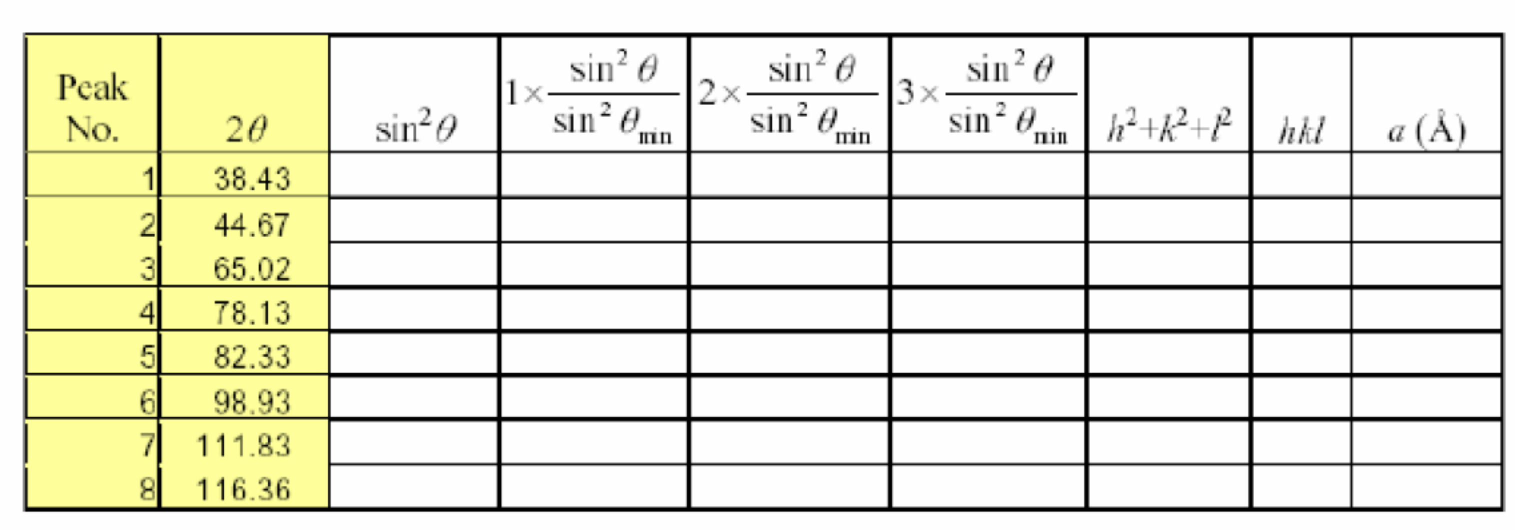
(4) Select the result from (3) that yields $h^2 + k^2 + l^2$ as an integer.

(5) Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice, e.g. BCC $h^2 + k^2 + l^2 = 2,4,6,8,\ldots$

(6) Calculate lattice parameters.

Worked Example cont…

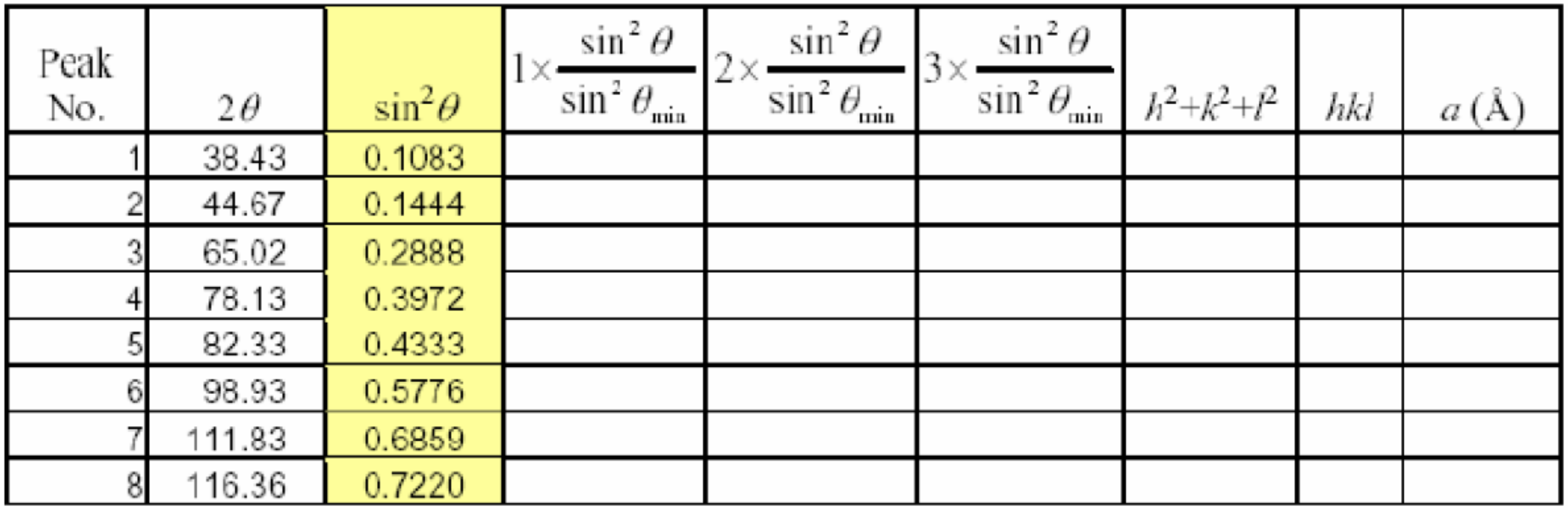
Step 1: Identify the peaks and their proper 2θ values. Eight peaks for this pattern.



Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

Worked Example cont…

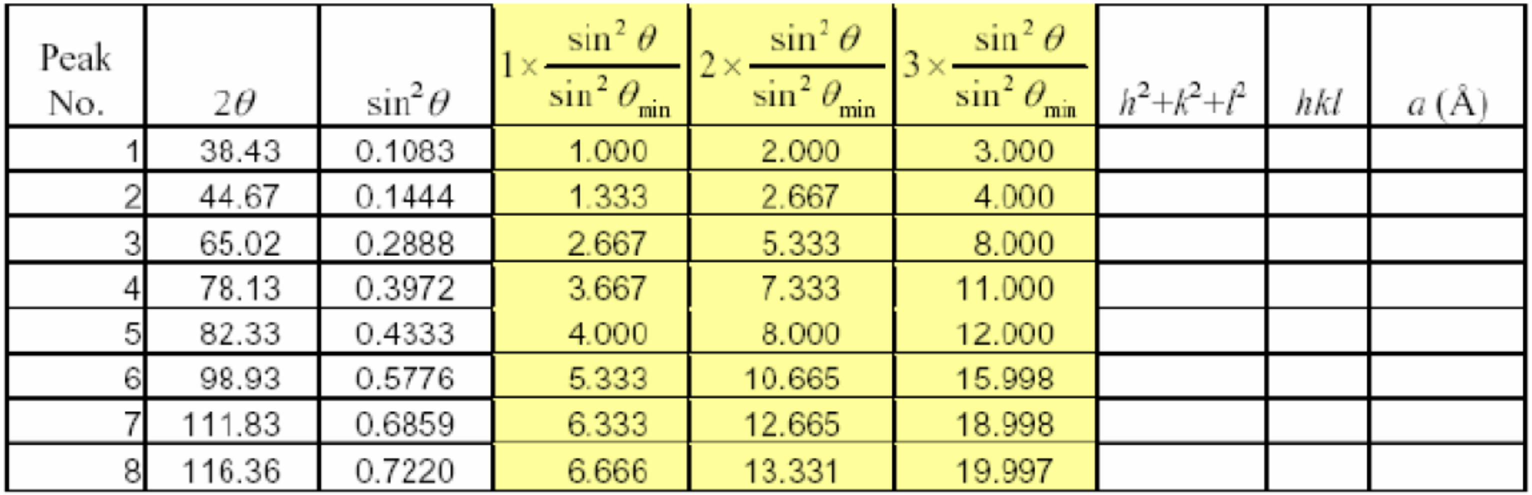
Step 2: Determine $\sin^2\theta$



Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

Worked Example cont…

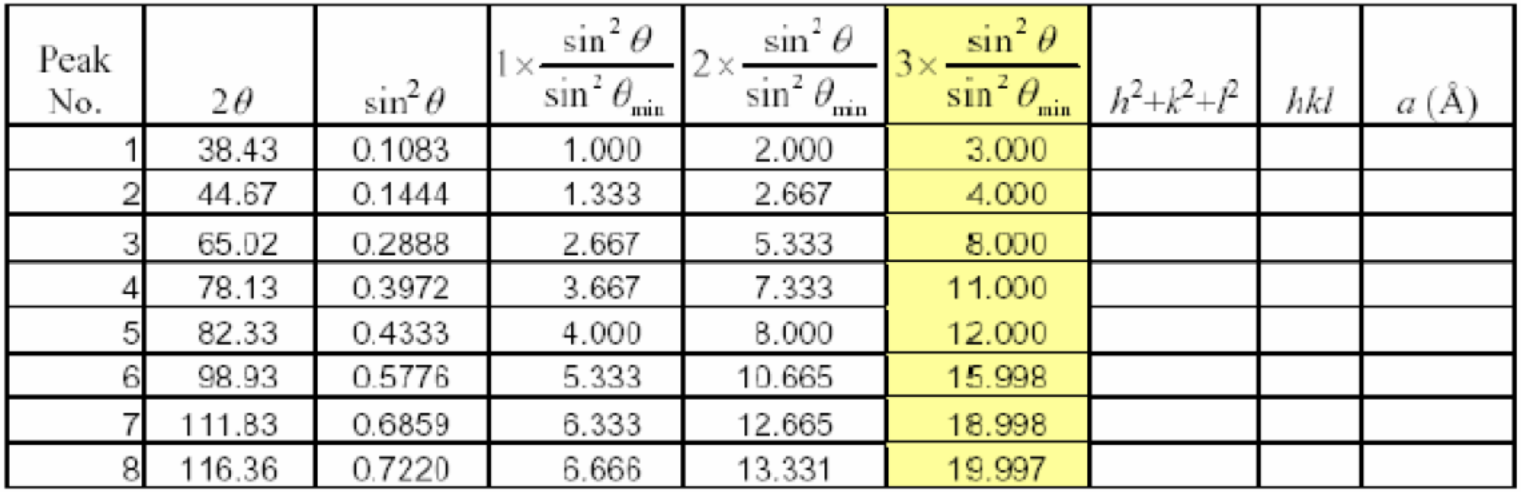
Step 3: Calculate the ratio $\sin^2\theta / \sin^2\theta_{\text{min}}$ and multiply by the appropriate integers.



Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{\text{min}}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{\text{min}}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{\text{min}}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

Worked Example cont…

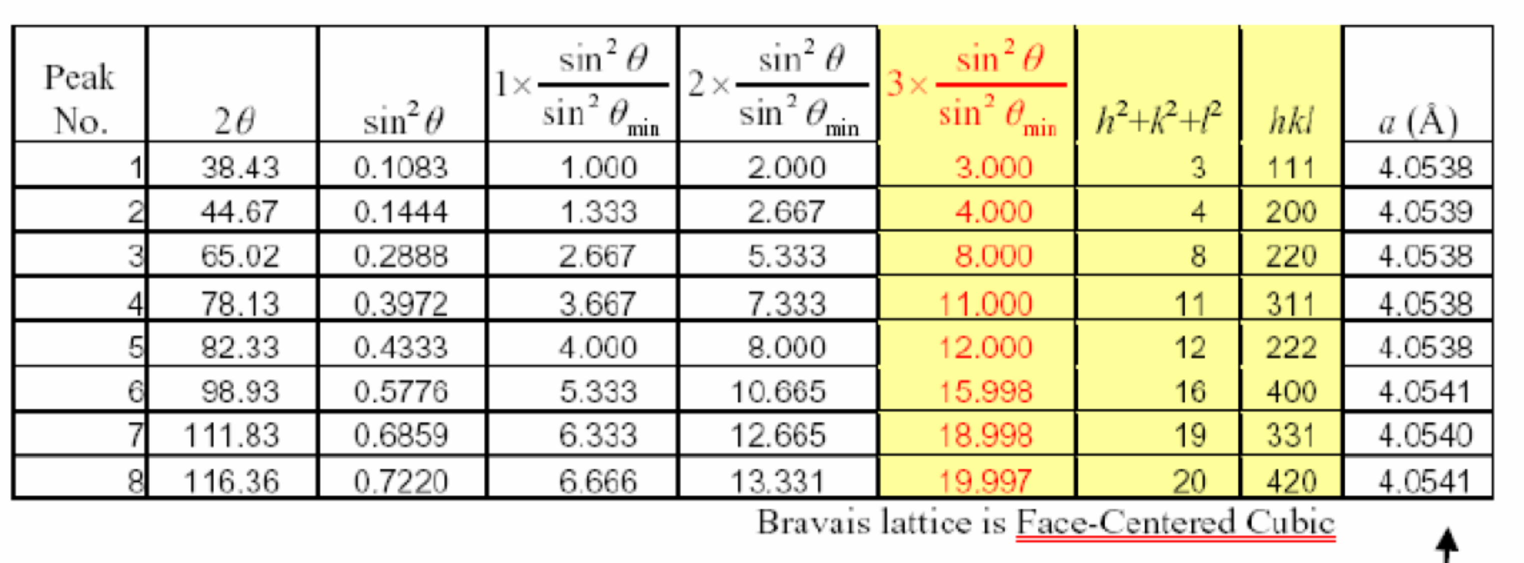
Step 4: Select the result from (3) that yields $h^2 + k^2 + l^2$ as a series of integers.



Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

Worked Example cont…

Step 5: Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice.



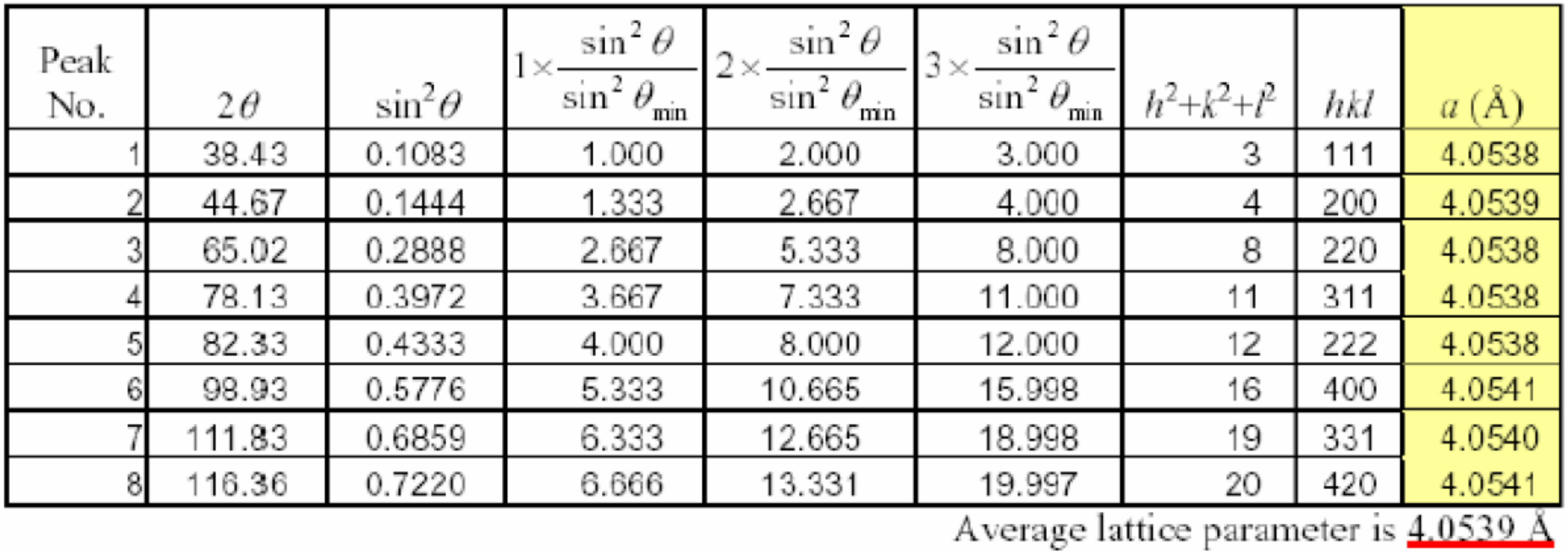
Peak No.	2θ	$\sin^2\theta$	$1 \times \frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$2 \times \frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$3 \times \frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Bravais lattice is Face-Centered Cubic

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2 + k^2 + l^2\right)$$

Worked Example cont…

Step 6: Calculate lattice parameters



Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Average lattice parameter is 4.0539 Å

Derivation of $sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2+l^2\right)$

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \qquad \lambda = 2d\sin\theta$$

$$d^2 = \frac{a^2}{h^2+k^2+l^2}; \qquad d = a\sqrt{\frac{1}{h^2+k^2+l^2}}$$

$$\lambda = 2a\sqrt{\frac{1}{h^2+k^2+l^2}}\,sin\,\theta$$

$$sin\,\theta = \frac{\lambda}{2a}\sqrt{h^2+k^2+l^2}$$

$$sin^2\theta = \frac{\lambda^2}{4a^2}h^2+k^2+l^2$$

Analytical

Recall: $\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2+k^2+l^2\right)$ and $\left(\frac{\lambda^2}{4a^2}\right)$ = constant for all patterns

Let $K = \frac{\lambda^2}{4a^2}$ then $\sin^2\theta = K\left(h^2+k^2+l^2\right)$

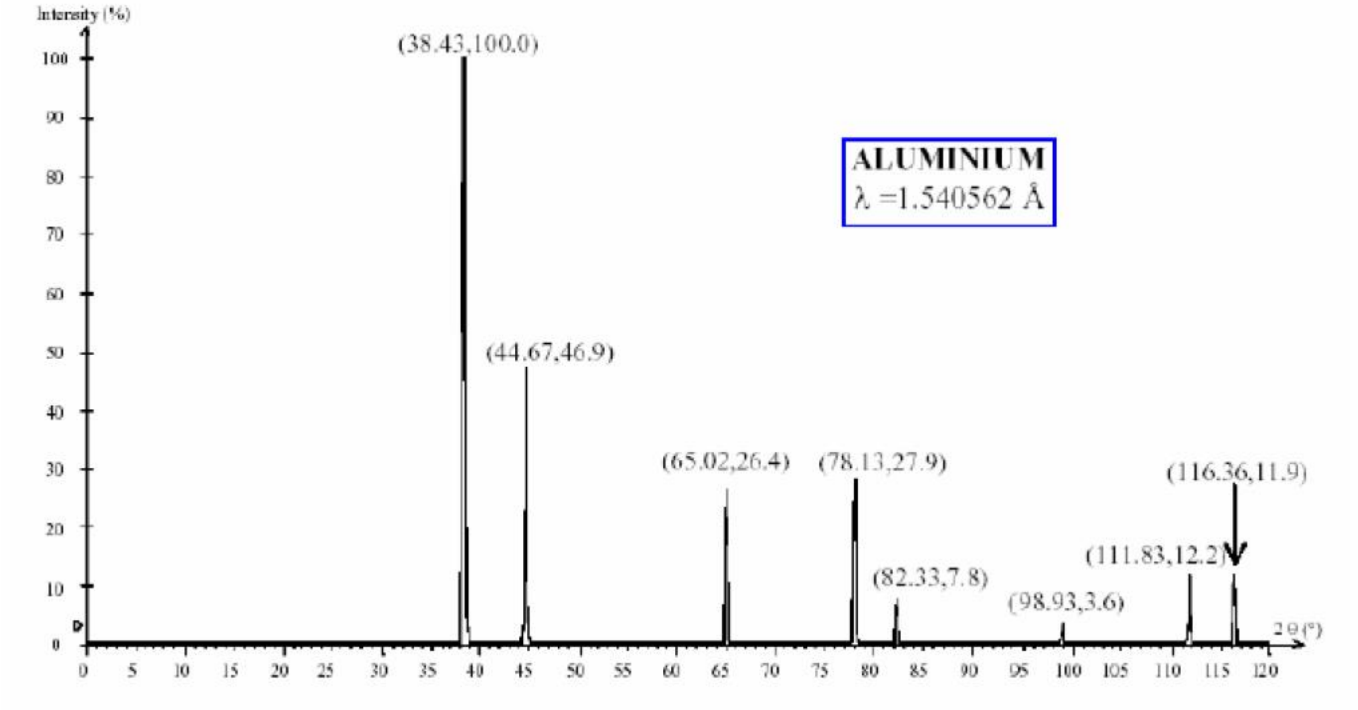
$$K = Sin^2\theta/(h^2+k^2+l^2)$$

For any cubic system, $h^2 + k^2 + l^2 = 1,2,3,4,5,6,8,9,10,11,12,\ldots$

If we determine $\sin^2\theta$ for each peak and divide the values by the integers 2,3,4,5,6,8,9,10,11…, we can obtain a common quotient, which is the value of K

Worked Example

Consider the following XRD pattern for Aluminum, which was collected using CuKα radiation.



Index this pattern and determine the lattice parameters.

Worked Example cont…

Steps:

(1) Identify the peaks.

(2) Determine $\sin^2\theta$

(3) Calculate the ratio $\sin^2\theta$/(integers)

$$\sin^2\theta = K\left(h^2 + k^2 + l^2\right)$$

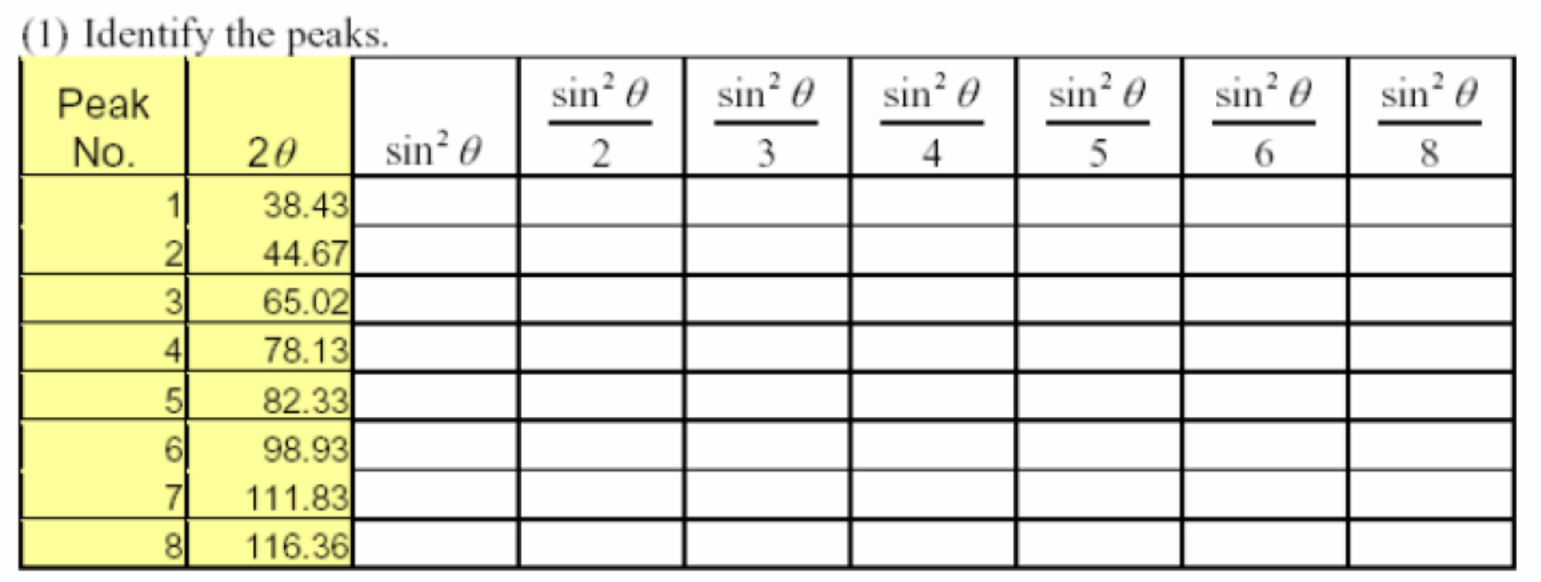
(4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be K.

(5) Divide $\sin^2\theta$ by K for each peak. This will give you a list of integers corresponding to $h^2 + k^2 + l^2$

(6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.

(7) Calculate lattice parameters.

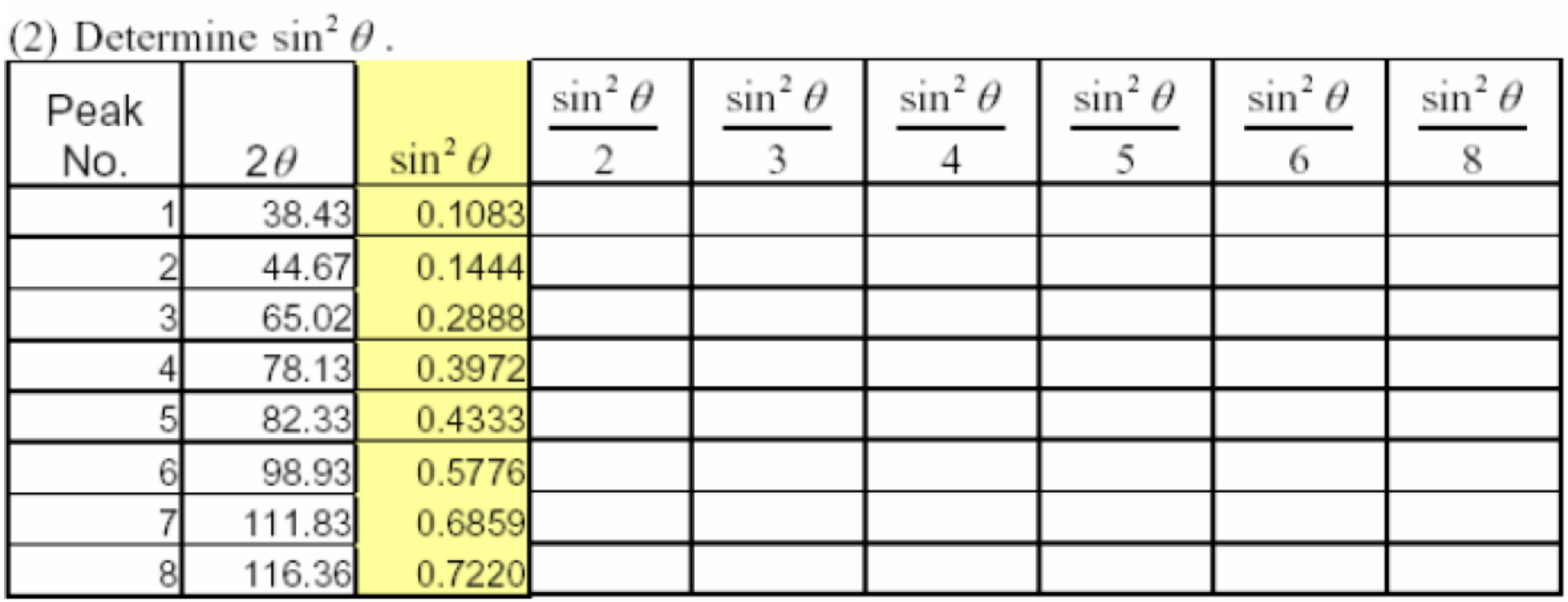
Worked Example cont…



(1) Identify the peaks.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

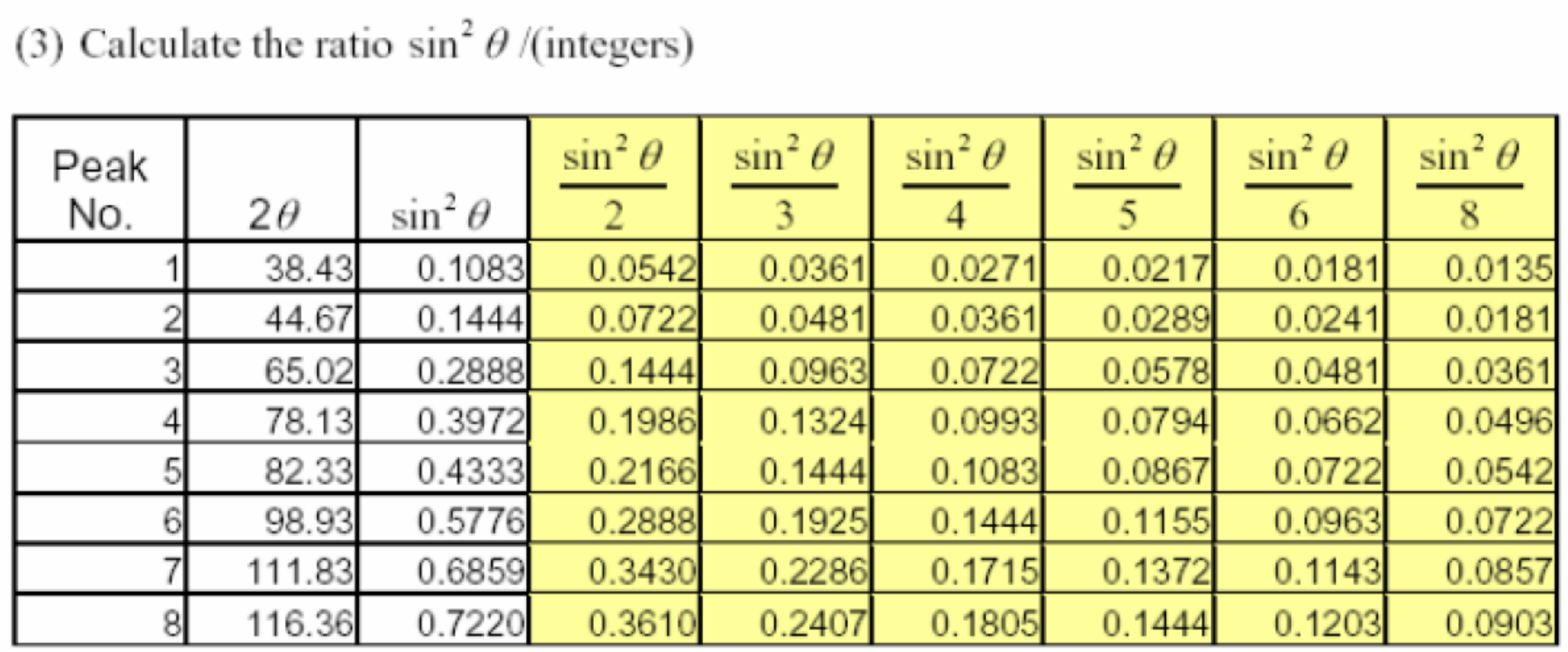
Worked Example cont…



(2) Determine $\sin^2\theta$.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

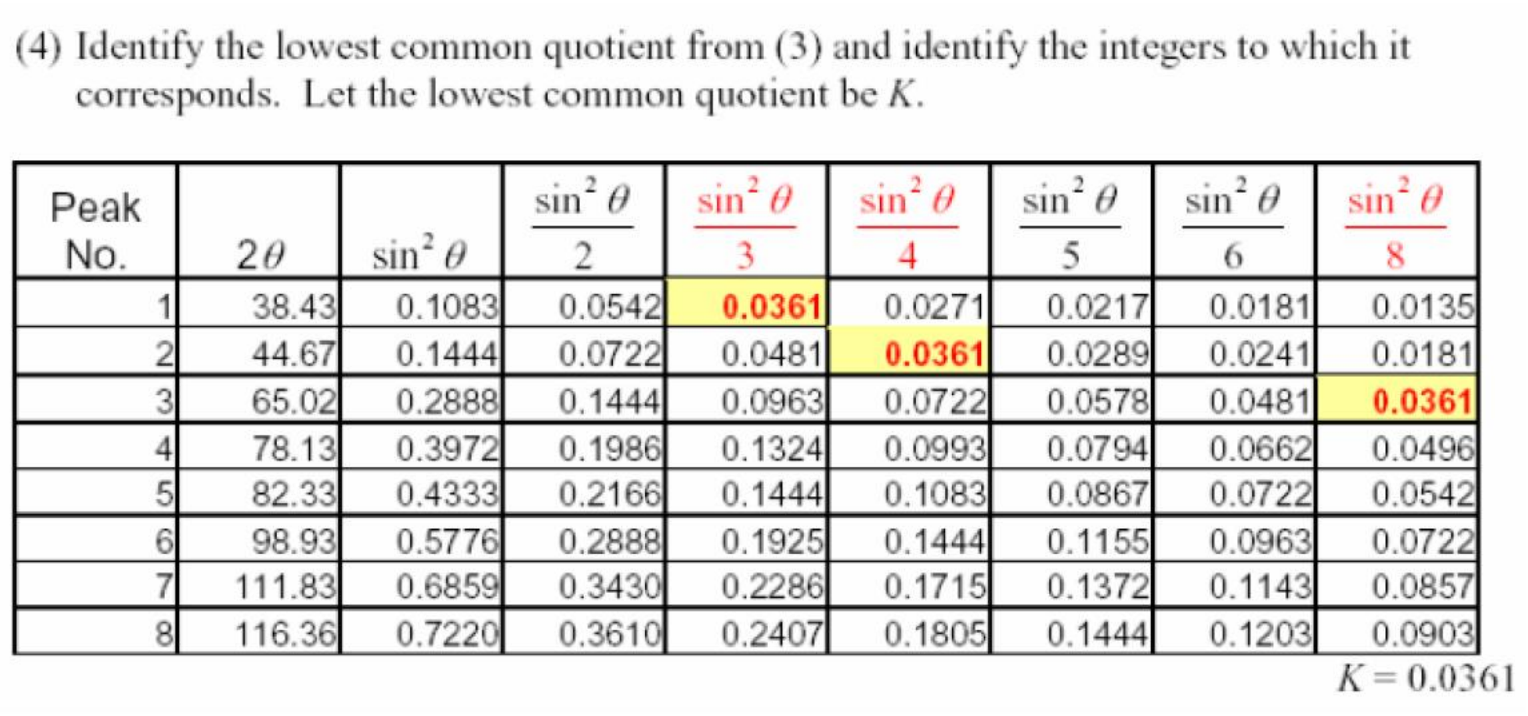
Worked Example cont…



(3) Calculate the ratio $\sin^2\theta$ /(integers)

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43	0.1083	0.0542	0.0361	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	0.0361	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	0.0361
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

Worked Example cont…

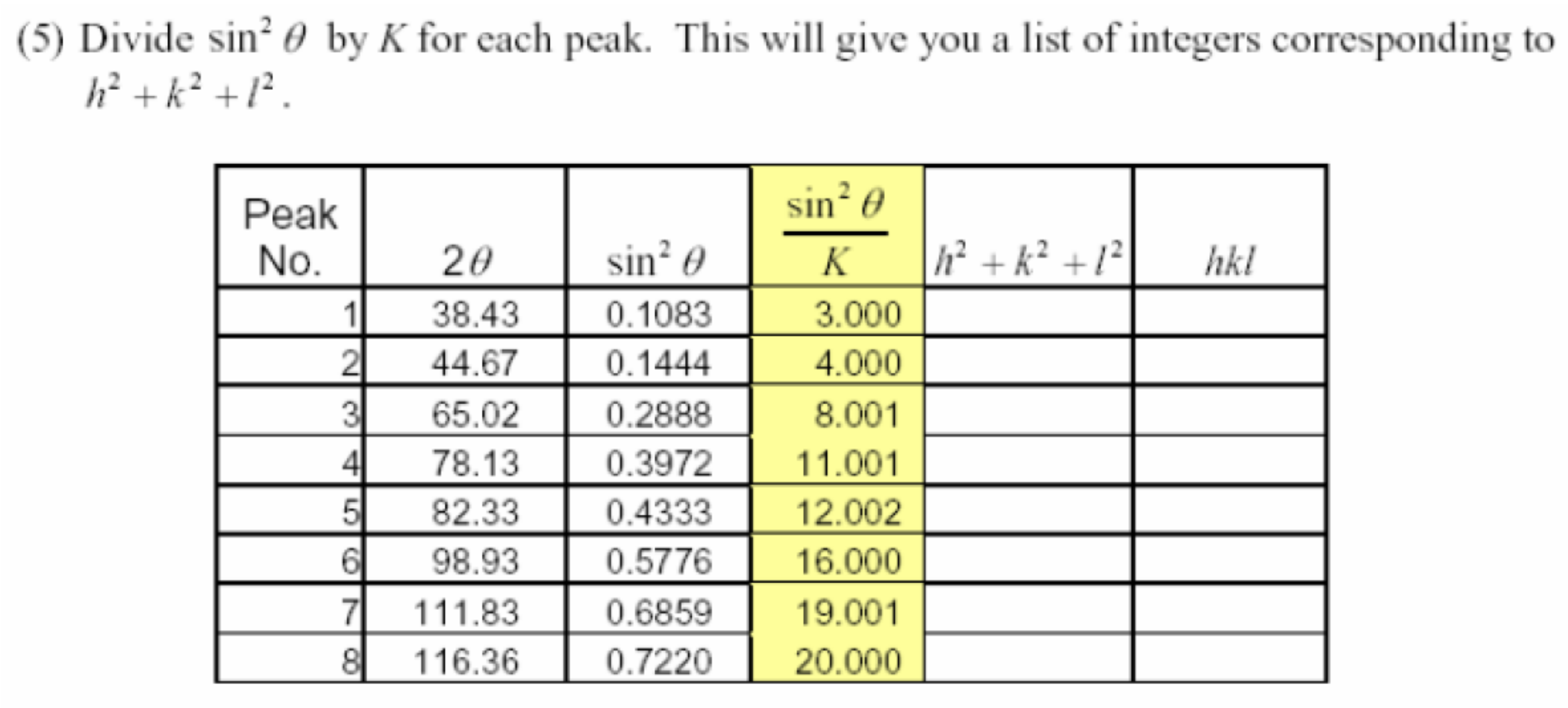


(4) Identify the lowest common quotient from (3) and identify the integers to which it corresponds. Let the lowest common quotient be *K*.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{2}$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{5}$	$\frac{\sin^2\theta}{6}$	$\frac{\sin^2\theta}{8}$
1	38.43	0.1083	0.0542	**0.0361**	0.0271	0.0217	0.0181	0.0135
2	44.67	0.1444	0.0722	0.0481	**0.0361**	0.0289	0.0241	0.0181
3	65.02	0.2888	0.1444	0.0963	0.0722	0.0578	0.0481	**0.0361**
4	78.13	0.3972	0.1986	0.1324	0.0993	0.0794	0.0662	0.0496
5	82.33	0.4333	0.2166	0.1444	0.1083	0.0867	0.0722	0.0542
6	98.93	0.5776	0.2888	0.1925	0.1444	0.1155	0.0963	0.0722
7	111.83	0.6859	0.3430	0.2286	0.1715	0.1372	0.1143	0.0857
8	116.36	0.7220	0.3610	0.2407	0.1805	0.1444	0.1203	0.0903

$K = 0.0361$

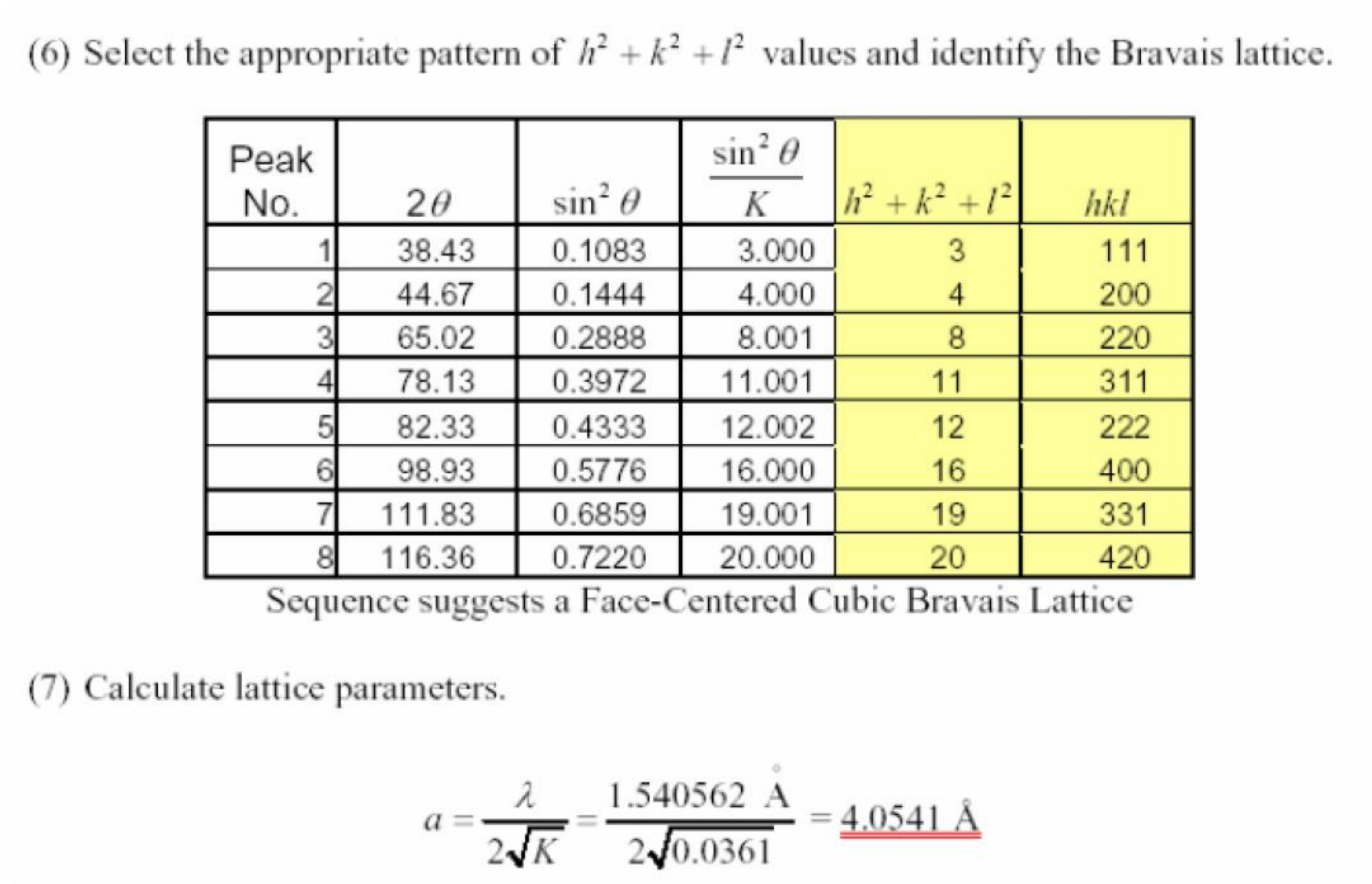
Worked Example cont…



(5) Divide $\sin^2\theta$ by K for each peak. This will give you a list of integers corresponding to $h^2+k^2+l^2$.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{K}$	$h^2+k^2+l^2$	hkl
1	38.43	0.1083	3.000		
2	44.67	0.1444	4.000		
3	65.02	0.2888	8.001		
4	78.13	0.3972	11.001		
5	82.33	0.4333	12.002		
6	98.93	0.5776	16.000		
7	111.83	0.6859	19.001		
8	116.36	0.7220	20.000		

Worked Example cont…



(6) Select the appropriate pattern of $h^2 + k^2 + l^2$ values and identify the Bravais lattice.

Peak No.	2θ	$\sin^2\theta$	$\frac{\sin^2\theta}{K}$	$h^2 + k^2 + l^2$	*hkl*
1	38.43	0.1083	3.000	3	111
2	44.67	0.1444	4.000	4	200
3	65.02	0.2888	8.001	8	220
4	78.13	0.3972	11.001	11	311
5	82.33	0.4333	12.002	12	222
6	98.93	0.5776	16.000	16	400
7	111.83	0.6859	19.001	19	331
8	116.36	0.7220	20.000	20	420

Sequence suggests a Face-Centered Cubic Bravais Lattice

(7) Calculate lattice parameters.

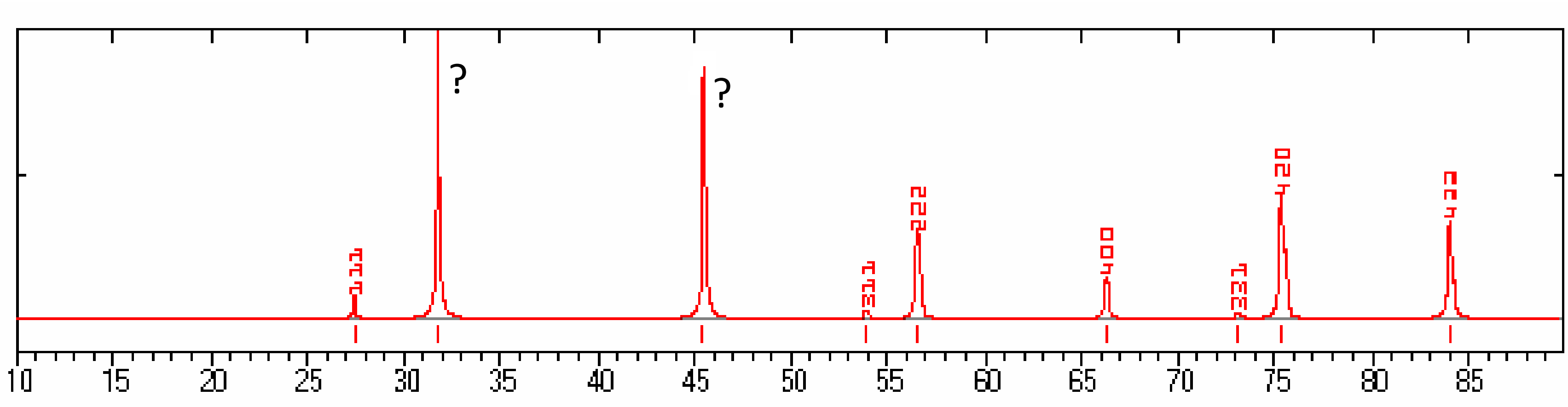
$$a = \frac{\lambda}{2\sqrt{K}} = \frac{1.540562\ \text{Å}}{2\sqrt{0.0361}} = \underline{4.0541\ \text{Å}}$$

Q. Use Bragg law to find out the indices of the first three reflections in a powder diffraction pattern taken from a simple cubic crystal.

3. Powder diffraction pattern are recorded with the help of monochromatic beam of X-Rays where as the samples consists of a large number of tiny crystals of random orientation. The condition of diffraction is given by Bragg's law: $2\,d\sin\theta = \lambda$ where 2θ is the angle between incident beam and the diffracted beam. The angle (sin θ) of diffraction is inversely proportional to inter planar spacing (d). The first three reflections therefore must come from the three most widely spaced crystal planes. The d spacing of a simple cubic crystal is given by $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$ where (h,k,l) are the Miller indices of the crystal planes. Clearly the lowest sum square value of (hkl) would have the highest d spacing. The first 3 values of $h^2 + k^2 + l^2$ are 1, 2 & 3 respectively. Therefore the indices of the first 3 reflections are (100), (110) & (111).

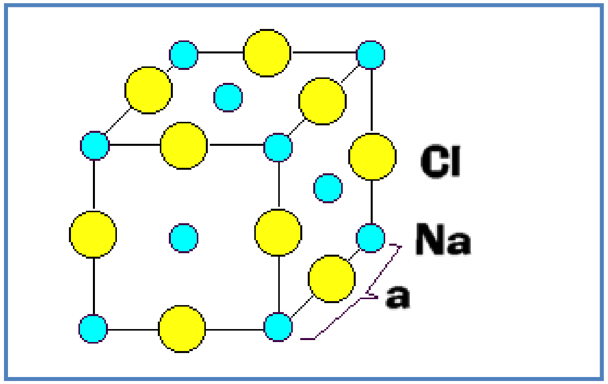
PROBLEM

NaCl shows a cubic structure. Determine *a* (Å) and the missing Miller indices (λ = 1.54056 Å).



Selected data from the NaCl diffractogram

2θ (°)	*h,k,l*
27.47	111
31.82	?
45.62	?
56.47	222



$$sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2 + k^2 + l^2\right)$$

a (Å)

Use at least two reflections and then average the results

$$a = \sqrt{\frac{\lambda^2\left(h^2+k^2+l^2\right)}{4\sin^2\theta}} = \sqrt{\frac{1.541^2\times 12}{4\times\sin^2\frac{56.473}{2}}} = 5.638 \text{ Å} \qquad (222)$$

Miller Indices

$$\sin^2\theta = \underbrace{\frac{\lambda^2}{4a^2}}_{K}\left(h^2 + k^2 + l^2\right)$$

$$\sin^2\theta = K\left(h^2 + k^2 + l^2\right)$$

$$K = \frac{\lambda^2}{4a^2} = \frac{1.54056^2}{4\times\left(5.638\right)^2} = 0.01867$$

$$\frac{\sin^2\theta}{K} = \left(h^2 + k^2 + l^2\right)$$

$$2\theta = 31.82^\circ \qquad \frac{sin^2\, 31.82/2}{0.01867} = 4.026 \approx 4 \qquad \left(h^2 + k^2 + l^2\right) = 4 \therefore \left(200\right)$$

$$2\theta = 45.62^\circ \qquad \frac{sin^2\, 45.62/2}{0.01867} = 8.052 \approx 8 \qquad \left(h^2 + k^2 + l^2\right) = 8 \therefore \left(220\right)$$

Identification of compounds

The powder diffractogram of a compound is its 'fingerprint' and can be used to identify the compound

Powder diffraction data from known compounds have been compiled into a **database (PDF)** by the Joint Committee on Powder Diffraction Standard, (**JCPDS**)

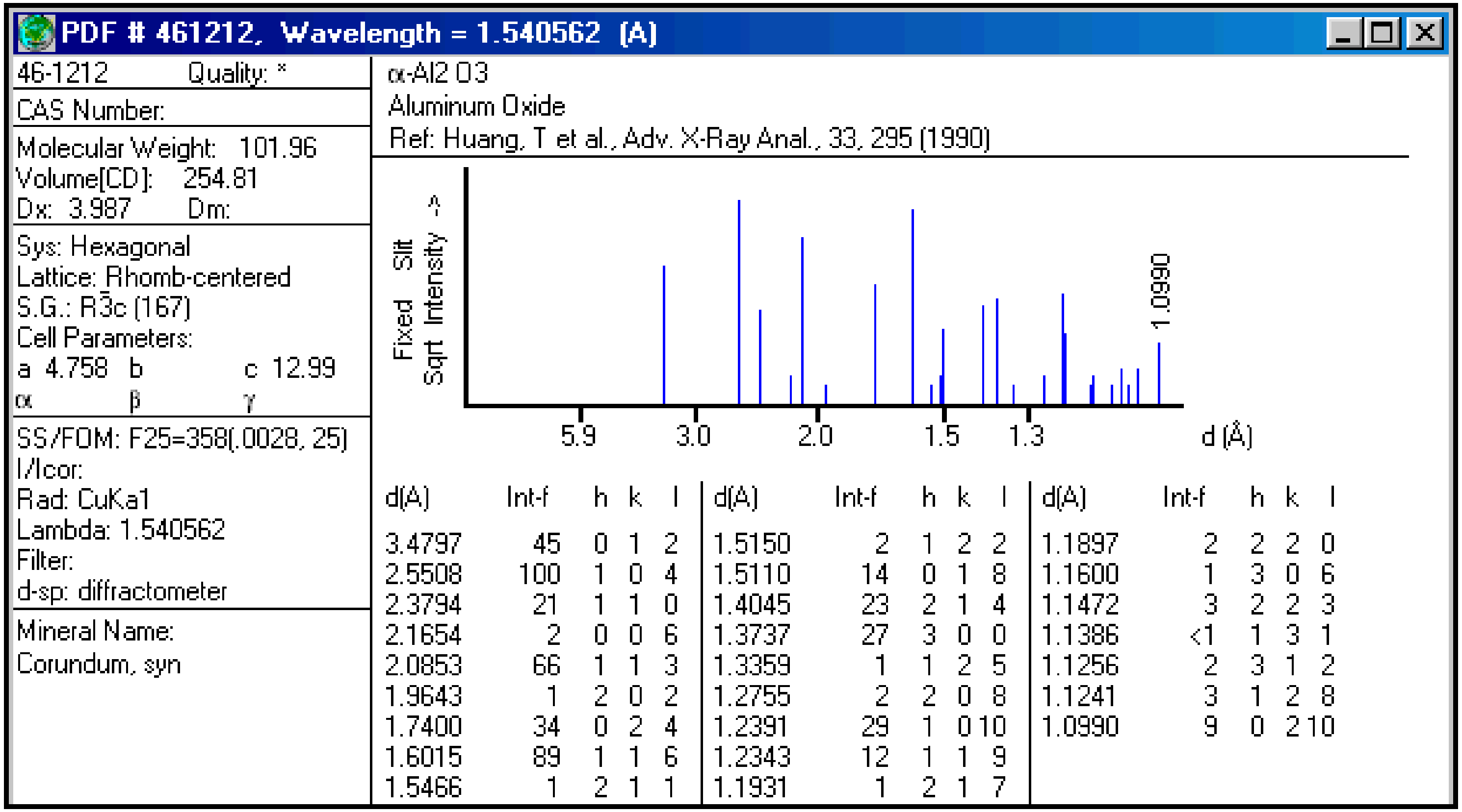
'Search-match' programs are used to ***compare*** experimental diffractograms with patterns of known compounds included in the database

This technique can be used in a variety of ways

PDF - Powder Diffraction File

A collection of patterns of inorganic and organic compounds

Data are added annually (2008 database contains 211,107 entries)



46-1212 Quality: *

CAS Number:

Molecular Weight: 101.96
Volume[CD]: 254.81
Dx: 3.987 Dm:

Sys: Hexagonal
Lattice: Rhomb-centered
S.G.: $R\bar{3}c$ (167)
Cell Parameters:
a 4.758 b c 12.99
α β γ

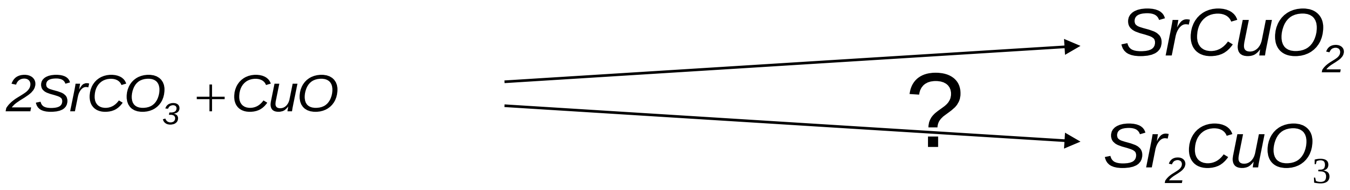
SS/FOM: F25=358(.0028, 25)
I/Icor:
Rad: CuKa1
Lambda: 1.540562
Filter:
d-sp: diffractometer

Mineral Name:
Corundum, syn

α-Al_2O_3
Aluminum Oxide
Ref: Huang, T et al., Adv. X-Ray Anal., 33, 295 (1990)

d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l
3.4797	45	0	1	2	1.5150	2	1	2	2	1.1897	2	2	2	0
2.5508	100	1	0	4	1.5110	14	0	1	8	1.1600	1	3	0	6
2.3794	21	1	1	0	1.4045	23	2	1	4	1.1472	3	2	2	3
2.1654	2	0	0	6	1.3737	27	3	0	0	1.1386	<1	1	3	1
2.0853	66	1	1	3	1.3359	1	1	2	5	1.1256	2	3	1	2
1.9643	1	2	0	2	1.2755	2	2	0	8	1.1241	3	1	2	8
1.7400	34	0	2	4	1.2391	29	1	0	10	1.0990	9	0	2	10
1.6015	89	1	1	6	1.2343	12	1	1	9					
1.5466	1	2	1	1	1.1931	1	2	1	7					

Outcomes of solid state reactions

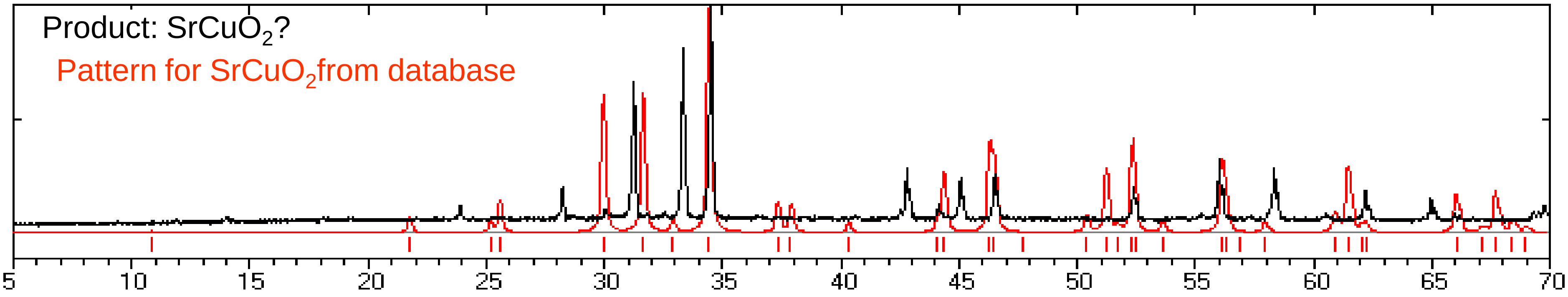


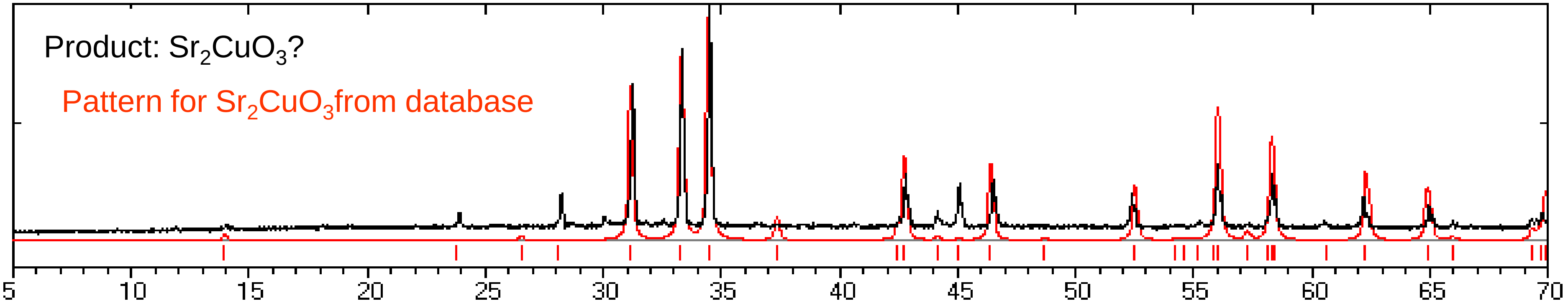
$2SrCO_3 + CuO$

?

$SrCuO_2$

Sr_2CuO_3





Determination of Number of Atoms in a Unit Cell

In structure determination process, the next step after establishing the shape and size of the unit cell is to find the number of atoms in the unit cell, because the number of atoms must be known before their positions can be determined.

When the unit cell volume, calculated from the lattice parameters, is multiplied by the measured density of the substance it gives the weight of all the atoms in the cell.

$$\sum A = \rho \frac{V}{1.66042}$$

Where $\sum A$ is the sum of the atomic weights of the atoms in the unit cell, ρ is the density (g/cm^3) and *V* is the volume of the unit cell (Å^3). If the substance is an element of atomic weight *A*, then

$$\sum A = n_1 A$$

Where *n1* is the number of atoms per unit cell. If the substance is a chemical compound then

$$\sum A = n_2 M$$

Where *n2* is the number of molecules per unit cell and *M* the molecular weight. The number of atoms per unit cell can then be calculated from *n2* and the composition of the phase.

Volume of the Unit Cell

The following equations are used to calculate the volume *V* of the unit cell:

Cubic:	$V = a^3$
Tetragonal:	$V = a^2c$
Orthorhombic:	$V = abc$
Monoclinic:	$V = abc \sin\beta$
Hexagonal:	$V = 0.866a^2c$

Atomic packing factor

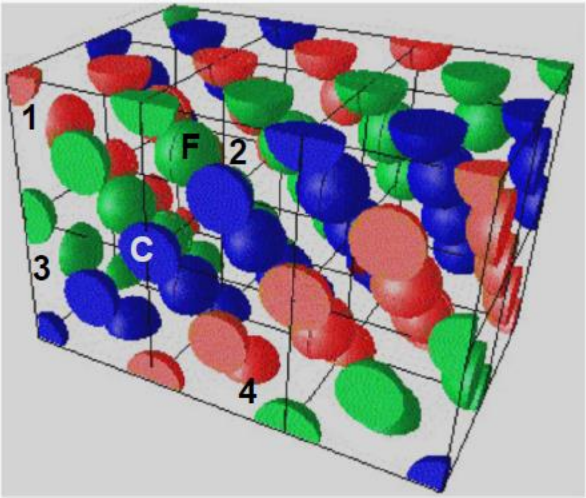
Atomic packing factor (APF) or packing efficiency indicates how closely atoms are packed in a unit cell and is given by the ratio of volume of atoms in the unit cell and volume of the unit cell

$$\mathrm{APF} = \frac{\text{Volme of atoms}}{\text{Volume of unit cell}}$$

Atomic packing factor

FCC lattice

In the FCC unit cell effective number of atoms = 8 corner atoms x (1/8) (each atom is shared by 8 unit cells) + 6 face-centered atoms x1/2 (each shared by two unit cells) = 4



The corner atom *C* is shared by unit cells *1, 2, 3, 4* and four more in front of each of them. The face-centered atom, *F* is shared between cells *1* and *2.*

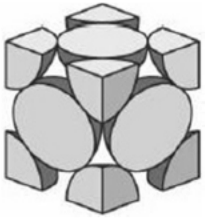
Atomic packing factor

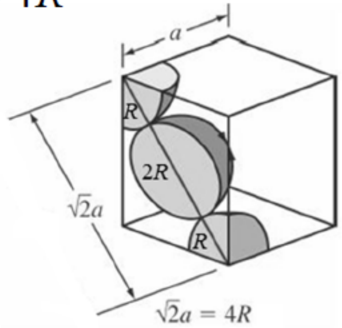
FCC lattice

Considering the atoms as hard spheres of radius *R*

$$\text{Total volume of atoms} = 4\times\frac{4}{3}\pi R^3$$

The relation between *R* and the FCC cell side a as shown in the figure below is $\sqrt{2}a = 4R$





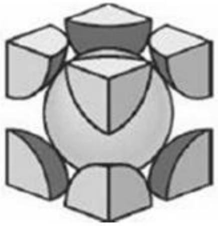
$$\boxed{APF(FCC) = \frac{4\times\frac{4}{3}\pi R^3}{a^3} = \frac{16\times 2\sqrt{2}\pi a^3}{3\times 64a^3} = 0.74}$$

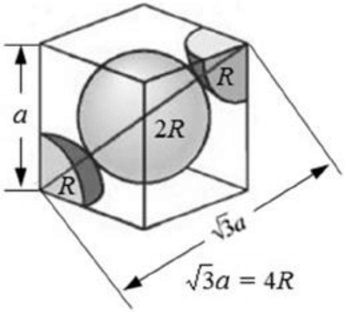
Atomic packing factor

BCC

For BCC crystals effective number of atoms per unit cell is 8 x 1/8 + 1 = 2 and the relation between *R* and a is

$$\sqrt{3}a = 4R$$





$$\boxed{APF(BCC) = \frac{2\times\frac{4}{3}\pi R^3}{a^3} = \frac{8\times3\sqrt{3}\pi a^3}{3\times64a^3} = 0.68}$$

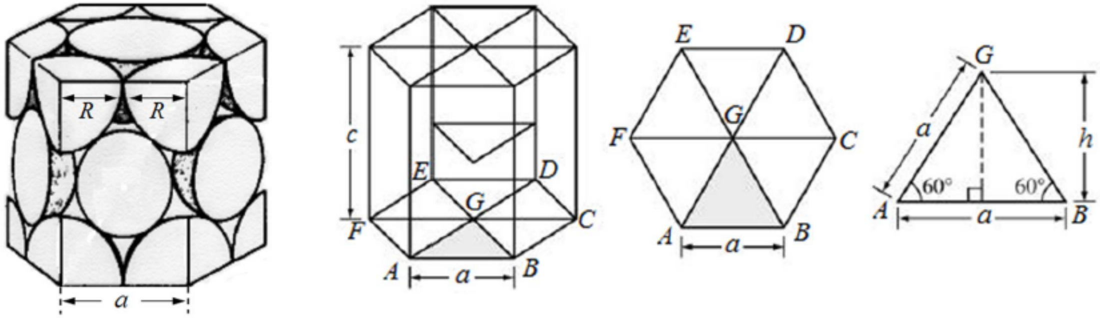
Atomic packing factor

Hexagonal lattice

In the Hexagonal unit cell, number of atoms = 12 corner atoms x 1/6 (shared by six unit cells) + Two face atoms x 1/2 + 3 interior = 6.

$$2R = a$$

Unit cell volume = (6 x ½ x a x h) x c = (3 x a x a sin60°) x c = $3a^2$ c sin60°



Examples

Ex. 1: Theoretical density calculation from crystal structure.

Theoretical density, $\rho = \frac{nA}{V_C N_A}$

n = number of atoms in the unit cell
A = atomic weight
V_C = volume of unit cell
N_A = Avogadro's number (6.023 x 10^{23} atoms/mol)

Calculate the theoretical density of Al.

Al is FCC, lattice parameter, a = 4.05 Å, n = 4.
Atomic weight of Al is 26.98 g/mol

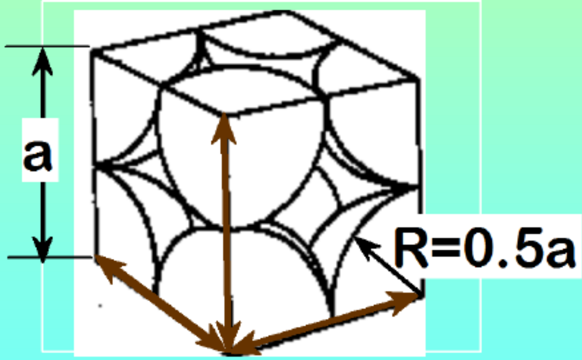
$$\rho = \frac{4 \times 26.98}{\left(4.05 \times 10^{-8}\right)^3 \times 6.023 \times 10^{23}} = 2.697 \, g/cc$$

Atomic Packing Factor (APF)

$$\text{APF} = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

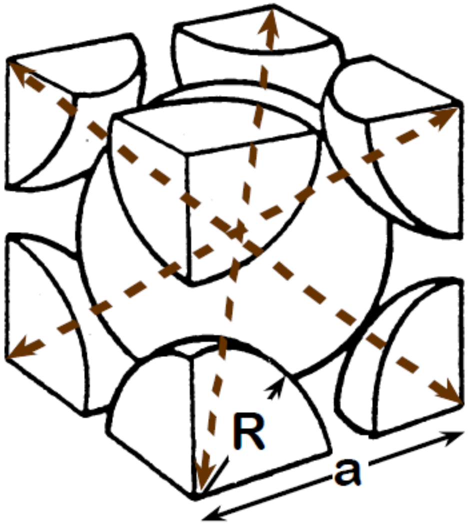
contains 8 x 1/8 =
1 atom/unit cell

$$\frac{\text{atoms}}{\text{unit cell}} \qquad \frac{\text{volume}}{\text{atom}}$$

$$\text{APF} = \frac{1 \quad \frac{4}{3}\pi\,(0.5a)^3}{a^3}$$

$$\frac{\text{volume}}{\text{unit cell}}$$

Body Centered Cubic (BCC) Structure



- **Coordination number** = 8
- **Close packed directions** are cube diagonals:

LD_{110}= 1 atom/(4R√(2/3))=1/(2R√8/3)
LD_{001} = 1 atom/(4R/√3))= 1/(2R √4/3)
LD_{111} = 2 atoms/4R = 1/(2R)

- **Unit cell contains:**

1 + 8 x 1/8 = **2** atoms/unit cell

- **APF** = 0.68:

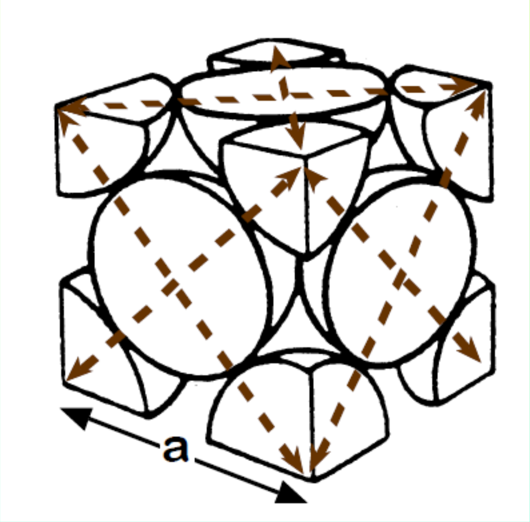
$\frac{\text{atoms}}{\text{unit cell}}$

$\frac{\text{volume}}{\text{atom}}$

$$\text{APF} = \frac{2\ \frac{4}{3}\pi(\sqrt{3}a/4)^3}{a^3}$$

$\frac{\text{volume}}{\text{unit cell}}$

Face-Centered Cubic (FCC) Structure



- **Coordination number** = 12
- **Close packed directions** are face diagonals:

LD_{110}= 2 atom/(4R)= 1/2R

LD_{001} = 1 atom/(2R√2))= 1/(2R √2)

LD_{111} = 1 atoms/4R = 1/(2R √6)

- **Unit cell contains**:

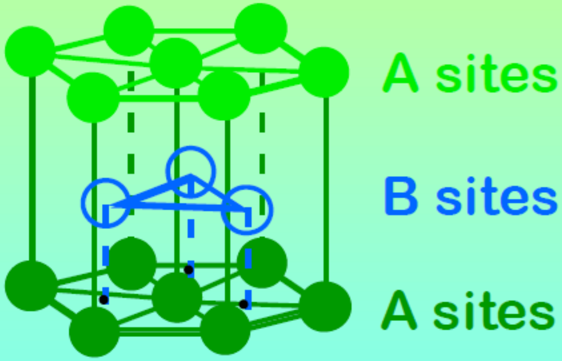
  6 x 1/2 + 8 x 1/8 = **4** atoms/unit cell

- **APF = 0.74**

$$\text{APF} = \frac{\overset{\frac{\text{atoms}}{\text{unit cell}}}{4}\ \overset{\frac{\text{volume}}{\text{atom}}}{\frac{4}{3}\pi(\sqrt{2}a/4)^3}}{\underset{\frac{\text{volume}}{\text{unit cell}}}{a^3}}$$

Hexagonal Close-Packed (HCP) Structure

- ABAB... Stacking Sequence
- 3D Projection



- 2D Projection

- Coordination number = ?
- APF = ?

Theoretical Density, ρ

 # atoms/unit cell → n

Atomic weight (g/mol) → A

$$\rho = \frac{n\,A}{V_C N_A}$$

Volume/unit cell
(cm^3/unit cell) → V_C

Avogadro's number
(6.023 x 10^{23} atoms/mol) → N_A

<u>Example: Copper</u>

- crystal structure **FCC**
- # atoms/unit cell **= 4**
- atomic weight = **63.55 g/mol**
- atomic radius R = **0.128 nm**

-7

- for FCC **a = 2R√2**; $V_c=a^3$; $V_c=4.75\ 10^{-23}$ cm^3

Result: theoretical ρ_{Cu} = 8.89 g/cm^3
Compare to actual: ρ_{Cu} = 8.94 g/cm^3

SIMPLE ANALYSIS OF SIMPLE PATTERNS

$$2d\sin\theta = n\lambda \quad \Rightarrow \quad \sin^2\theta \propto \frac{1}{d_{hkl}^2}$$

For cubic crystals: $d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

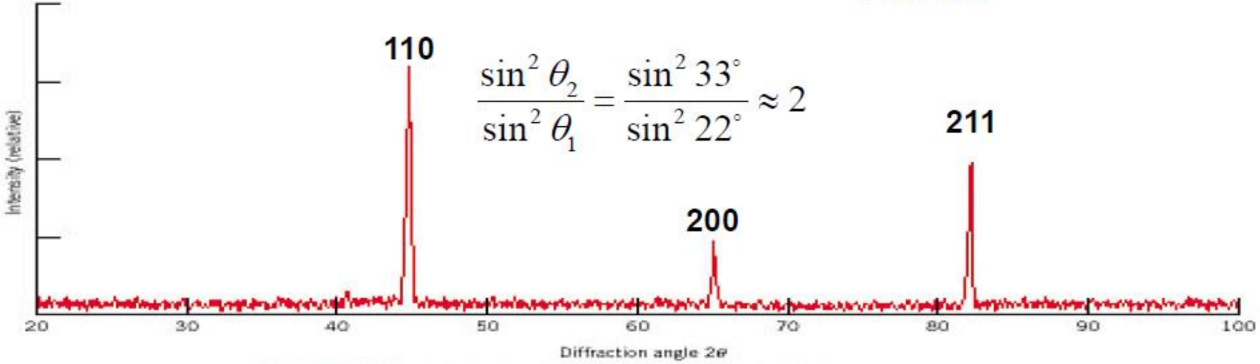
$$\sin^2\theta \propto (h^2+k^2+l^2)$$

$$\frac{\sin^2\theta_{n\text{th peak}}}{\sin^2\theta_{\text{1st peak}}} = \frac{(h^2+k^2+l^2)_{n\text{th peak}}}{(h^2+k^2+l^2)_{\text{1st peak}}}$$

SIMPLE ANALYSIS OF SIMPLE PATTERNS

α-Fe is cubic. Is it FCC or BCC?

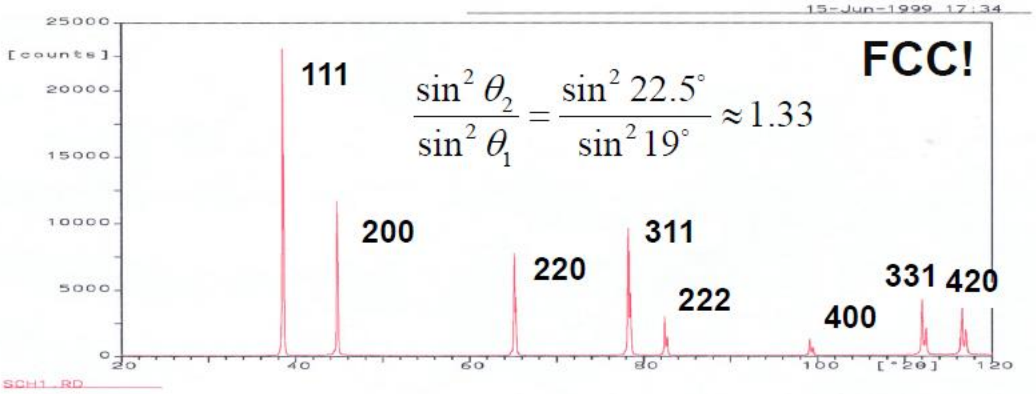
BCC!



$$\frac{\sin^2\theta_2}{\sin^2\theta_1}=\frac{\sin^2 33^\circ}{\sin^2 22^\circ}\approx 2$$

FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

What about Al?



FCC!

$$\frac{\sin^2\theta_2}{\sin^2\theta_1}=\frac{\sin^2 22.5^\circ}{\sin^2 19^\circ}\approx 1.33$$

Ex: An element, BCC or FCC, shows diffraction peaks at 2θ: 40, 58, 73, 86.8,100.4 and 114.7. Determine:(a) Crystal structure?(b) Lattice constant? (c) What is the element?

2theta	theta	$\sin^2\theta$	normalized $h^2+k^2+l^2$	(*hkl*)
40	20	0.117	1	(110)
58	29	0.235	2	(200)
73	36.5	0.3538	3	(211)
86.8	43.4	0.4721	4	(220)
100.4	50.2	0.5903	5	(310)
114.7	57.35	0.7090	6	(222)

BCC, *a* =3.18 Å → W

Q.

Copper forms cubic crystals when an X-ray powder pattern of crystalline copper is taken using X-rays from a copper target with λ = 1.5405 Å, reflections are found at θ (degree) = 21.65, 25.21, 37.06, 44.96, 47.58.

i) What is the type of lattice formed?
ii) What is the unit cell length?
iii) What is the density of copper ?

Q.

The edge of the cubic unit cell of lead is 4.92 Å. The density of lead is 11.55 gm/cc. Calculate the smallest angle with respect to the incident beam at which constructive interference of X-rays of wavelengths 1.5418 Å would occur for 110 planes of this crystal.

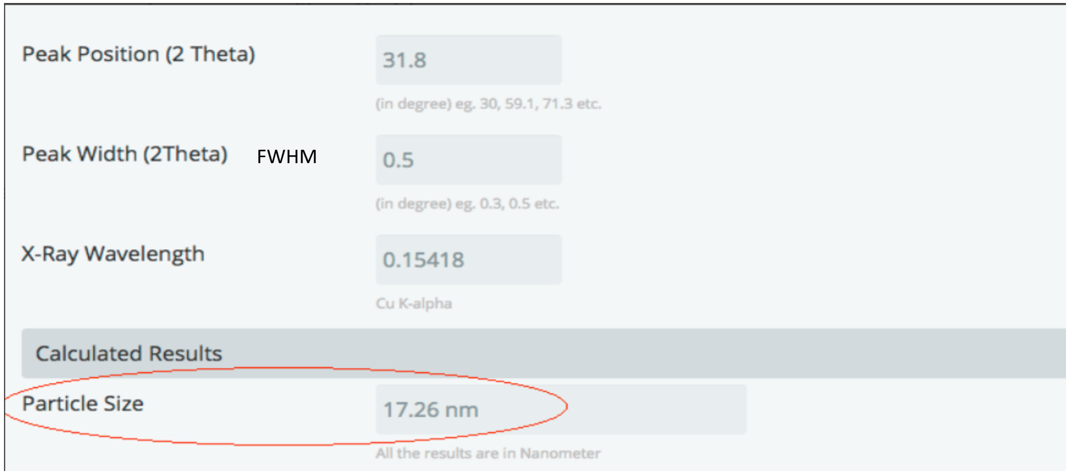
Q.

The X-ray diffraction pattern of a crystal is obtained using X-rays from a copper target and a certain reflection is found at $10.27^{o.}$ With another metal target, the same reflection was found at 4.73^{o} Given the wavelength of the X-rays from the copper target is 1.540 Å, calculate the wavelength of the X-rays from the other metal target and identify the metal.

Q.1 The distance between a set of planes in NaCl is 564.02 pm. Using an x-ray source of 75 pm, at what diffraction angle (2θ) should peaks be recorded for the first order of diffraction ($n = 1$) ?

Hint: To calculate the angle θ from $\sin\theta$, the $\sin^{-1}$ function on the calculator must be used

Q. 4: Calculate the particles size by using the following value?



Peak Position (2 Theta): 31.8

(in degree) eg. 30, 59.1, 71.3 etc.

Peak Width (2Theta) FWHM: 0.5

(in degree) eg. 0.3, 0.5 etc.

X-Ray Wavelength: 0.15418

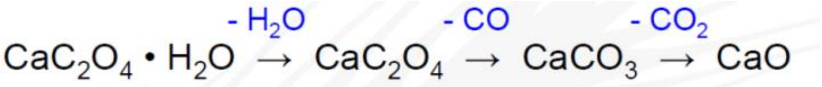
Cu K-alpha

Calculated Results

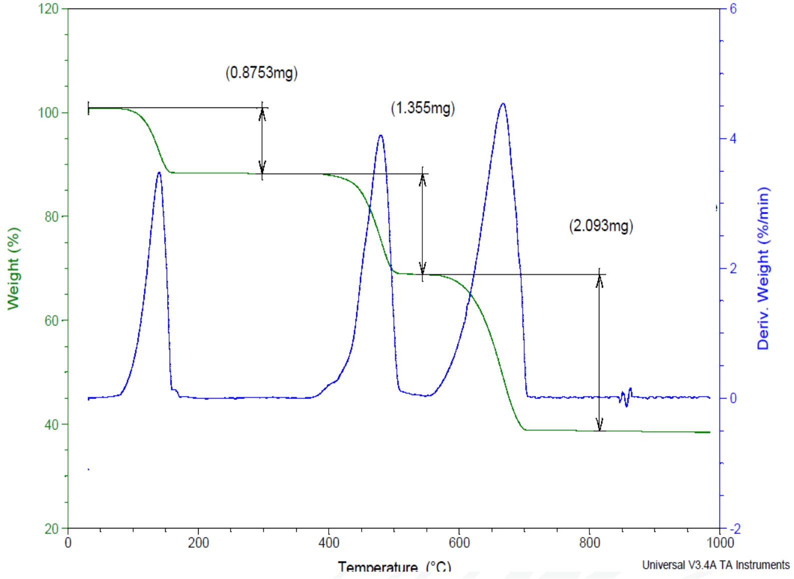
Particle Size: 17.26 nm

All the results are in Nanometer

Q.3: Mark the TG/DTA peak of byproduct with respect to given weight obtained after decomposition of Calcium Oxalate?



$$CaC_2O_4 \cdot H_2O \xrightarrow{-H_2O} CaC_2O_4 \xrightarrow{-CO} CaCO_3 \xrightarrow{-CO_2} CaO$$



Q.4: X-ray diffraction of copper, which has a face-centered cubic sturucture, is done using X-rays with a wavelength of 0.154 nm, one peak in the XRD pattern is at $2\theta = 43.2^o$

What are the miller indices for this peak?

Q. 5. X-ray diffractometers are not used to identify the physical properties of which of the following?

a) Metals

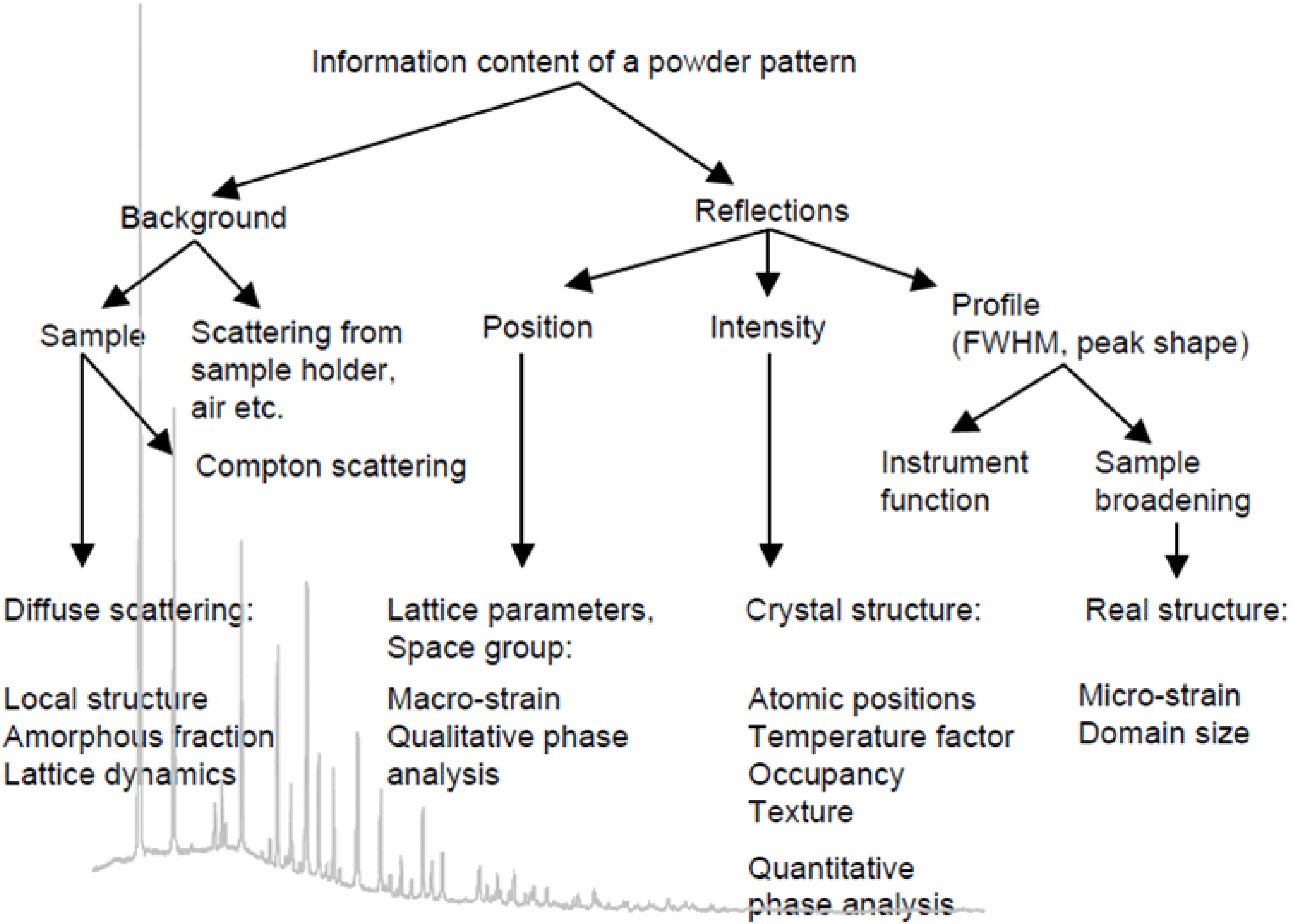
b) Liquids

c) Polymeric materials

d) Solids

Selection Rules for Reflections in Cubic Crystals

(*hkl*)	$h^2 + k^2 + l^2$	SC	BCC	FCC
100	1	✓	×	×
110	2	✓	✓	×
111	3	✓	×	✓
200	4	✓	✓	✓
210	5	✓	×	×
211	6	✓	✓	×
220	8	✓	✓	✓
300, 221	9	✓	×	×
310	10	✓	✓	×
311	11	✓	×	✓
222	12	✓	✓	✓
320	13	✓	×	×
321	14	✓	✓	×
400	16	✓	✓	✓
410, 322	17	✓	×	×
411, 330	18	✓	✓	×
331	19	✓	×	✓
420	20	✓	✓	✓
421	21	✓	×	×



Information content of a powder pattern

Background

Sample

Scattering from sample holder, air etc.

Compton scattering

Diffuse scattering:

Local structure
Amorphous fraction
Lattice dynamics

Reflections

Position

Lattice parameters, Space group:

Macro-strain
Qualitative phase analysis

Intensity

Crystal structure:

Atomic positions
Temperature factor
Occupancy
Texture

Quantitative phase analysis

Profile (FWHM, peak shape)

Instrument function

Sample broadening

Real structure:

Micro-strain
Domain size