

Powder X-ray Diffraction

Brendan J. Kennedy
School of Chemistry
The University of Sydney

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

Structure Refinement

Rietveld Method

Structure Solution

Reciprocal Space Methods
Real Space Methods

Thermal expansion and Phase Transitions

Quantitative Analysis

Lattice Parameter Determination
Phase Fraction Analysis

Peak Shape Analysis

Crystallite Size Distribution
Microstrain Analysis
Extended Defect Concentration

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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

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What is special about a crystal?

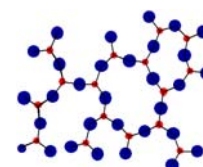
Solid phases are often crystalline, but need not be - e.g. glass an “amorphous material”

Glass

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

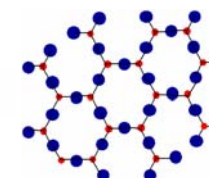
Crystal

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



• Si

• Oxygen



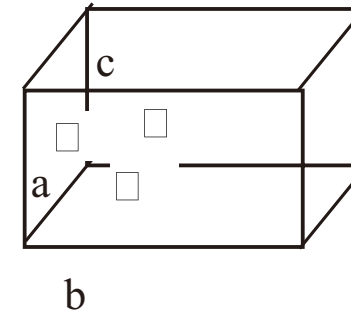
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Crystal Structure

- **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.

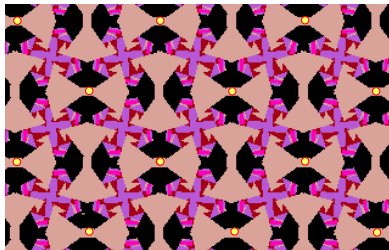
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The Unit Cell



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.

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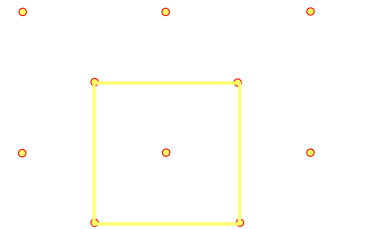


Example of 2D symmetry in a wallpaper pattern

To show symmetry:

1. Pick a point
2. Find all equivalent points

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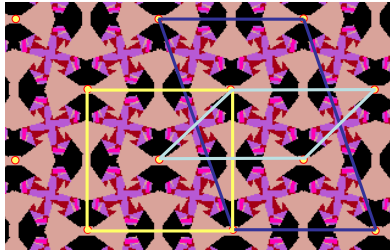


Example of 2D symmetry in a wallpaper pattern

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*

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Example of 2D symmetry in a wallpaper pattern

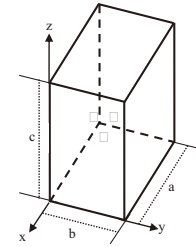
• Connecting 4 lattice points to form a parallelogram gives a possible *unit cell*

• *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

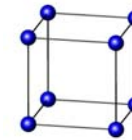
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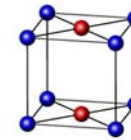
Lattice parameters:
 $a, b, c; \alpha, \beta, \gamma$

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

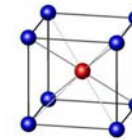
P



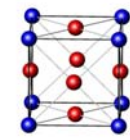
C



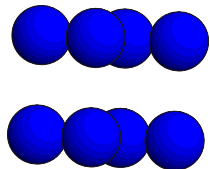
I



F



PC Lattice

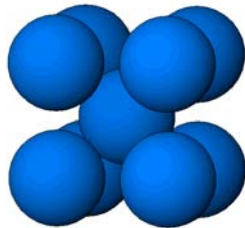


α -Po is **primitive-Cubic**

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

Lattice type P

BCC Lattice



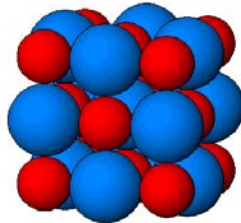
α -Iron is **Body-Centered Cubic**

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

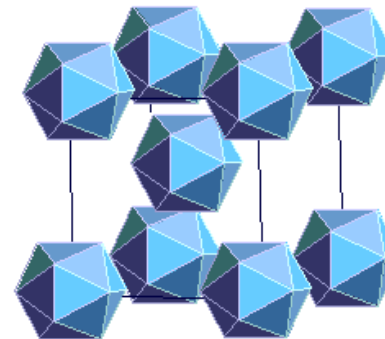
Rocksalt structure

Lattice type F

Also NaF, KBr, MgO....

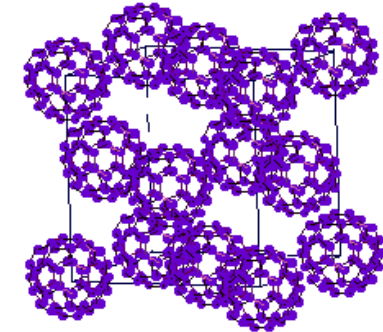
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FOOT & MOUTH VIRUS



BCC

BUCKMINSTERFULLERENE

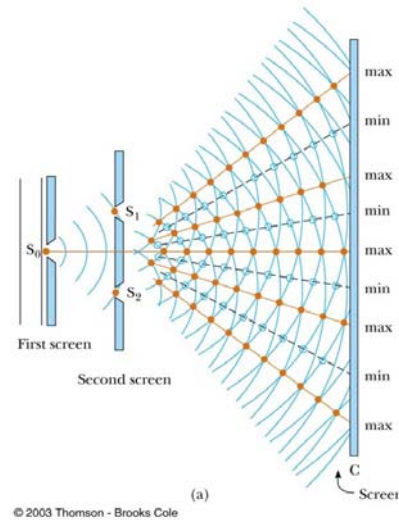


FCC

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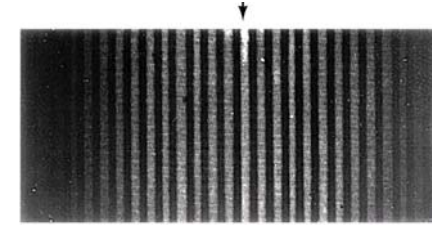
Young's Double Slit Experiment

- Thomas Young first demonstrated interference in light waves from two sources in 1801
- Light is incident on a screen with a narrow slit, S_0
- 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



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Resulting Interference Pattern

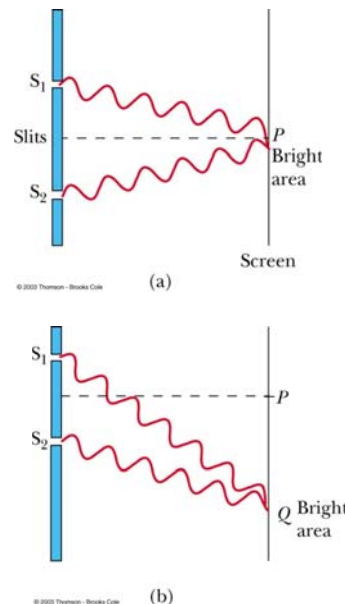


- The light from the two slits form a visible pattern on a screen
- The pattern consists of a series of bright and dark parallel bands called *fringes*
- **Constructive interference** occurs where a bright fringe occurs
- **Destructive interference** results in a dark fringe

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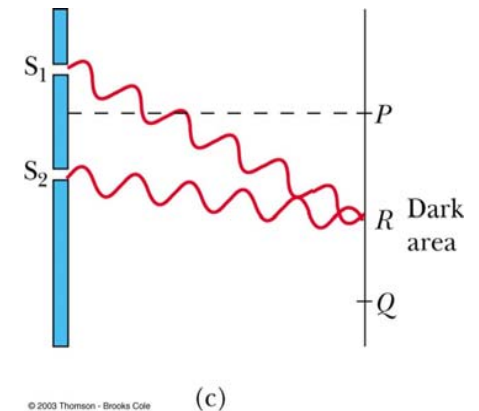
Interference Patterns

- Constructive interference occurs at the center point
- The two waves travel the same distance
 - Therefore, they arrive in phase
- The upper wave travels one wavelength farther than the lower wave
 - Therefore, they arrive in phase
- A bright fringe occurs



Interference Patterns

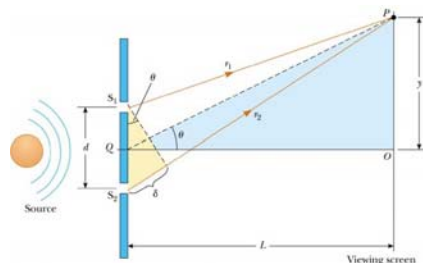
- The upper wave travels one-half of a wavelength farther than the lower wave
- The trough of the bottom wave overlaps the crest of the upper wave (180° phase shift)
- This is destructive interference
 - A dark fringe occurs



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Interference Equations

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



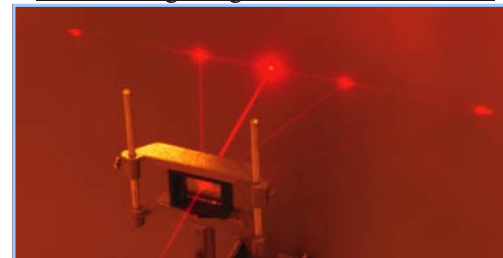
- For a bright fringe, produced by **constructive interference**, the path difference must be either zero or some integral multiple of the wavelength
- $\delta = d \sin \theta_{\text{bright}} = m \lambda$
 - $m = 0, \pm 1, \pm 2, \dots$
 - m is called the *order number*

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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.

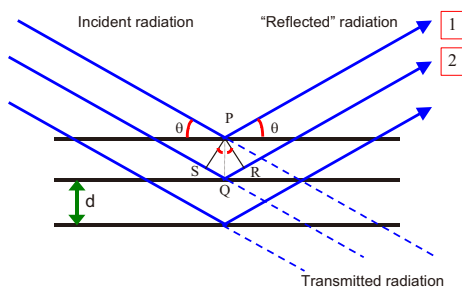
Diffraction grating and helium-neon laser



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Bragg's Law



Beam "2" travels the extra distance SQR

$$\begin{aligned} n\lambda &= \overline{SQ} + \overline{QR} \\ &= d_{hkl} \sin \theta + d_{hkl} \sin \theta \\ &= 2d_{hkl} \sin \theta \end{aligned}$$

But not all planes result in diffraction !!!

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Society of Crystallographers in Australia and New Zealand
SCANZ

Asian Crystallographic Association

2-5 December 2012

AsCA 12/ CRYSTAL 28:
Celebrating 100 years of X-Ray Crystallography

Adelaide Convention Centre, Adelaide, South Australia

A Joint Meeting of the Asian Crystallographic Association (AsCA),
Society of Crystallographers in Australia and New Zealand (SCANZ) in
association with the BRAGG Symposium.

Microsymposia Topics:

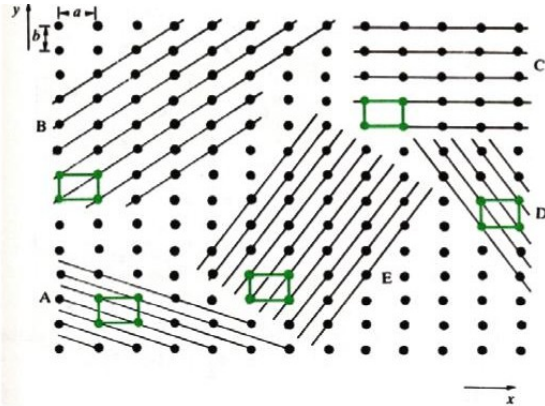
<ul style="list-style-type: none"> Hot structures in Biology Diffraction Physics and applications of crystallography Membrane Proteins Energy related materials Macromolecular assemblies (Viral proteins) Small angle scattering Structural proteomics and bioinformatics 	<ul style="list-style-type: none"> Metallo-organic structural chemistry Non-ambient and in-situ Diffraction Studies Synchrotron and neutron sources, instrumentation and application Dynamic aspects of molecular and solid state crystals Crystal growth and engineering Drug discovery Enzymes Diffraction imaging and XFELS
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Further details on invited speakers and the program will be available as updates at
www.sapmea.asn.au/crystal2012

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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 Indices

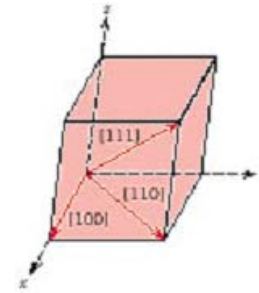


Crystallographic Directions And Planes

Lattice Directions

Individual directions: $[uvw]$

Symmetry-related directions: $\langle uvw \rangle$



Miller Indices:

- Find the intercepts on the axes in terms of the lattice constant a, b, c
- Take the reciprocals of these numbers, reduce to the three integers having the same ratio

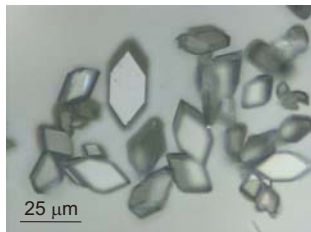
(hkl)

Set of symmetry-related planes: $\{hkl\}$

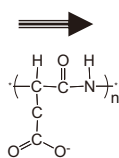
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Calcium oxalate solvates: COM & COD

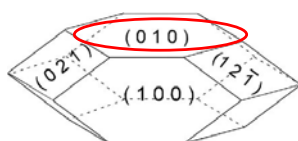
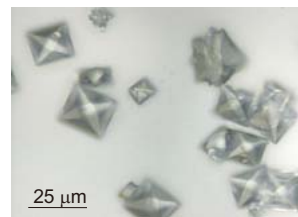
CaOx Monohydrate
(symptomatic)



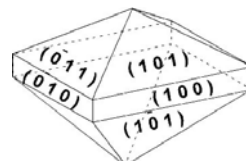
polyD



CaOx Dihydrate
(protective)

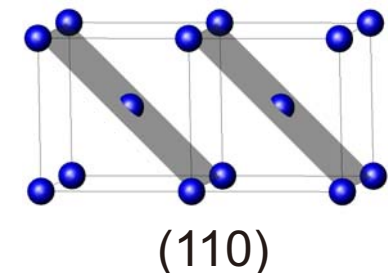
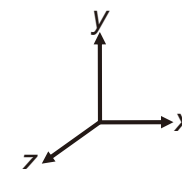
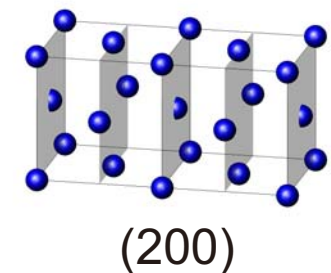
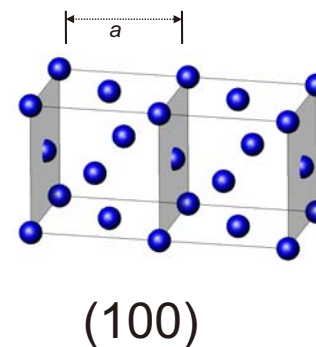


$P2_1/c$
($a = 6.290 \text{ \AA}$, $b = 14.580 \text{ \AA}$, $c = 10.116 \text{ \AA}$, $\beta = 109.46^\circ$)



$I4/m$
($a = b = 12.371 \text{ \AA}$, $c = 7.357 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$)

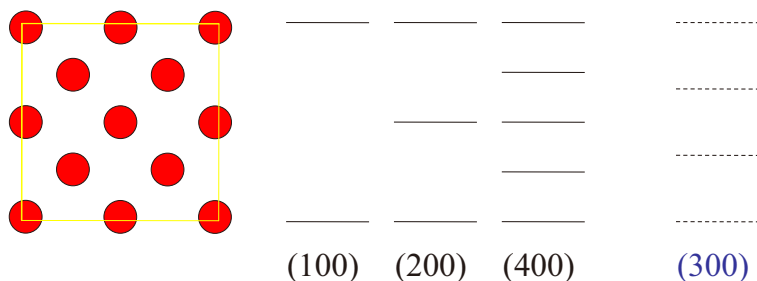
Examples of Miller Indices



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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

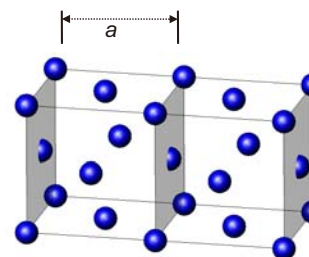


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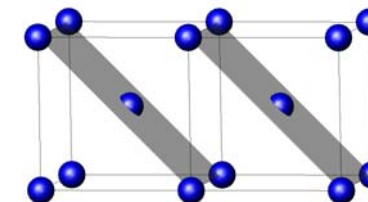
Lattice Spacing

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

For cubic system with $a = 4.0 \text{ \AA}$



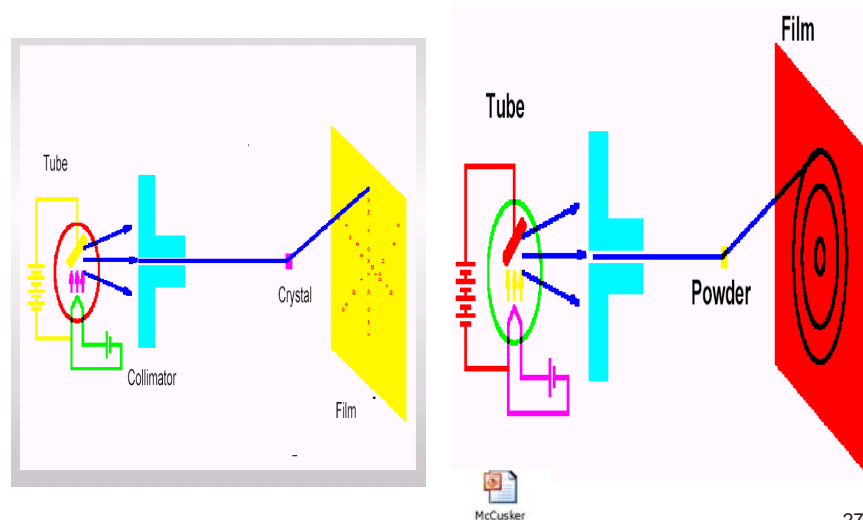
$$d_{100} = 4.0$$



$$d_{110} = 2.828$$

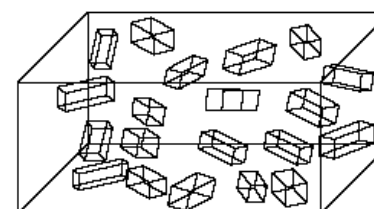
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Single Crystal vs Powder



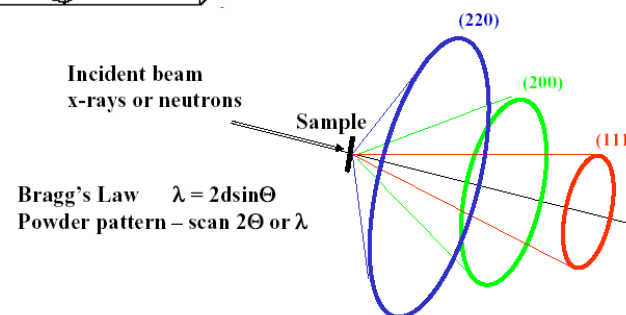
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Powder – A Polycrystalline Mass

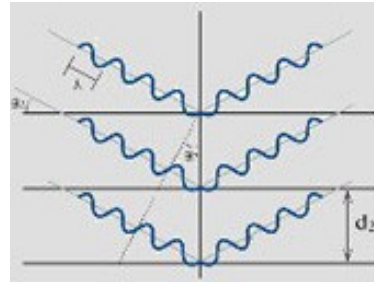
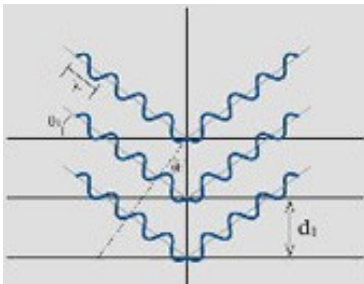


All orientations of crystallites possible

Single crystal reciprocal lattice - smeared into spherical shells



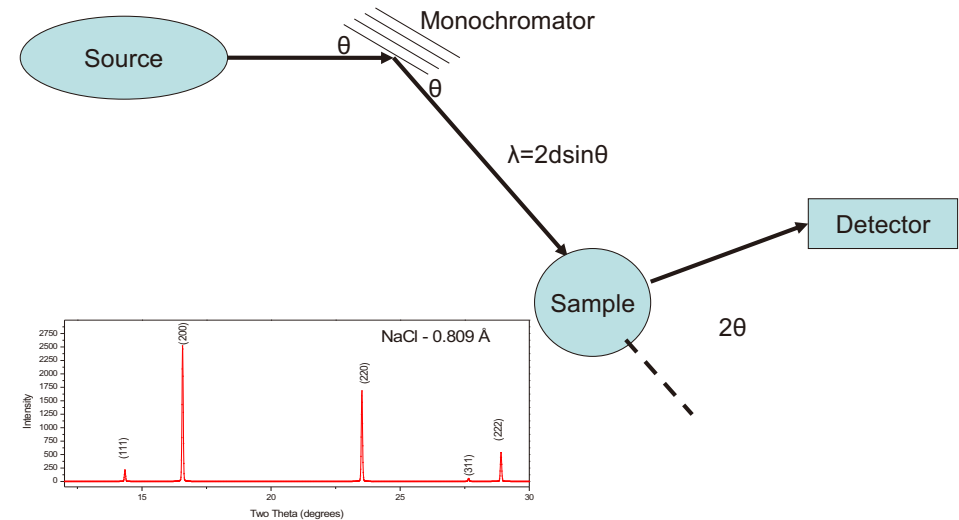
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- By varying the angle θ , the Bragg's Law conditions are satisfied by different d -spacings in polycrystalline materials.
- Plotting the angular positions and intensities of the resultant diffracted peaks produces a pattern which is characteristic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

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Powder Diffraction



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Information Contained in a Diffraction Pattern

Peak Positions

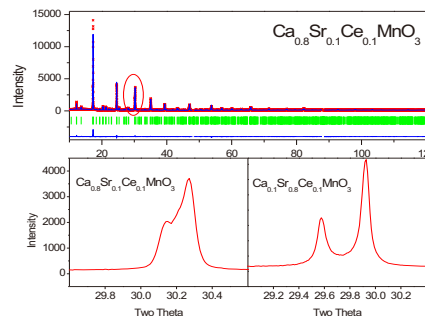
Crystal System
Space Group Symmetry
Unit Cell Dimensions
Qualitative Phase Identification

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.)

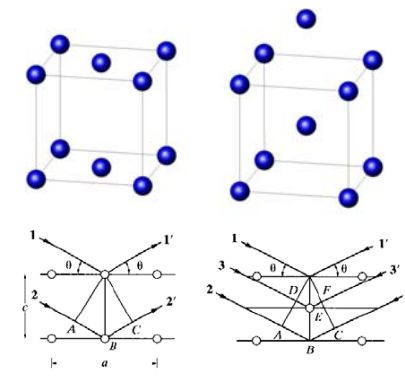


Changes in symmetry and microstrain upon chemical substitution can be established by examination of the patterns

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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 $\lambda/2$ and destructive interference in (b) will lead to no diffracted intensity

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Centering and Absences

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

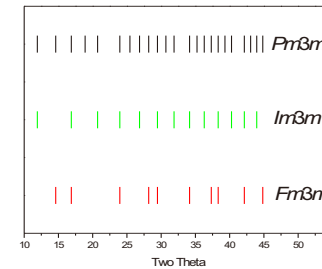
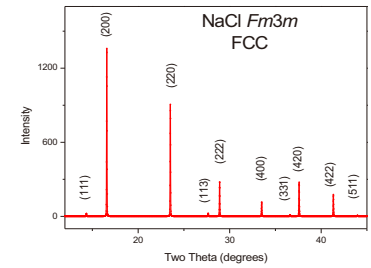
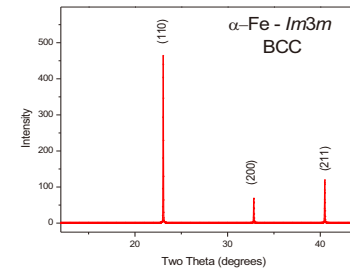
<i>Bravais lattice</i>	<i>Reflections that must be absent</i>
<i>Simple (Primitive)</i>	<i>none</i>
<i>Base (C) centered</i>	<i>h and k mixed</i>
<i>Body (I) centered</i>	<i>(h+k+l) odd</i>
<i>Face (F) centered</i>	<i>h, k and l mixed</i>

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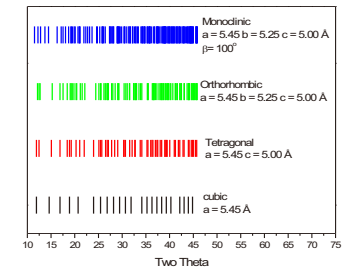
Multiplicity

- 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 it 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

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Influence of centering



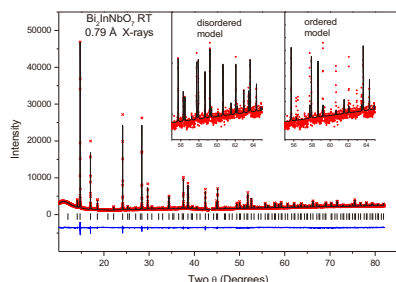
Influence of symmetry 34

Diffraction Patterns

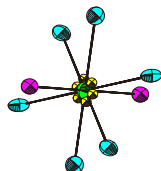
- Spacing of peaks depends on size of unit cell and the space group.
- The bigger the unit cell and/or the lower the symmetry the more diffraction peaks are observed.
- Intensity of peaks depends on (amongst other things) the arrangement of the atoms in the unit cell.
- For two materials that had identical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

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Need for High Q



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

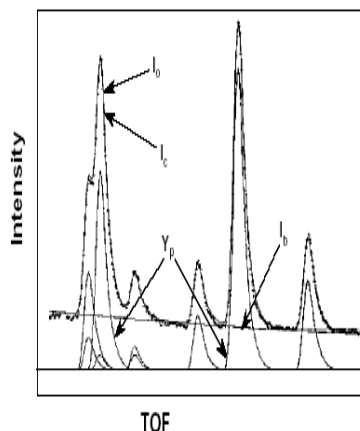


Refinement of structure gave unusual displacement parameters for the Bi cations, indicative of cation disorder. The patterns could only be adequately fitted by including 6-fold disorder of the Bi. This involves a displacement along the (1 -1 0) direction

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)

Peak Overlap

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

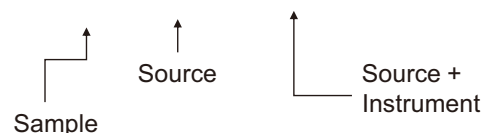


Need for High Resolution

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

Differentiating Braggs Law gives the resolution as:

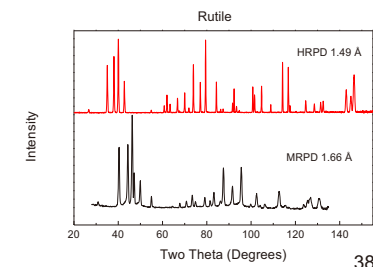
$$\lambda = 2d \sin \theta$$



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.



The Solution - Rietveld

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

- 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,
- $k_1 \dots k_2$ are the reflections contributing intensity to point i,
- the superscript p corresponds to the possible phases present in the sample.

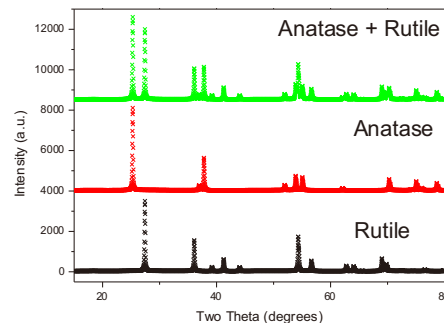


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The Answers

- The Profile R
$$R_p = \frac{\sum |y_{iobs} - y_{icalc}|}{\sum y_{iobs}}$$
- The weighted Profile R
$$R_{wp} = \left[\frac{\sum w_i (y_{iobs} - y_{icalc})^2}{\sum w_i y_{iobs}^2} \right]^{1/2}$$
- 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.

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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

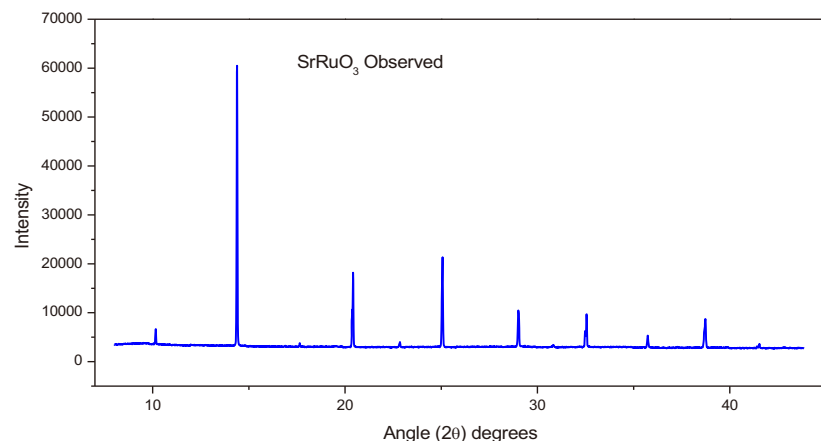
I is the index running over all phases

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

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An Example

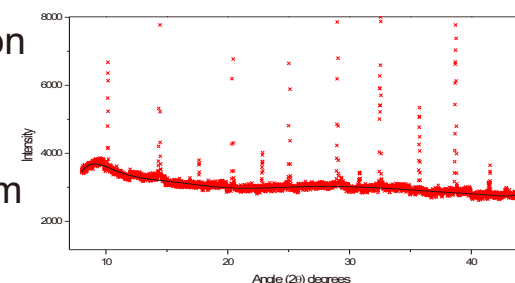
- Synchrotron X-ray Diffraction pattern for SrRuO_3



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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

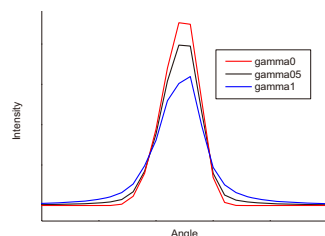


- Background can be either fitted or estimated.
- Here the capillary is a feature.

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Peak Shapes

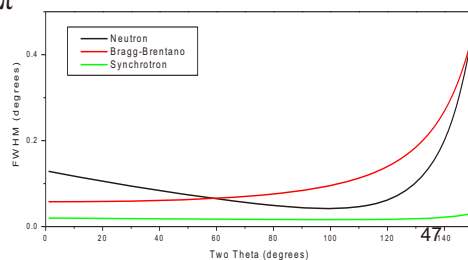
- Different Diffractometers have different peak shapes.
- The most widely function is a pseudo-Voigt (mixed Gaussian and Lorentzian).



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

- The width of peaks is usually not constant.

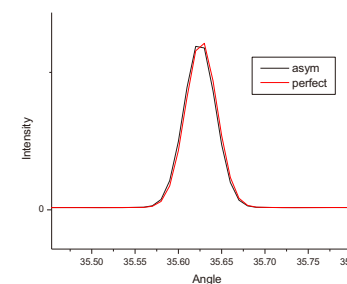
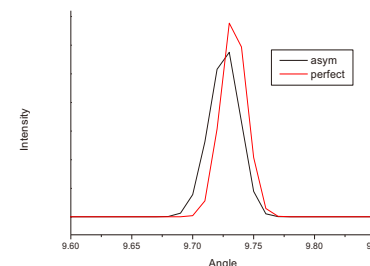
$$H^2 = U \tan^2 \theta + V \tan \theta + W$$



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Peak Asymmetry

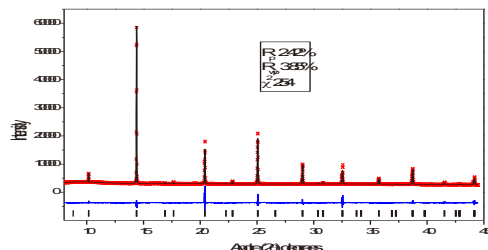
- Beam Divergence can result in asymmetric peaks at low angles.
- Results from not integrating over the entire Debye cone.



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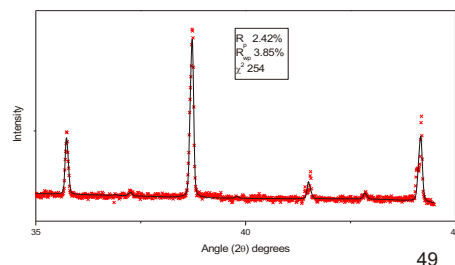
The Simple Structural Model

- The fit to a single phase sample looks good



• BUT.....

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



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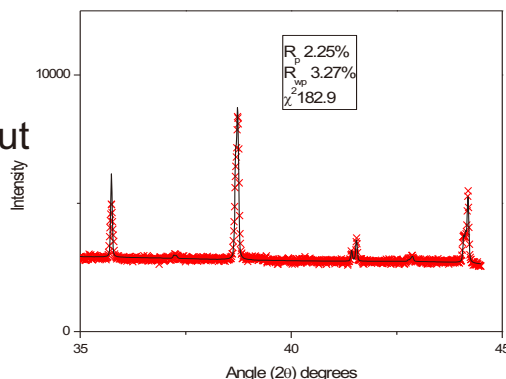
A Common Problem

- 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

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An Alternate Model

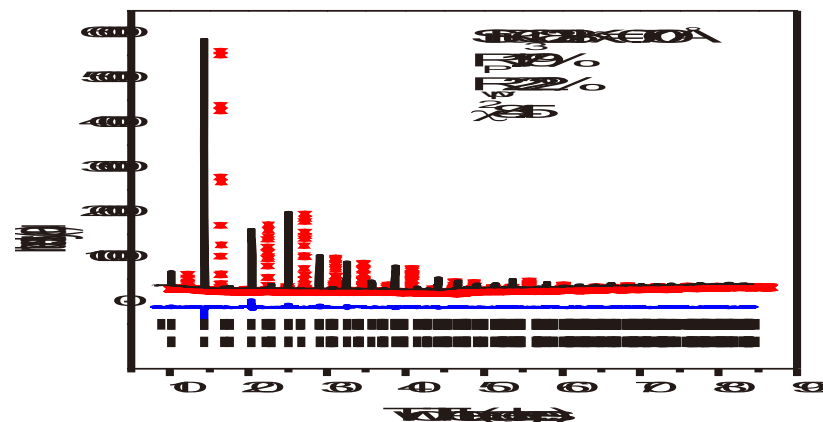
- The high angle splitting is well modeled by a tetragonal model - but this overestimates some intensities.



- The Truth lies somewhere in the middle

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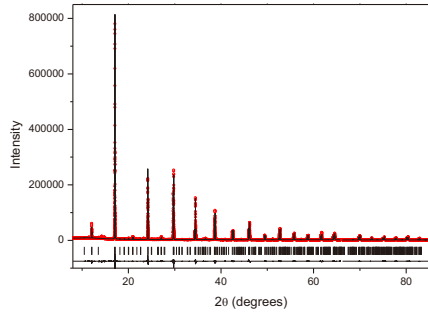
The finished Product



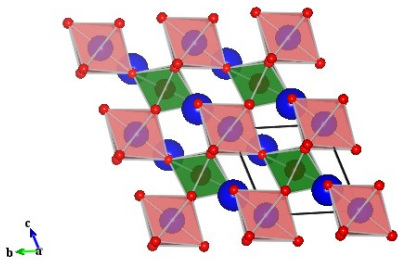
- The sample contains a mixture of both phases!

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Crystallography gives average structure



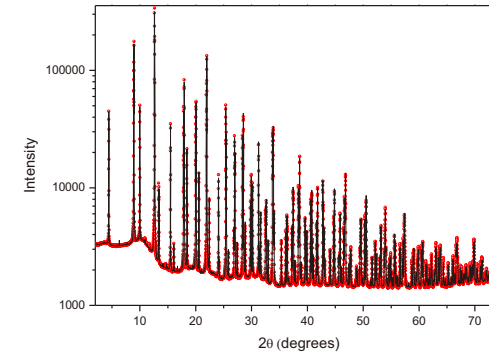
- *The Rietveld method has served us well for over 45 years – but it only uses part of the information of the diffraction experiments, namely the intensity of the Bragg peaks*



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Crystallography challenged: materials with disorder

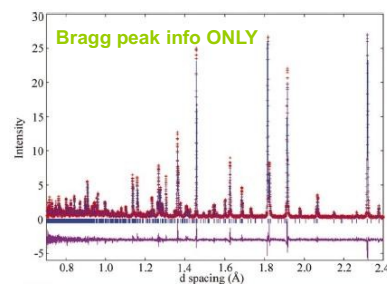
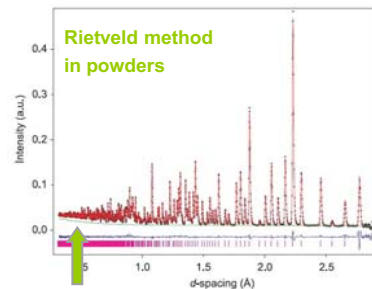
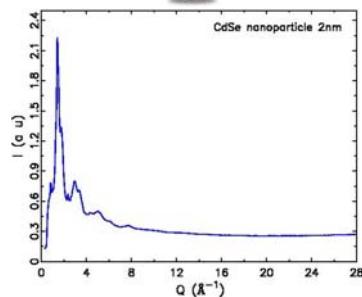
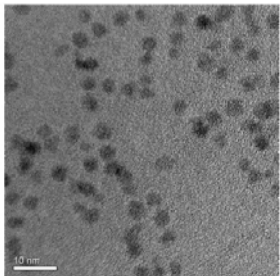
Rietveld approach assumption: **crystals are perfectly periodic...**
...but this is not always the case!



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

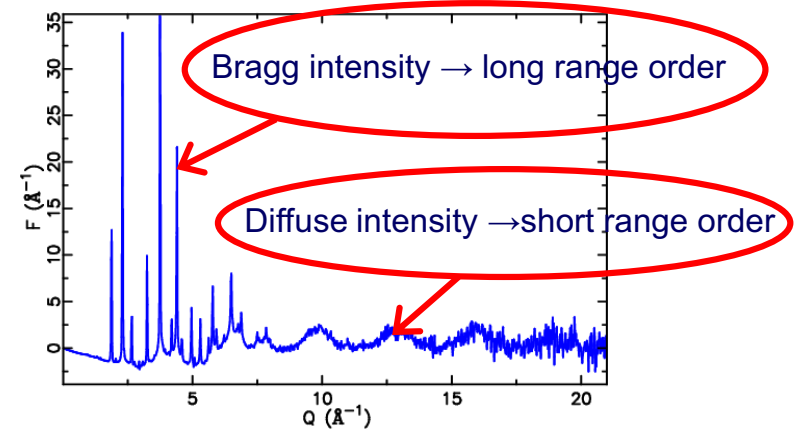
Crystallography challenged: nano-crystals

From E. Bozin BNL



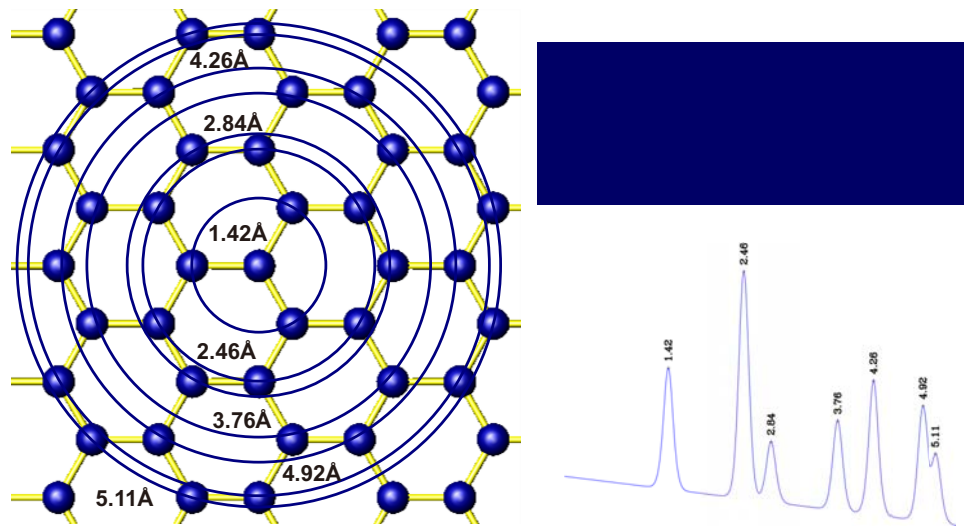
Diffuse intensity contains information on short-range order

From E. Bozin BNL



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

Total Scattering - PDF



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.

Anomalous X-ray Scattering

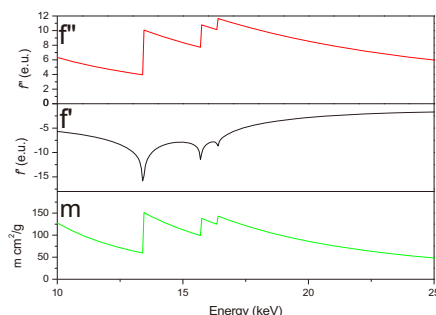
$$f_i^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$$

- *Anomalous scattering* or *anomalous dispersion* occurs when the incident X-ray energy is sufficient to cause photoelectric x-ray production in a target atom. The process is called fluorescence. This phenomenon is responsible for “absorption edge” observed when certain elements interacting with particular wavelength x-rays. In this process a characteristic X-ray photon is produced in the target; subsequent interaction produces coherent X - rays which are slightly out of phase with other coherently scattered X-rays. The net result is a reduction of the scattered intensity from the element.

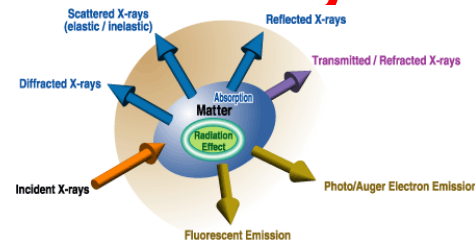
Bi Wavelength Dependence

Just as the absorption coefficient shows large jumps at “edges” the scattering power of elements shows rapid changes near edges.

- Minimum absorption is obtained near 13.31 eV (0.93 Å)
- Maximum $\Delta f'$ is ca 8 electrons by measuring at 13.3 and 13.5 eV.



Interaction of X-rays and Matter



Scattering.

coherent, incoherent
elastic (Thomson), inelastic (Compton)

Absorption.

atoms: can then be emitted as fluorescence, photoelectrons, Auger electrons
molecules: can emit fluorescence, phosphorescence, transfer heat, (stimulated emission)

Diffraction. The bending of waves due to obstructions and small apertures, as with crystals.

Refraction. The bending of a wave as it passes from one medium to another

Reflection. Radiation bouncing back from one medium to the original medium, where the wavelength \ll size of the object.

Dynamics

Equilibrium

- B factors
- Diffuse scatter

Non-equilibrium

- Laue crystallography
- Rapid Mixing and Small angle scattering

The temperature (B) factor

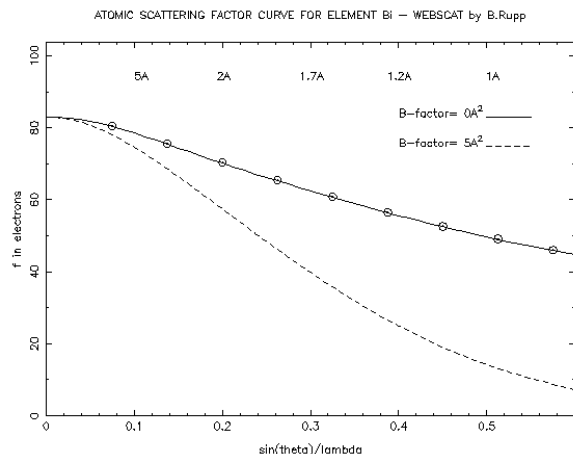
- Atoms are not located at fixed points - undergo vibrations about their mean positions.
- The amplitude of these vibrations increase as the temperature increases.
- Due to such motion, the scattering factor falls off exponentially. The greatest reduction in intensity is at high angles (low d-values).

$$f_B = f \cdot e^{-B(\sin \theta / \lambda)^2}$$

Debye-Waller temperature factor $B = 8\pi^2 \langle u^2 \rangle$

Where $\langle u^2 \rangle$ is mean-square amplitude of atomic vibration. This is directional and can be anisotropic

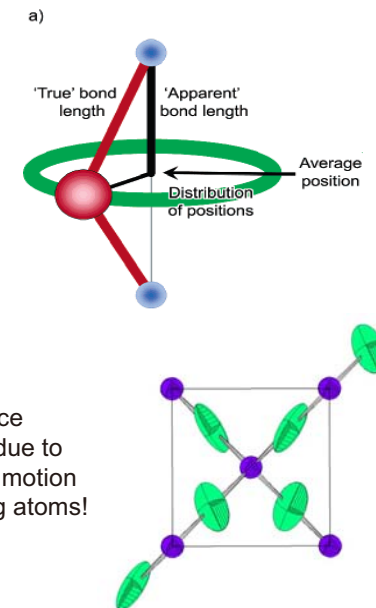
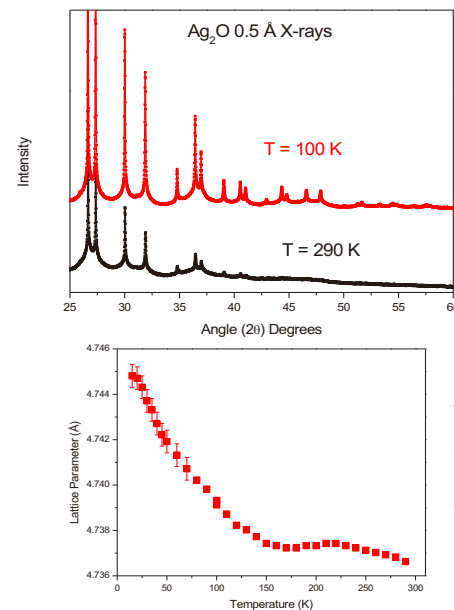
The temperature (B) factor



$$f_B = f \cdot e^{-B(\sin \theta / \lambda)^2}$$

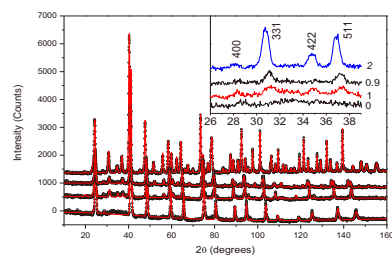
Debye-Waller temperature factor $B = 8\pi\langle u^2 \rangle$

Effect of Temperature Ag_2O

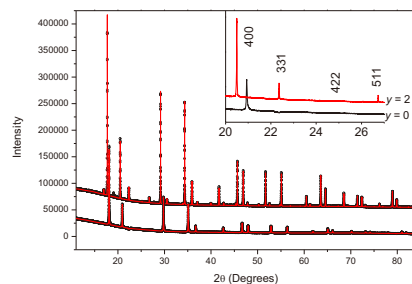


X-rays and Neutrons, Same Same but Different

Neutron

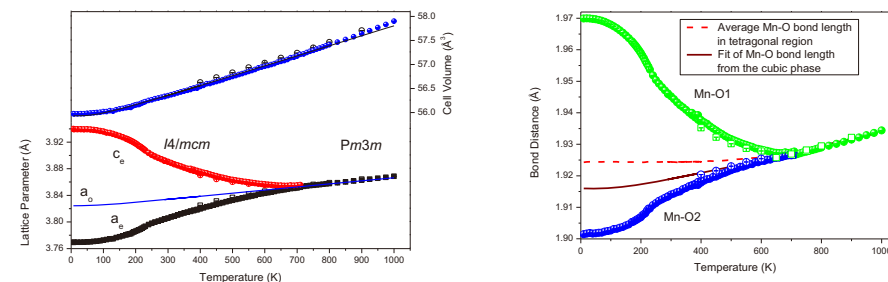


S-XRD



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

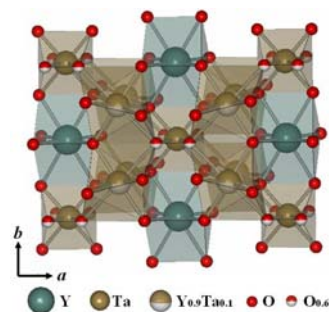
$\text{Sr}_{0.65}\text{Pr}_{0.35}\text{MnO}_3$ – structural parameters



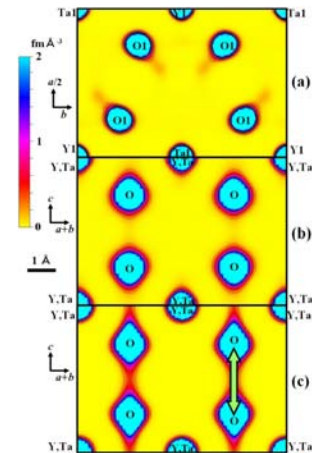
Single structural phase transition observed. Apparently conventional thermal expansion of the cell volume (fitted as $V_0 = V_1 + V_2 \coth(\Theta/T)$)

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 $\langle 100 \rangle$ directions

Acetylene Absorption in Framework Solids

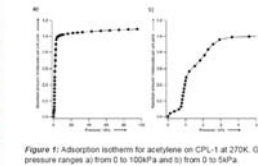
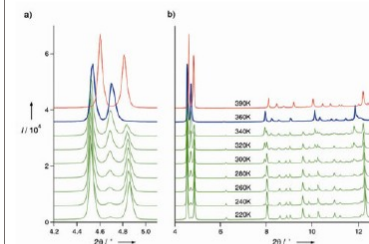
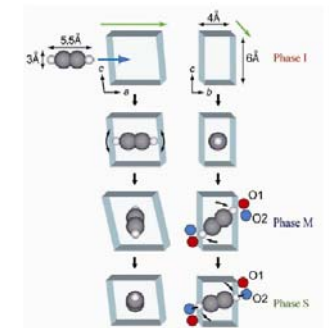


Figure 1: Adsorption isotherms for acetylene on CPV-1 at 270K. Gas pressure ranges a) from 0 to 100 kPa and b) from 0 to 50 kPa.



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.

