An Introduction to X-Ray Powder Diffraction

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LATTICE ARRAYS AND BRAVAIS LATTICES

Crystalline materials differ from amorphous materials in that in the former there is order in the arrangement of the molecular contents whereas in the latter there is no order or at best a tendency for a short-range order.

The packing of atoms, molecules or ions within a crystal occurs in a symmetrical manner and furthermore this symmetrical arrangement is repetitive.
A most important common characteristic that crystals may share is the manner in which repetition occurs. This will be expressed in a common lattice array.

A lattice array is constructed from the arrangement of atomic material within the crystal as follows:

A 2-dimensional Lattice

Pick any position within the 2 dimensional lattice in Fig. 1(a) and note the arrangement about this point. The chosen position can be indicated by a point (a lattice point). In view of the repetitive arrangement, there will be a 2 dimensional array of identical positions and if these are also marked by a point a 2-dimensional lattice will result if the points are joined.
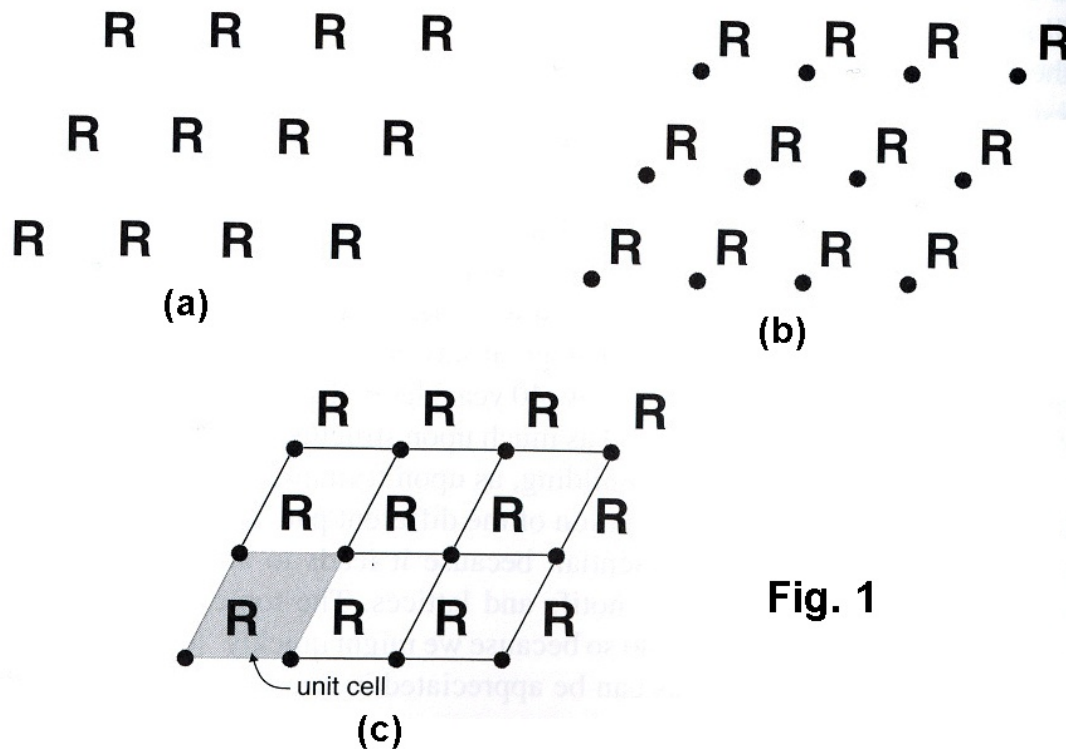

Fig. 1

In a real 3-dimensional crystal lattice the same ideas apply.

When crystal structures are represented by lattices, it transpires that all crystals break down into one of fourteen three dimensional lattice arrangements. **Bravais** demonstrated mathematically that there are only fourteen ways in which repetitive symmetry can occur and the fourteen lattices representing the ways in which repetition can occur are referred to as the **Bravais** lattices.

UNIT CELL

A unit cell can be any unit of a lattice array which when repeated in all directions, and *always **maintaining the same orientation in space***, generates the lattice array.
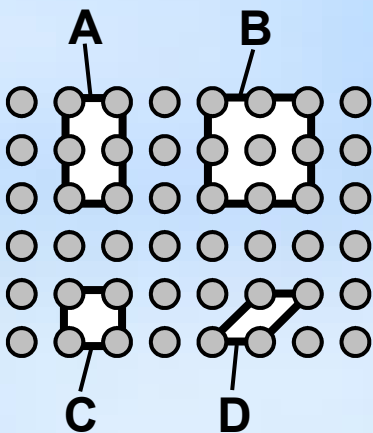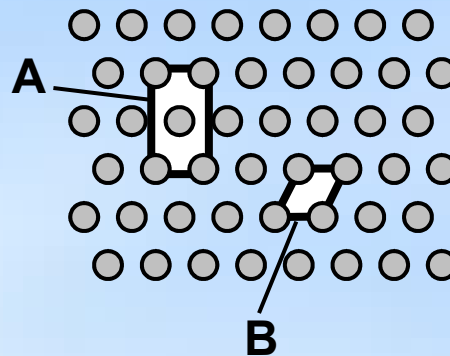
There is no unique way of choosing a unit cell. For example, each of the cells (**A** to **D**) in Fig. 2 are OK. However, the cell favoured by crystallographers is the one of smallest volume that displays all of the symmetry of the lattice. Thus, cells **C** and **A** are the preferred unit cells for the lattices of Figs. 2 and 3 respectively.

Fig. 2

Fig. 3

UNIT CELL TYPES and THE SEVEN CRYSTAL SYSTEMS

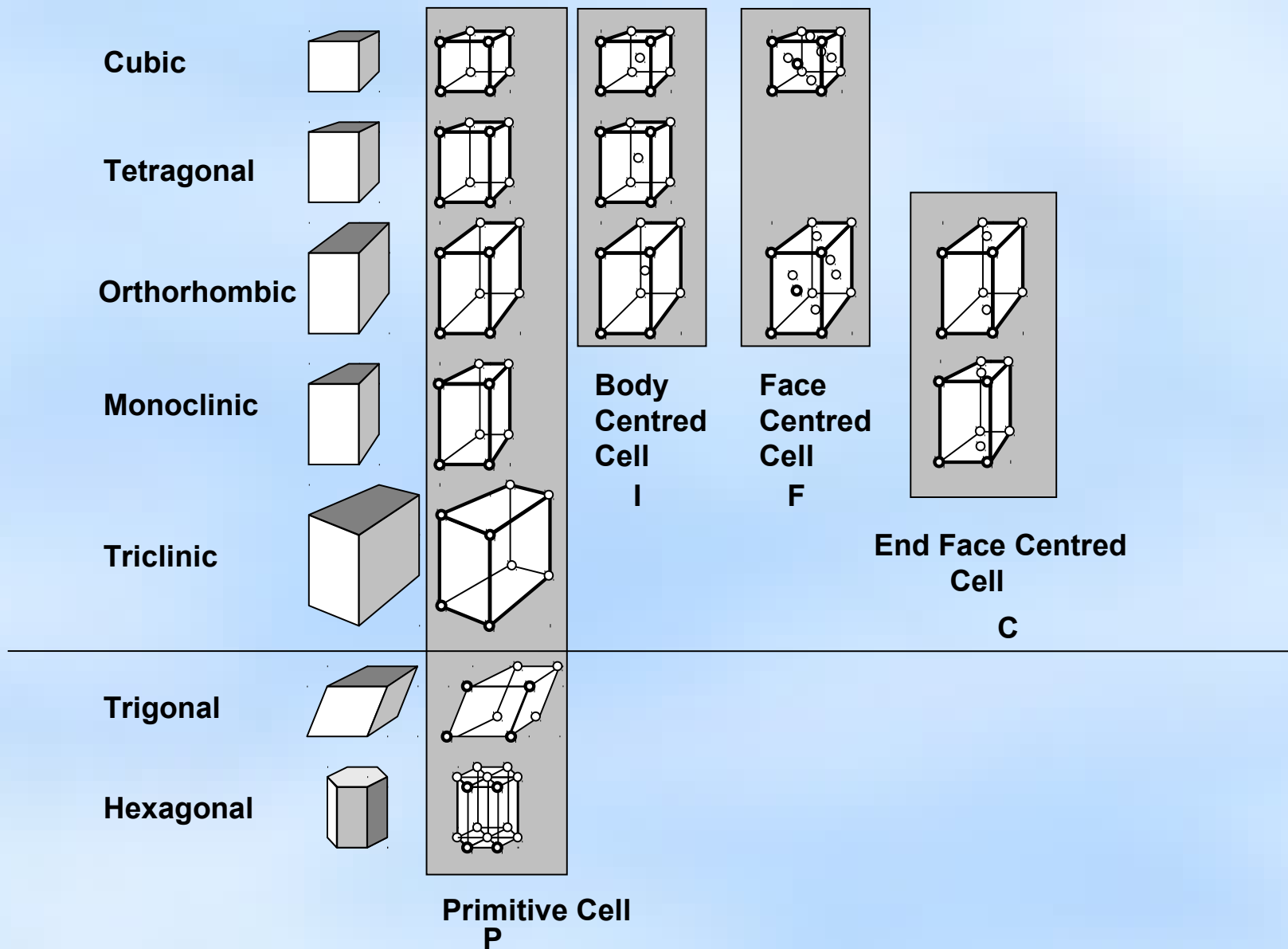|		
Cubic	$a = b = c$.	$\alpha = \beta = \gamma = 90°$.
Tetragonal	$a = b \neq c$.	$\alpha = \beta = \gamma = 90°$.
Orthorhombic	$a \neq b \neq c$.	$\alpha = \beta = \gamma = 90°$.
Monoclinic	$a \neq b \neq c$.	$\alpha = \gamma = 90°, \beta \neq 90°$.
Triclinic	$a \neq b \neq c$..	$\alpha \neq \beta \neq \gamma \neq 90°$.
Rhombohedral (or Trigonal)	$a = b = c$.	$\alpha = \beta = \gamma \neq 90°$.
Hexagonal	$a = b \neq c$.	$\alpha = \beta = 90°, \gamma = 120°$.
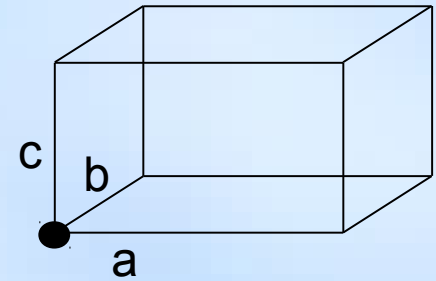
Orthorhombic
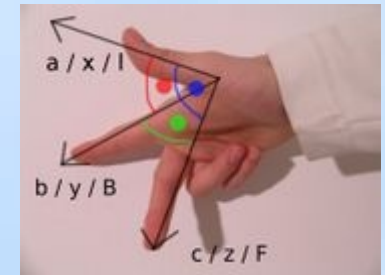
In general, six parameters are required to define the shape and size of a unit cell, these being three cell edge lengths (conventionally, defined as a, b, and c), and three angles (conventionally, defined as α, β, and γ). In the strict mathematical sense, a, b, and c are vectors since they specify both length and direction.
α is the angle between b and c, β is the angle between a and c, γ is the angle between a and b. The unit cell should be right handed. Check the cell above with your right hand

When these unit cells are combined with possible "centering" there are 14 different Bravais lattices.

Cubic

Tetragonal

Orthorhombic

Monoclinic

Triclinic

Trigonal

Hexagonal

Body Centred Cell I

Face Centred Cell F

End Face Centred Cell C

Primitive Cell P

Fig. 3

SYMMETRY: POINT GROUP SYMMETRY AND SPACE GROUP SYMMETRY

Point group theory is not dealt with here. What follows is just a summary.

Point group symmetry defines the symmetry of an isolated object or group of objects, whereas space group symmetry further defines the systematic fashion in which an object, or group of objects is repeated in space to generate an infinite periodic array in 3D.

Point group symmetry is quantified in terms of symmetry elements (existing within the object or group of objects) and their associated operations. Four symmetry elements are used to quantify point group symmetry

Symmetry Element	Symmetry Operation
Rotation axis (n-fold)	Rotation
Mirror plane	Reflection
Centre of Symmetry	Inversion
Rotor-reflection axis (n-fold)	Rotation and reflection
or	
Rotor-inversion axis (n-fold)	Rotation and inversion

Point Group and Space Group Symmetry

To generate a 3D lattice from an object it is necessary to add translational symmetry to point group symmetry. The two important space group symmetry operations which move objects are glide planes and screw axes. These operations combine translation and reflection and translation and rotation respectively.
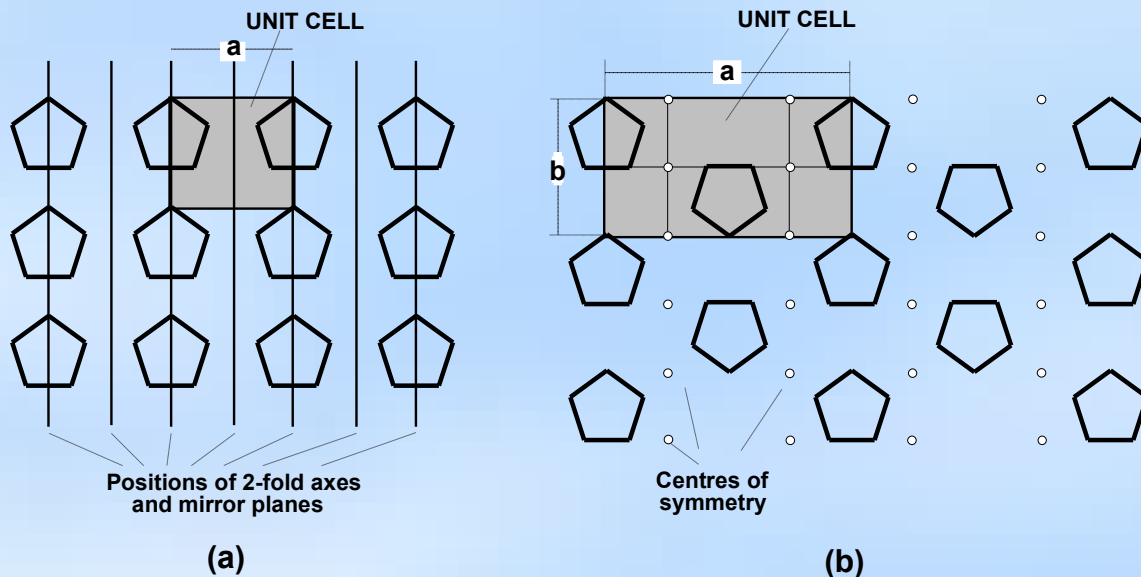

(a)

(b)

Fig. 5

The pentagons on the left are related by simple translation. In 5(b) the pentagon on the top left of the cell is related to the one in the centre by translation a/2 followed by either reflection or rotation. Centres of inversion in 5(b) are marked with tiny circles.

The 230 Space Groups

There is an infinite number of combinations of the four symmetry elements. *However, if there is a restriction on the order of the rotation axes to 2, 3, 4, and 6, as is the case for repetitive symmetry (crystallographic symmetry) this leaves only 32 unique combinations. These are the 32 crystallographic point groups. Adding screw axes and glide planes gives the 230 space groups*. The overall breakdown of symmetry for crystals then is as shown in Fig. 9.

CRYSTAL SYSTEMS (7)	BRAVAIS LATTICES (14)	SPACE GROUPS (230)	
Cubic	P	15	
	F	11	36
	I	10	
Tetragonal	P	49	68
	I	19	
Orthorhombic	P	30	
	F	5	59
	I	9	
	C and A	15	
Monoclinic	P	8	13
	C	5	
Triclinic	P	2	2
Rhombohedral	P and R	25	25
Hexagonal	P	27	27

Fig. 9

The International Tables for Crystallography list the symmetry properties for all 230 Space Groups. The 2nd edition was in one volume and edited by Kathleen Lonsdale. The current edition runs to 7 volumes. The CSD or Cambridge Data Base is a repository for the structures of organic and organometallic compounds.

Space Group determination is an important step in crystal structure determination.

CRYSTAL PLANES AND MILLER INDICES

The use of crystal planes to describe the structure of crystals goes back to the start of crystallography and crystal planes were used by Bragg to explain diffraction as will be seen later.
Crystal planes are defined by the intercepts they make on the crystal axes of the unit cell.
The inverse of these fractions are the Miller Indices of the planes.

In (a) the intercepts are ½, ½, 1 and the Miller Indices are (2 2 1).
In (c) the intercepts on b and c are at infinity the inverse of which is 0 and the plane is the (2 0 0).
In (d) the plane cuts the negative c axis at -1 and thus is (1 1 -1). In crystallography -1 is often written $\bar{1}$ and pronounced "Bar 1".
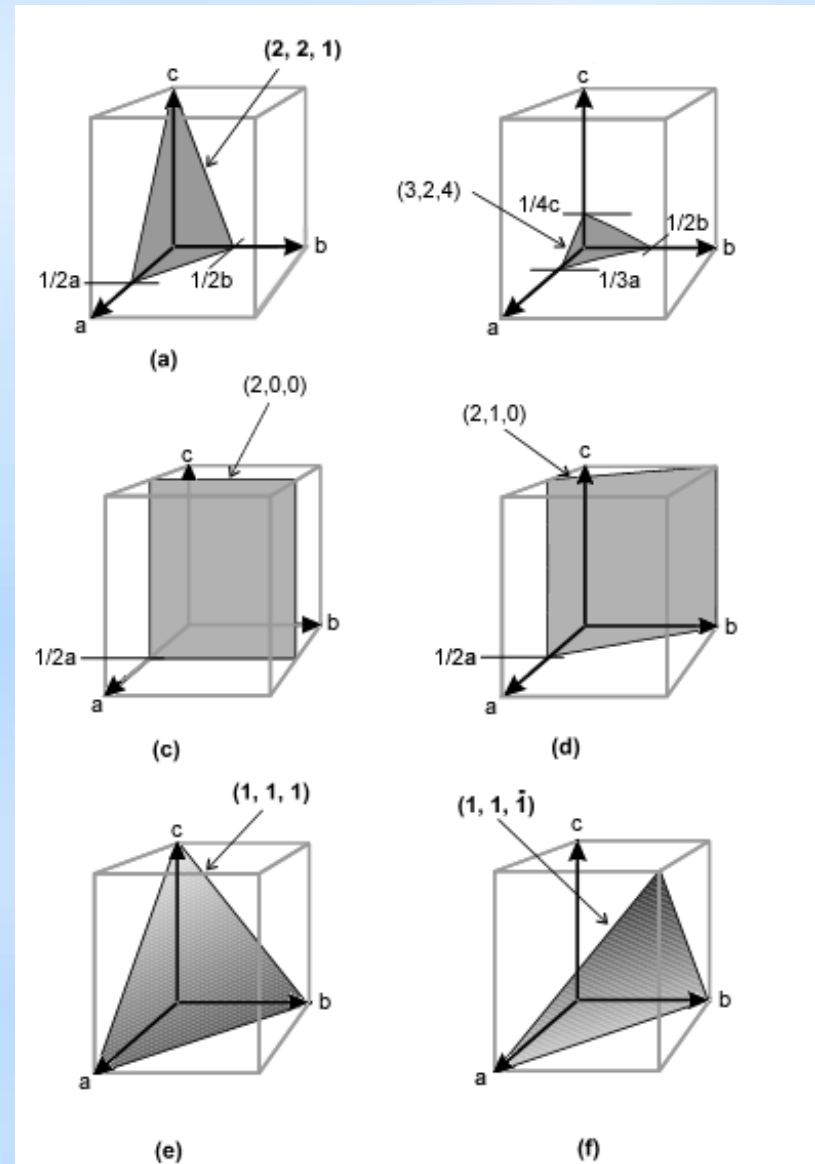
Crystalline materials are characterized by the orderly periodic arrangements of atoms.

The (200) planes of atoms in NaCl
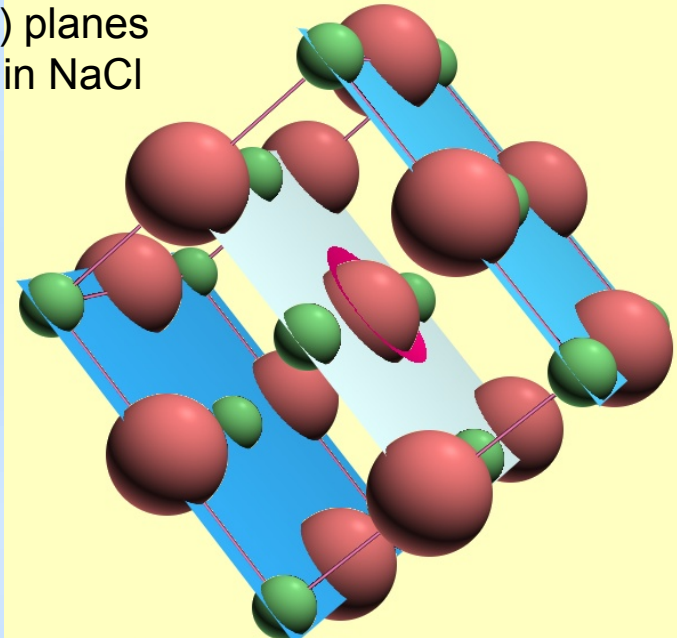
The (220) planes of atoms in NaCl
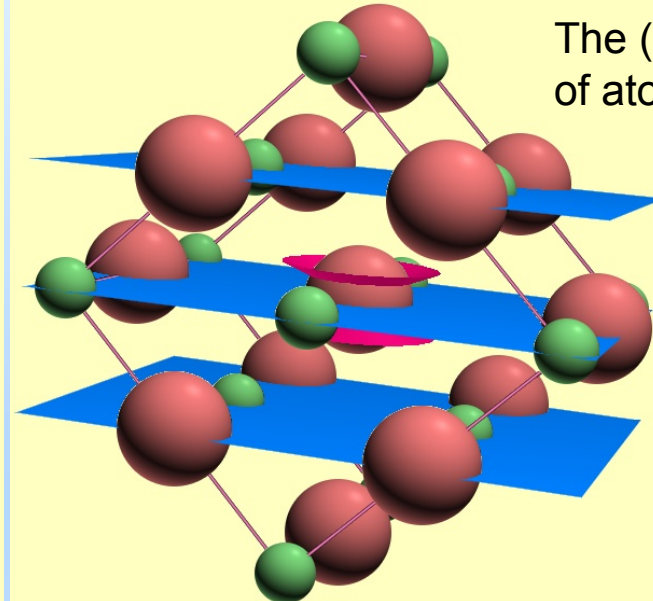
- The unit cell is the basic repeating unit that defines a crystal.
- Parallel **planes of atoms** intersecting the unit cell are used to define directions and distances in the crystal.
  - These crystallographic planes are identified by **Miller indices**.

DIFFRACTION AND THE BRAGG EQUATION

Max von Laue was the first to suggest that crystals might diffract X-rays and he also provided the first explanation for the diffraction observed. However, it is the explanation provided by Bragg that is simpler and more popular.

In the Bragg view crystal planes act a mirrors. Constructive interference is observed when the path difference between the two reflected beams in (a) = $n\lambda$. The path difference in (a) is $2my$. Since $my/d = \sin\theta$

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

where d is the interplanar spacing.

(a)

(b)
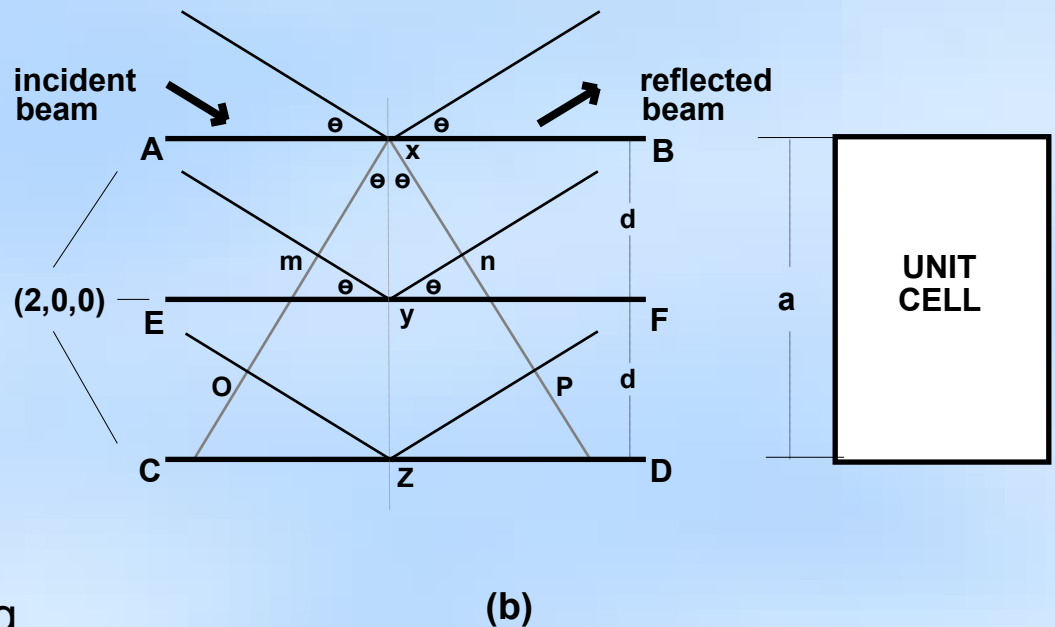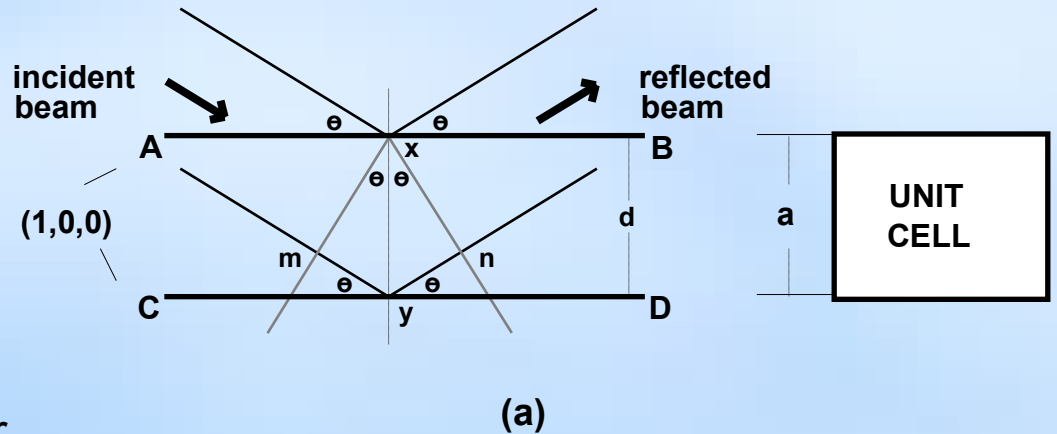
Fig. 11

Diagram Of An Area Detector X-Ray Data Collection System.

The first crystallographic
data collection systems used
photographic methods. These
were replaced by automated
diffractometers which measured
reflections one at a time. A typical
data collection took several days.
modern systems use area detectors
which measure 100s at a time.

marView [V5.1.3] - /data/aol1/aol1_001.image (1200 pixels & 11 > 65535)

File   Options   Help

Spots
Show
Edit
961

Avg Int: 75.2
Max Int: 98161 (*)
Lambda: 0.7110 Ang.
Distance: 100.00 mm
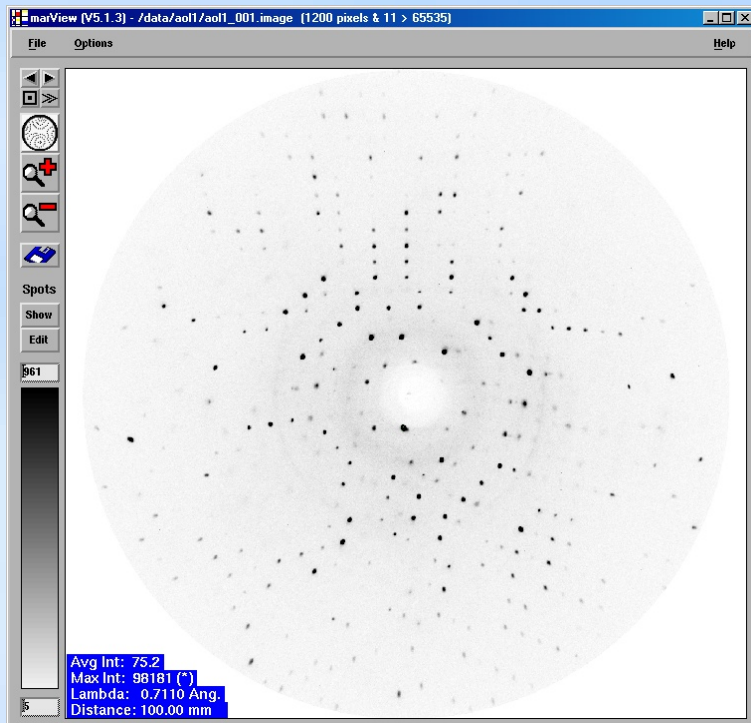
The crystal is oscillated over < 2°
while an image is collected then
rotated by the same amount
and oscillated again. The process is
repeated over a total range of about 180°.
Each image is exposed for < 100s.
Thus if readout time is ignored total
data collection time is often < 3 hr.
A typical image shown to the left.
A computer program is used to predict
the unit cell from several images.

Determination of the Lattice type and Space Group

High symmetry can lead to reflections being systematically absent from the data set. Absent reflections have no measurable intensity. There are two types of absences, **General Absences** and **Special Absences**.
The general absences determine the lattice type;
  Primitive (**P**) has no general absences and no restrictions on h, k or l.
 End Centered (**C**) h+k=2n+1 are all absent.
  Face Centered (**F**) only h, k, l, all even or all odd are observed.
  Body Centered (**I**) h+k+l=2n+1 are all absent.

The special absences refer to specific sets of reflections and are used to detect the presence of glide planes and screw axes. Some Space Groups are uniquely determined by special absences but in many cases several Space Groups will have to be considered.

Computer programs are able to lay out the data in tables with absences indicated and possible Space Groups can be suggested however the choice of Space Group will often need much thought.

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.
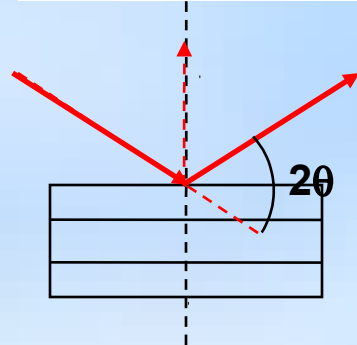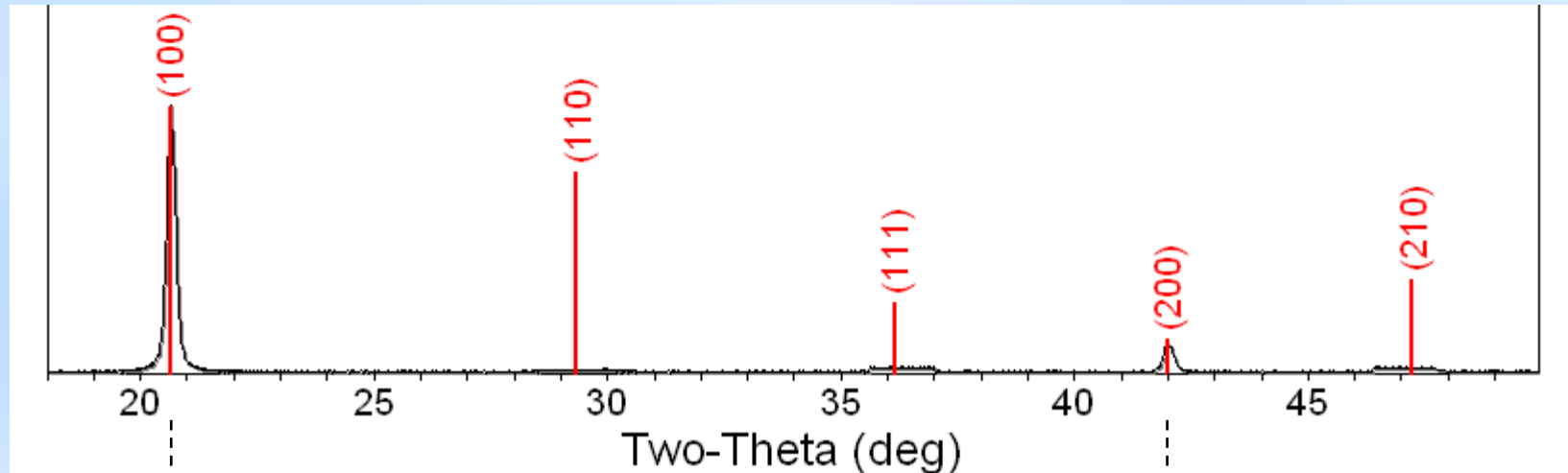
At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.
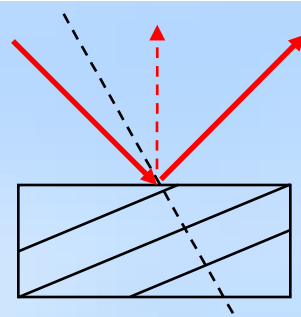
The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.
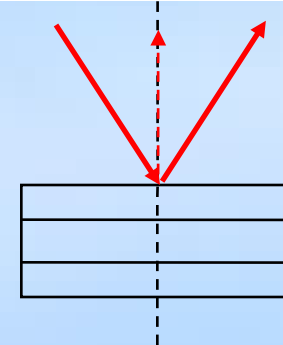
The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.
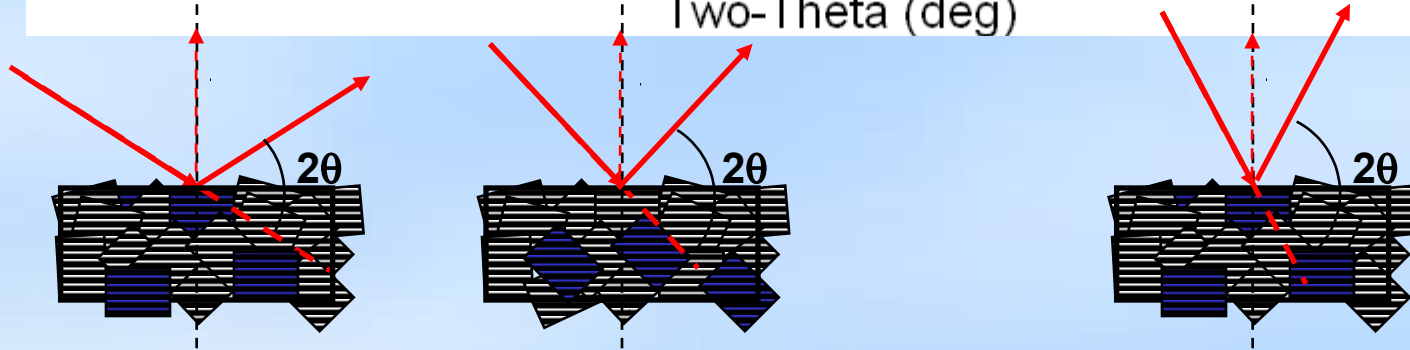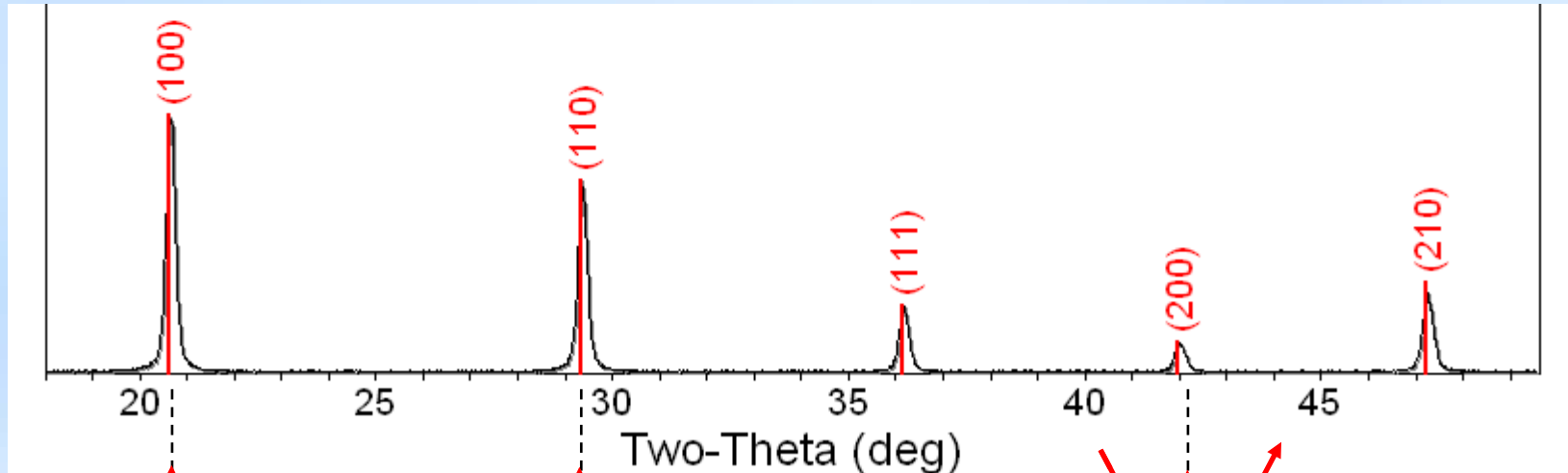
- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.
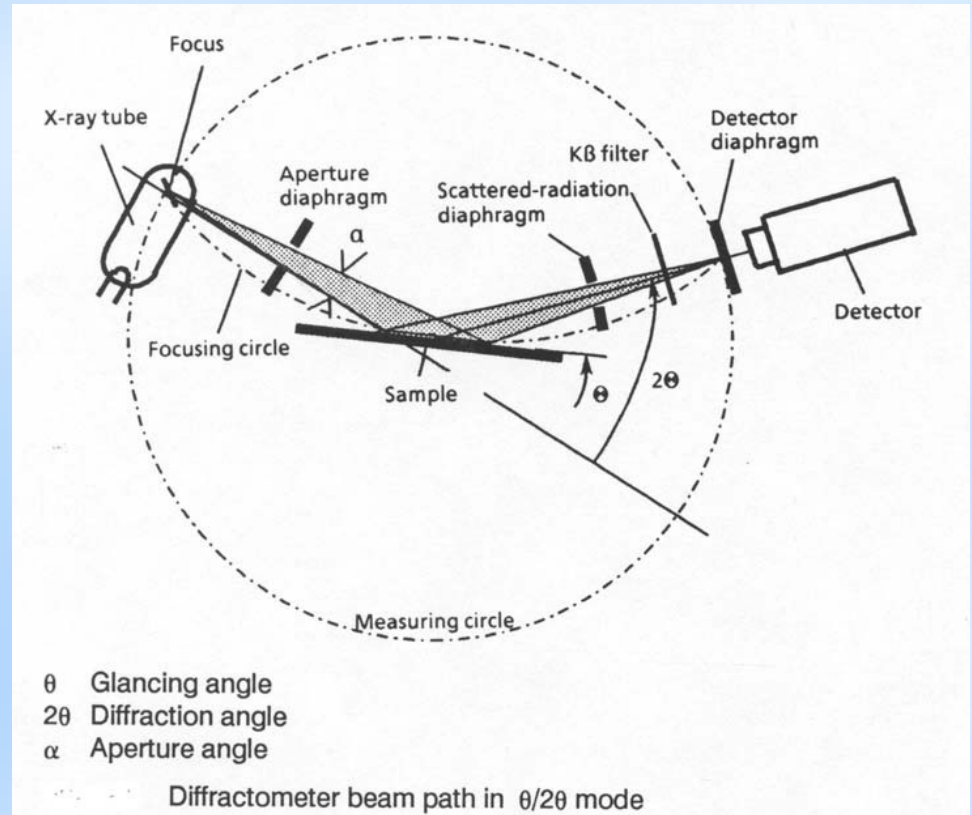
POWDER X-RAY DIFFRACTOMETRY

A crystalline powder sample will diffract X-rays but since the orientations of the individual crystals are random the data set produced is a plot of intensity *v.s.* diffraction angle or Bragg angle θ.

Here the sample is sitting on a flat plate and the plate is turned about the centre of the diffractometer at half the rate through which the counter moves. This is the θ/2θ or Bragg scan method.

Notice the plot contains 2θ on the X-axis and X-ray intensity on the y-axis.

θ   Glancing angle
2θ   Diffraction angle
α   Aperture angle

Diffractometer beam path in θ/2θ mode

50/50 CALCITE - ARAGONITE MIXTURE
RANDOMLY ORIENTED AGGREGATE MOUNT
Cu Kα
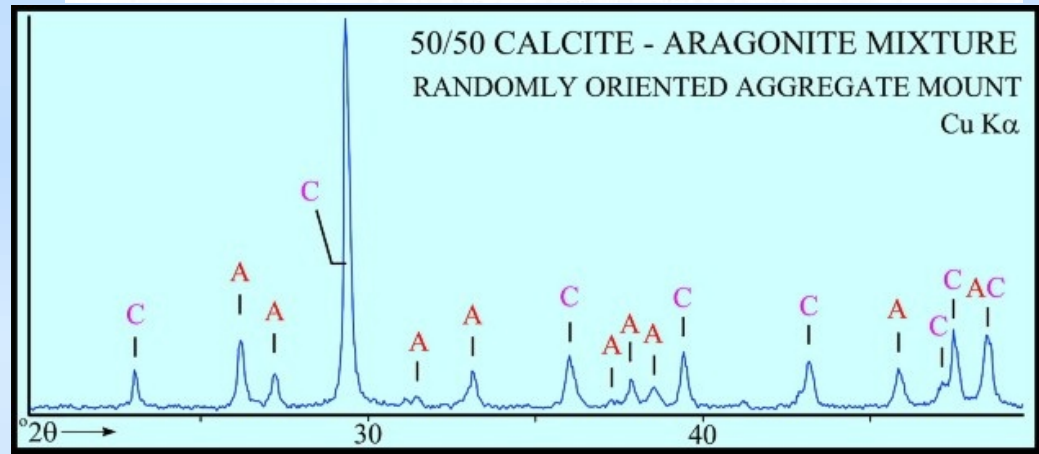
Uses of X-ray Powder Diffraction

In general, powder diffraction data are unsuitable for solving crystal structures. Some advances have recently been made using the Rietveld method. However this is far from trivial and it works best in relatively simple cases. It is very difficult to be sure that the unit cell is correct as the reflections overlap and are difficult to resolve from one another.

Important advantages and uses of powder diffraction:
1. The need to grow crystals is eliminated.
2. A powder diffraction pattern can be recorded very rapidly and the technique is non-destructive.
3. With special equipment very small samples may be used (1-2mg.)
4. A powder diffraction pattern may be used as a fingerprint. It is often superior to an infrared spectrum in this respect.
5. It can be used for the qualitative, and often the quantitative, determination of the ***crystalline components*** of a powder mixture.
6. Powder diffractometry provides an easy and fast method for the detection of crystal polymorphs. Powder patterns are provided when a drug is being registered with the FDA. (Polymorphs are different crystal forms of the same substance.)

Calculations using X-ray powder diffraction patterns.

For an orthogonal system ($\alpha = \beta = \gamma = 90°$) the relationship between interplanar spacing (d) and the unit cell parameters is given by the expression:

$$\frac{1}{d_{(h,k,l)^2}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

This is the expression for an orthorhombic crystal.
For the tetragonal system it reduces to

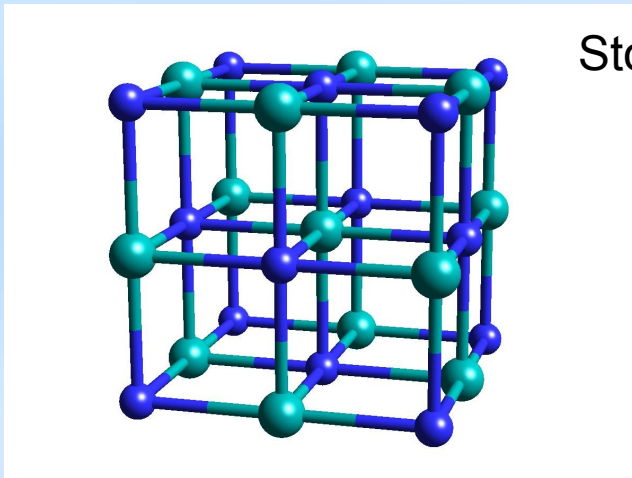$$\frac{1}{d_{(h,k,l)^2}} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2}$$

and, for the cubic system, it further reduces to

$$\frac{1}{d_{(h,k,l)^2}} = \frac{(h^2 + k^2 + l^2)}{a^2}$$

Important Cubic Lattice Types

Two of the most important cubic lattice types are the NaCl type and the CsCl type.

NaCl crystallizes in the Space Group **Fm-3m**

Stoichiometry (formula) from the Unit Cell

Site	Na^+	Cl^-
Central	0	1
Face	6/2	0
Edge	0	12/4
Corner	8/8	0
Total	4	4

In the CsCl structure both ions have coordination numbers of 8 and the structure is a simple primitive one with no centring.

Formula Cs at centre = 1
$$8 \times 1/8 Cl = 1 = CsCl$$
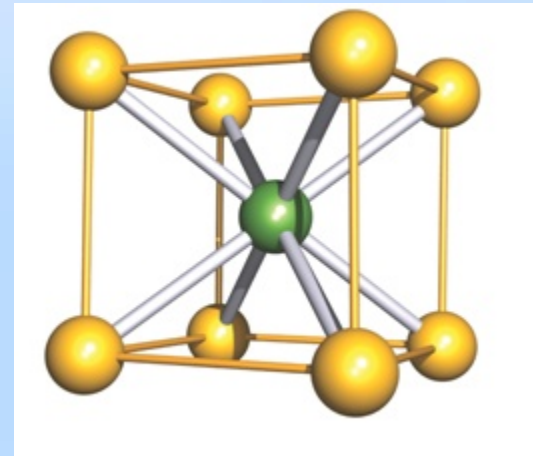
- Powder Diffraction
  - Samples can be powder, sintered pellets, coatings on substrates, engine blocks, …
- If the crystallites are randomly oriented, and there are enough of them, then they will produce a continuous Debye cone.
- In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point; thus giving the appearance of a discrete diffraction peak.
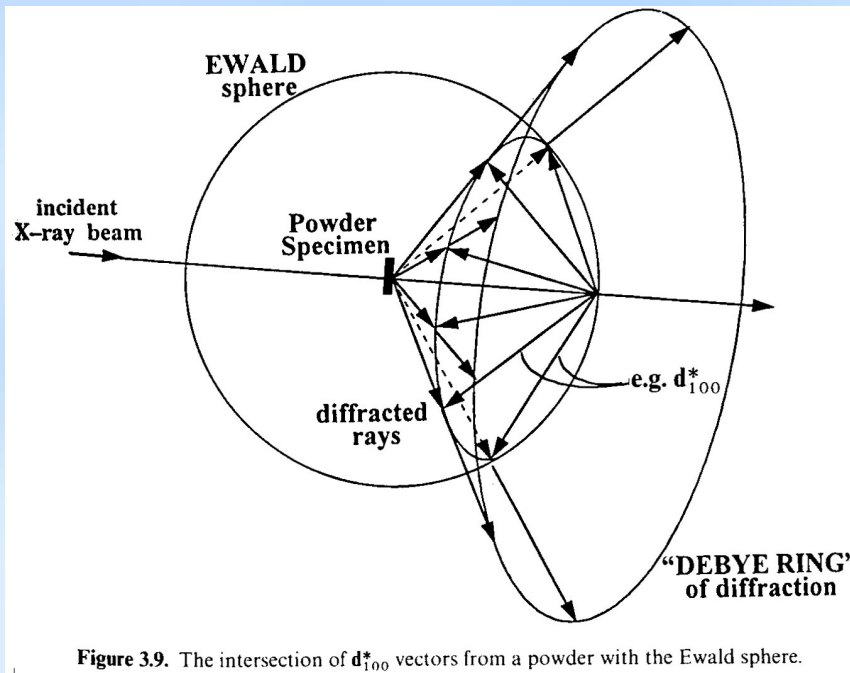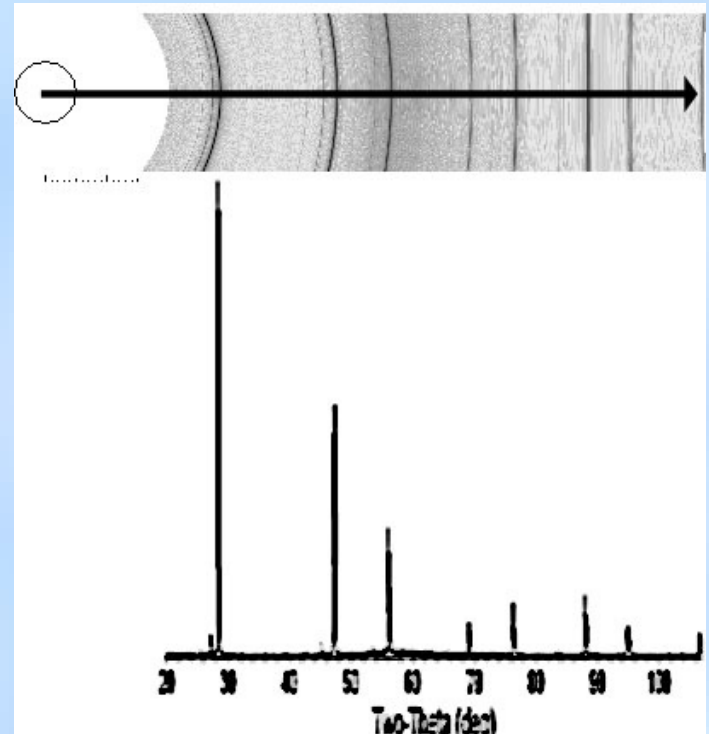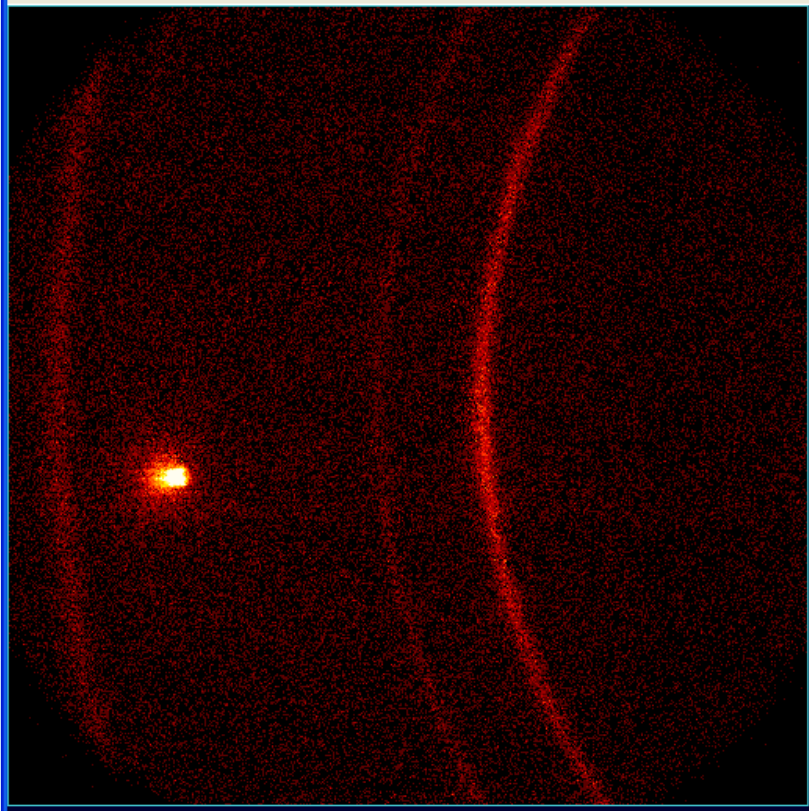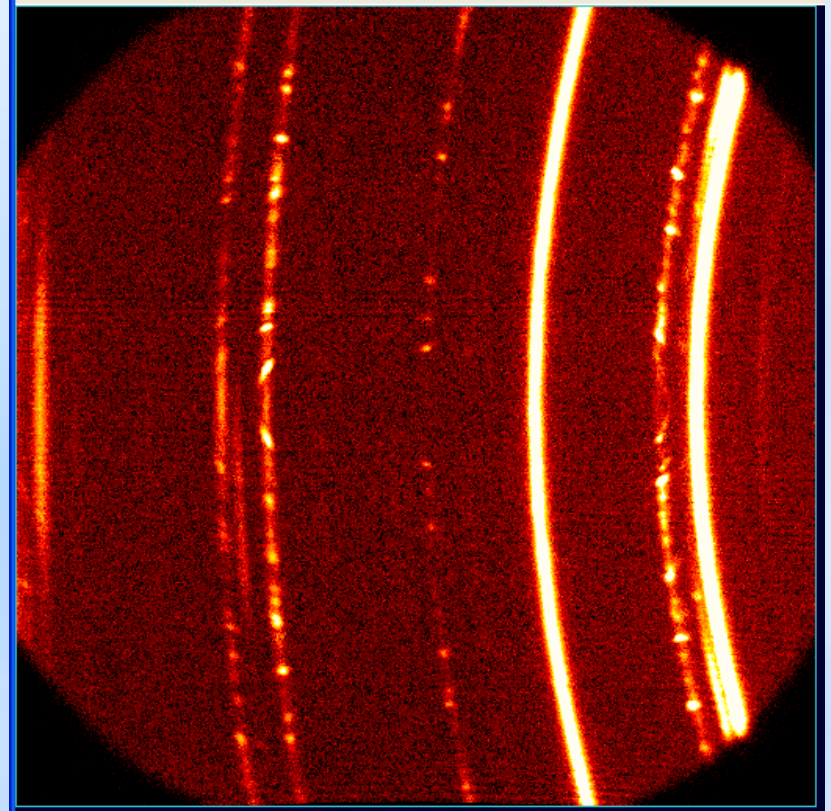

Figure 3.9. The intersection of $\mathbf{d}^*_{100}$ vectors from a powder with the Ewald sphere.

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

Polycrystalline thin film on a single crystal substrate

Mixture of fine and coarse grains in a metallic alloy

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

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

[HighRes_run113_12hr scan.xml] run113 mono-Y2O3 OVD
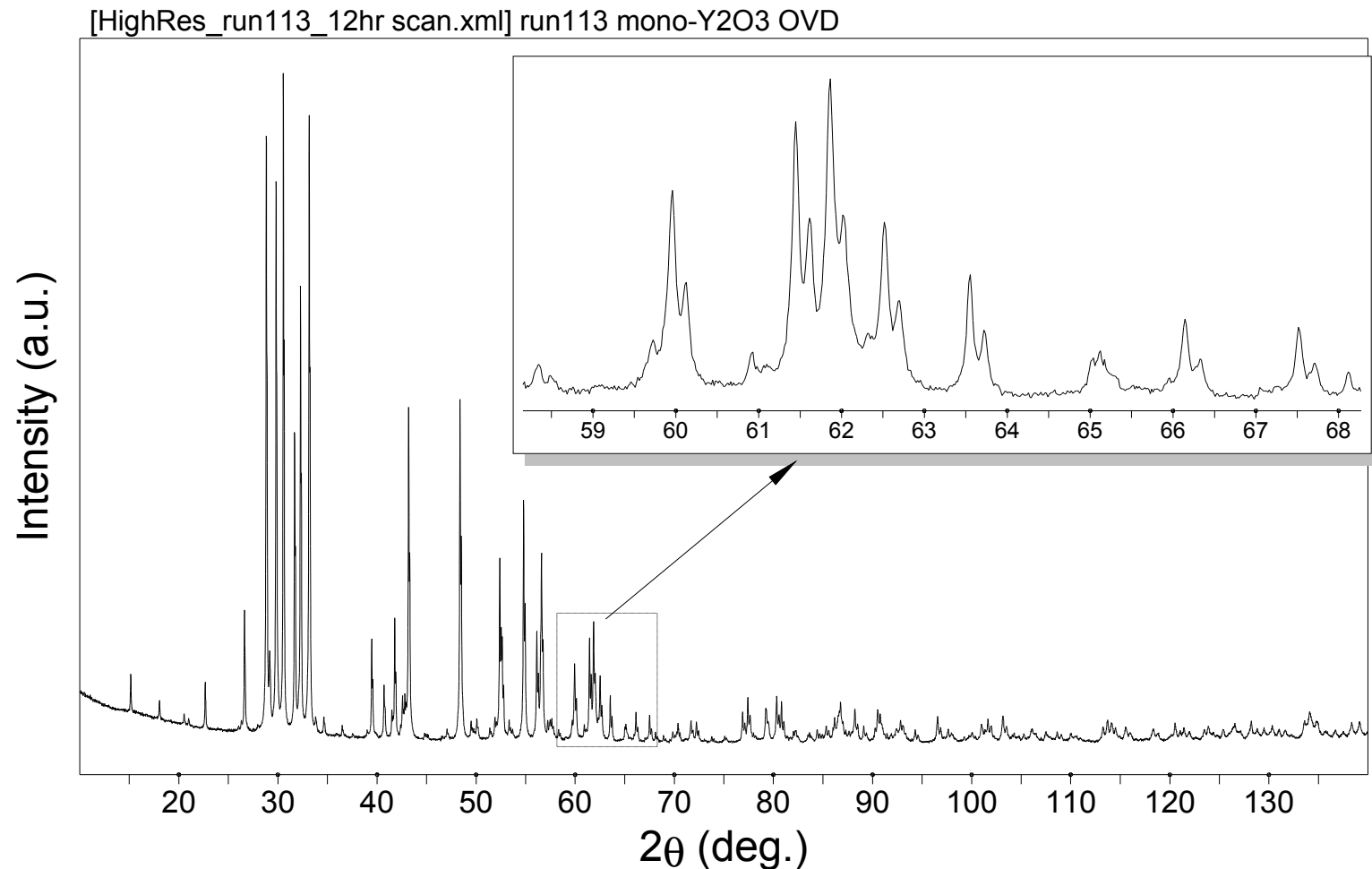
Diffraction patterns are best reported using d_{hkl} and relative intensity rather than 2θ and absolute intensity.

- 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.

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

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

Raw Data

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

[DEMO08.MDI] Demo08: Corundum
00-010-0173> Corundum - Al₂O₃
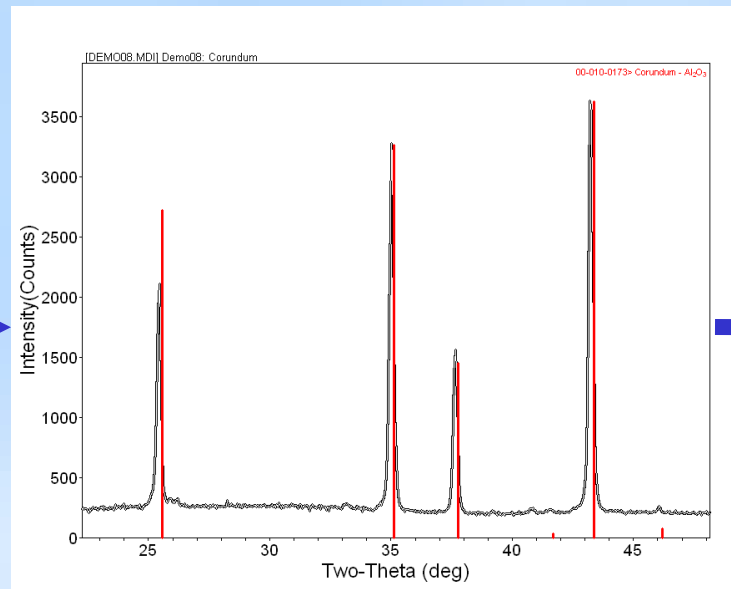
Reduced dI list

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

You can use XRD to determine

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

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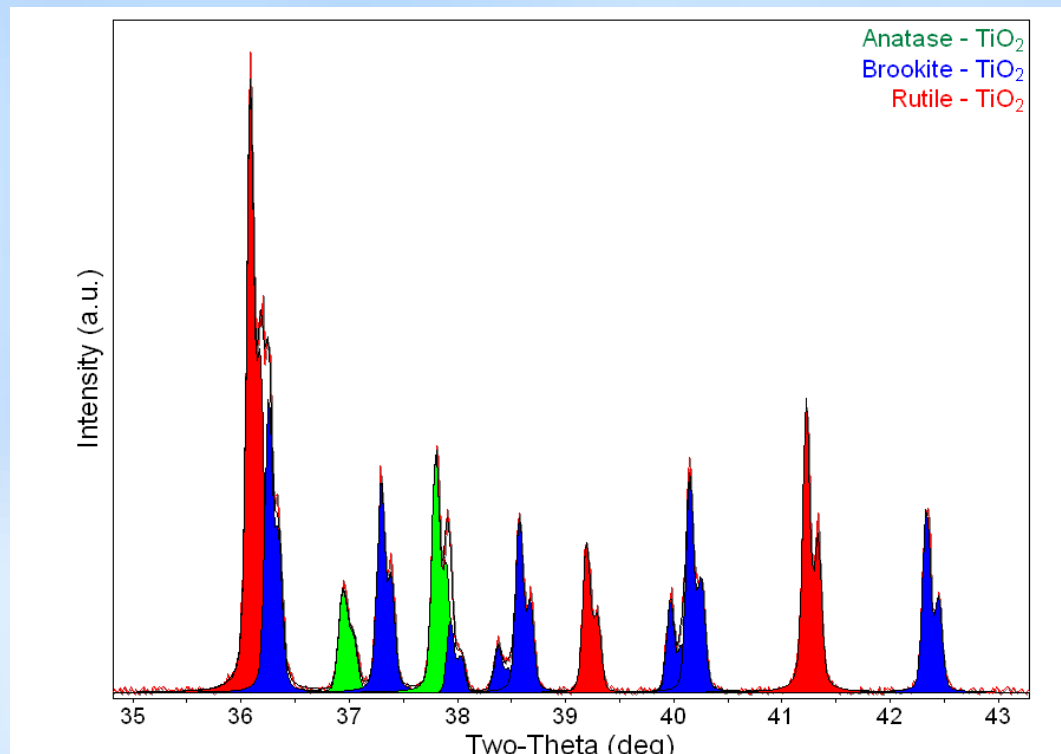
Databases such as the Powder Diffraction File (PDF) contain lists for thousands of crystalline phases.

- The PDF contains over 200,000 diffraction patterns.

- Modern computer programs can help you determine what phases are present in your sample by quickly comparing your diffraction data to all of the patterns in the database.

- The PDF card for an entry contains a lot of useful information, including literature references.
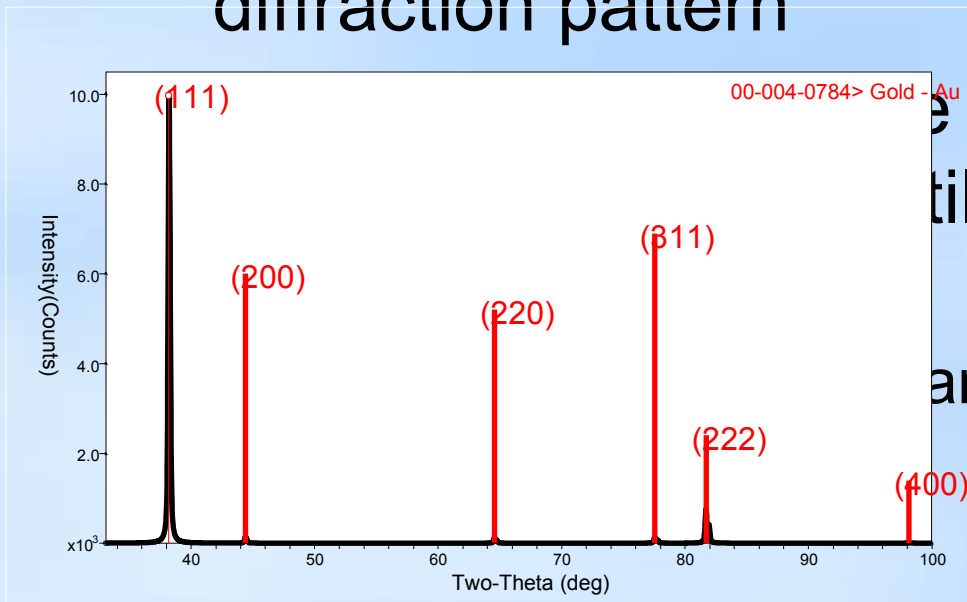
Crystallite Size and Microstrain

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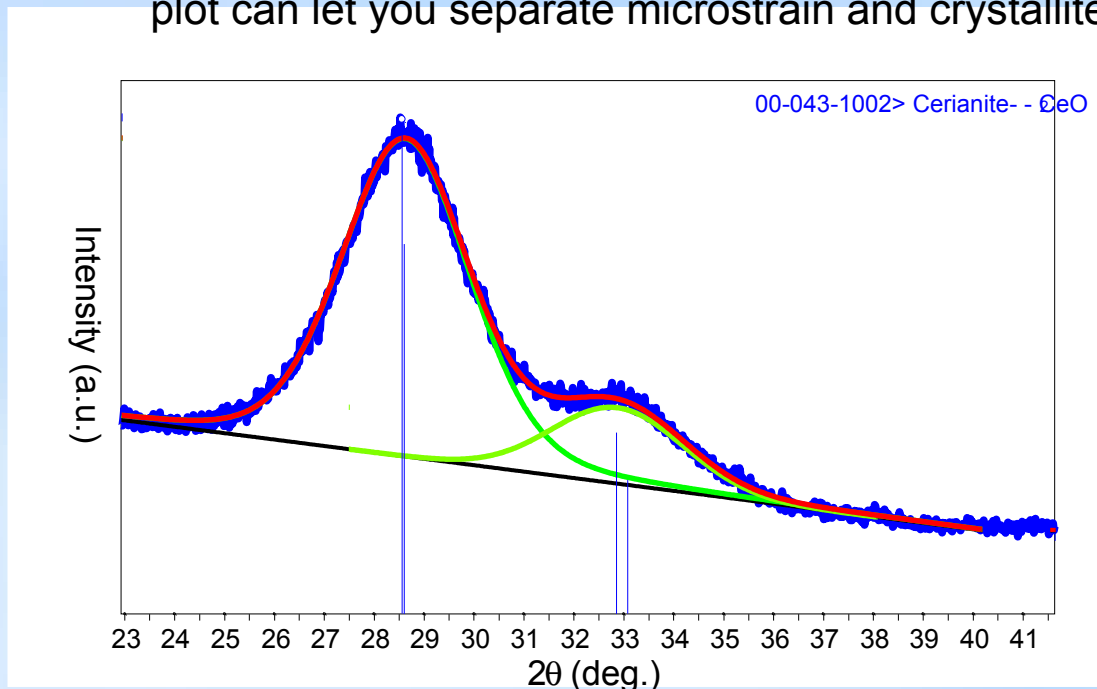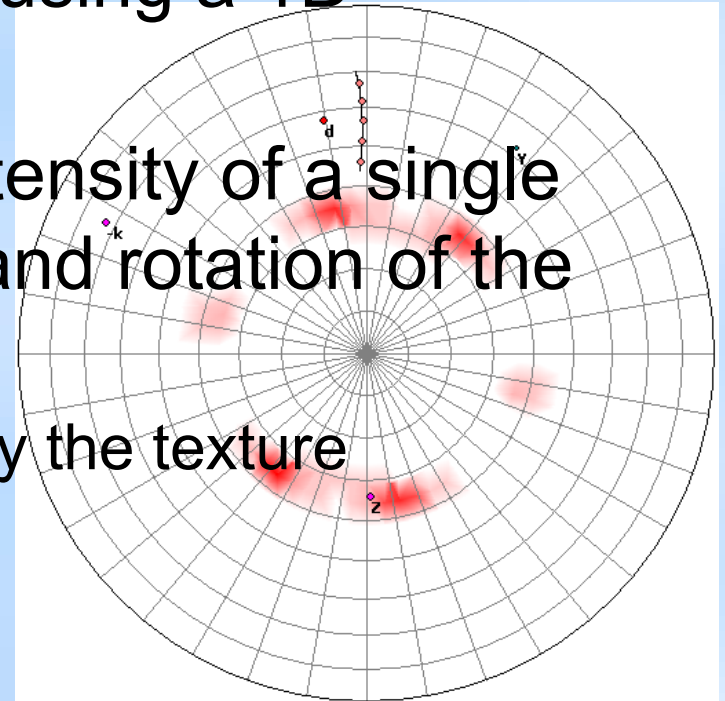

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

Preferred Orientation (texture)

- Preferred orientation of crystallites can create a systematic variation in diffraction peak intensities
  - can qualitatively analyze using a 1D diffraction pattern
  - e intensity of a single
    tilt and rotation of the
  - antify the texture

Essential Parts of the Diffractometer

- X-ray Tube: the source of X Rays

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

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

- The sample & sample holder

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

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

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

- Sealed X-ray tubes tend to operate at 1.8 to 3 kW.

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

- Both sources generate X rays by striking the anode target wth an electron beam from a tungsten filament.
  - The target must be water cooled.
  - The target and filament must be contained in a vacuum.
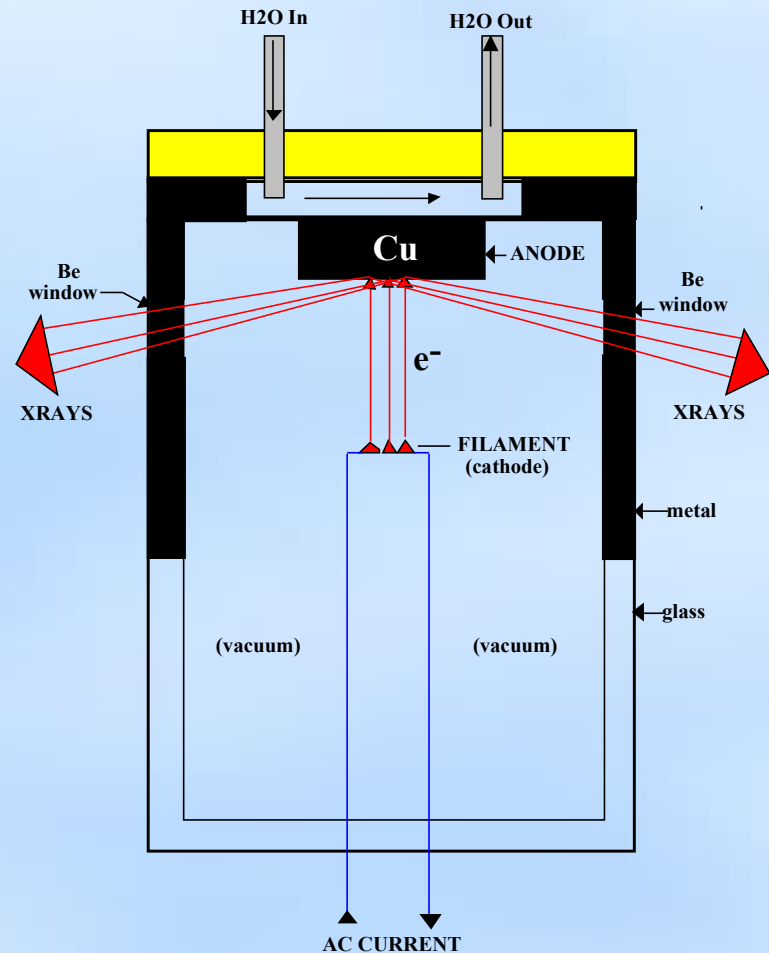
The wavelength of X rays is determined by the anode of the X-ray source.

- Electrons from the filament strike the target anode, producing characteristic radiation via the photoelectric effect.
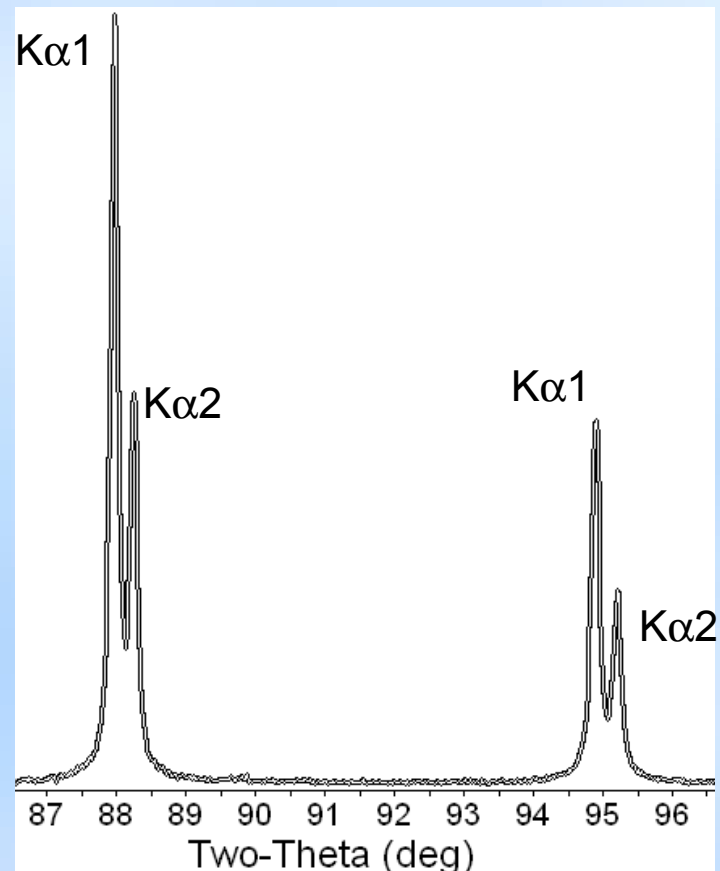
- The anode material determines the wavelengths of characteristic radiation.

- While we would prefer a monochromatic source, the X-ray beam actually consists of several characteristic wavelengths of X rays.
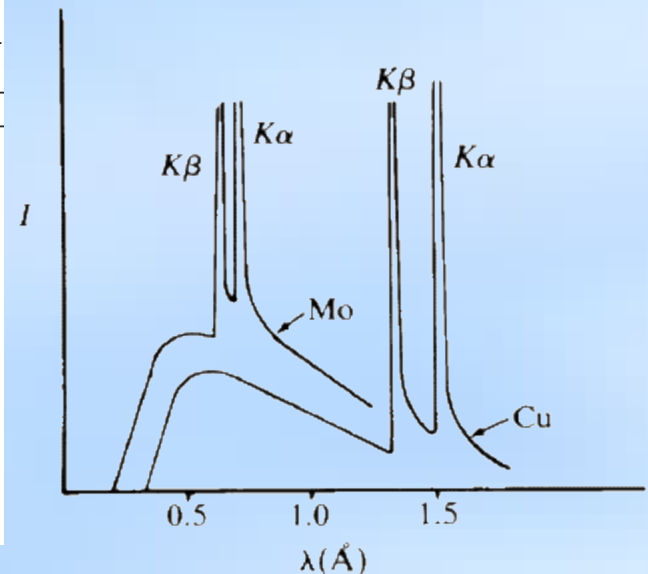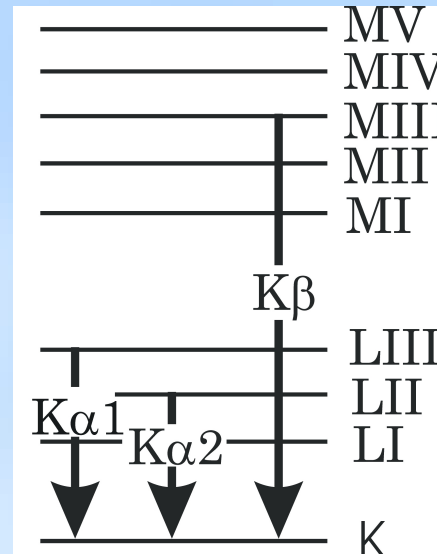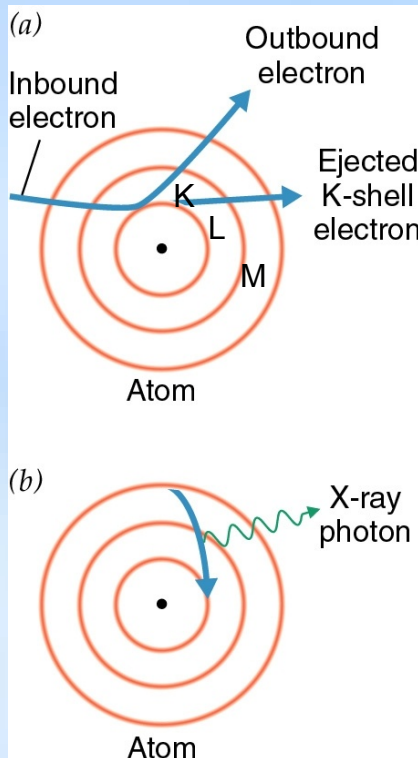
Spectral Contamination in Diffraction Patterns
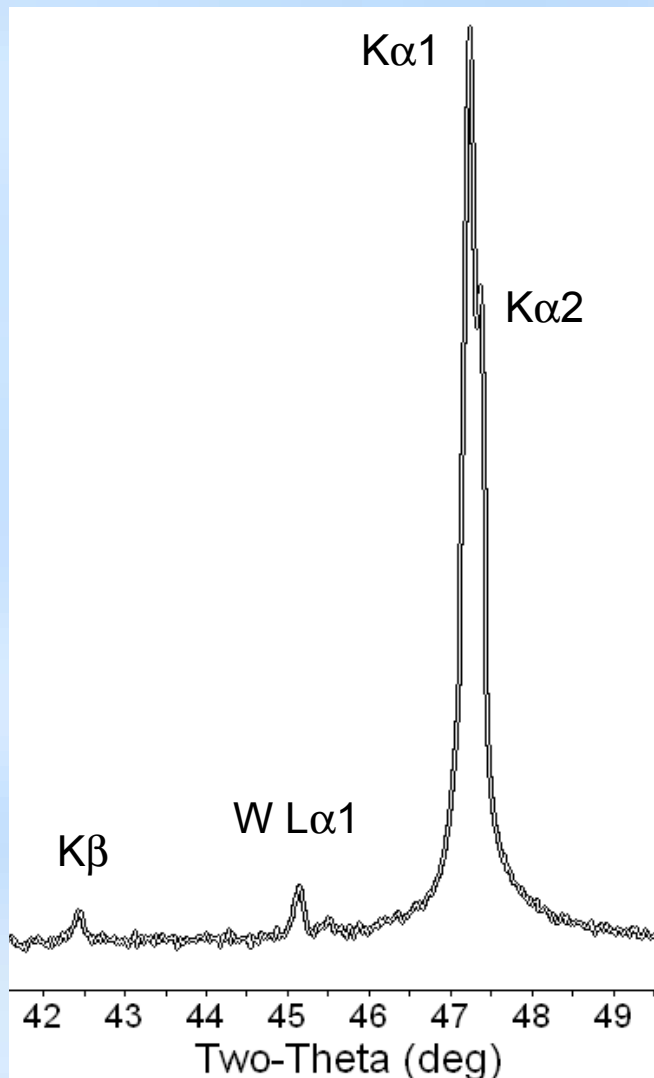
- The Kα1 & Kα2 doublet will almost always be present
  - Very expensive optics can remove the Kα2 line
  - Kα1 & Kα2 overlap heavily at low angles and are more separated at high angles
- W lines form as the tube ages: the W filament contaminates the target anode and becomes a new X-ray source
- W and Kβ lines can be removed with optics

Wavelengths for X-Radiation

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)
- Has your XRD analysis software been updated?

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

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

- The slits block X-rays that have too great a divergence.

- The size of the divergence slit influences peak intensity and peak shapes.

- Narrow divergence slits:
  - reduce the intensity of the X-ray beam
  - reduce the length of the X-ray beam hitting the sample
  - produce sharper peaks
    - the instrumental resolution is improved so that closely spaced peaks can be resolved.
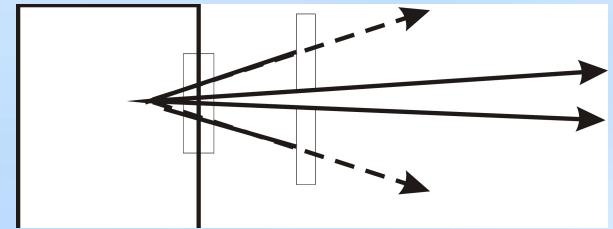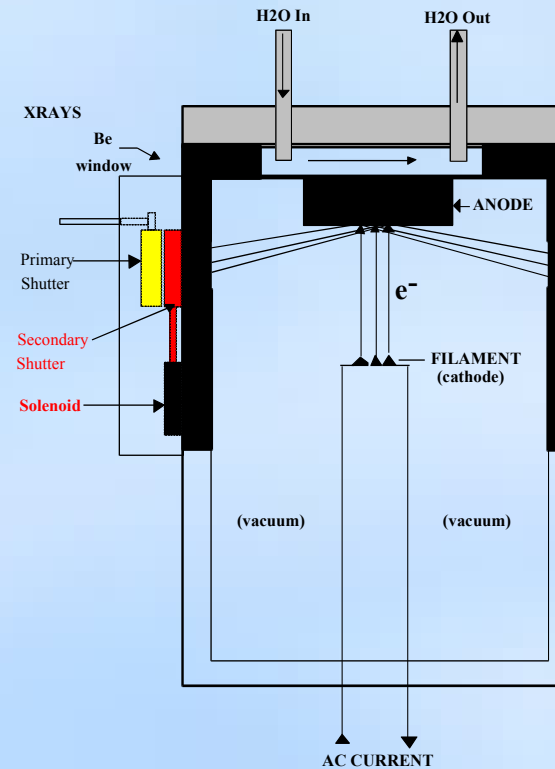
Preparing a powder specimen

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

Important characteristics of samples for XRPD

- Densely packed
- Randomly oriented grains/crystallites
- Grain size less than 10 microns

- Reflection mode - 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 rough surfaces
  - 'Infinitely' thick

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.

END and additional slides