Powder X-ray Diffraction

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Uses of Powder Diffraction

Qualitative Analysis

- Identification of single-phase materials
- Identification of multiple phases in microcrystalline mixtures
- Recognition of amorphous materials in partially crystalline mixtures

Quantitative Analysis

- Lattice Parameter Determination
- Phase Fraction Analysis

Peak Shape Analysis

- Crystallite Size Distribution
- Microstrain Analysis
- Extended Defect Concentration

Structure Refinement

- Rietveld Method

Structure Solution

- Reciprocal Space Methods
- Real Space Methods

Thermal expansion and Phase Transitions

Three Unique Features of Synchrotron Radiation

- **Intensity**
- *Enables Rapid Data Collection*
  - Kinetics
  - Unstable Compounds
  - Environmental Cells
  - –*Enables Focussing*
  - Small Samples
  - Small areas/volumes

- **Energy Range**
- *Enables Spectroscopy*
  - –Elemental Identification
  - –Bonding Studies
  - –Speciation
- *Enables Optimal Conditions*
  - –Environmental Cells
  - –Selected Elements

- **Low Divergence**

Enables High Resolution

- Micro Beams
- Small Volumes
- Complex Materials

What is special about a crystal?

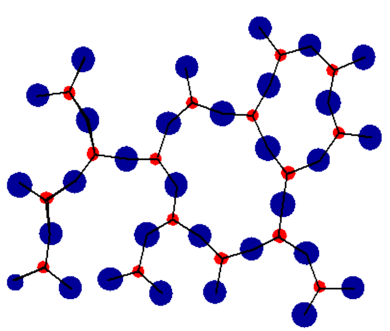
Solid phases are often crystalline, but need not be - e.g. glass an “amorphous material”

Glass

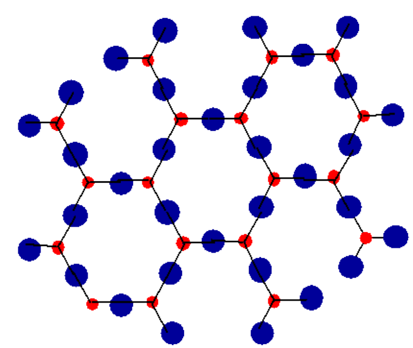
- Fractures into shards
- Takes on any shape, depending on preparation
- Properties do not vary with orientation.

Crystal

- Cleaves along preferred directions
- Grows with well developed crystal faces
- Properties depend on orientation in which they are measured.



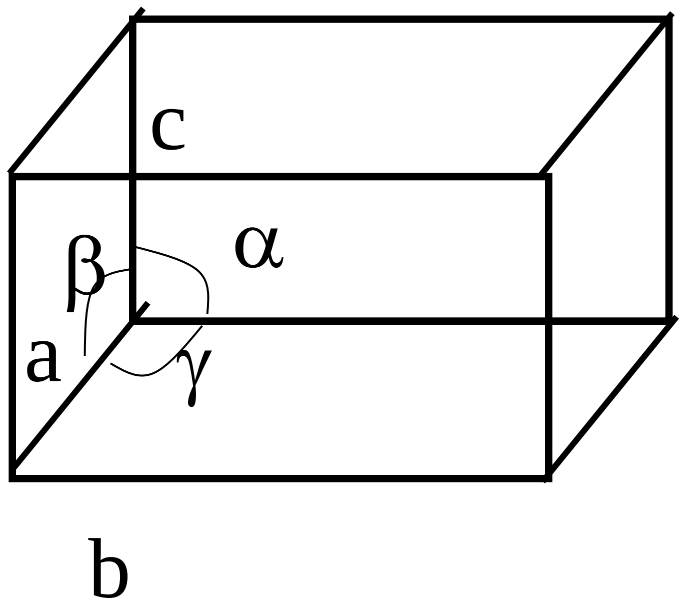
• Si • Oxygen



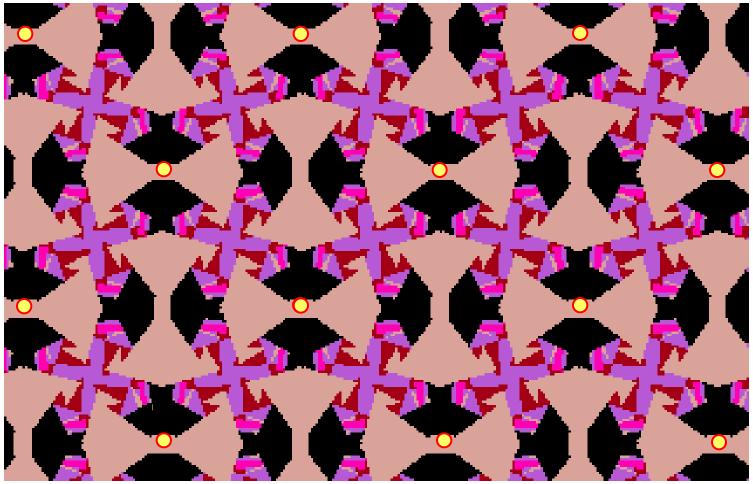
Crystal Structure

- CRYSTAL: Contains a periodical array of atoms/ions. This can be represented by a simple lattice of points.
- A group of atoms is associated with each lattice points.
- LATTICE: An infinite array of points in space, in which each point has identical surroundings to all others.
- CRYSTAL STRUCTURE: The periodic arrangement of atoms in the crystal.

The Unit Cell



The unit cell is a basic parallelopiped shaped block from which the whole volume of the crystal may be built by repetition in 3 dimensions. Any point in the unit cell may be specified with respect to the origin by parameters x, y, z measured parallel to the unit cell axes and expressed as fractions.



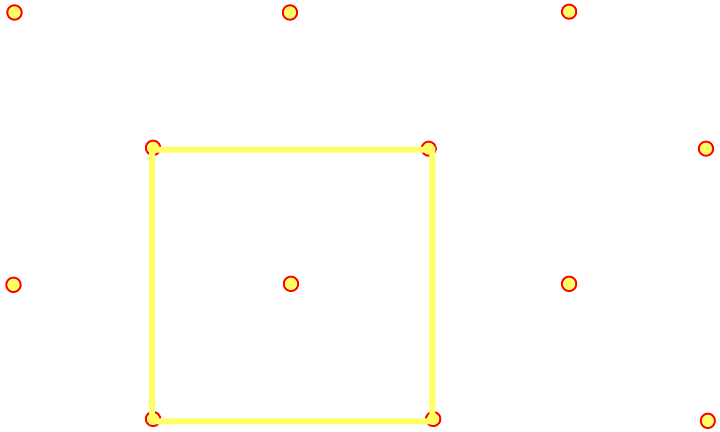
Example of 2D symmetry in a wallpaper pattern

To show symmetry:

1. Pick a point

2. Find all equivalent points

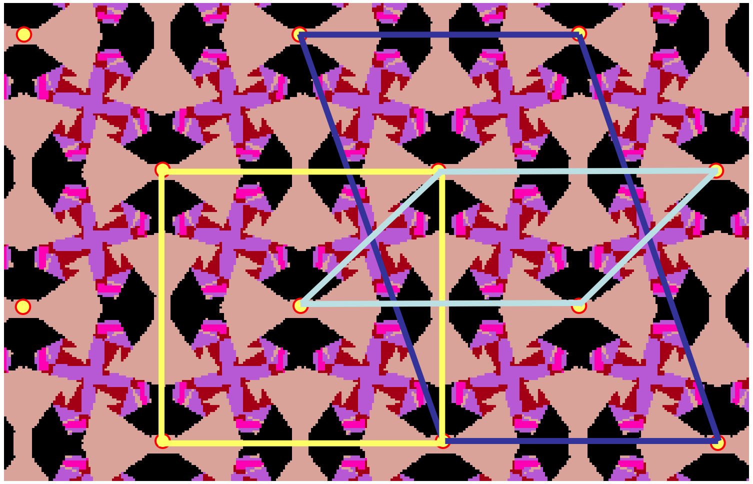
(http://www.clarku.edu/~djoyce/wallpaper/)



Example of 2D symmetry in a wallpaper pattern

To show symmetry:

- 1. Pick a point
- 2. Find all equivalent points
- These points form a 2D lattice
- Connecting 4 lattice points to form a parallelogram gives a possible *unit cell*



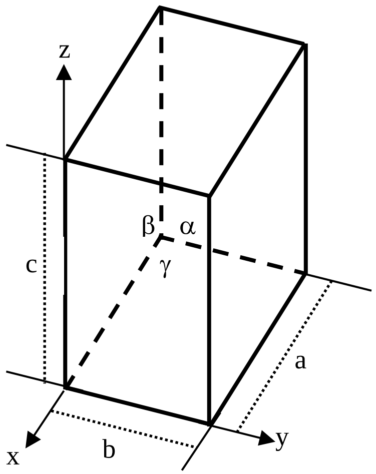
Example of 2D symmetry in a wallpaper pattern

- Connecting 4 lattice points to form a parallelogram gives a possible *unit cell*

- *Unit cell* – the basic unit that repeats in every direction

- Different *unit cells* can be chosen

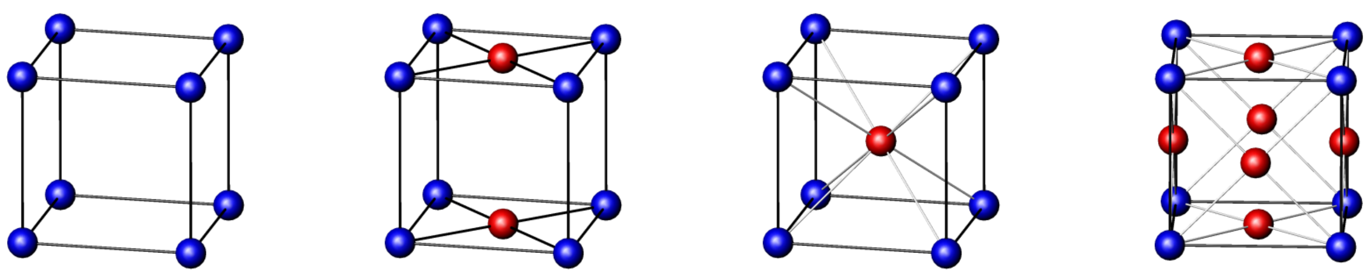
- But some *unit cells* are preferable for higher symmetry



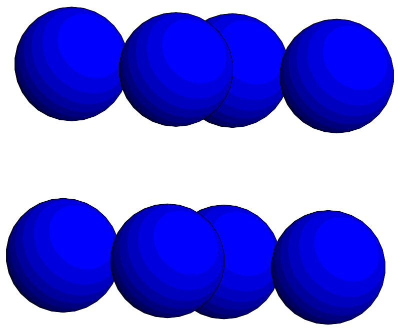
Lattice parameters:
a, b, c; α, β, γ

Name	Bravis Lattice	Conditions
Triclinic	1 (P)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2 (P, C)	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$
Orthorhombic	4 (P,F,I,A)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2 (P, I)	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$
Cubic	3 (P, F,I)	$a = b = c$ $\alpha = \beta = \gamma = 90°$
Trigonal	1 (P)	$a = b = c$ $\alpha = \beta = \gamma < 120° \neq 90°$
Hexagonal	1 (P)	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$

P **C** **I** **F**



PC Lattice

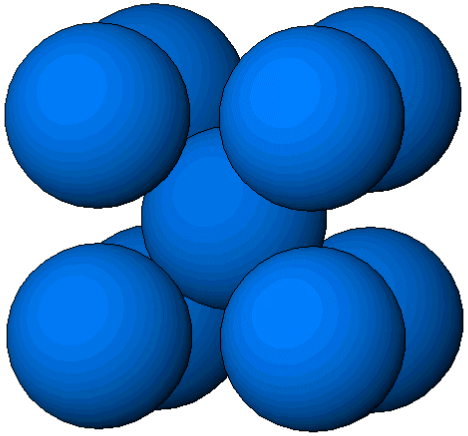


α-Po is **primitive-Cubic**

Identical atoms at corners but nothing at the and body or face centers.

Lattice type P

BCC Lattice



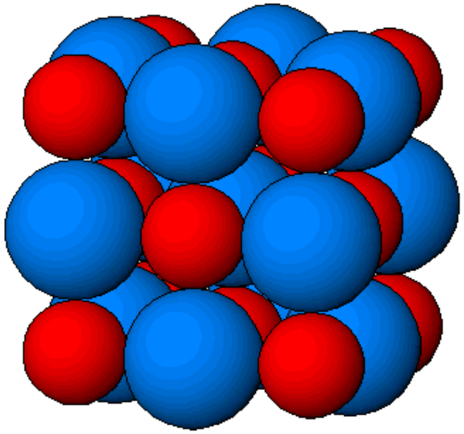
α-Iron is **Body-Centered Cubic**

Identical atoms at corners and body center (nothing at face centers)

Lattice type I

Also Nb, Ta, Ba, Mo...

FCC Lattice



Sodium Chloride (NaCl) Na is much smaller than Cl

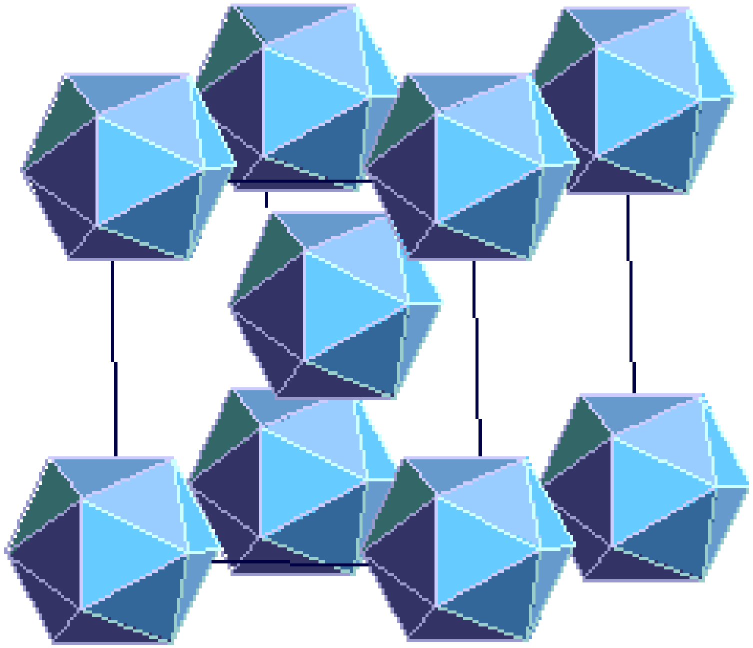
Face Centered Cubic

<u>Rocksalt structure</u>

Lattice type F

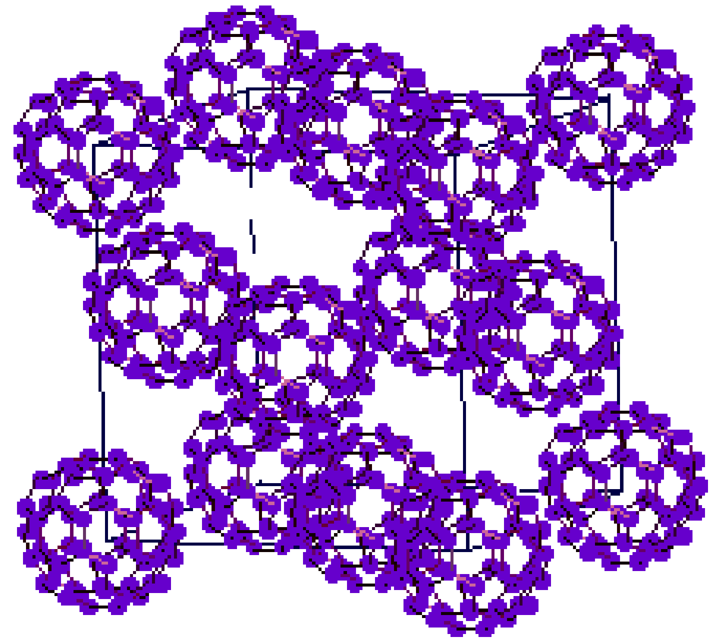
Also NaF, KBr,MgO….

FOOT & MOUTH VIRUS



BCC

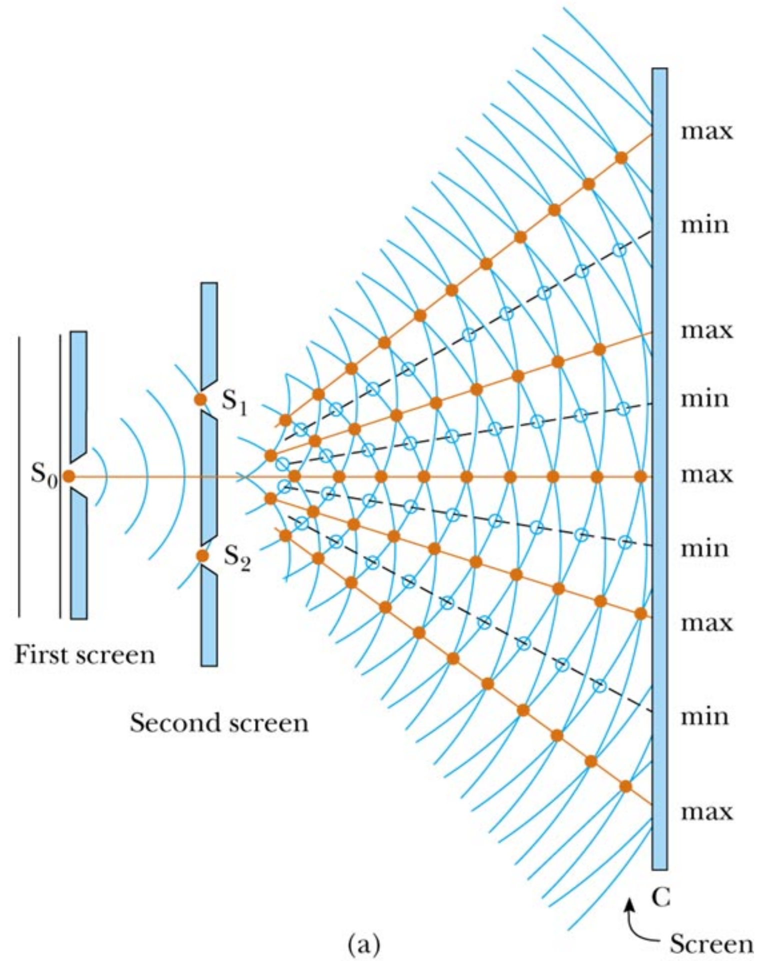
BUCKMINSTERFULLERENE



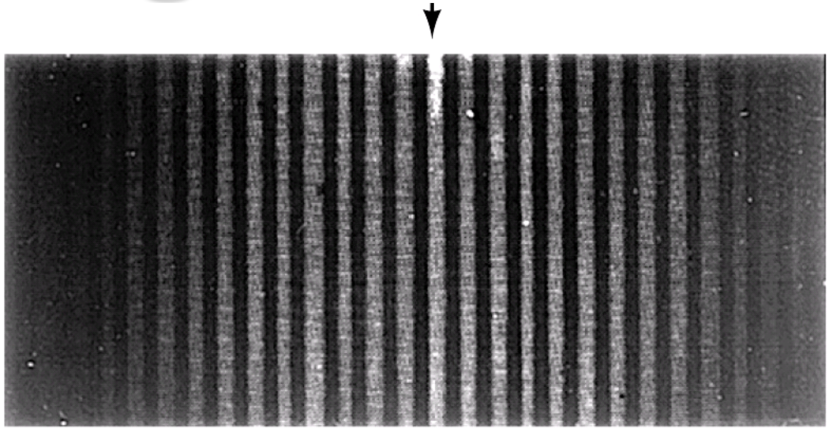
FCC

Young's Double Slit Experiment

- Thomas Young first demonstrated interference in light waves from two sources in 1801
- Light is incident on a screen with a narrow slit, S_o
- The light waves emerging from this slit arrive at a second screen that contains two narrow, parallel slits, S_1 and S_2
- The narrow slits, S_1 and S_2 act as sources of waves
- The waves emerging from the slits originate from the same wave front and therefore are always in phase



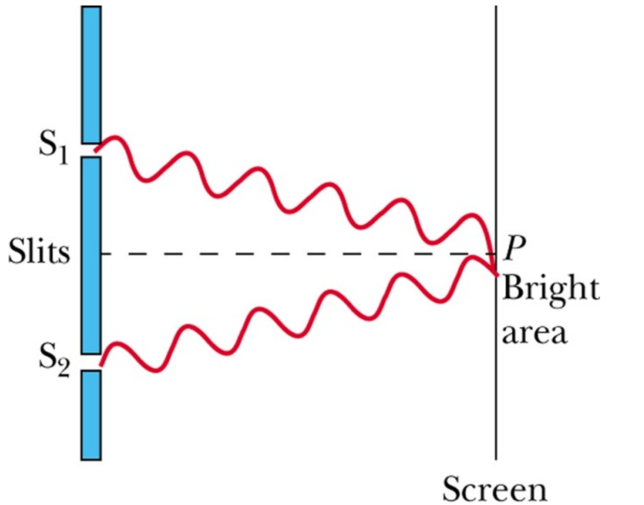
Resulting Interference Pattern



- The light from the two slits form a visible pattern on a screen
- The pattern consists of a series of bright and dark parallel bands called *fringes*
- ***Constructive interference*** occurs where a bright fringe occurs
- ***Destructive interference*** results in a dark fringe

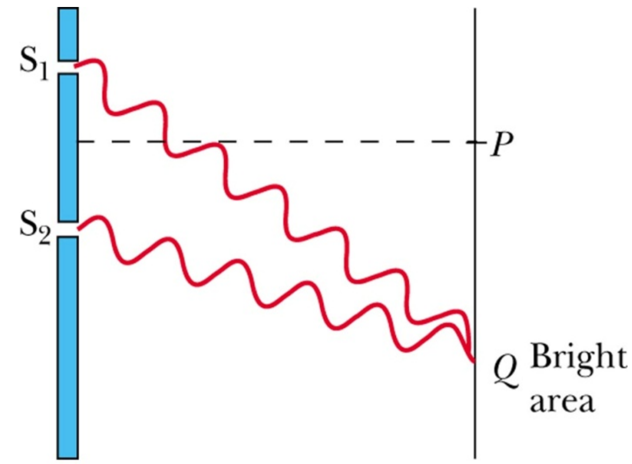
Interference Patterns

- Constructive interference occurs at the center point
- The two waves travel the same distance
  - Therefore, they arrive in phase



(a)

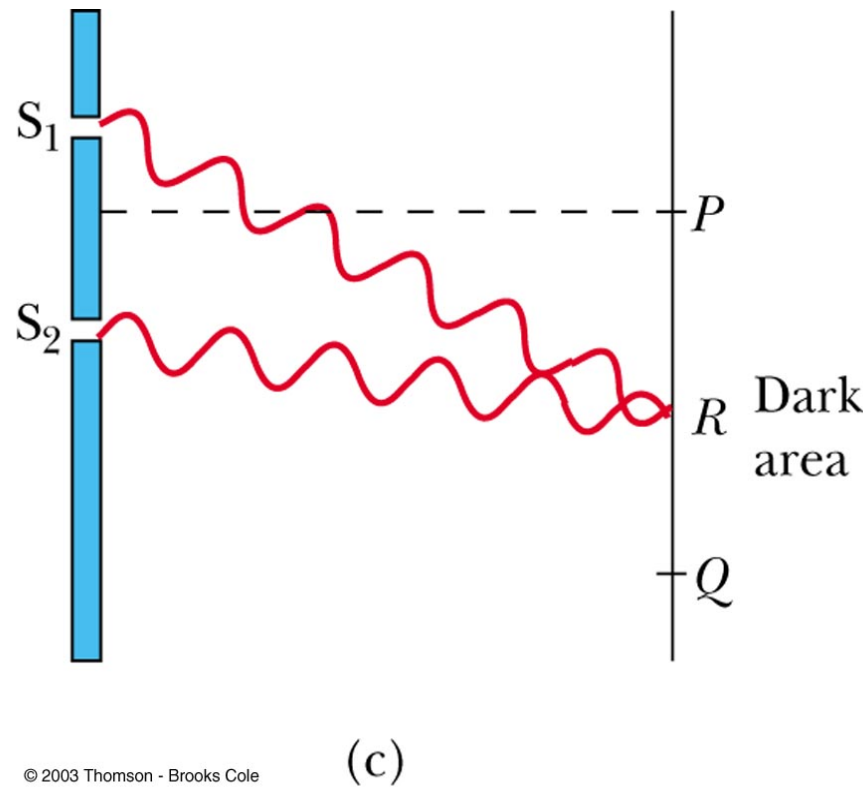
- The upper wave travels one wavelength farther than the lower wave
  - Therefore, they arrive in phase
- A bright fringe occurs



(b)

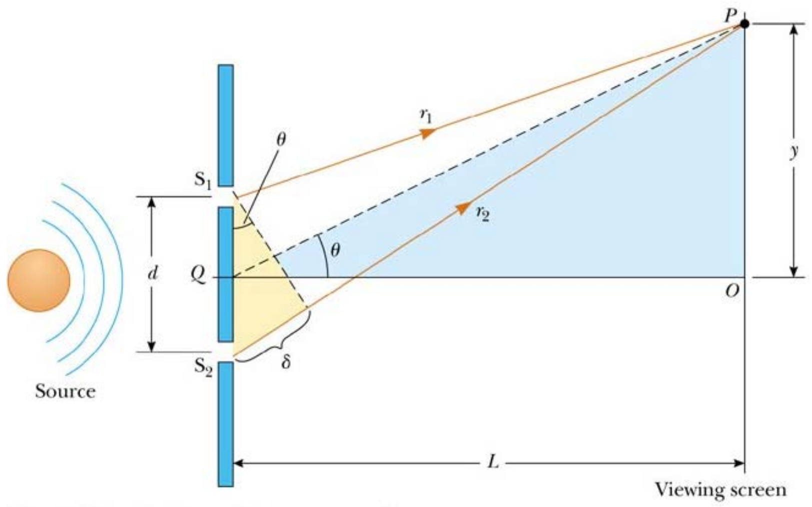
Interference Patterns

- The upper wave travels one-half of a wavelength farther than the lower wave
- The trough of the bottom wave overlaps the crest of the upper wave (180° phase shift)
- This is destructive interference
  - A dark fringe occurs



Interference Equations

- The path difference, δ, is found from the tan triangle
- $\delta = r_2 - r_1 = d \sin \theta$



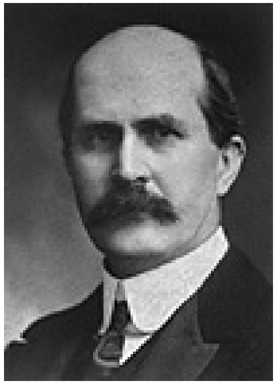
- For a bright fringe, produced by constructive interference, the path difference must be either zero or some integral multiple of of the wavelength
- $\delta = d \sin \theta_{bright} = m \lambda$
  - $m = 0, \pm 1, \pm 2, \ldots$
  - m is called the *order number*

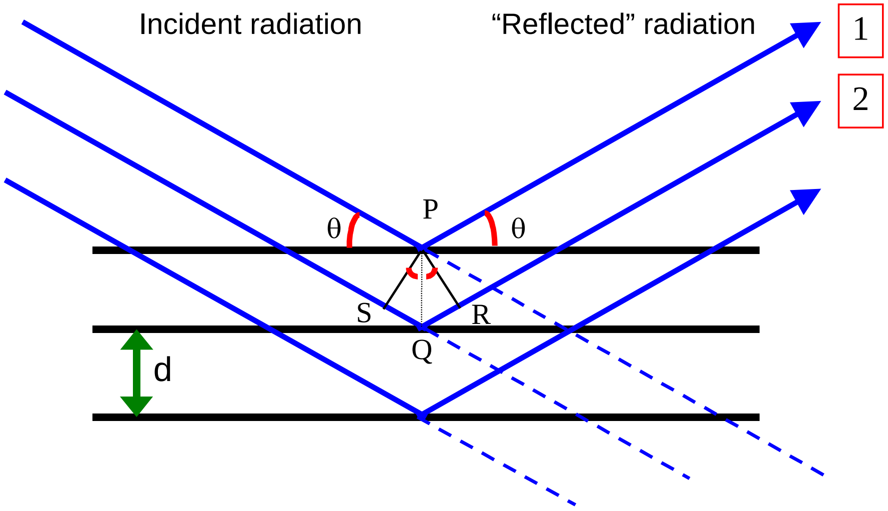
Diffraction of X-ray Waves

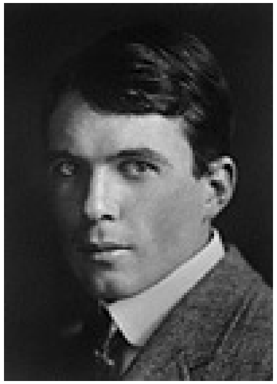
- **Diffraction:** When light passes sharp edges or goes through narrow slits the rays are deflected and produce fringes of light and dark bands.

Diffraction grating and helium-neon laser

Bragg's Law







Beam "2" travels the extra distance SQR

$$n\lambda = \overline{SQ} + \overline{QR}$$

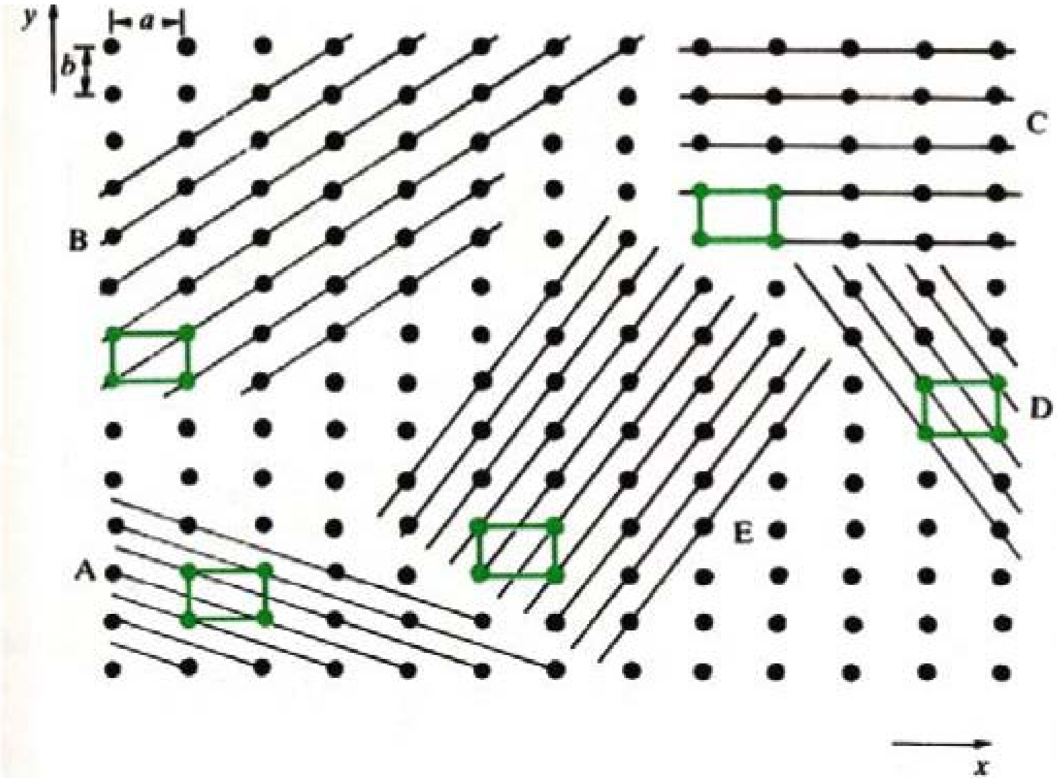
$$= d_{hkl} \sin\theta + d_{hkl} \sin\theta$$

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

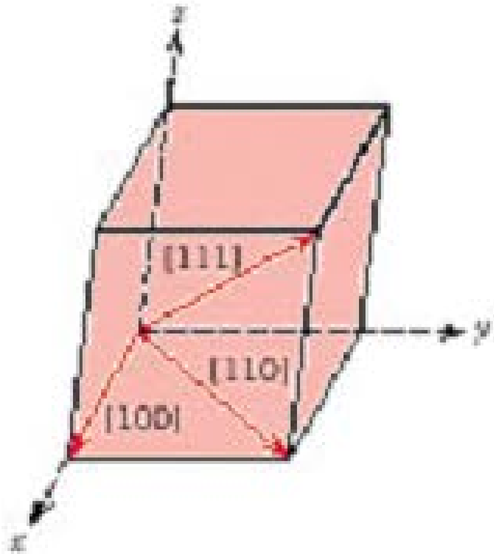
But not all planes result in diffraction !!!

Lattice Planes

- It is possible to describe certain directions and planes with respect to the crystal lattice using a set of integers referred to as Miller Indicies



Crystallographic Directions And Planes



Lattice Directions

Individual directions: [uvw]

Symmetry-related directions: <uvw>

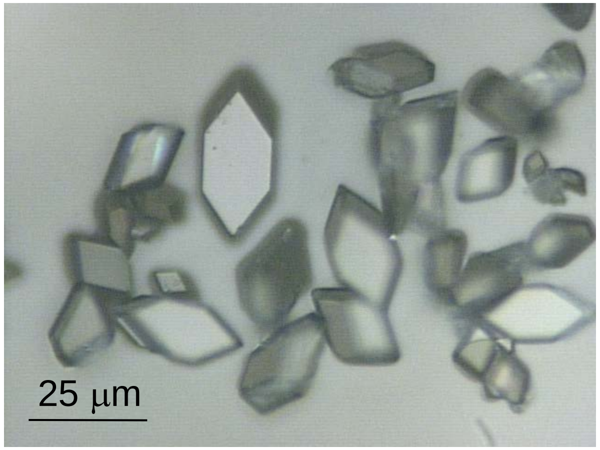
Miller Indices:

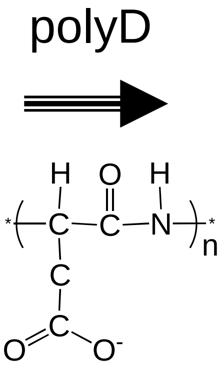
1. Find the intercepts on the axes in terms of the lattice constant a, b, c
2. Take the reciprocals of these numbers, reduce to the three integers having the same ratio **(hkl)**

Set of symmetry-related planes: {hkl}

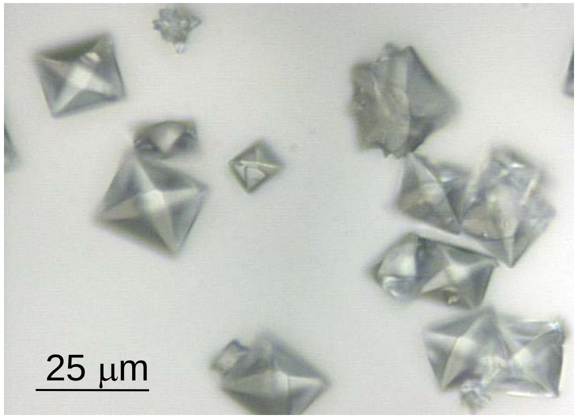
Calcium oxalate solvates: COM & COD

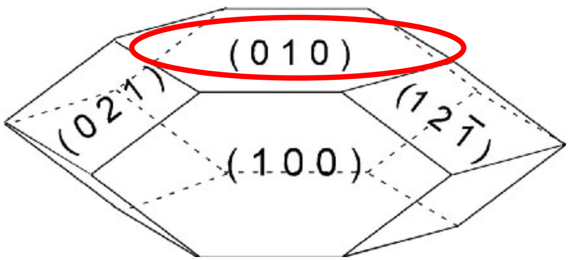
CaOx **Monohydrate**
(symptomatic)

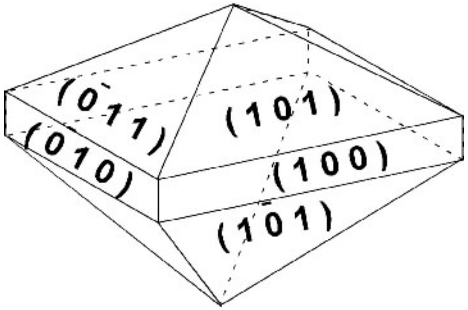




CaOx **Dihydrate**
(protective)



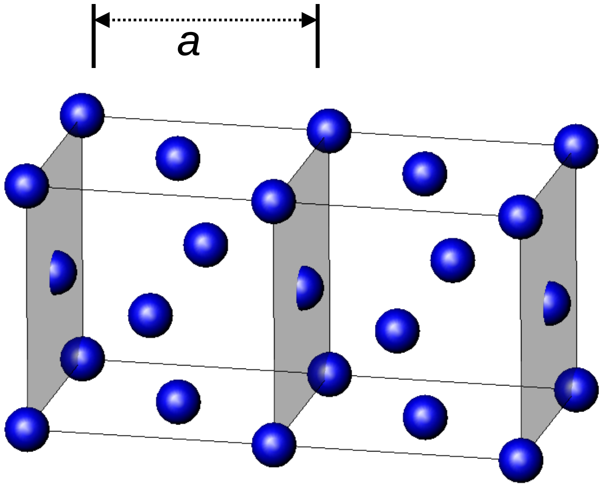




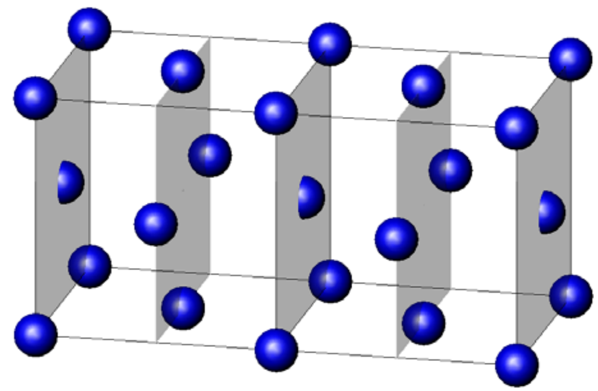
$P2_1/c$
(a = 6.290 Å, b = 14.580 Å, c = 10.116 Å, β = 109.46°)

$I4/m$
(a = b = 12.371 Å, c =7.357 Å, $\alpha = \beta = \gamma$ = 90°)

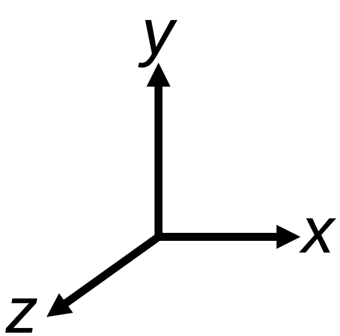
Examples of Miller Indices

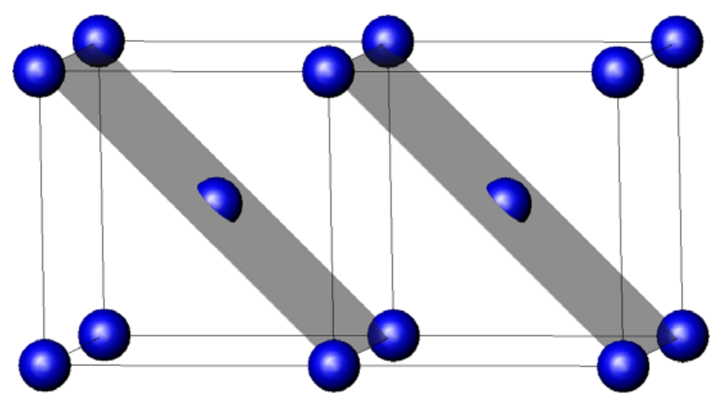


(100)



(200)

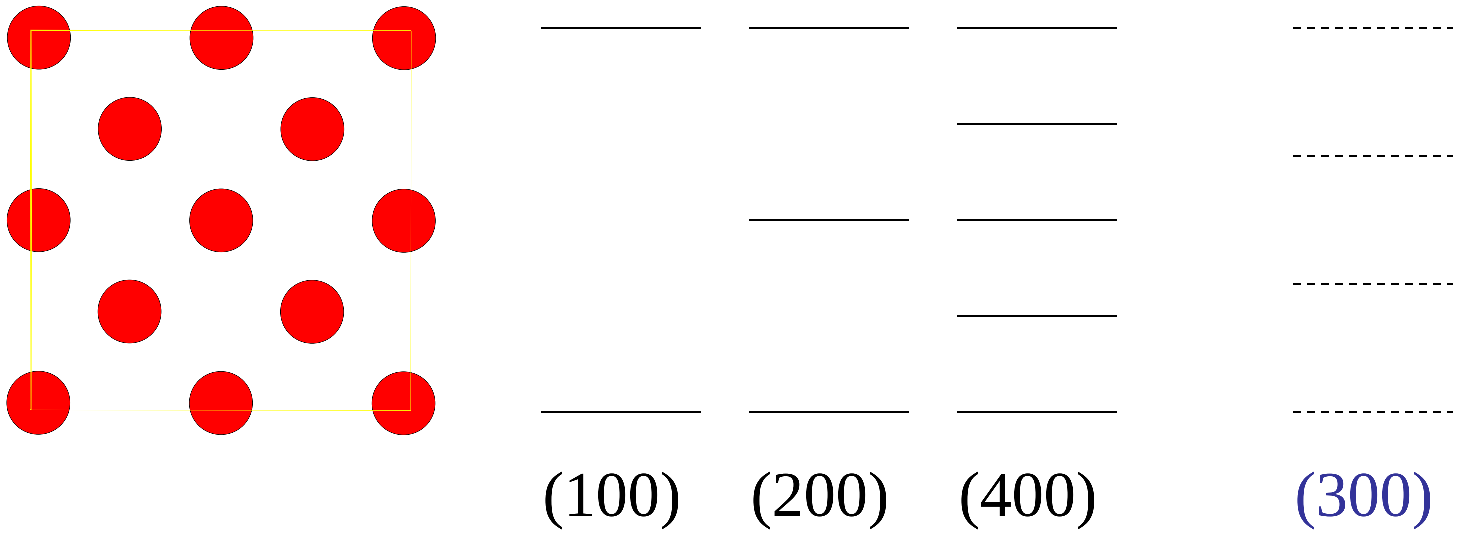




(110)

Families of Planes

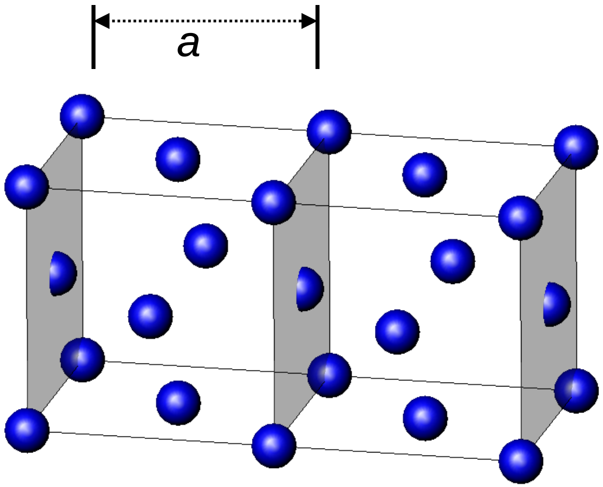
- Miller indices describe the orientation of a family of planes
  - the spacing between adjacent planes in a family is referred to as a "d-spacing"
- different families of planes
  - d-spacing between (400) planes is 1/4 that of the (100) spacing.
  - The (300) plane does not contain atoms and so is not observed



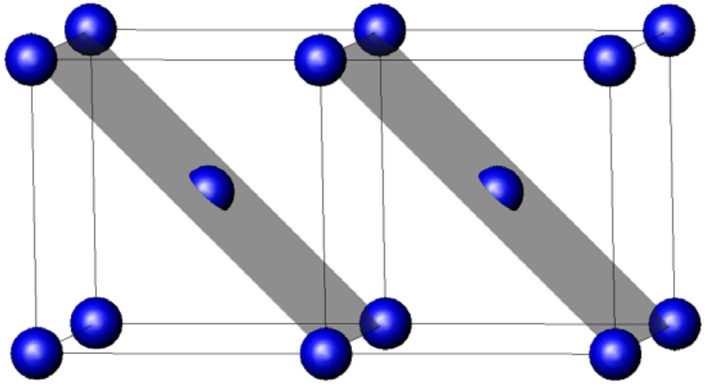
Lattice Spacing

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

For cubic system with a = 4.0 A

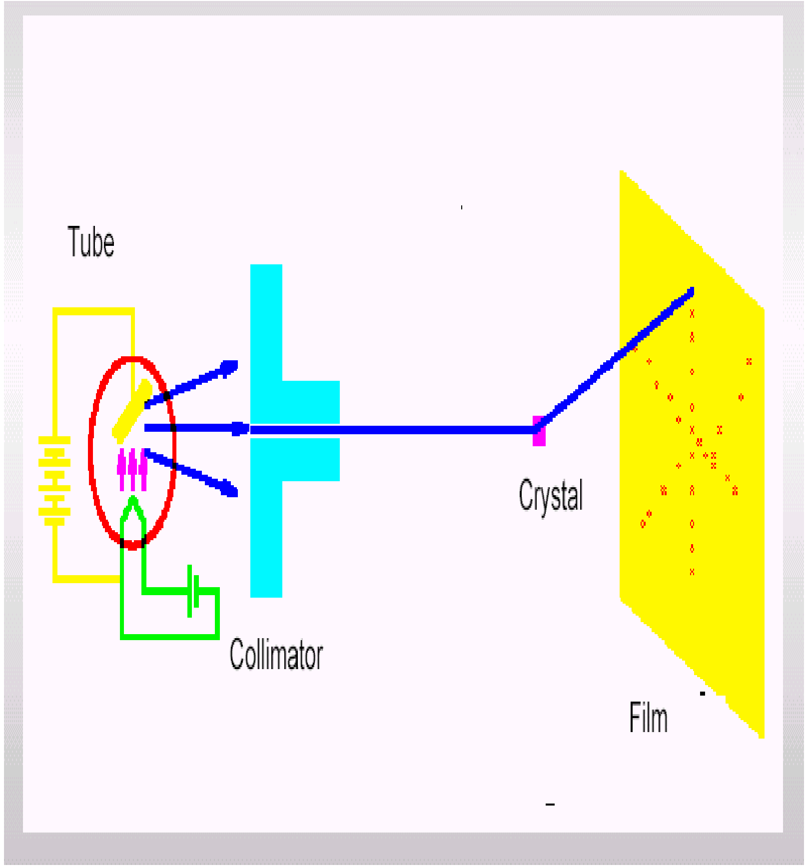


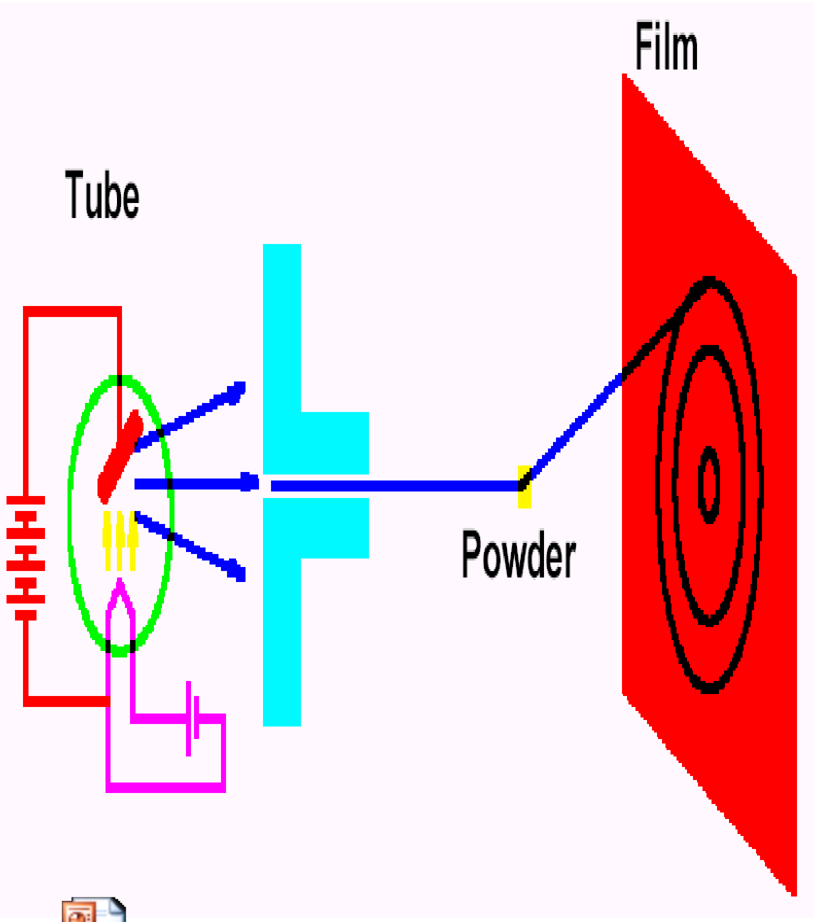
d_{100} = 4.0



d_{110} = 2.828

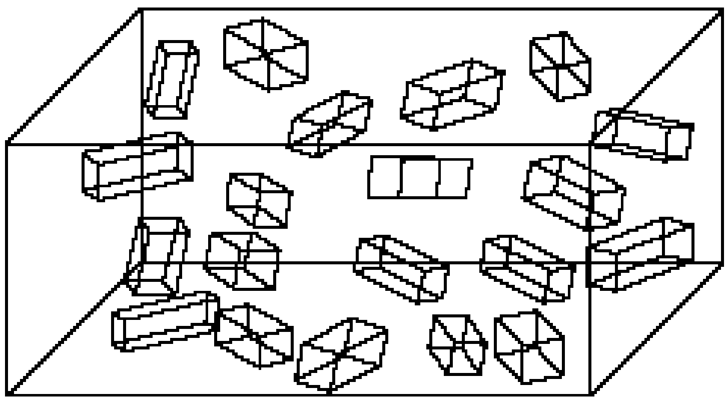
Single Crystal vs Powder





McCusker

Powder – A Polycrystalline Mass

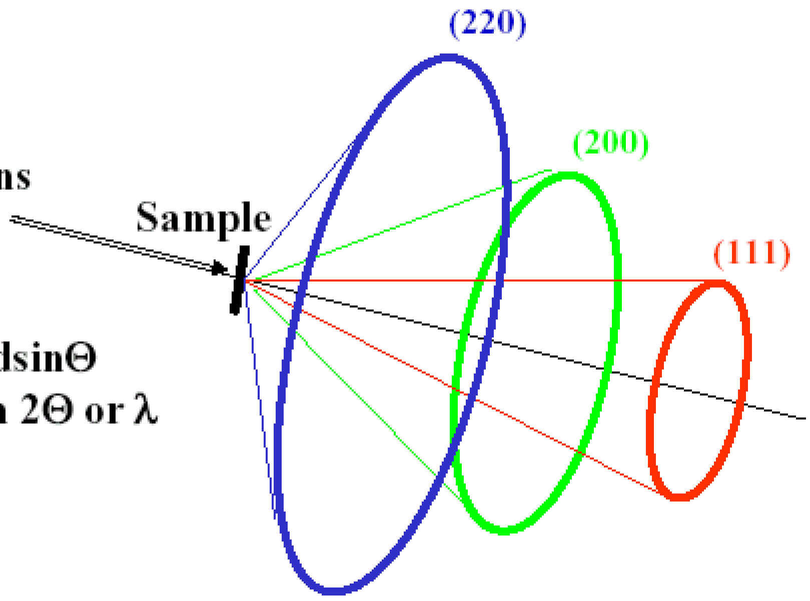


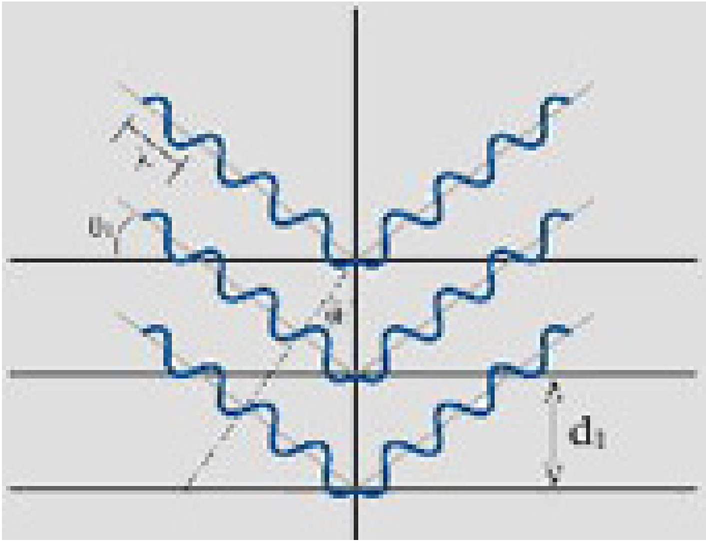
All orientations of crystallites possible

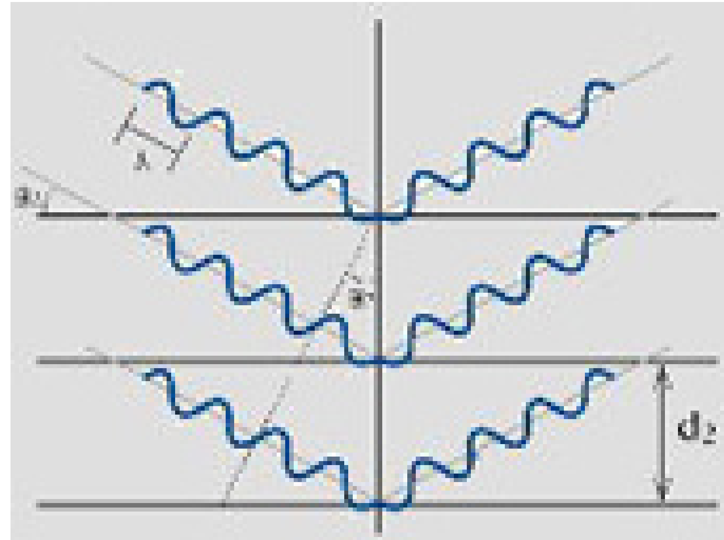
Single crystal reciprocal lattice - smeared into spherical shells

Incident beam
x-rays or neutrons

Bragg's Law $\lambda = 2d\sin\Theta$
Powder pattern – scan 2Θ or λ

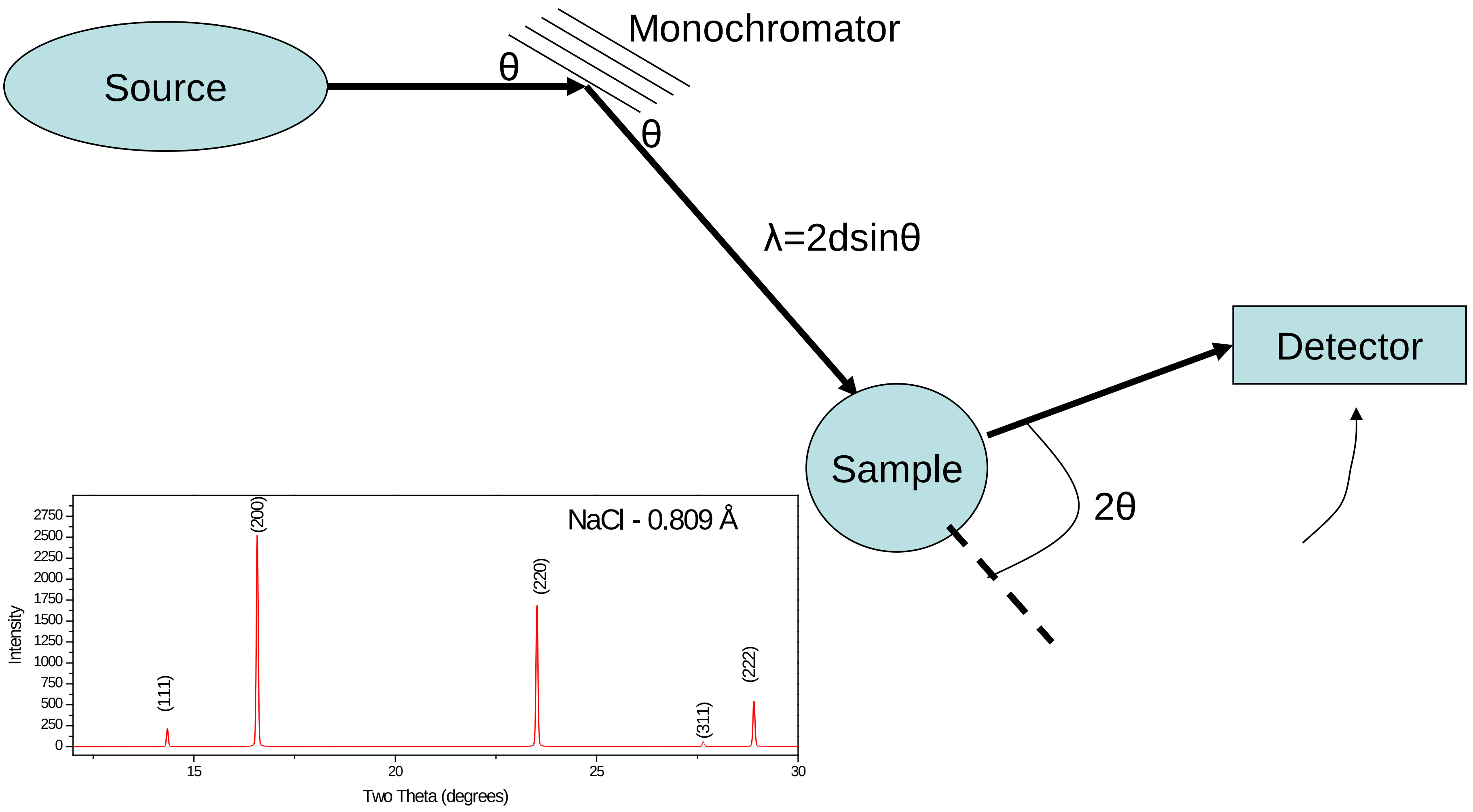




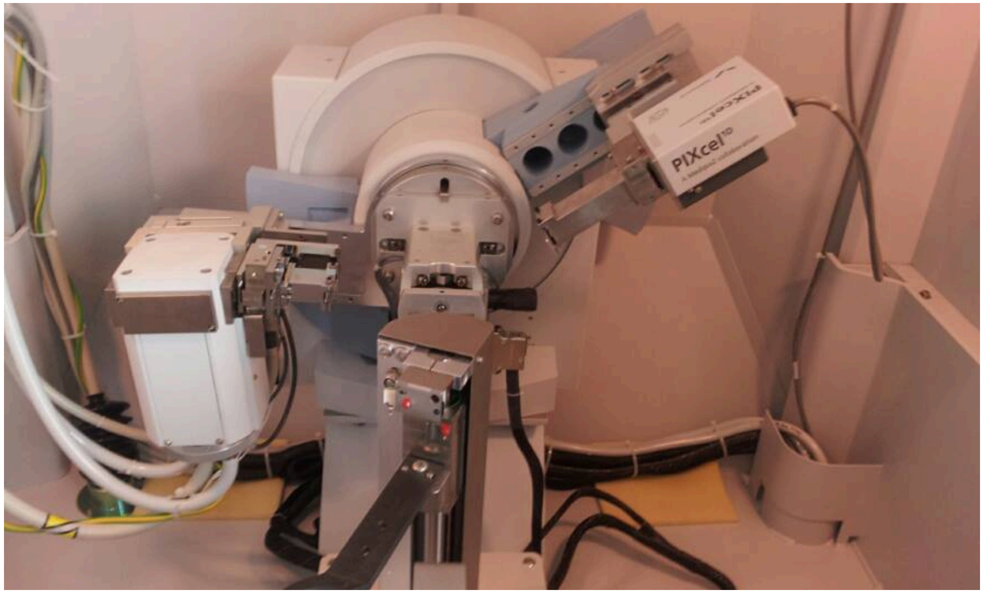


- By varying the angle θ, the Bragg's Law conditions are satisfied by different d-spacings in polycrystalline materials.
- Plotting the angular positions and intensities of the resultant diffracted peaks produces a pattern which is characteristic of the sample.

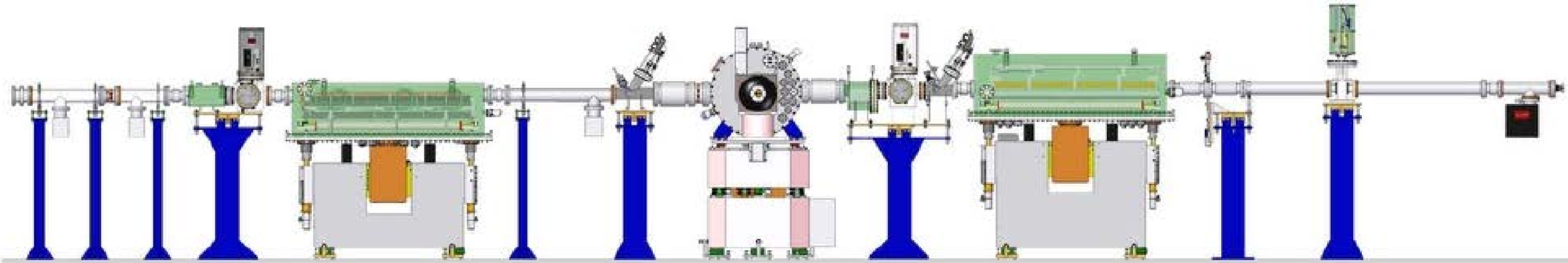
Powder Diffraction



My Powder X-ray Diffraction Beamline



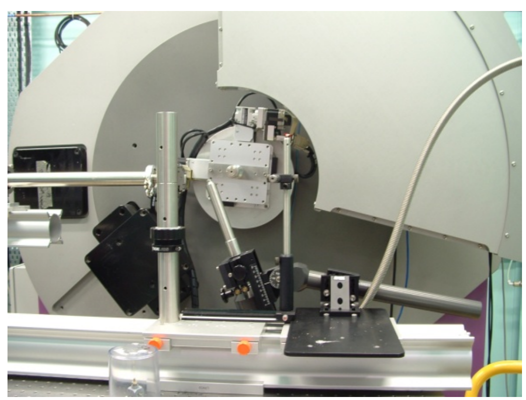
Powder Diffraction Beamline

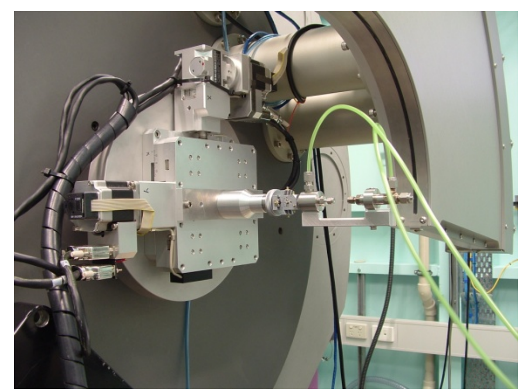


Vertical collimating mirror

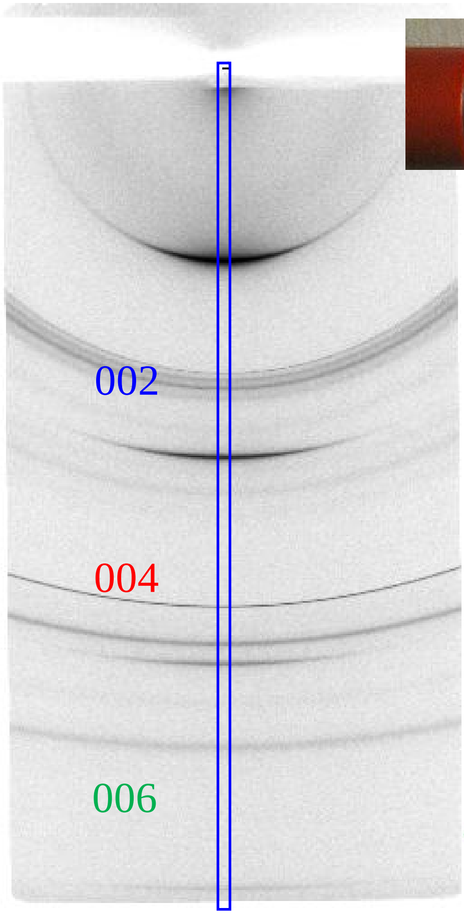
Double crystal monochromator
Si(111) flat pair
Si(311) flat/bent pair

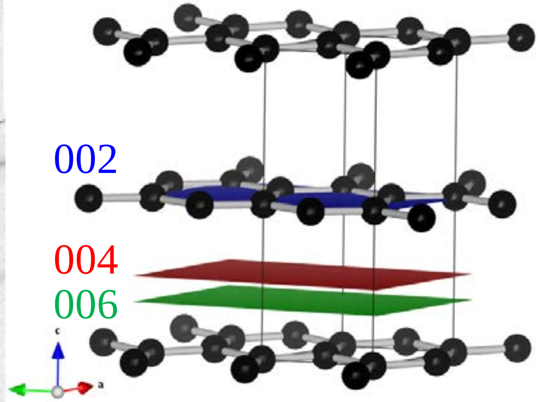
Vertical focusing mirror

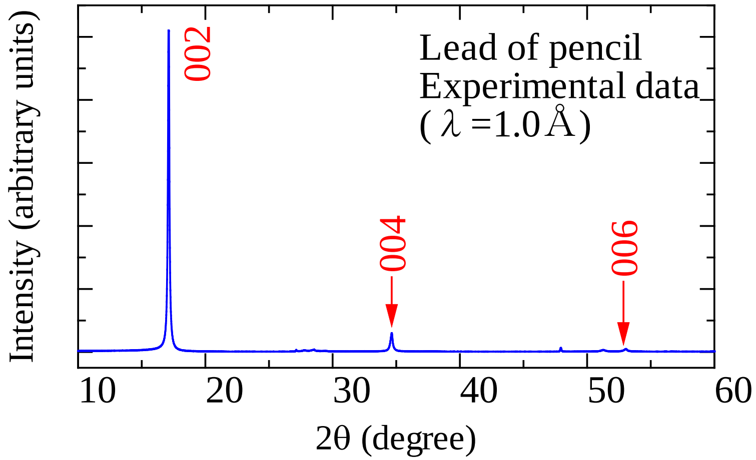


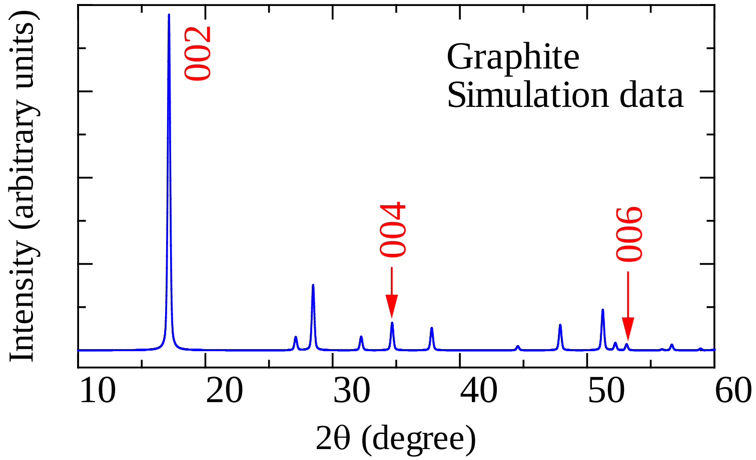


Preferred orientation of lead pencil









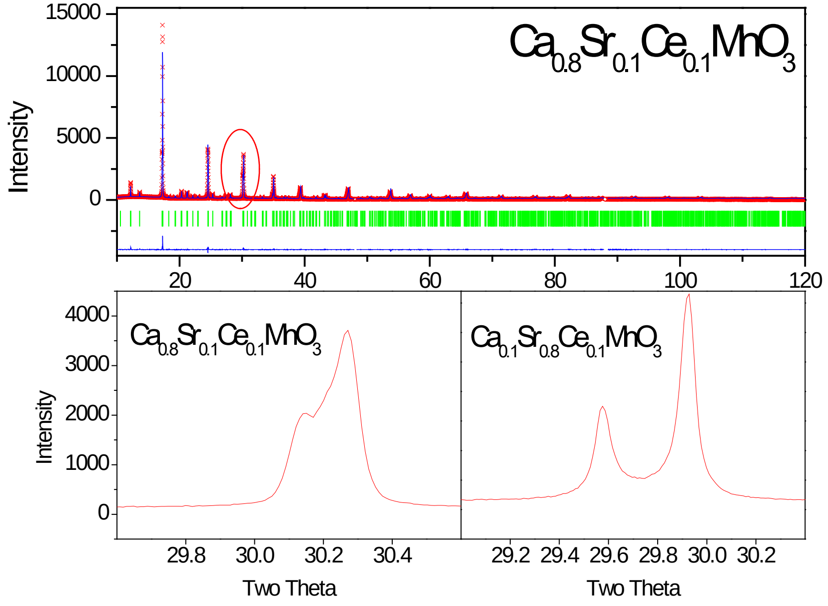
Kim BL02B2 Spring-8

Information Contained in a Diffraction Pattern

Peak Positions
- Crystal System
- Space Group Symmetry
- Unit Cell Dimensions
- Qualitative Phase Identification

Peak Intensities
- Unit Cell Contents
- Point Symmetry
- Quantitative Phase Fractions

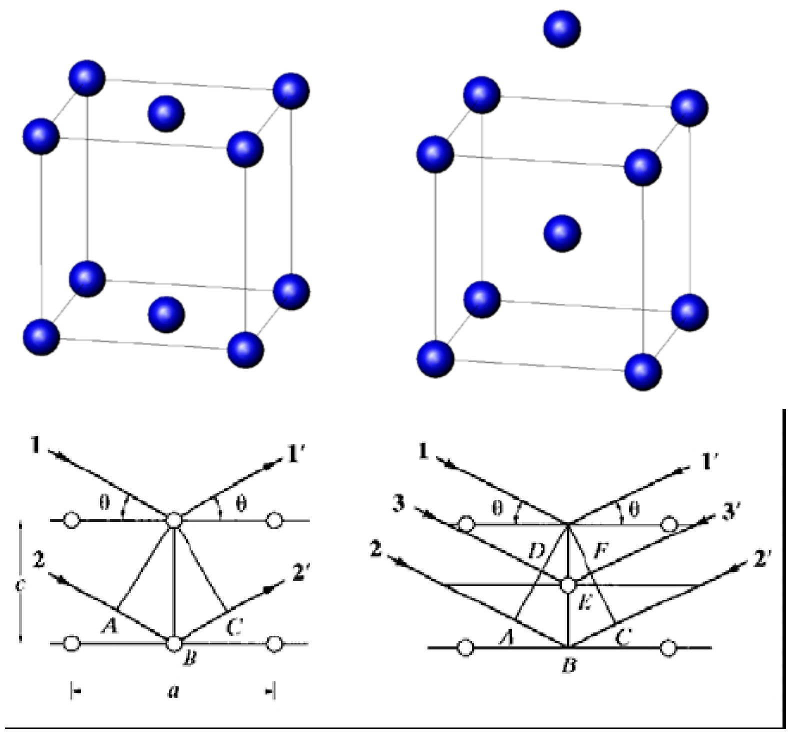
Peak Shapes & Widths
- Crystallite Size (2-200 nm)
- Non-uniform microstrain
- Extended Defects (stacking faults, etc.)



Changes in symmetry and microstrain upon chemical substitution can be established by examination of the patterns

Centering and Absences

- The positions of the atoms in a unit cell determine the intensities of the reflections
- Consider diffraction from (100) planes in

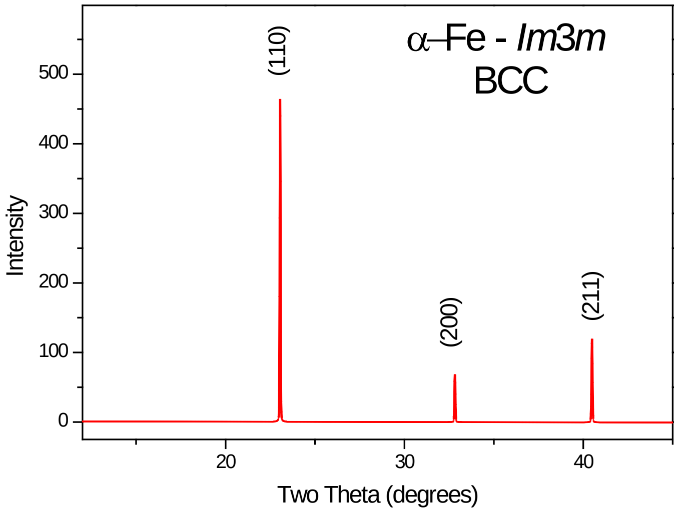


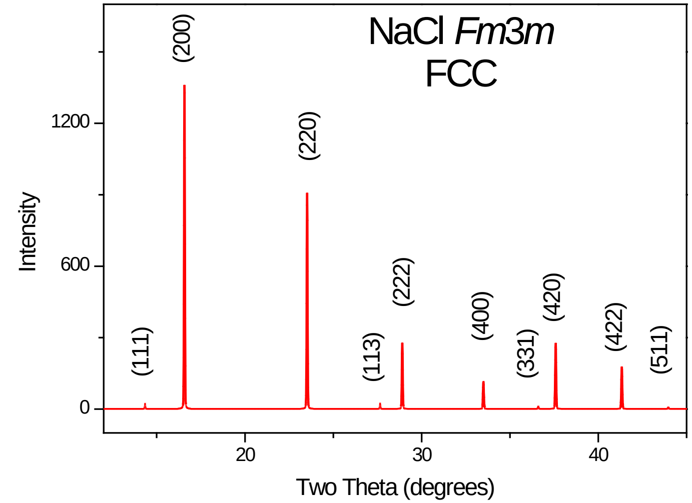
If the pathlength between rays 1 and 2 differs by λ, the path length between rays 1 and 3 will differ by λ/2 and destructive interference in (b) will lead to no diffracted intensity

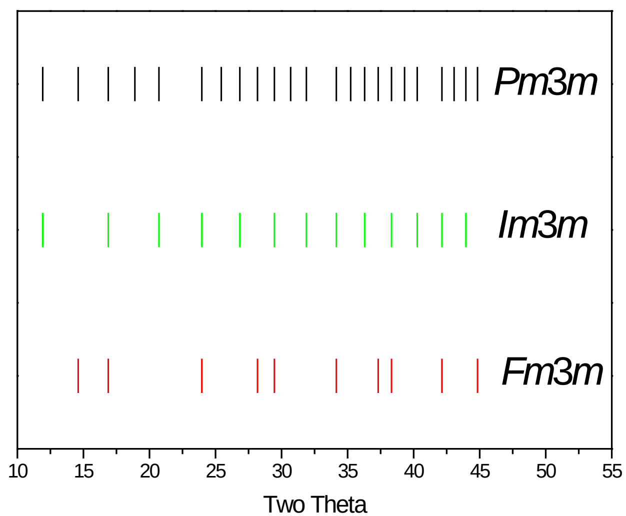
Centering and Absences

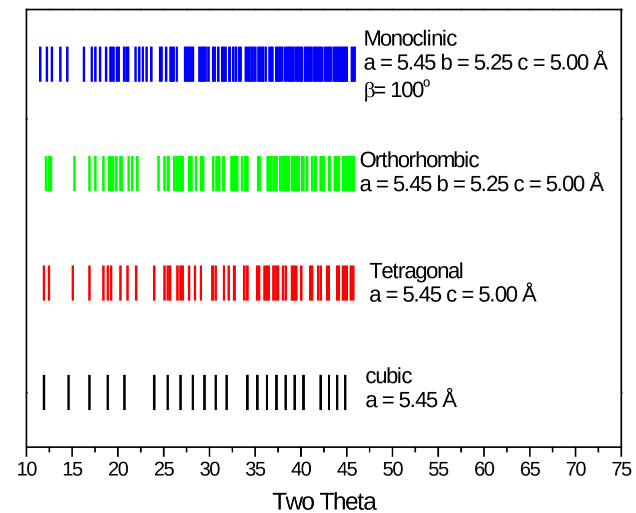
- We can extend these types of calculation to include other modes of lattice centering. They all lead to systematic absences

Bravais lattice	**Reflections that must be absent**
Simple (Primitive)	none
Base (C) centered	h and k mixed
Body (I) centered	(h+k+l) odd
Face (F) centered	h, k and l mixed









Influence of centering

Influence of symmetry

Multiplicity

- For high symmetry materials the Bragg angles and d-spacings for different reflections may be equivalent to one another

  For example (100), (010), (001) etc are equivalent in a cubic material

- In a powder, all planes with the same d-spacing contribute to the scattered intensity at a given Bragg angle

- The number of planes that are symmetry equivalent is referred to as the multiplicity and its appears as a multiplicative term in powder diffraction intensity calculations

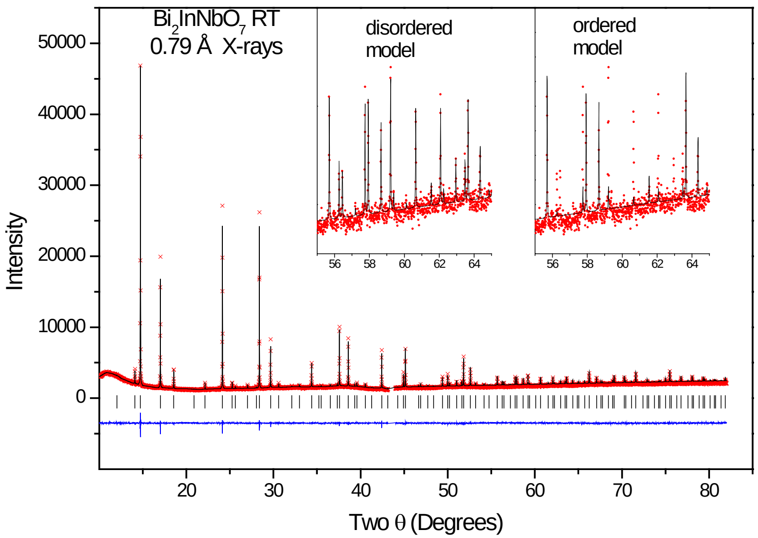
- The multiplicity of a reflection depends upon the symmetry of the crystal

  Multiplicity of {100} for cubic is 6, but for tetragonal it would only be 4 as (100) and (001) are not equivalent

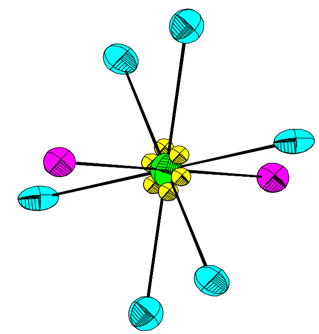
Diffraction Patterns

- Spacing of peaks depends on size of unit cell and the space group.
- The bigger the unit cell and/or the lower the symmetry the more diffraction peaks are observed.
- Intensity of peaks depends on (amongst other things) the arrangement of the atoms in the unit cell.
- For two materials that had identical unit cells, the peak positions would be IDENTICAL, however their intensities would be DIFFERENT.

Need for High Q



There are many more reflections at higher Q. Therefore, most of the structural information is at higher Q



Refinement of structure gave unusual displacement parameters for the Bi cations, indicative of cation disorder. The patterns could only be adequately fitted by including 6-fold disorder of the Bi. This involves a displacement along the (1 -1 0) direction

Atom	Site	x	y	z	B_{iso}
Model 1. Ordered Bi. R_p 4.08 R_{wp} 6.07%					
Bi	16d	0	0.25	0.75	2.74(6)
In/Nb	16c	0	0	0	3.00(8)
O(1)	48f	0.350(3)	0.125	0.125	7.6(7)
O(2)	8b	0.375	0.375	0.375	7.6(7)
Model 2. Disordered Bi R_p 3.09 R_{wp} 3.93%					
Bi	96h	0	0.2249(1)	0.7751(1)	0.96(7)
In/Nb	16c	0	0	0	0.61(3)
O(1)	48f	0.322(1)	0.125	0.125	1.7(2)
O(2)	8b	0.375	0.375	0.375	1.7(2)

Need for High Resolution

$$\frac{\Delta d}{d} = \frac{\Delta \lambda}{\lambda} + \frac{\Delta \theta}{\tan \theta}$$

Differentiating Braggs Law gives the resolution as:

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

Sample

Source

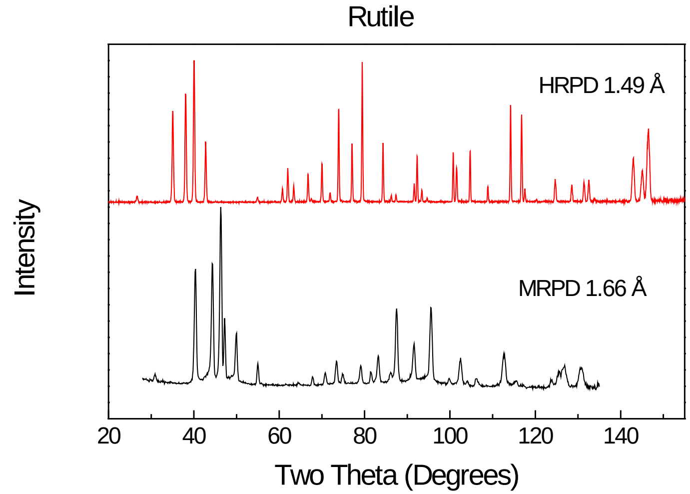
Source + Instrument

Resolution

In Powder Diffraction it typically refers to the width of the peaks.

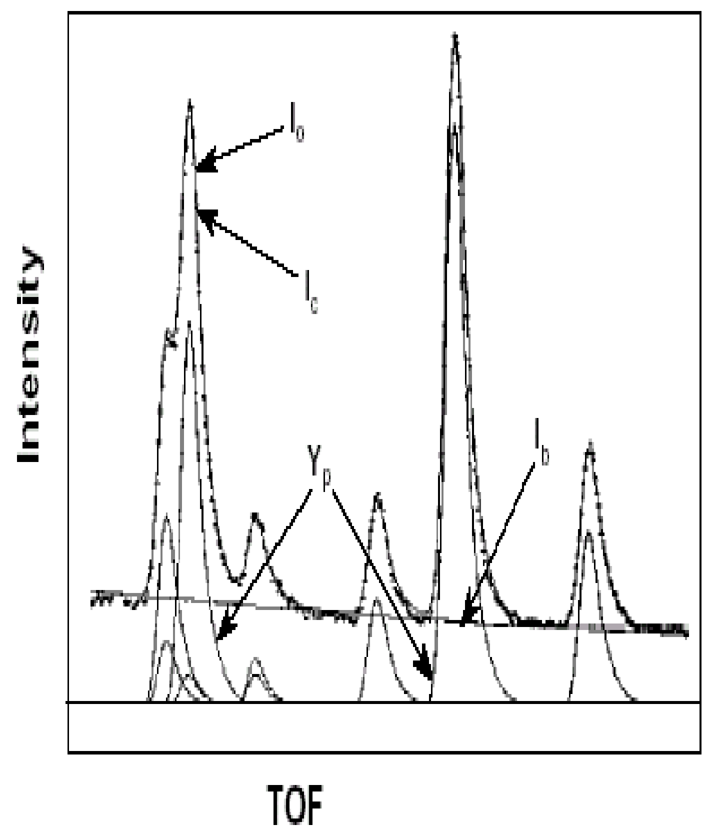
In Single Crystal Diffraction it typically refers to the minimum d-space studied.

Both definitions are relevant.



Peak Overlap

- Powder Diffraction patterns are a one dimensional representation of a three dimensional structure.
- Often peaks due to individual Bragg reflections overlap



The Solution - Rietveld

$$y_{icalc} = y_{iback} + \sum_{p} \sum_{k=k_1^p}^{k_2^p} G_{ik}^p I_k^2$$

- y_{ic} the net intensity calculated at point i in the pattern,
- y_{iback} is the background intensity,
- G_{ik} is a normalised peak profile function,
- I_k is the intensity of the k^{th} Bragg reflection,
- k_1 ... k_2 are the reflections contributing intensity to point i,
- the superscript p corresponds to the possible phases present in the sample.



The Answers

- The Profile R

$$R_p = \frac{\sum |y_{iobs} - y_{icalc}|}{\sum y_{iobs}}$$

- The weighted Profile R

$$R_{wp} = \left[\frac{\sum w_i \left(y_{iobs} - y_{icalc} \right)^2}{\sum w_i y_{iobs}^2} \right]^{1/2}$$

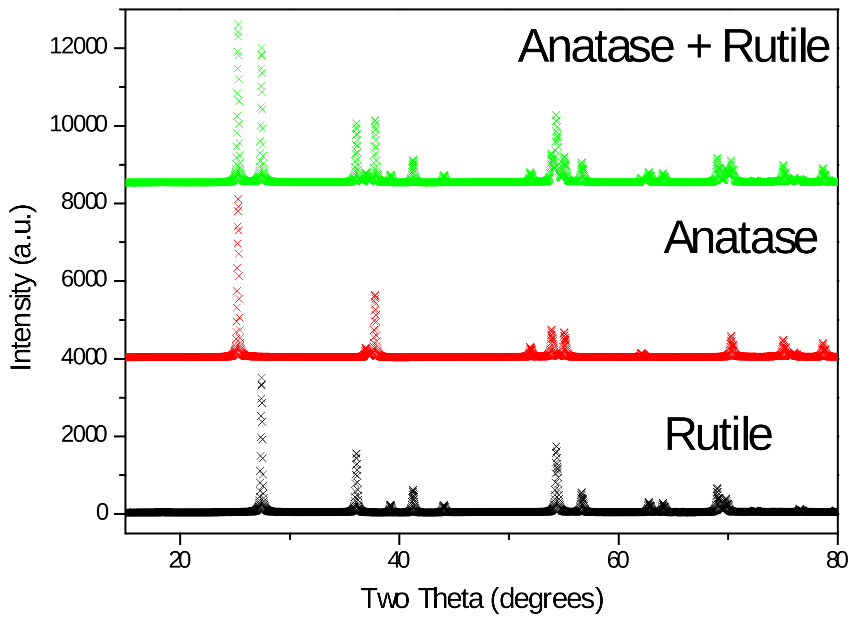
- The expected Profile R

$$R_{exp} = \left[\frac{N - P}{\sum w_i y_{iobs}^2} \right]^{1/2}$$

- The Goodness of fit

$$\chi^2 = \frac{\sum w_i (y_{iobs} - y_{icalc})^2}{N - P} = \left[\frac{R_{wp}}{R_{exp}} \right]^2$$

Phase Analysis



- Where a mixture of different phases is present, the resultant diffraction pattern is formed by addition of the individual patterns.
- The intensity of the peaks is proportional to the amount of the phase present.

Quantitative Phase Analysis

- Bragg scattering is proportional to N/V where N is the number of unit cells and V the unit cell volume. There for the weight of a phase in the beam is:

$$W_P = \frac{(SZMV)_P}{\sum_i (SMPV)_i}$$

S - the scale factor

Z the number of formula unites per unit cell

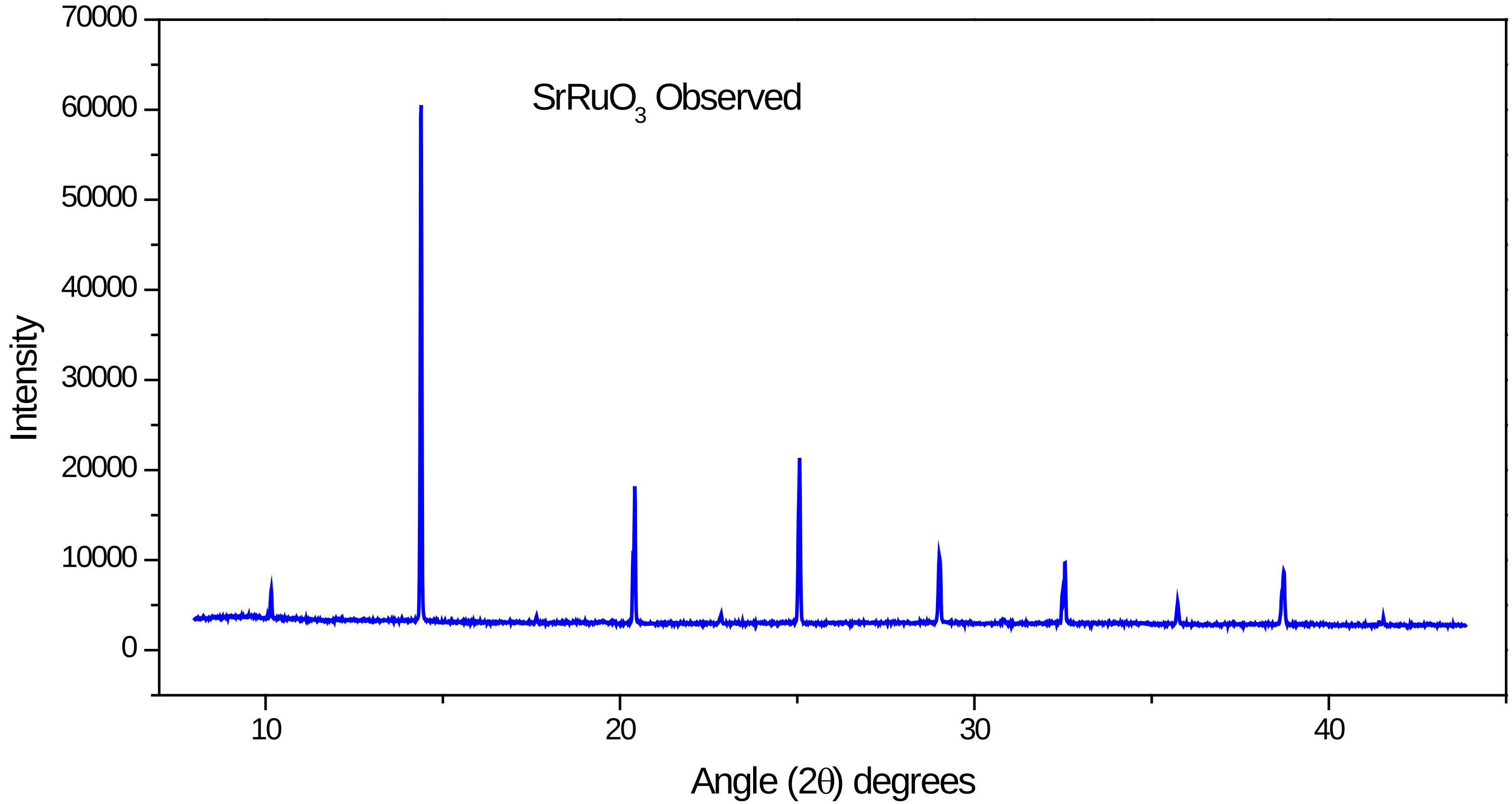
M the molecular weight of the formula unit

I is the index running over all phases

- Hence SZVM is proportional to the weight of the diffracting sample

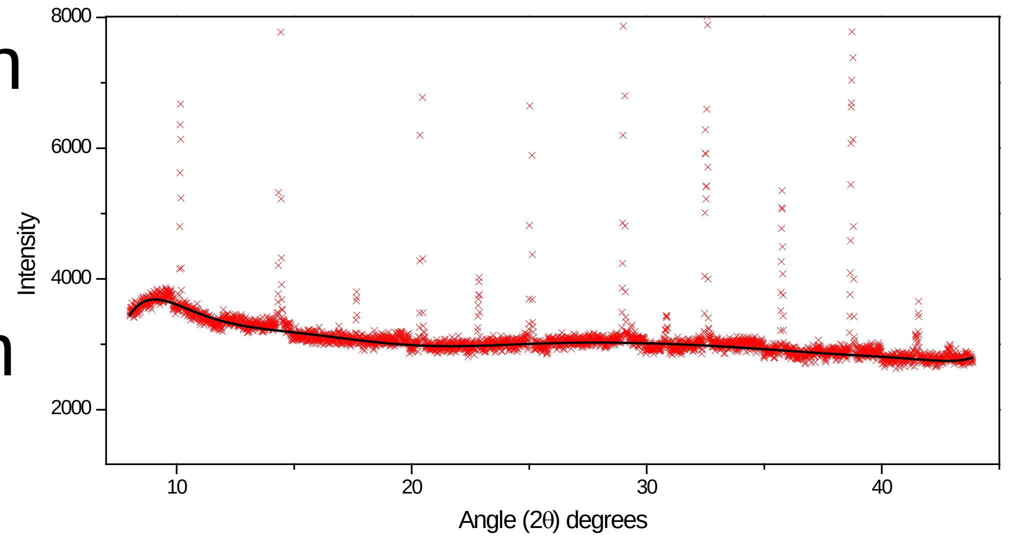
An Example

- Synchrotron X-ray Diffraction pattern for $SrRuO_3$



The background

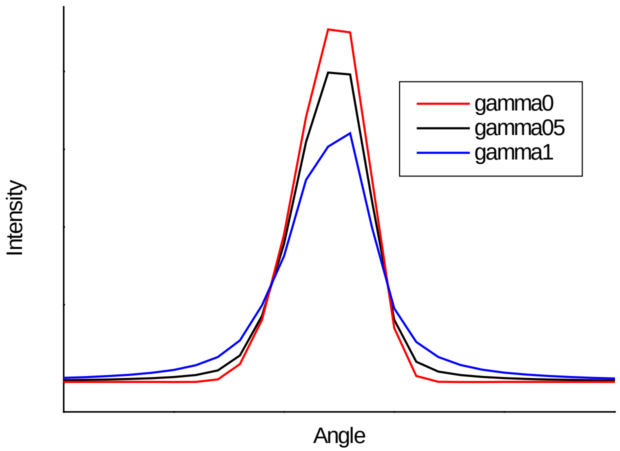
- Fluorescent radiation from the sample
- Diffraction from the continuous spectrum
- Diffuse scattering
  - Incoherent
  - Temperature diffuse
  - Short range order
- Other materials
  - Specimen holder
  - air etc



- Background can be either fitted or estimated.
- Here the capillary is a feature.

Peak Shapes

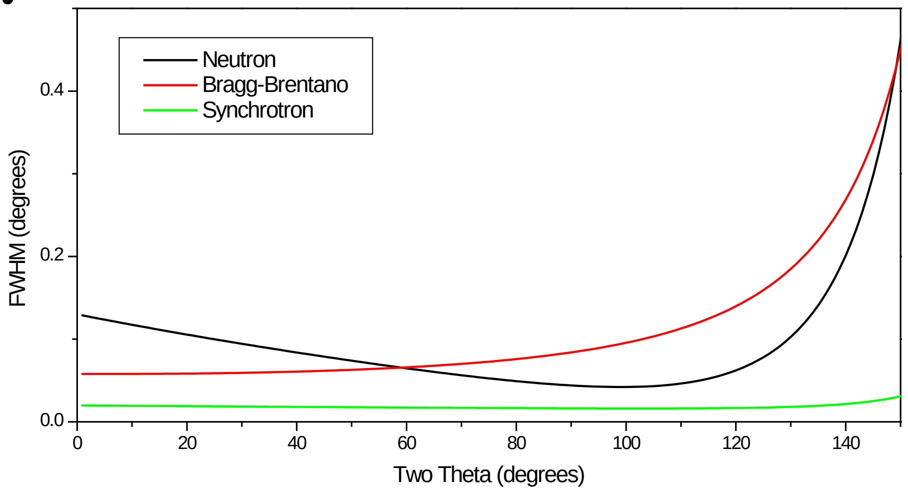
- Different Diffractometers have different peak shapes.
- The most widely function is a pseudo-Voigt (mixed Gaussian and Lorentzian).



$$G_{ik} = \gamma \frac{C_0^{1/2}}{H_k \pi}\left[1 + C_0 X_{ik}^2\right]^{-1} + (1+\gamma)\frac{C_1^{1/2}}{H_k \pi^{1/2}} \exp\left[-C_1 X_{ik}^2\right]$$

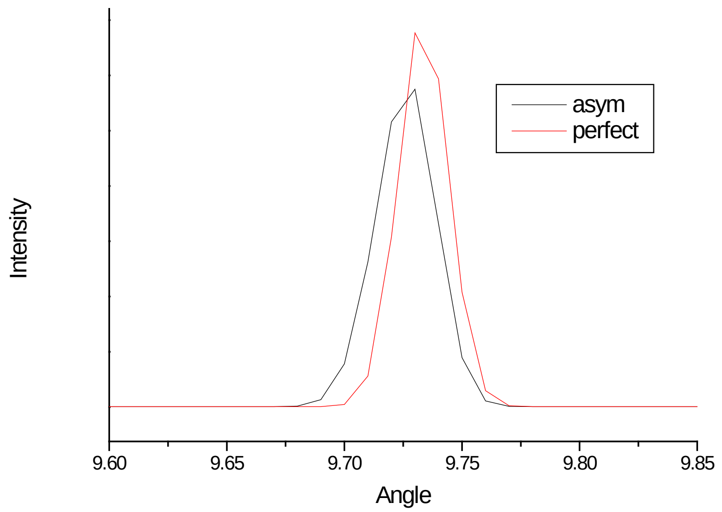
- The width of peaks is usually not constant.

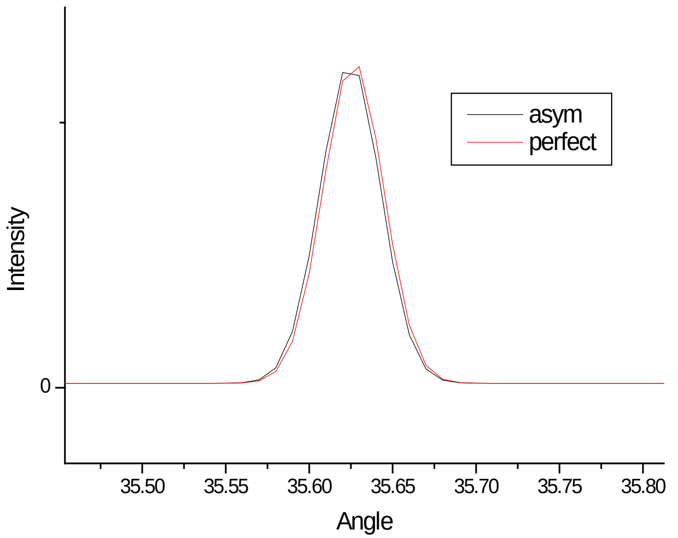
$$H^2 = U\tan^2\theta + V\tan\theta + W$$



Peak Asymmetry

- Beam Divergence can results in asymmetric peaks at low angles.
- Results from not integrating over the entire Debye cone.



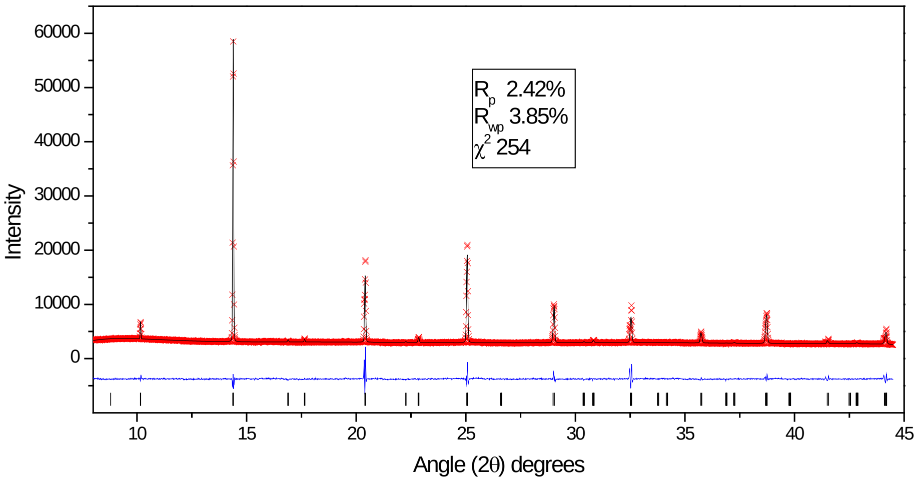


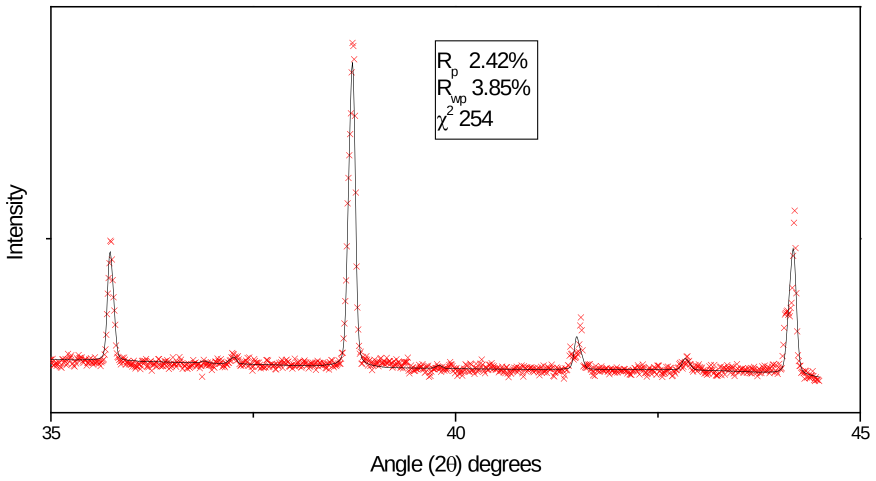
The Simple Structural Model

- The fit to a single phase sample looks good

  - BUT……

- The detail of the fit is not satisfactory - the model is missing something!



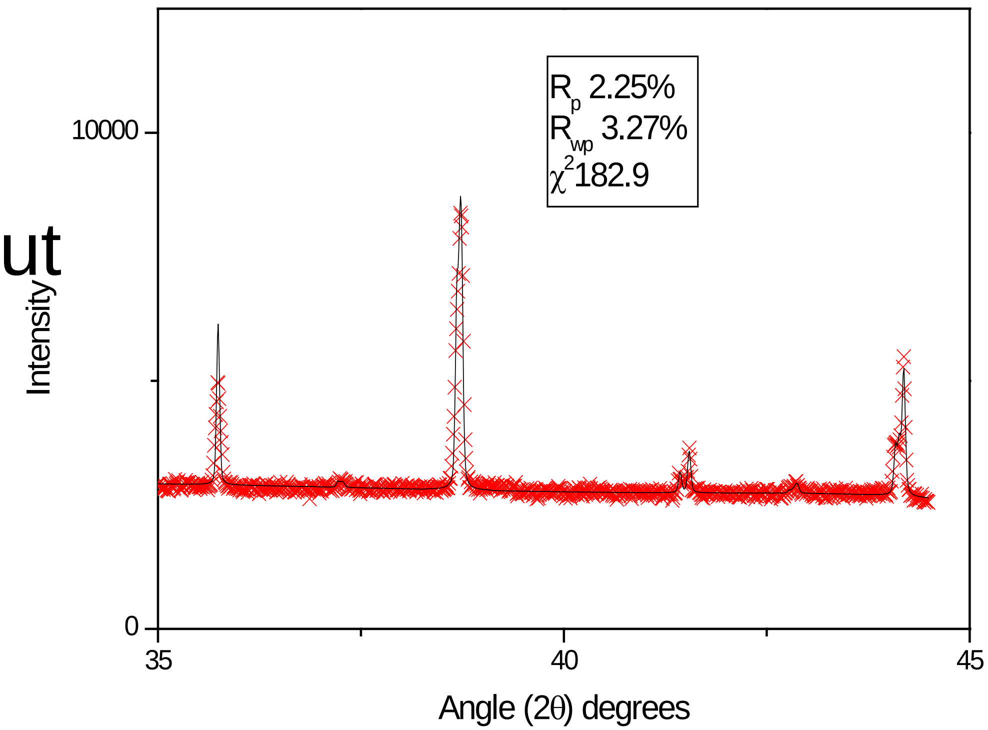


A Common Problem

- If the structural model is wrong then the most common response of Rietveld programs is to:
  - broaden the peaks,
  - Increase the displacement parameters,
- The former is most noticeable at high angles where intensity is lowest.
- Due to absorption of the X-rays powder X-ray diffraction often yields poor displacement parameters

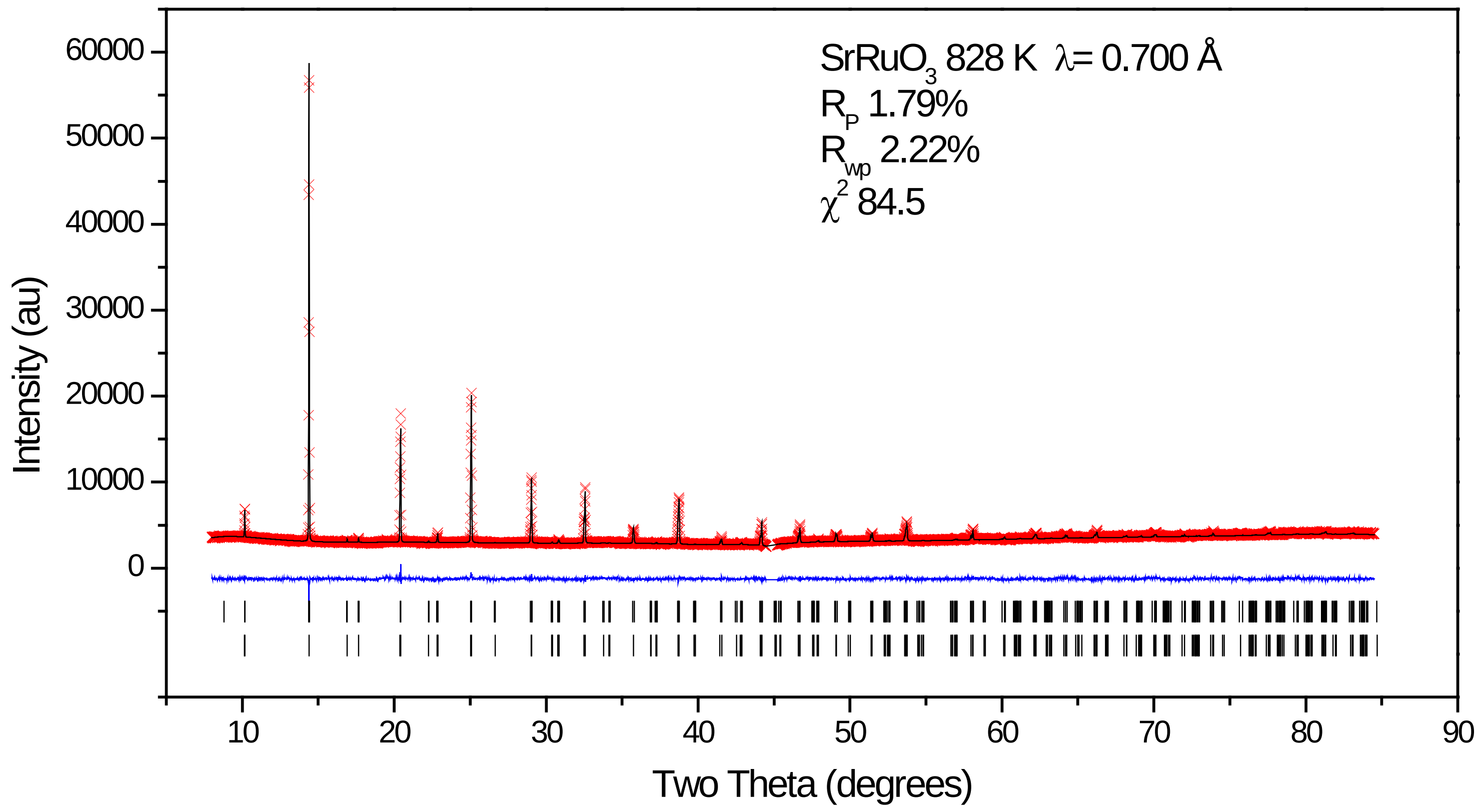
An Alternate Model

- The high angle splitting is well modeled by a tetragonal model - but this overestimates some intensities.



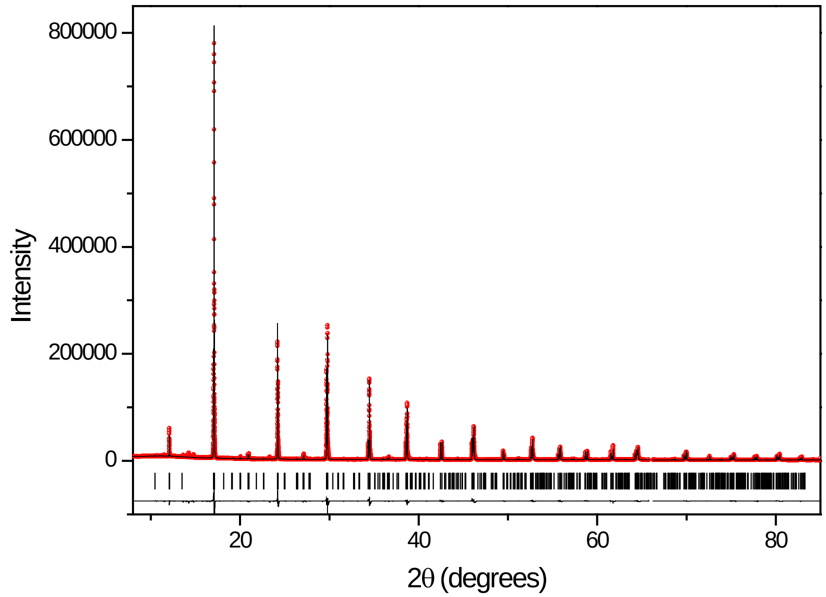
- The Truth lies somewhere in the middle

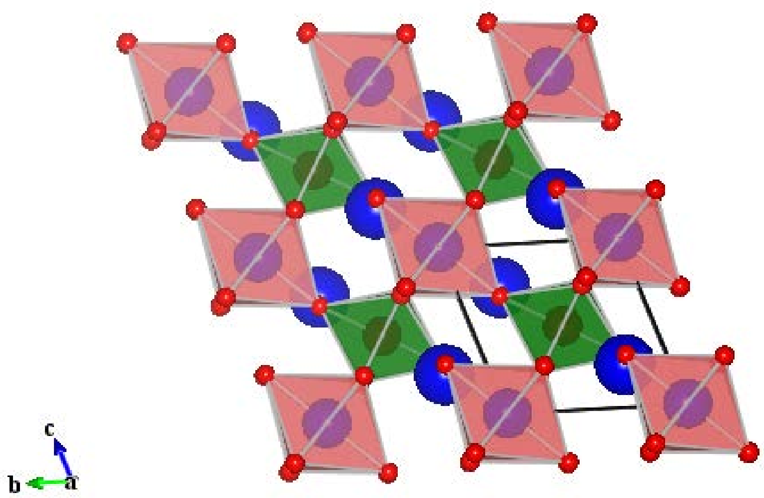
The finished Product



- The sample contains a mixture of both phases!

Crystallography gives average structure



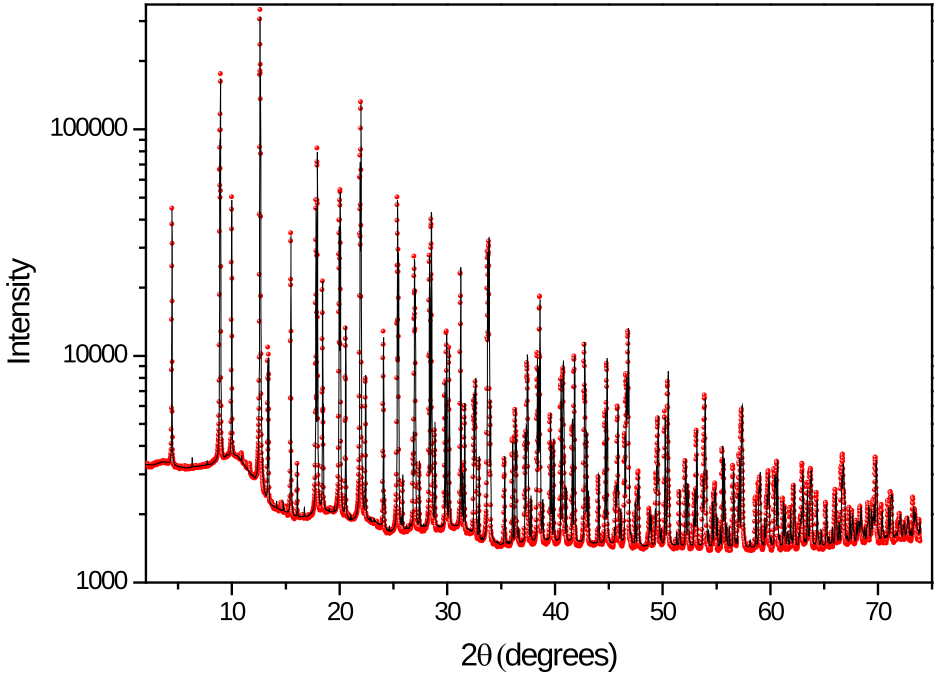


- The Rietveld method has served us well for over 45 years – but it only uses part of the information of the diffraction experiments, namely the intensity of the Bragg peaks

Crystallography challenged: materials with disorder

Rietveld approach assumption: **crystals are perfectly periodic…**

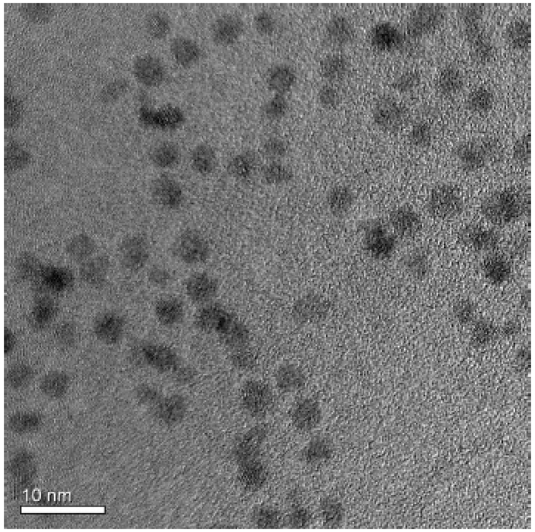
…but this is not always the case!

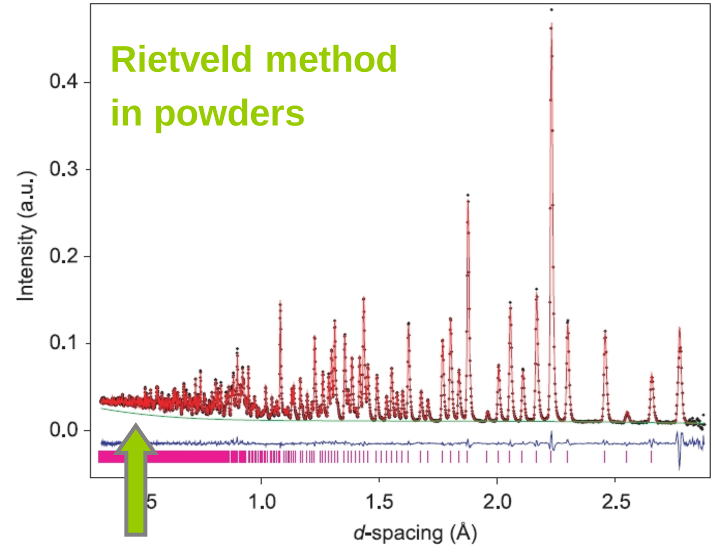


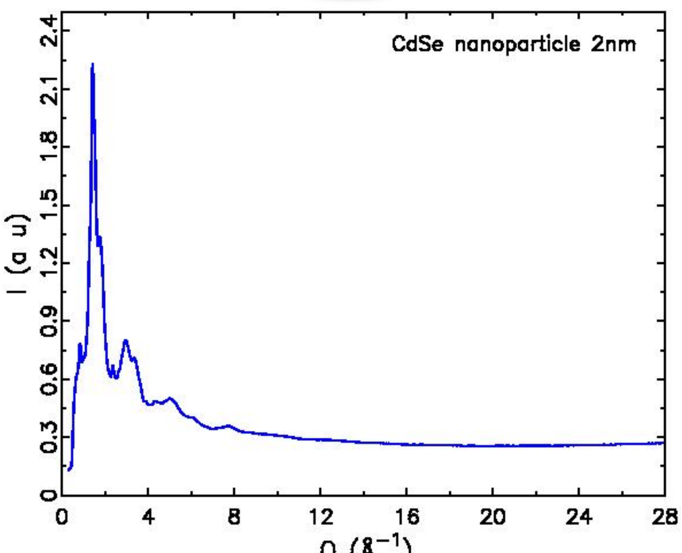
Just using the Bragg reflections means that we “ignore” the information in the background, but what information is this?

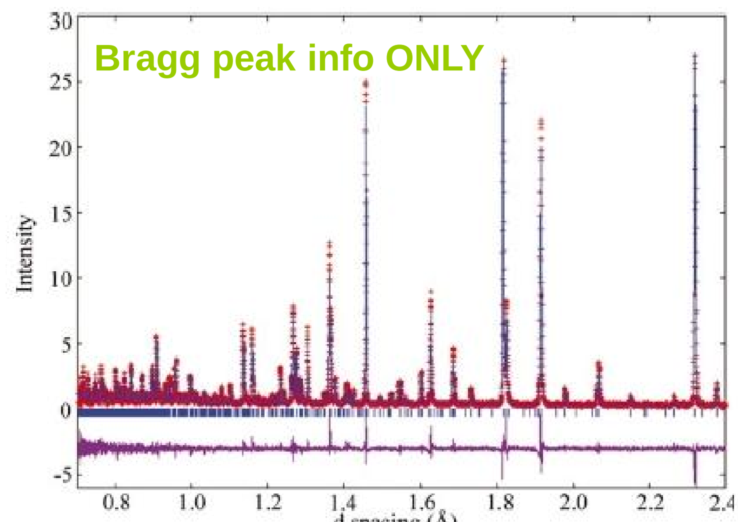
Crystallography challenged: nano-crystals

From E. Bozin BNL



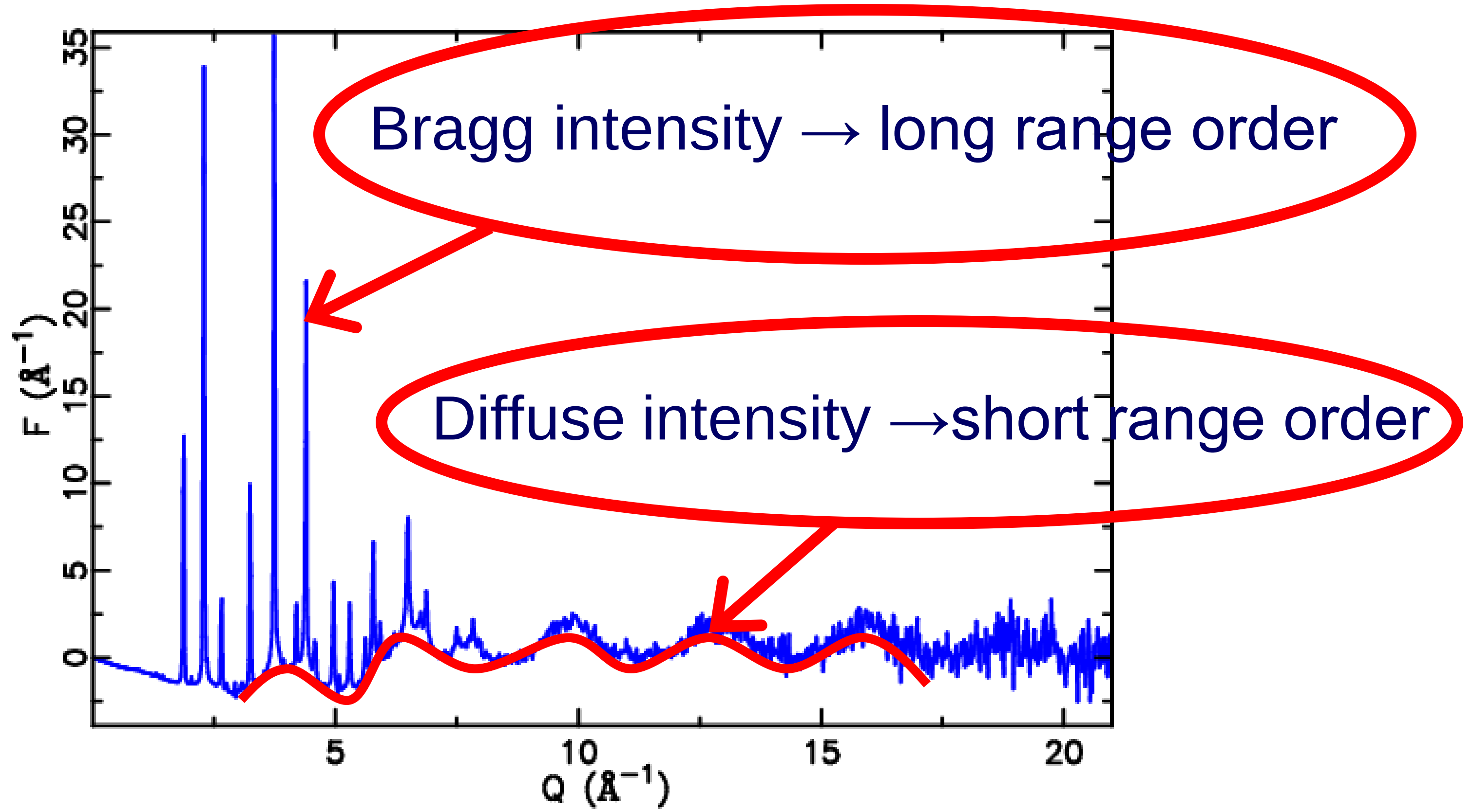






Diffuse intensity contains information on short-range order

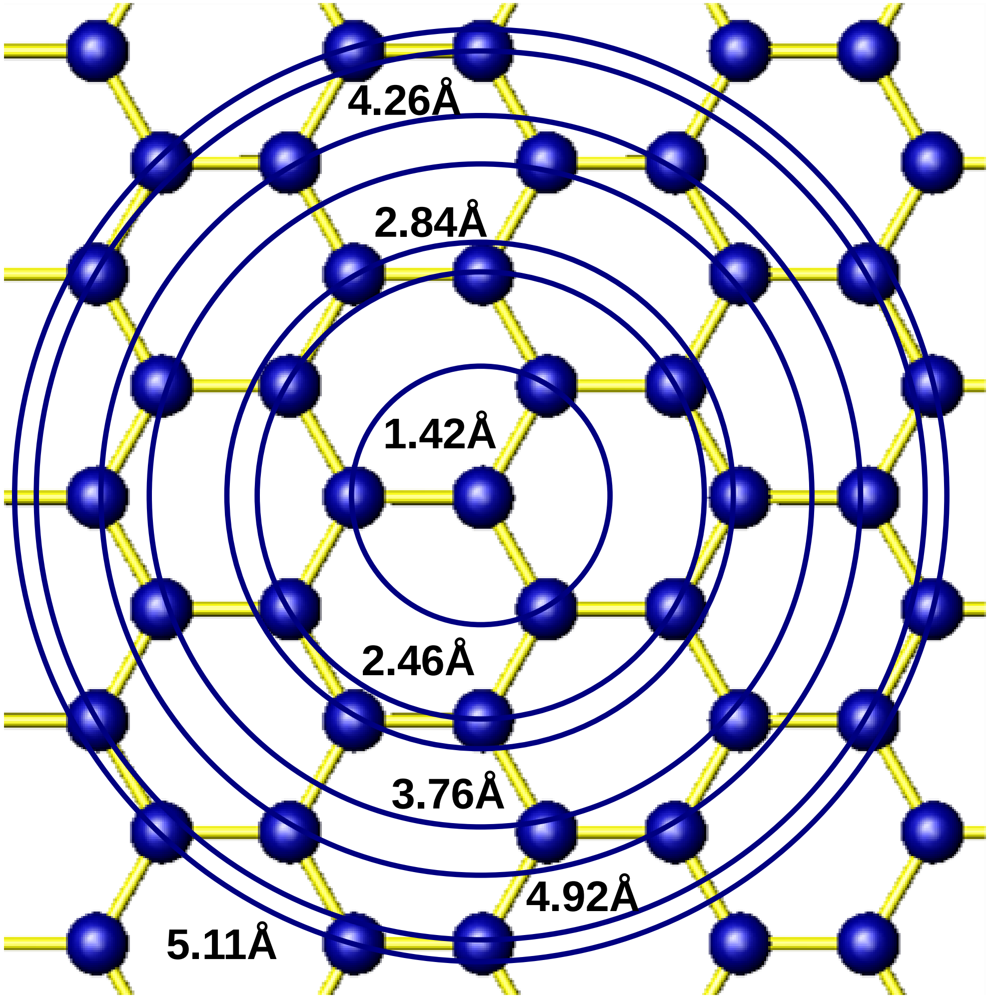
From E. Bozin BNL



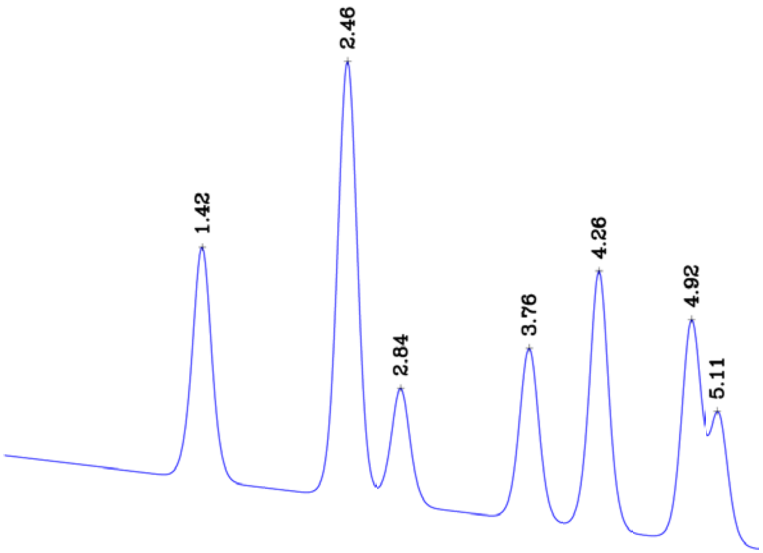
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$

From E. Bozin BNL

Total Scattering - PDF



Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.



Strengths and Limitations of Powder X-ray Diffraction

Strengths

- Non-destructive – small amount of sample
- Relatively rapid
- Identification of compounds / phases – not just elements
- Quantification of concentration of phases – (sometimes)
- Classically for powders, but solids possible too
- Gives information regarding crystallinity, strain, crystallite size, and orientation

Limitations

- Bulk technique – generally – unless a microfocus source is used
- Not a “stand-alone” technique – often need chemical data
- Complicated appearance
- multiphase materials – identification /quantification can be difficult

Experiment Design Issues

What Wavelength?

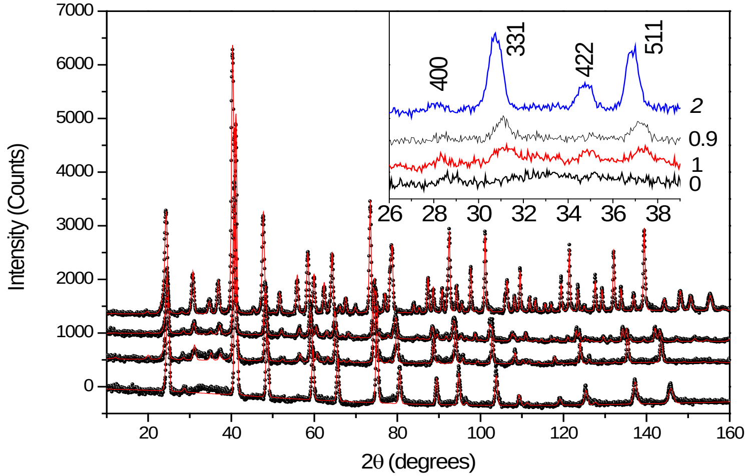
- Absorption is your enemy!
- Short Wavelengths are best! BUT….
- Consider required resolution. And…
- Avoid Absorption Edges.

What Size Capillary?

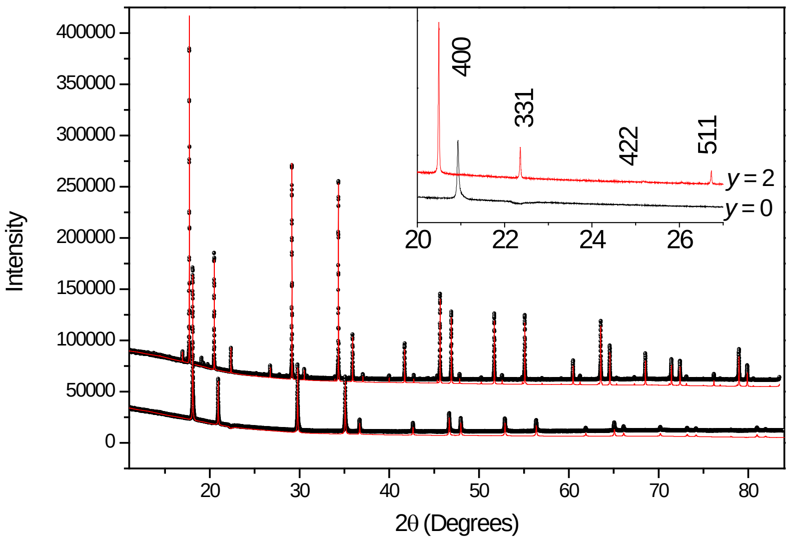
- Small capillaries reduce absorption AND (with area detectors) improve resolution.
- BUT reduce amount of material.

X-rays and Neutrons, Same Same but Different

Neutron



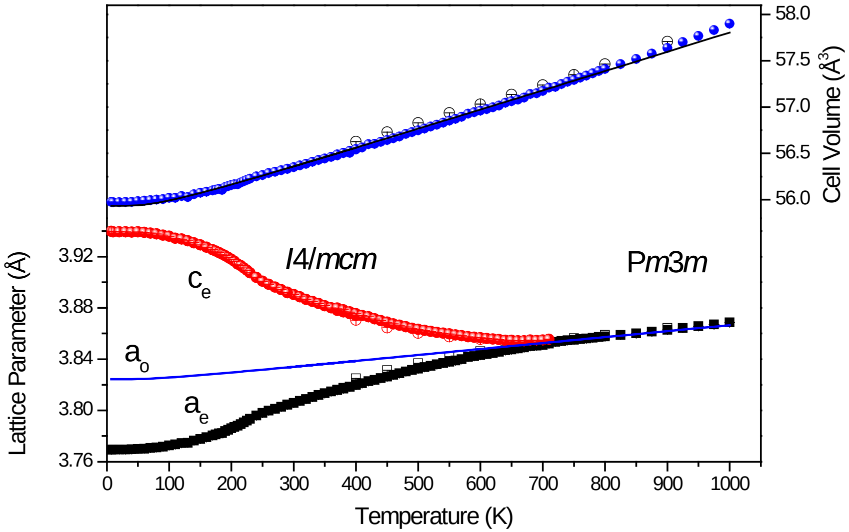
S-XRD

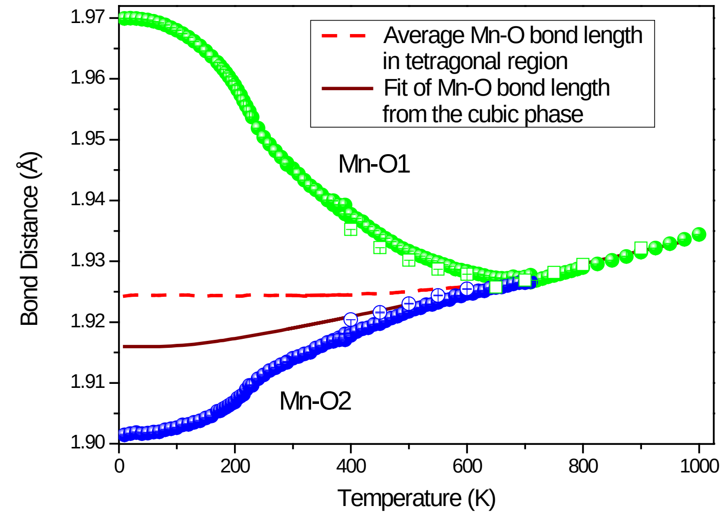


Anion disorder clearly evident in neutron profiles but absent in XRD patterns
No evidence for cation disorder in the XRD patterns

J. Solid State Chem 2011 184 2108

$Sr_{0.65}Pr_{0.35}MnO_3$ – structural parameters

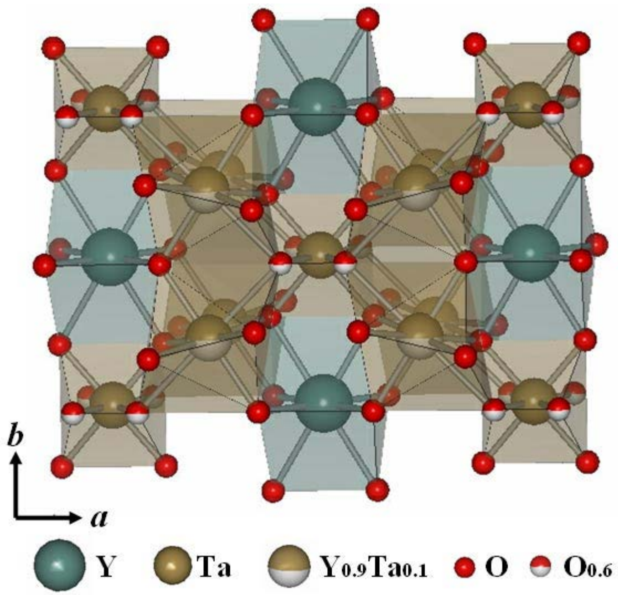




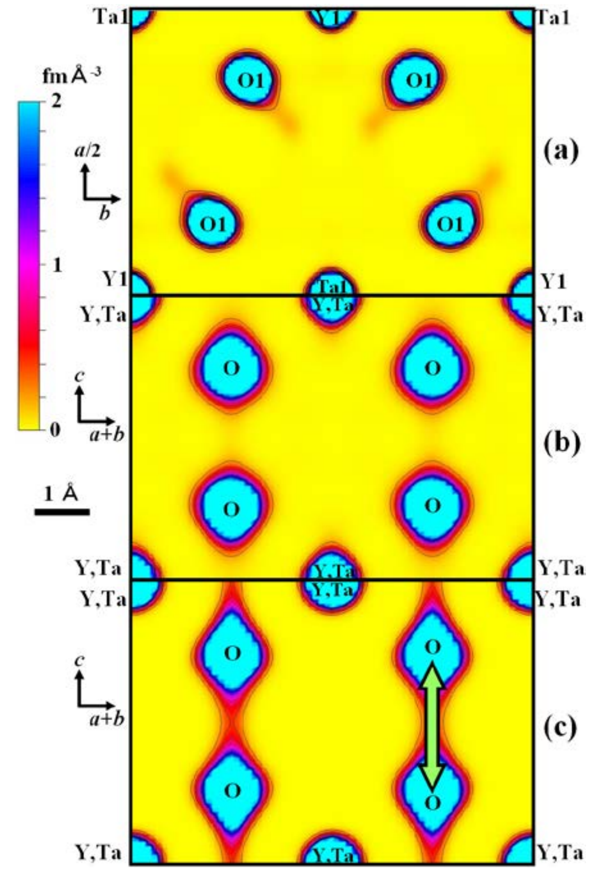
Single structural phase transition observed. Apparently conventional thermal expansion of the cell volume (fitted as $V_o = V_1 + V_2\Theta\coth(\Theta/T)$ *)*

Clear change in the anisotropy of the unit cell near 250 K.
Large tetragonal distortion of the MnO_6 octahedra. Consequence of the JT active Mn^{3+} cations – evidence for orbital ordering and suggests coupling between the lattice and the orbitals

Oxygen Conduction in $Y_{1-x}Ta_xO_{1.5+x}$

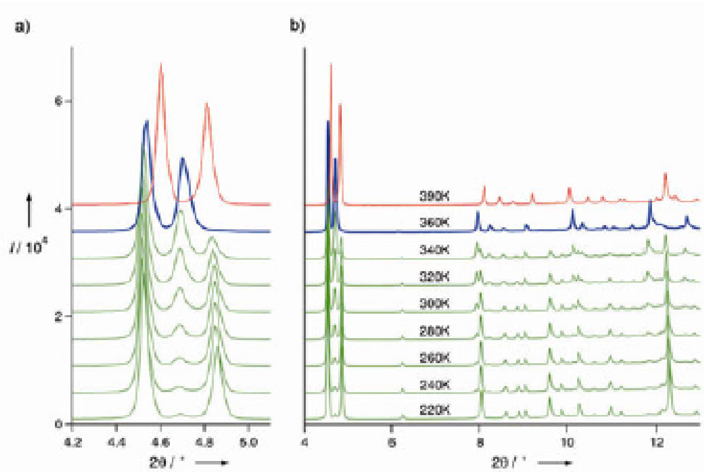


Representation of the fluorite structure of $Y_{1-x}Ta_xO_{1.5+x}$



Scattering amplitude distribution (a) on the (002) plane of the orthorhombic *Cmmm* fluorite-related $Y_{0.7}Ta_{0.3}O_{1.8}$, and on the (110) planes of the cubic fluorite-type $Y_{0.785}Ta_{0.215}O_{1.715}$ (b) at 299 K and (c) at 808 K.. Lines with arrows indicate the diffusion paths along the <100> directions

Acetylene Absorption in Framework Solids



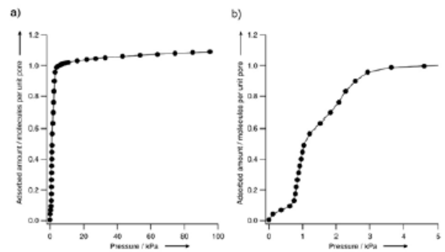
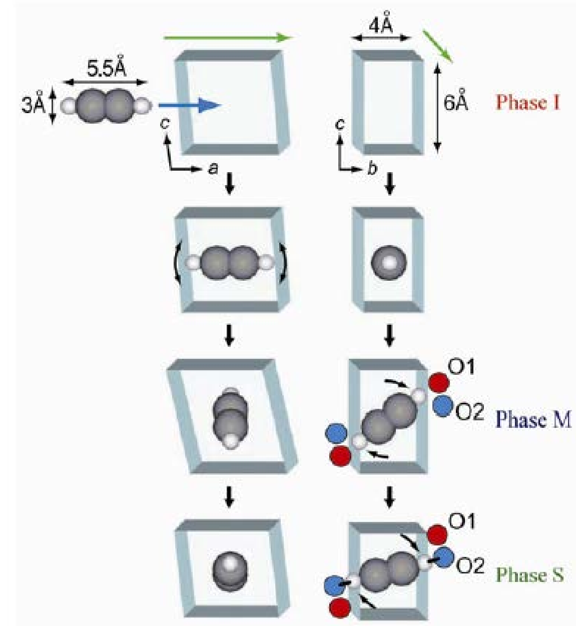
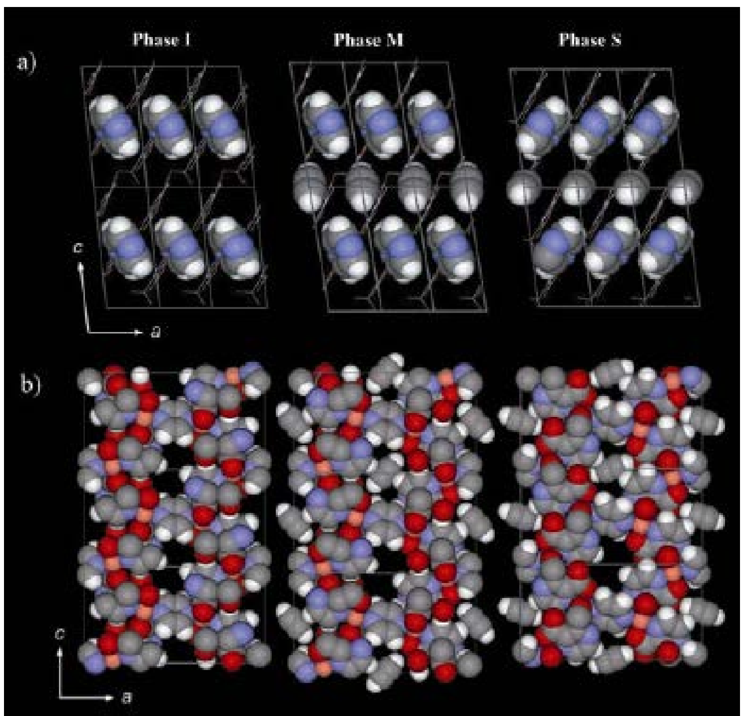
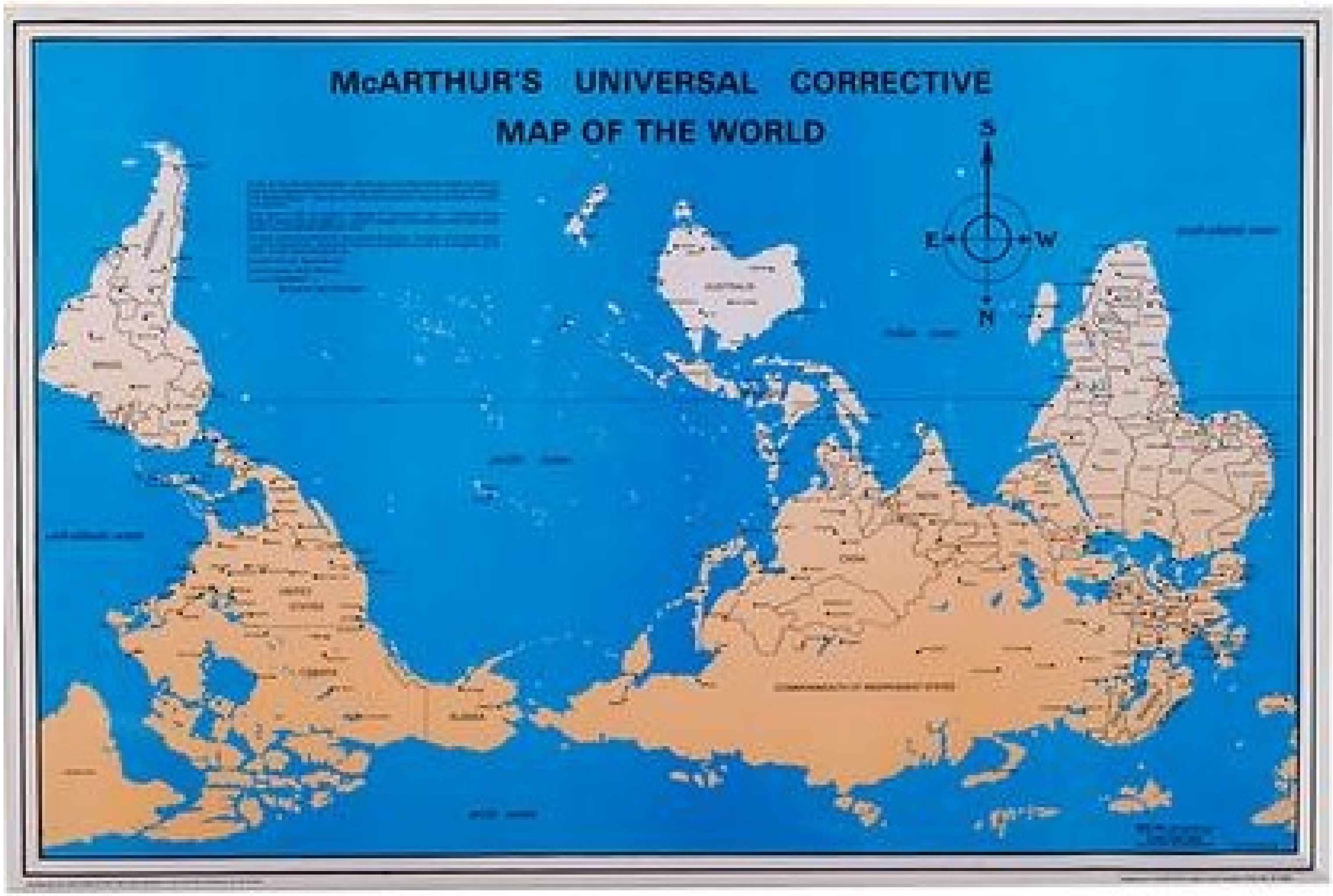


Figure 1: Adsorption isotherm for acetylene on CPL-1 at 270K. Gas pressure ranges a) from 0 to 100kPa and b) from 0 to 5kPa.





Crystal structures with the adsorption of acetylene.
a) Views from the side of the nanochannels. Pillar-molecules (pyrazine) and adsorbed acetylene molecules are shown by CPK model. Otherwise are connected by lines. b) Views from the nanochannel direction by the CPK model. Adsorbed acetylene molecules are omitted in the lower central pore in the phase M and S.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