Basics of X-Ray Powder Diffraction

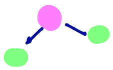
Modified from the slides of
Scott A Speakman, Ph.D.

Introduction to Crystallography and X-Ray Diffraction Theory

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

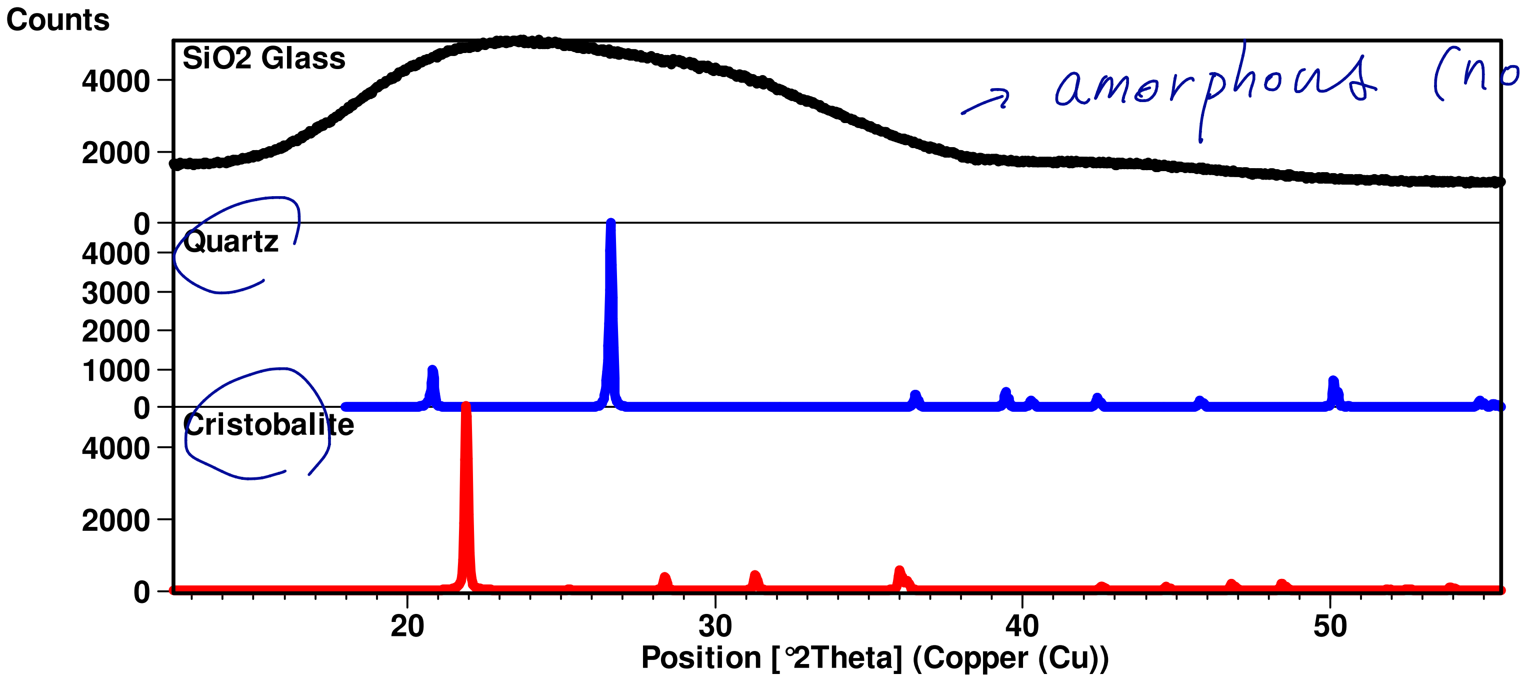
- The electrons in an atom coherently scatter light.
  - We can regard each atom as a coherent point scatterer
  - The strength with which an atom scatters light is proportional to the number of electrons around the atom.
- The atoms in a crystal are arranged in a periodic array and thus can diffract 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

SiO_2

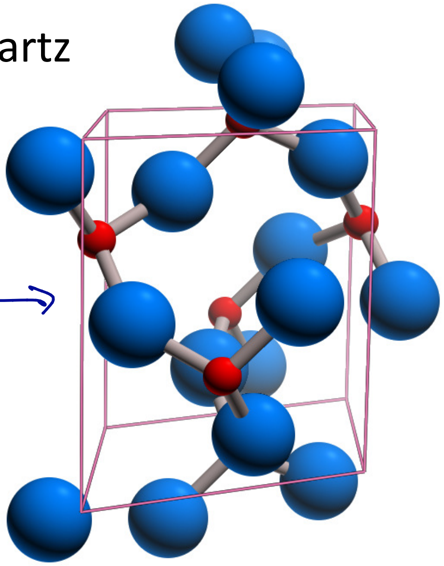


→ amorphous (not crystalline)

diffraction patterns

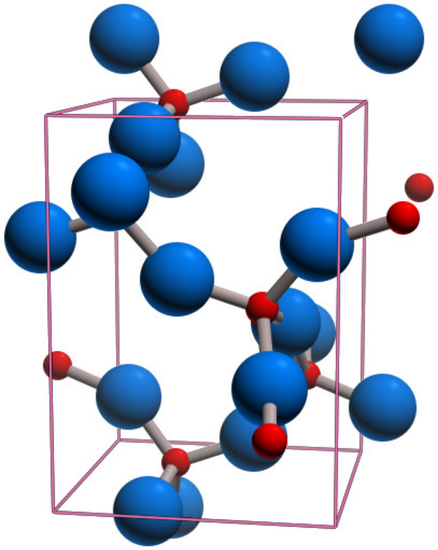
- These three phases of SiO_2 are chemically identical
- Quartz and cristobalite have two different crystal structures
  - The Si and O atoms are arranged differently, but both have structures with long-range atomic order
  - The difference in their crystal structure is reflected in their different diffraction 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

unit cell



Cristobalite

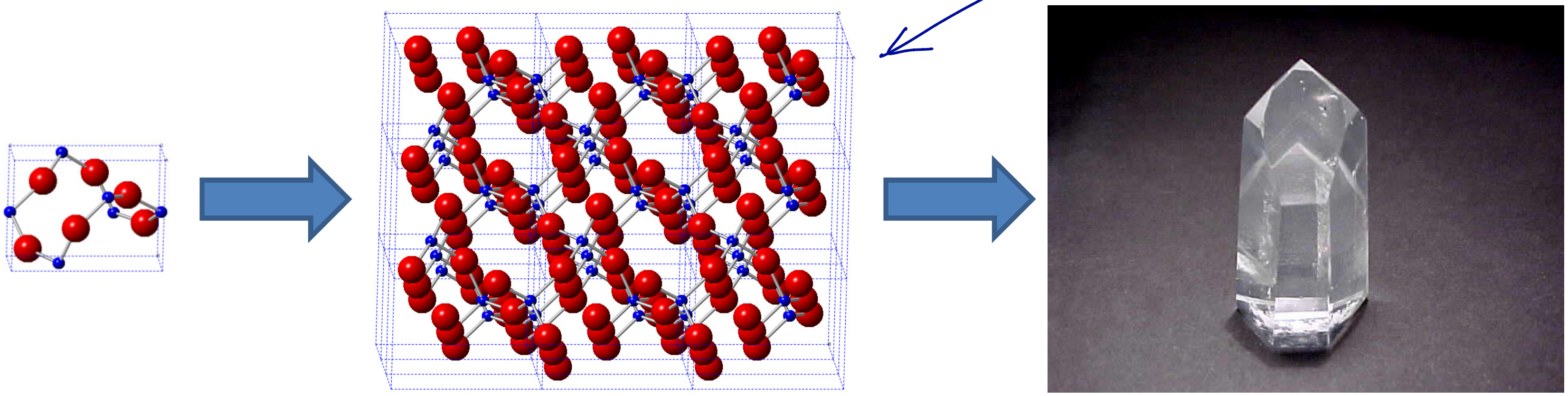
- The crystal structure describes the atomic arrangement of a material.
- When the atoms are arranged differently, a different diffraction pattern is produced (ie quartz vs cristobalite)

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:
$\overset{a}{4.9134}$ x $\overset{b}{4.9134}$ x $\overset{c}{5.4052}$ Å
($\underset{\alpha}{90}$ x $\underset{\beta}{90}$ x $\underset{\gamma}{120°}$)



Crystal structures focus on symmetry elements to define the atomic arrangement

- Symmetry in crystal structures is a product of energy minimization in the atomic arrangement
- Symmetry in the crystal structure often produces symmetry in material properties and behavior

Quartz
Crystal System: hexagonal
Bravais Lattice: primitive
Space Group: $P3_221$
Lattice Parameters: 4.9134 x 4.9134 x 5.4052 Å
(90 x 90 x 120°)

Atom Positions:

	x	y	z
Si	0.47	0	0.667
O	0.414	0.268	0.786

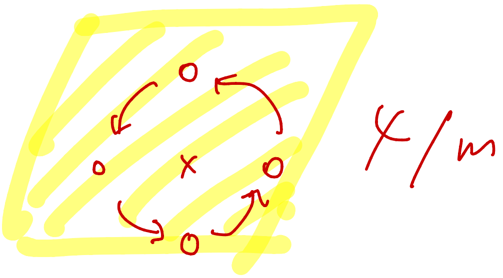
Primitive Bravais Lattice
3_2 screw axis
2-fold rotational axis

1 : no symmetry.

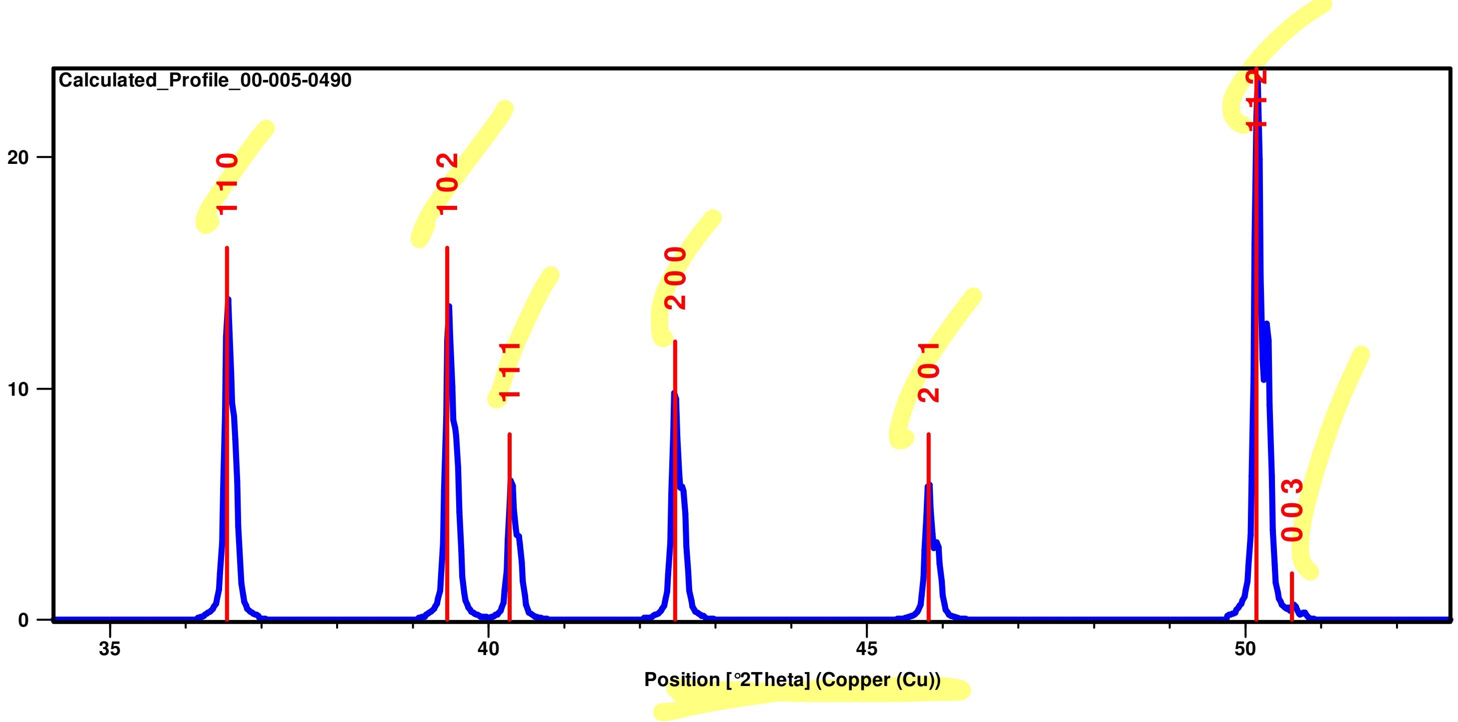
Symmetry elements are used to define seven different crystal systems

Crystal System 7	Bravais Lattices 14	Symmetry	Axis System
Cubic	P, I, F	m3m	a=b=c, α=β=γ=90
Tetragonal	P, I	4/mmm	a=b≠c, α=β=γ=90
Hexagonal	P, R	6/mmm	a=b≠c, α=β=90 γ=120
Rhombohedral*	R	3m	a=b=c, α=β=γ≠90
Orthorhombic	P, C, I, F	mmm	a≠b≠c, α=β=γ=90
Monoclinic	P, C	2/m	a≠b≠c, α=γ=90 β≠90
Triclinic	P	1	a≠b≠c, α≠β≠γ≠90

Quartz
Crystal System: hexagonal
Bravais Lattice: primitive
Space Group: $P322_1$
Lattice Parameters: 4.9134 x 4.9134 x 5.4052 Å
(90 x 90 x 120°)



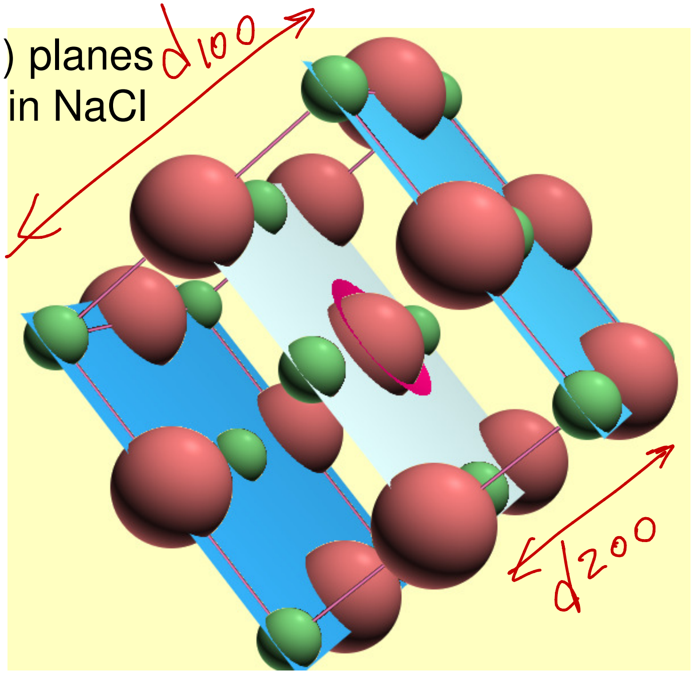
Diffraction peaks are associated with planes of atoms

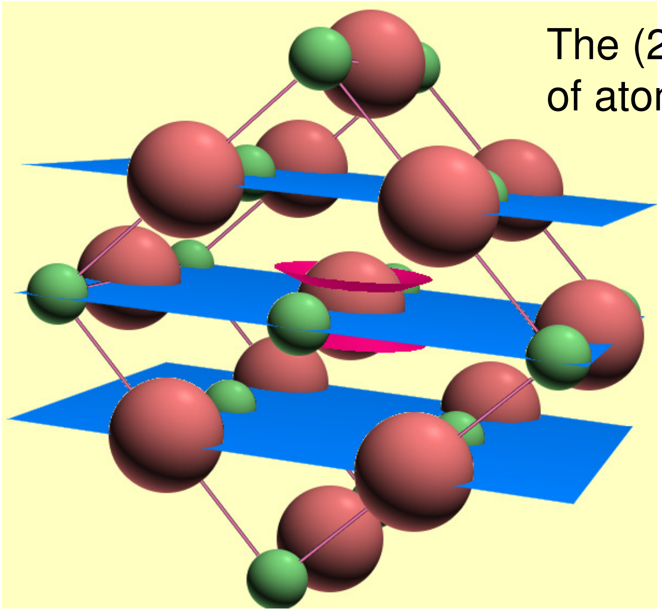


- Miller indices (hkl) are used to identify different planes of atoms
- Observed diffraction peaks can be related to planes of atoms to assist in analyzing the atomic structure and microstructure of a sample

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

The (200) planes of atoms in NaCl





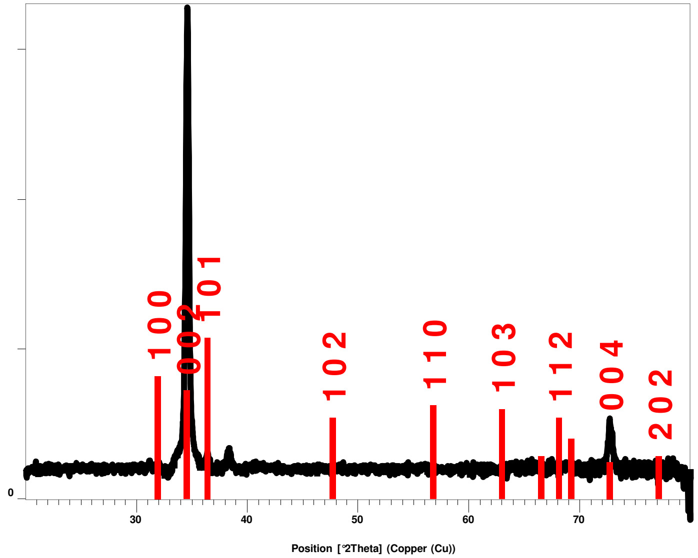
The (220) planes of atoms in NaCl

- The Miller indices (hkl) define the reciprocal of the axial intercepts
- The crystallographic direction, [hkl], is the vector normal to (hkl)
- d_{hkl} is the vector extending from the origin to the plane (hkl) and is normal to (hkl)
- The vector d_{hkl} is used in Bragg's law to determine where diffraction peaks will be observed

Useful things to remember about Miller indices

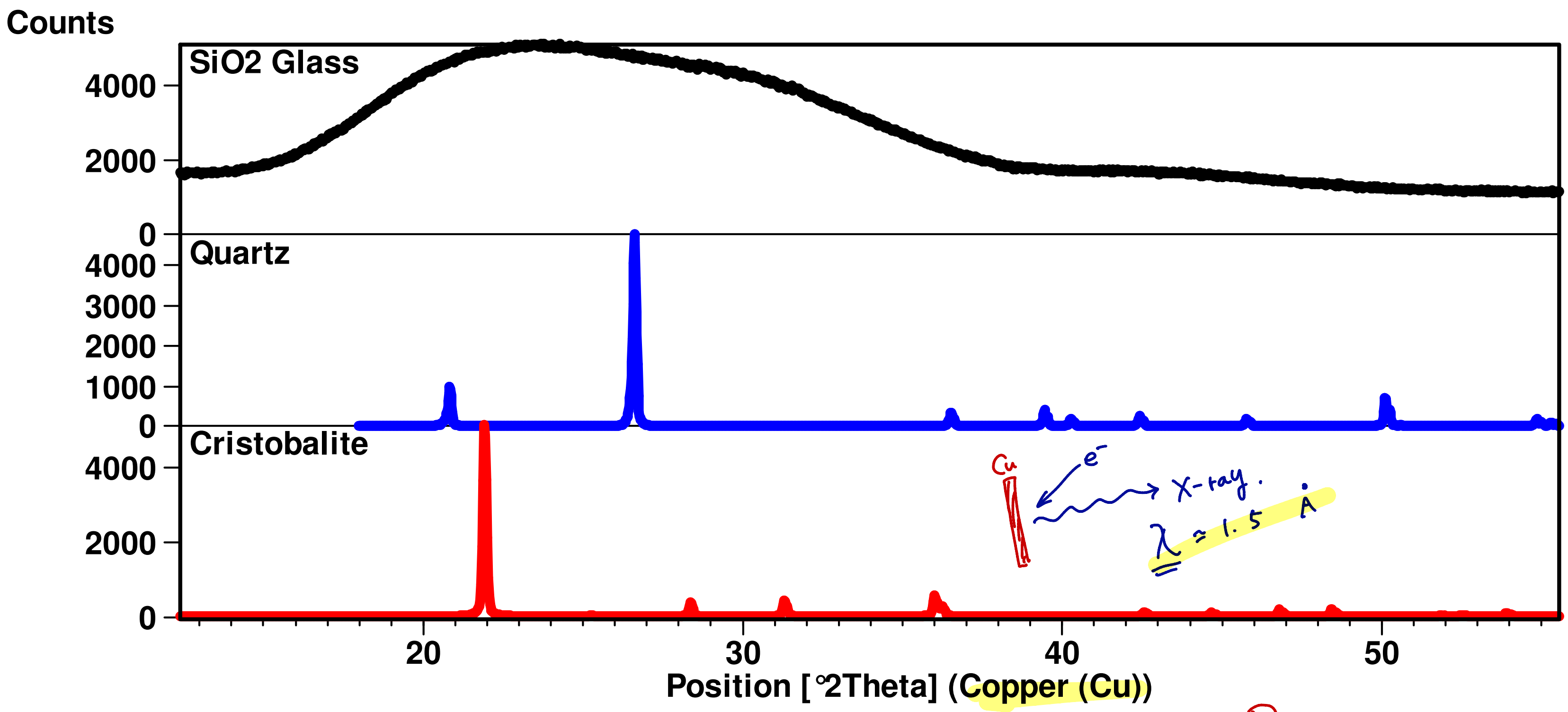
- (hkl) is parallel to (n*h n*k n*l)
  - For example, (110) // (220) // (330) // (440) …
- Planes are orthogonal if (hkl) • (h’k’l’) = 0
- Some planes may be equivalent because of symmetry
  - In a cubic crystal, (100) (010) and (001) are equivalent
  - They are the family of planes {100}
- [h00] is parallel to the a-axis, [0k0] // b-axis, [00l] // c-axis

- **When analyzing XRD data, we look for trends corresponding to directionality in the crystal structure by analyzing the Miller indices of diffraction peaks.**



In this figure, the (002) and (004) peaks (which are parallel to each other) are much more intense than expected– this provides information about the microstructure of the sample

The position and intensity of peaks in a diffraction pattern are determined by the crystal structure



Cu e^- X-ray.

$\lambda \approx 1.5$ Å

→ 2θ

The diffraction peak position is recorded as the detector angle, 2θ.

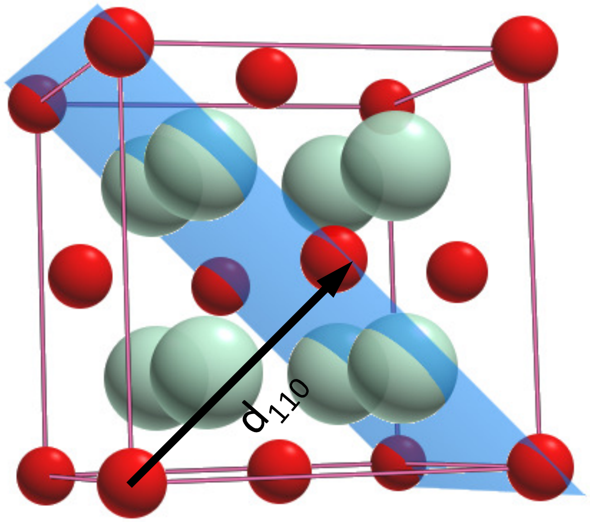
←

d-spacing

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

Bragg's Law

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



- 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.
- $\mathbf{d_{hkl}}$ is the vector drawn from the origin of the unit cell to intersect the crystallographic plane (hkl) at a 90° angle.
  - d_{hkl}, the vector magnitude, is the distance between parallel planes of atoms in the family (hkl)
  - d_{hkl} is a geometric function of the size and shape of the unit cell

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

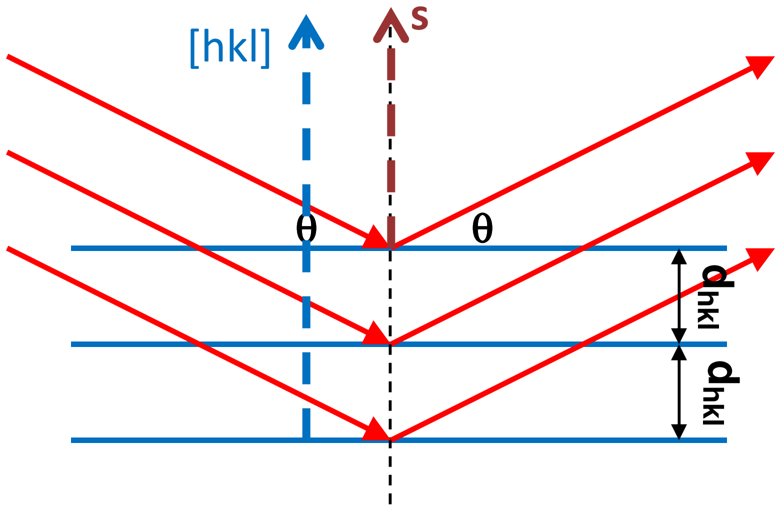
$$I_{hkl} \propto |F_{hkl}|^2$$

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

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

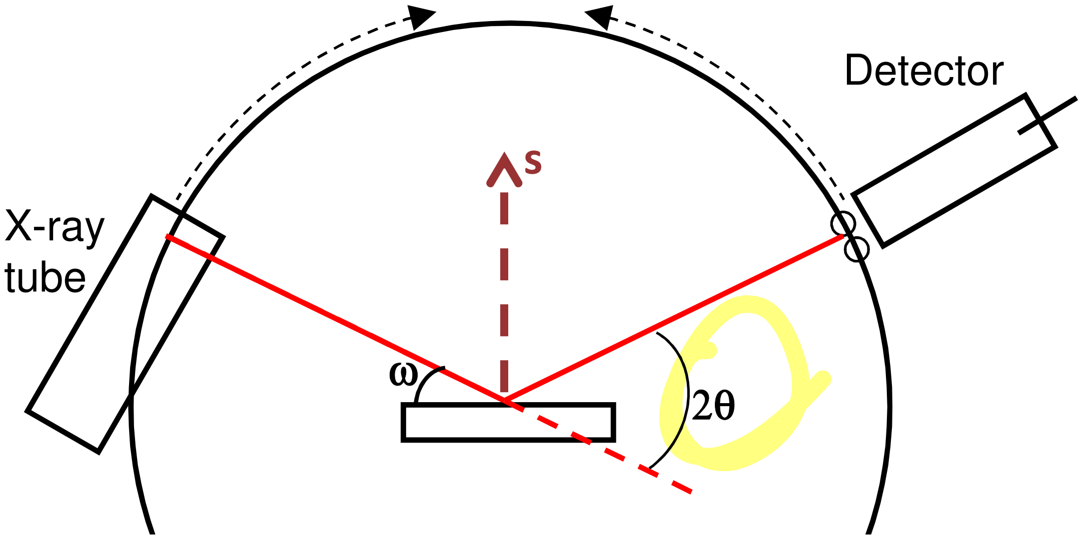
Bragg's law provides a simplistic model to understand what conditions are required for diffraction.

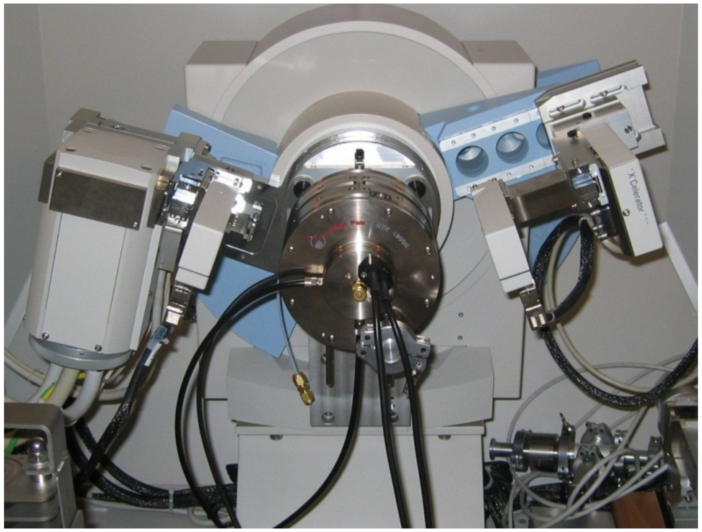
$$\lambda = 2d_{hkl}\sin\theta$$



- For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied.
  - In our diffractometers, the X-ray wavelength λ is fixed.
  - 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

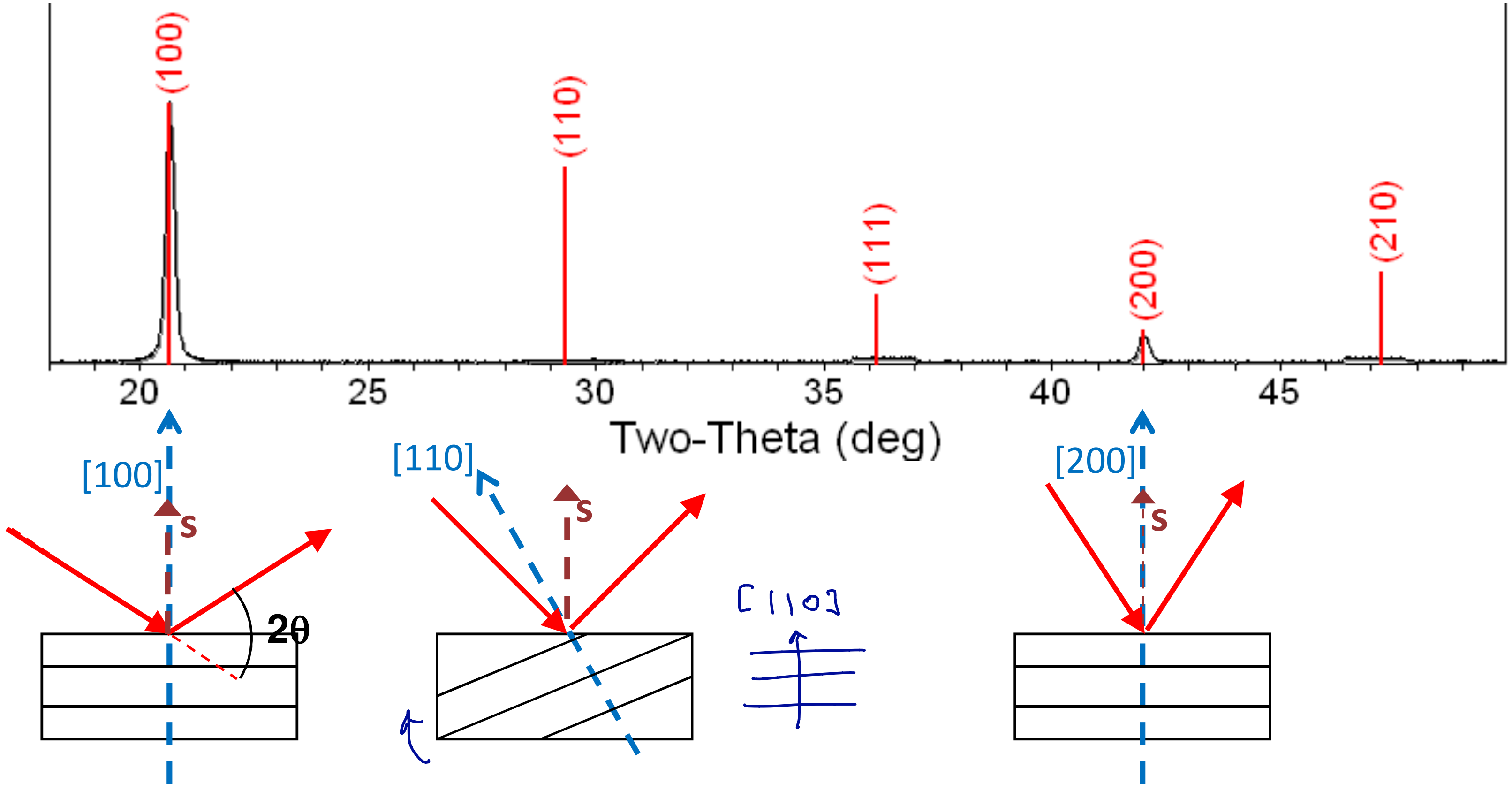
Our powder diffractometers typically use the Bragg-Brentano geometry.





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

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

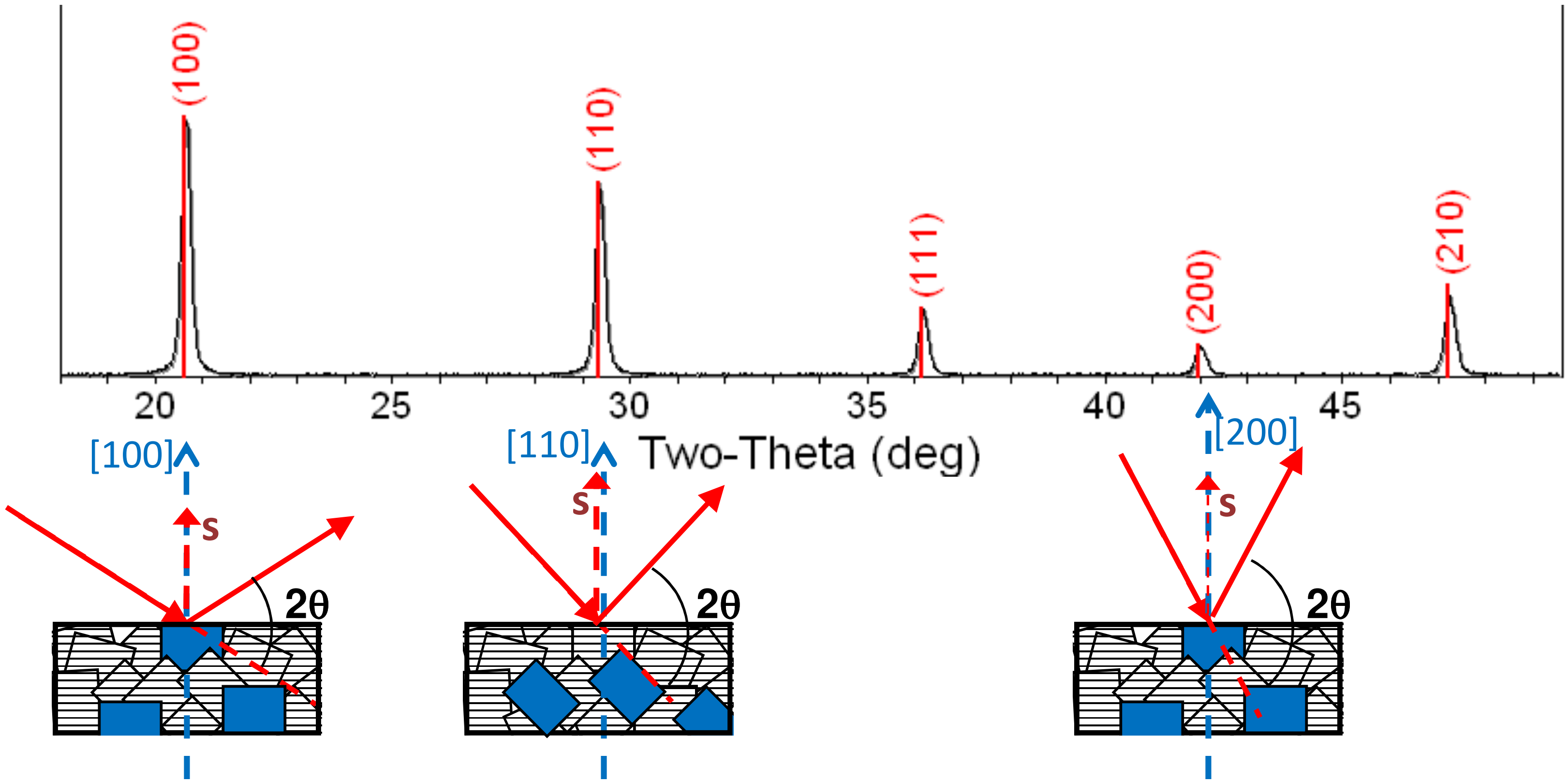


At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

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

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

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



- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

Powder diffraction is more aptly named polycrystalline diffraction

- Samples can be powder, sintered pellets, coatings on substrates, engine blocks...
- The ideal “powder” sample contains tens of thousands of randomly oriented crystallites
  - Every diffraction peak is the product of X-rays scattering from an equal number of crystallites
  - Only a small fraction of the crystallites in the specimen actually contribute to the measured diffraction pattern
    - XRPD is a somewhat inefficient measurement technique
- Irradiating a larger volume of material can help ensure that a statistically relevant number of grains contribute to the diffraction pattern
  - Small sample quantities pose a problem because the sample size limits the number of crystallites that can contribute to the measurement

X-rays are scattered in a sphere around the sample

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

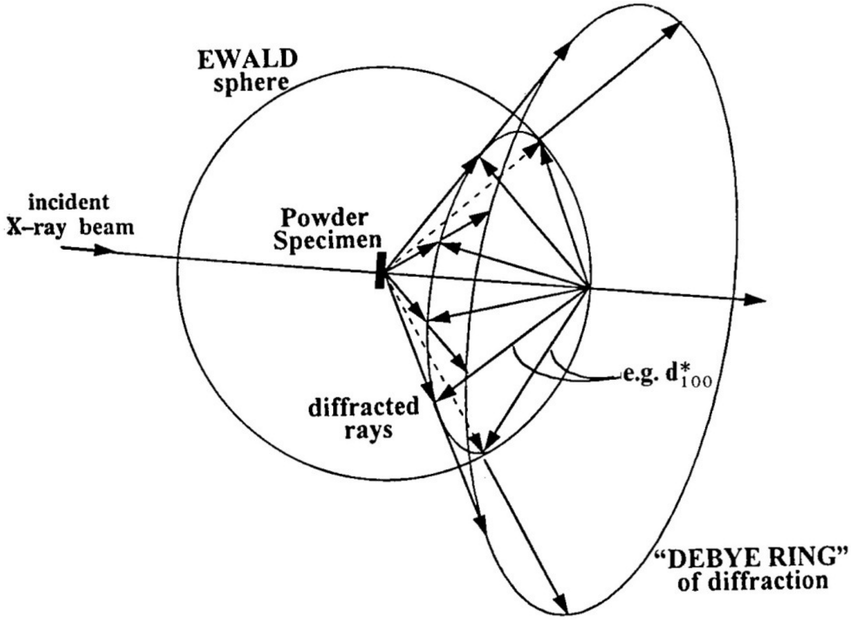
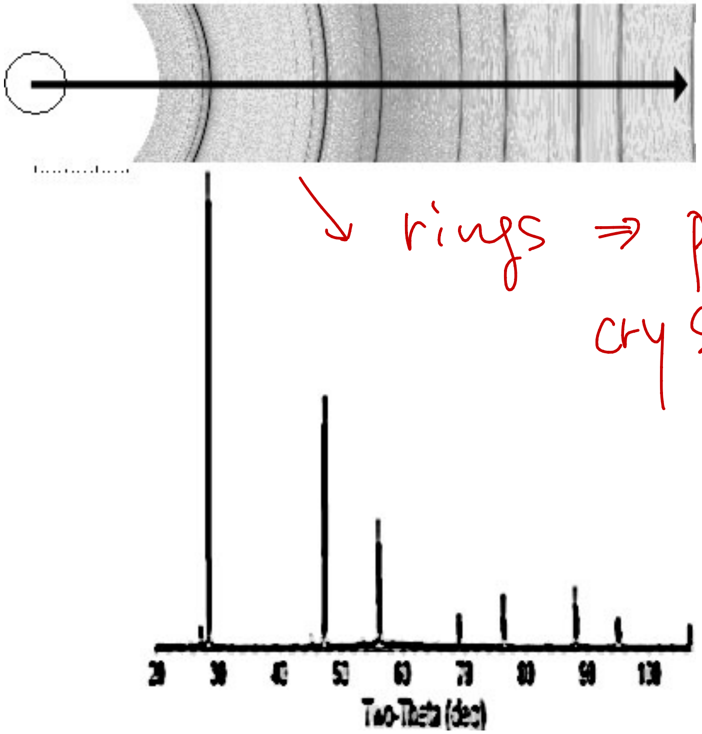


Figure 3.9. The intersection of d^*_{100} vectors from a powder with the Ewald sphere.

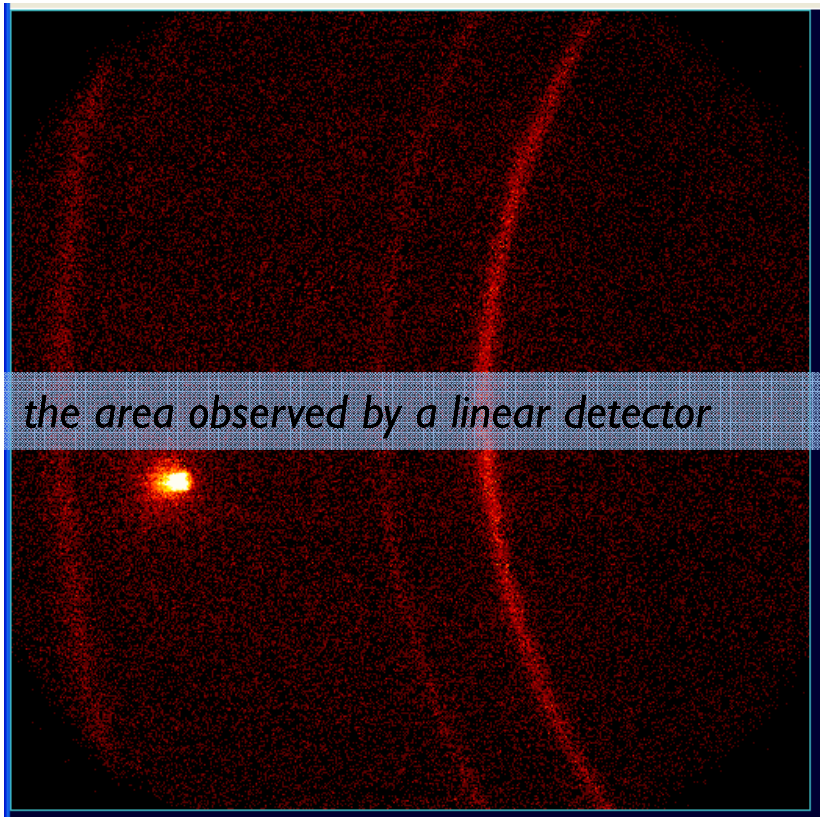


↘ rings ⇒ polycrystalline.

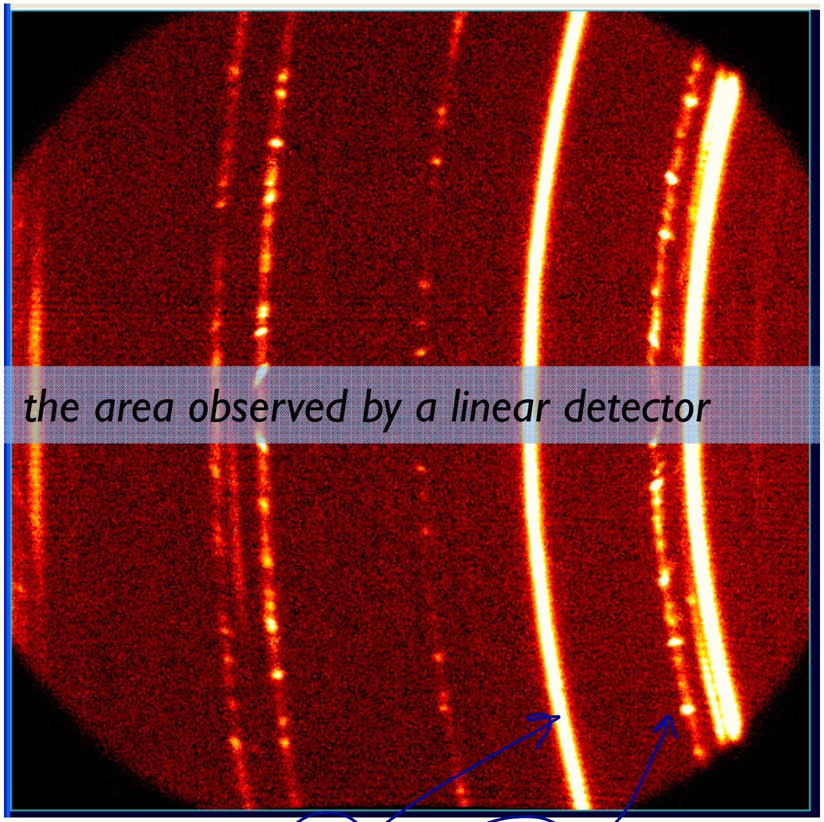
X-Ray Powder Diffraction (XRPD) is a somewhat inefficient measurement technique

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

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



Polycrystalline thin film on a single crystal substrate

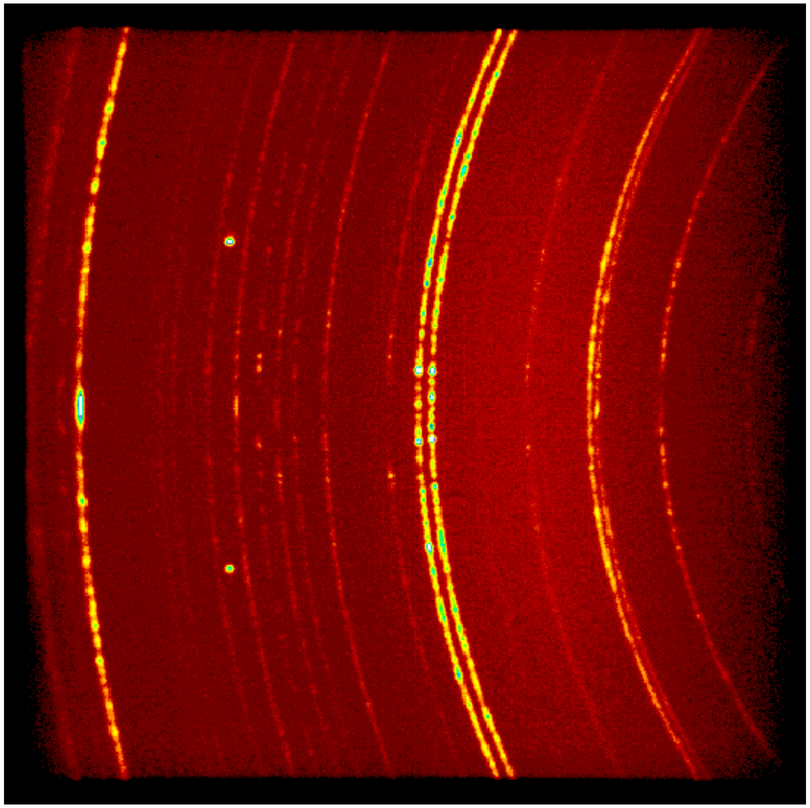


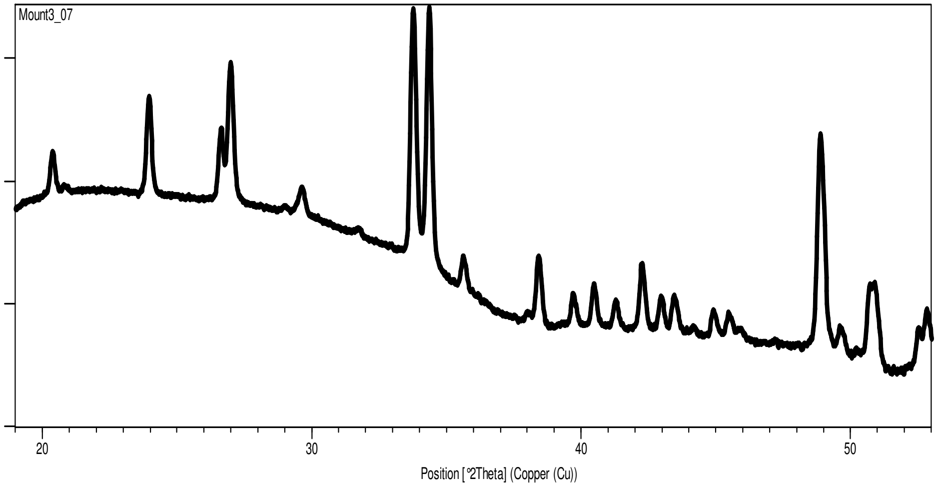
Mixture of fine and coarse grains in a metallic alloy

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

Non-Ideal Samples: a “spotty” diffraction pattern

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

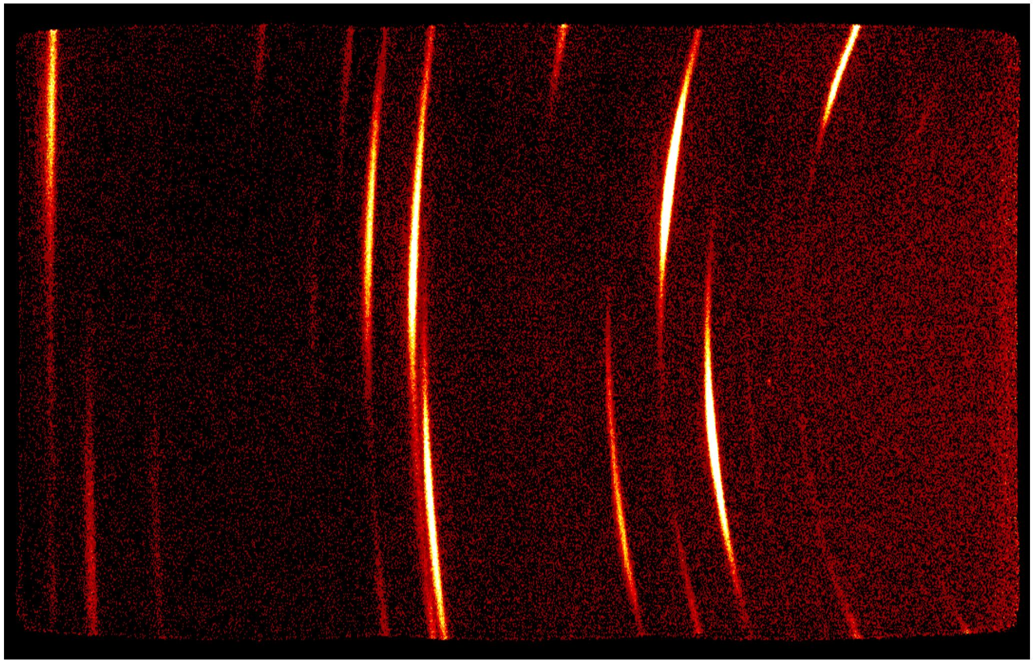


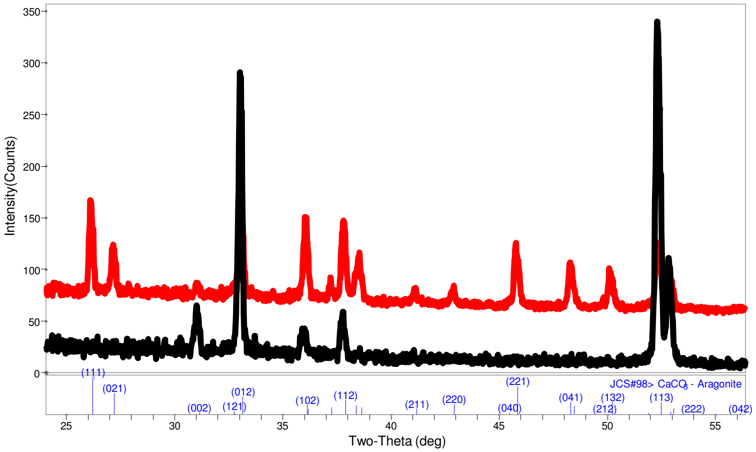


The poor particle statistics cause random error in the observed diffraction peak intensities.

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

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





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

$$d = \frac{n\lambda}{2\sin\theta} \quad (n = 1)$$

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

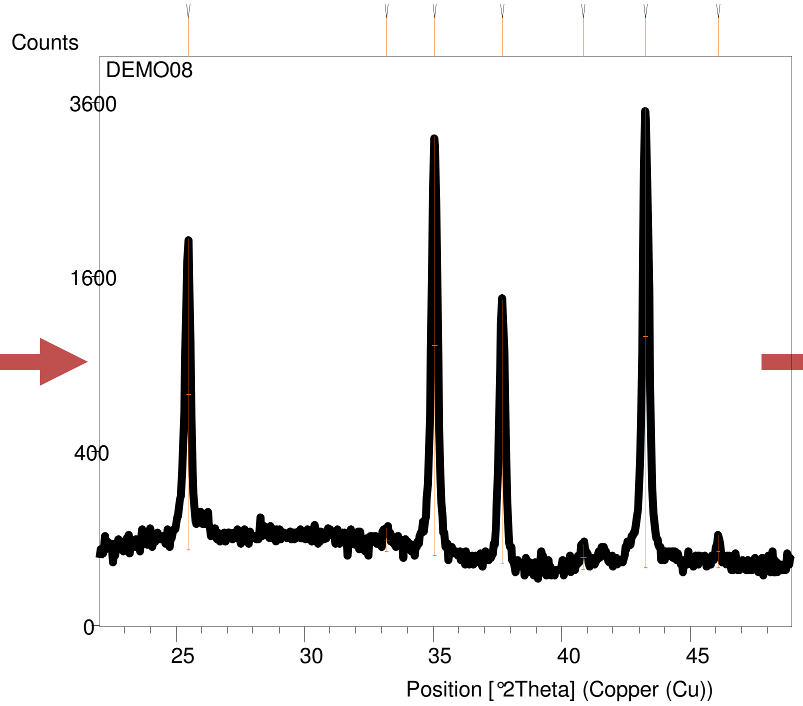
- The peak position as 2θ depends on instrumental characteristics such as wavelength.
  - The peak position as d_{hkl} is an intrinsic, instrument-independent, material property.
    - Bragg's Law is used to convert observed 2θ positions to d_{hkl}.
- The absolute intensity, i.e. the number of X rays 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.

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

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

Raw Data

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



Reduced dI list

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

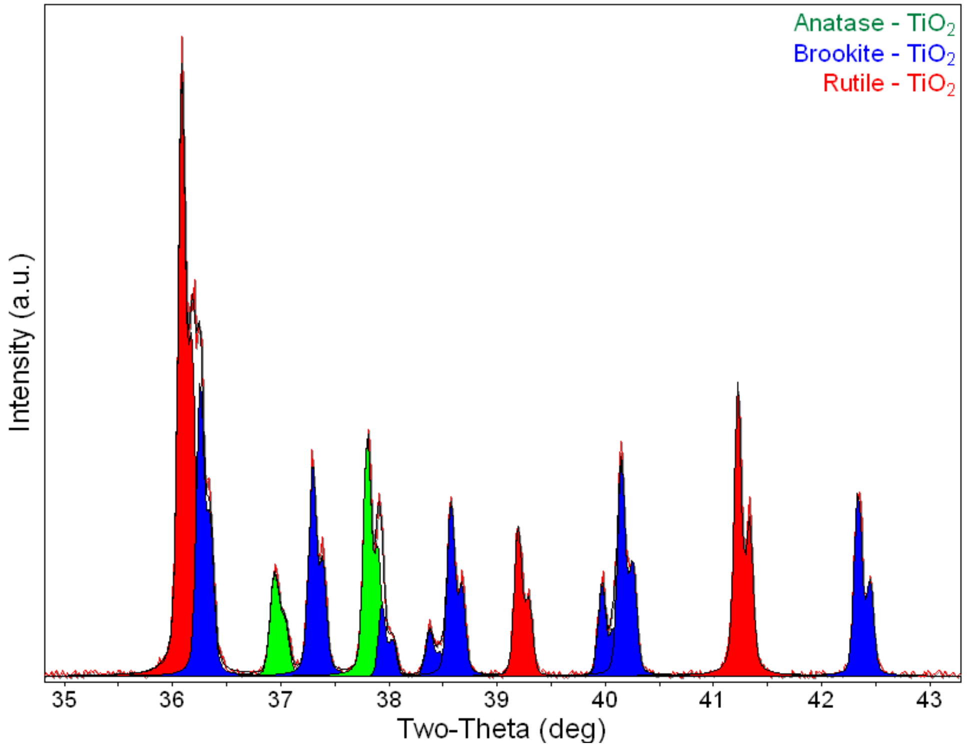
Applications of XRPD

You can use XRD to determine

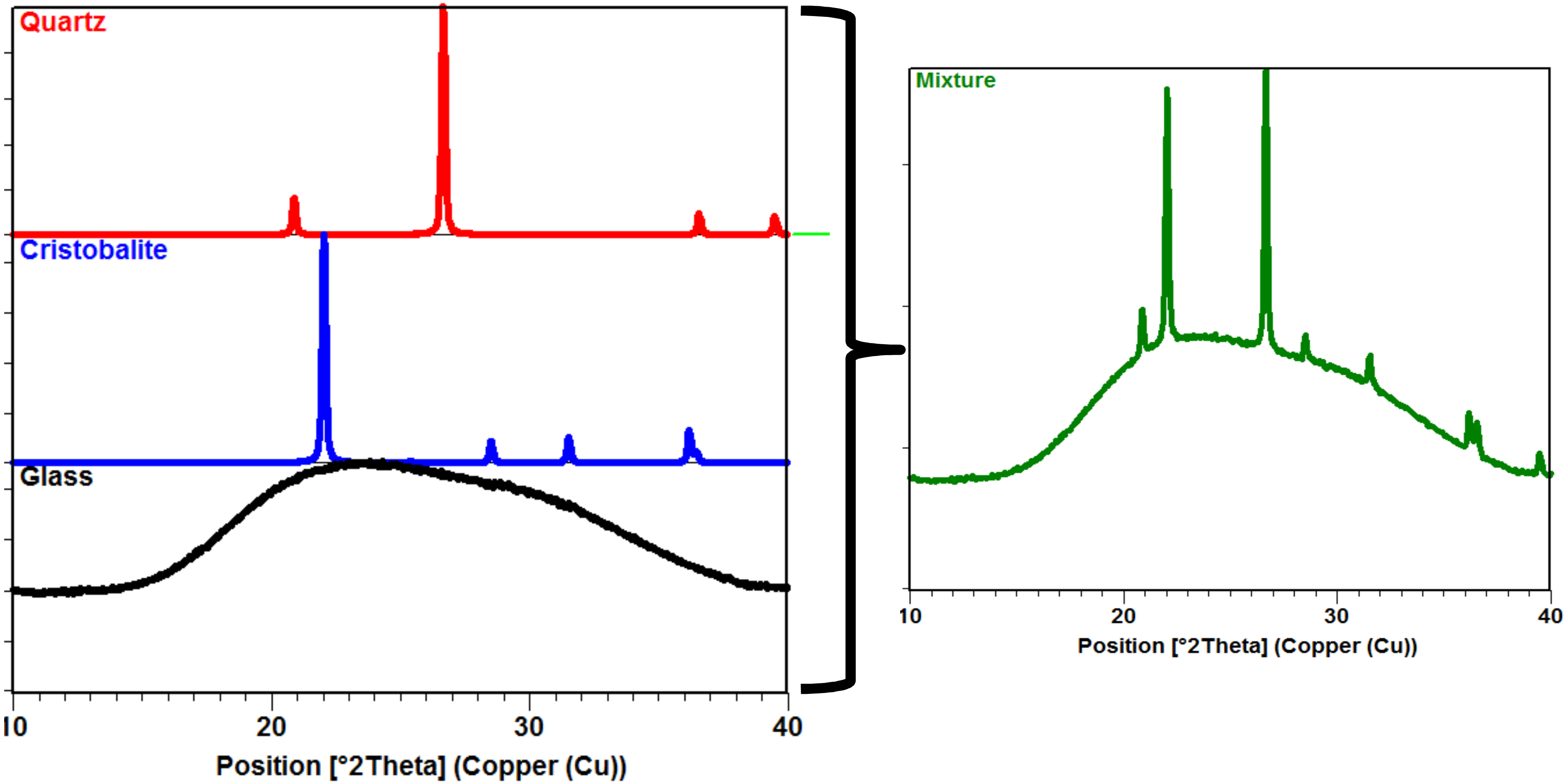
- Phase Composition of a Sample
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and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



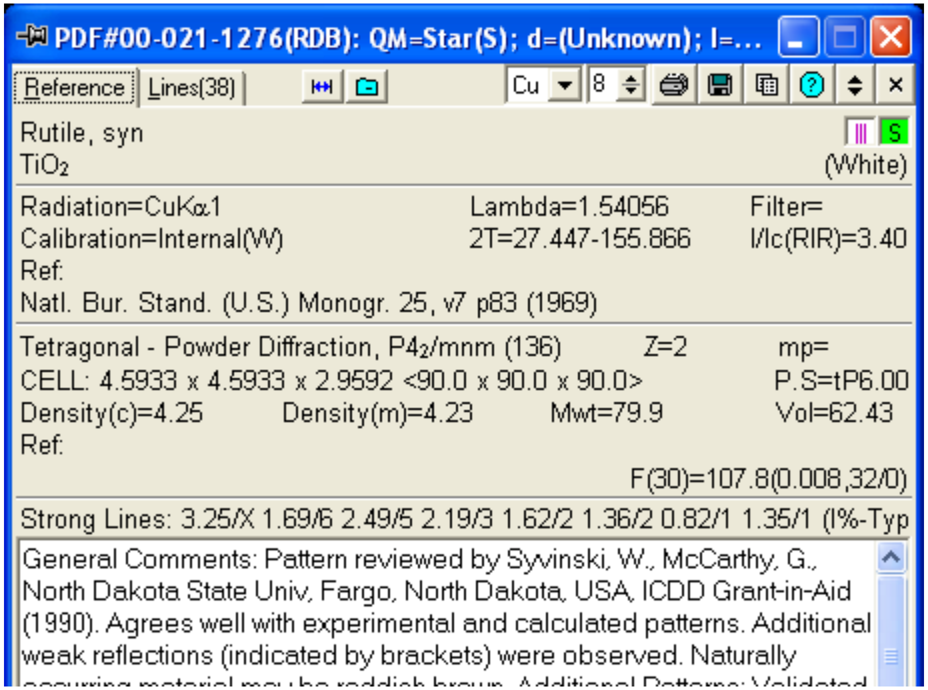
The diffraction pattern of a mixture is a simple sum of the scattering from each component phase



{ Pawley
LeBail } decomposition to know abc , αβγ ⇒ Rietveld analysis to get atomic positions

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

- The PDF contains over 300,000 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.



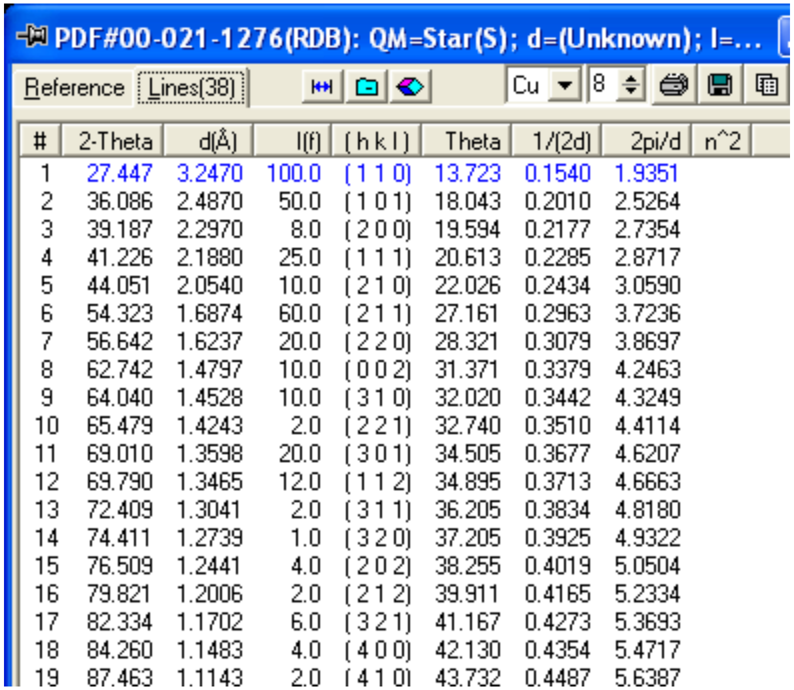
Rutile, syn
TiO_2 (White)

Radiation=CuKα1 Lambda=1.54056 Filter=
Calibration=Internal(W) 2T=27.447-155.866 I/Ic(RIR)=3.40
Ref:
Natl. Bur. Stand. (U.S.) Monogr. 25, v7 p83 (1969)

Tetragonal - Powder Diffraction, $P4_2/mnm$ (136) Z=2 mp=
CELL: 4.5933 x 4.5933 x 2.9592 <90.0 x 90.0 x 90.0> P.S=tP6.00
Density(c)=4.25 Density(m)=4.23 Mwt=79.9 Vol=62.43
Ref:
F(30)=107.8(0.008,32/0)

Strong Lines: 3.25/X 1.69/6 2.49/5 2.19/3 1.62/2 1.36/2 0.82/1 1.35/1 (I%-Typ

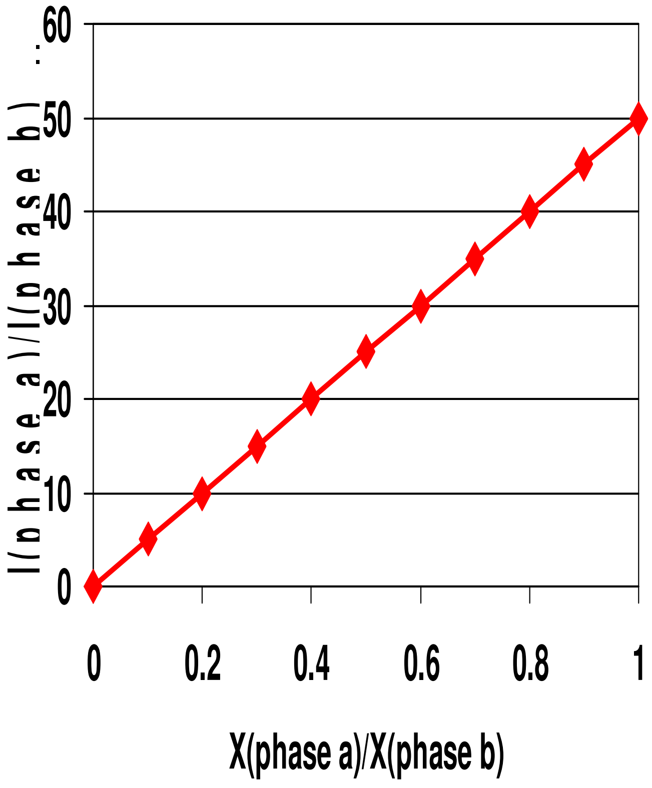
General Comments: Pattern reviewed by Syvinski, W., McCarthy, G., North Dakota State Univ, Fargo, North Dakota, USA, ICDD Grant-in-Aid (1990). Agrees well with experimental and calculated patterns. Additional weak reflections (indicated by brackets) were observed. Naturally



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

Quantitative Phase Analysis

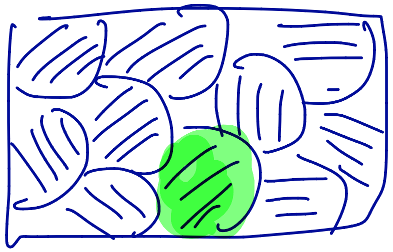
- With high quality data, you can determine how much of each phase is present
  - must meet the constant volume assumption (see later slides)
- The ratio of peak intensities varies linearly as a function of weight fractions for any two phases in a mixture
  - $\frac{I_\alpha}{I_\beta} = K * \frac{X_\alpha}{X_\beta}$
  - need to know the constant of proportionality
- RIR method is fast and gives semi-quantitative results
  - $K = \frac{RIR_\alpha}{RIR_\beta}$
- Whole pattern fitting/Rietveld refinement is a more accurate but more complicated analysis



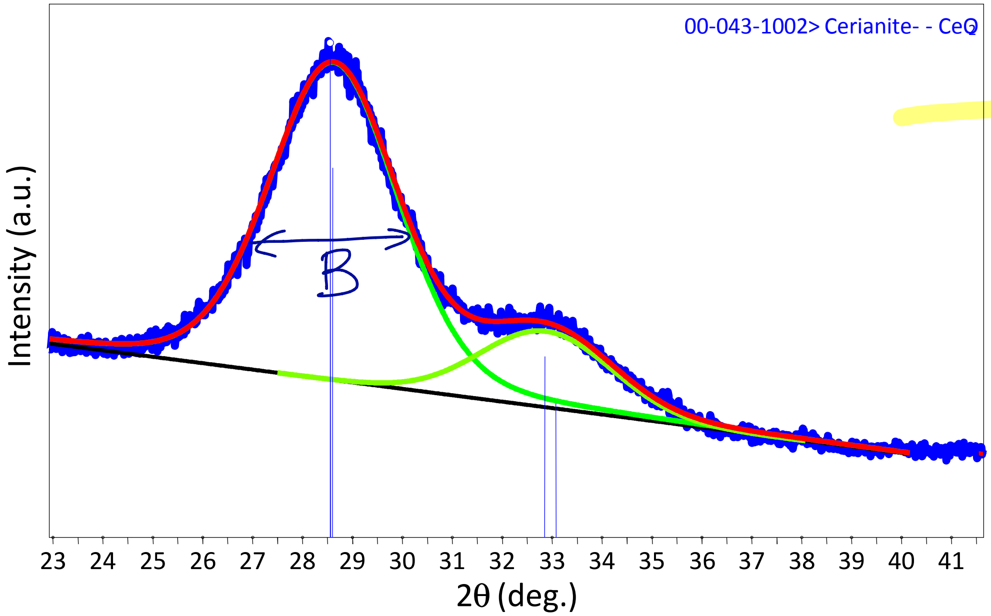
Unit Cell Lattice Parameter Refinement

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

Crystallite Size and Microstrain



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



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

crystallite size

Preferred Orientation (texture)

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