Powder X-ray Diffraction

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State of the Art on Earth1912



Laue X-ray Diffractometer



Bragg's X-ray tube



State of the Art on Mars 2012



Prototype of CheMin Diffractometer



Crab Nebula. The bluish glow from the central region of the nebula is due to synchrotron radiation.





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

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.



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 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

0

0

.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: $a, b, c; \alpha, \beta, \gamma$

	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)	$a = b \neq c$ $\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$
	Ρ	C I	F











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



BUCKMINSTERFULLERENE



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, S₁ and S₂
- The narrow slits, S₁ and S₂ act as sources of waves
- The waves emerging from the slits originate from the same wave front and thus 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
- 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



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
- $\delta = d \sin \theta_{\text{bright}} = m \lambda$
 - $-m = 0, \pm 1, \pm 2, \dots$
 - *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







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
- 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 CaOx Dihydrate (symptomatic) (protective) polyD 25 µm 25 µm 1077 (101) 010) Tai, 010 102 (100) (- 1- 0-0-). (101)

 $P2_1/c$ (*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, $\alpha = \beta = \gamma = 90^{\circ}$)

Examples of Miller Indices



(100)





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



For cubic system with a = 4.0 A





 $d_{110} = 2.828$

 $d_{100} = 4.0$

Single Crystal vs Powder



Powder – A Polycrystalline Mass



All orientations of crystallites possible

Single crystal reciprocal lattice - smeared into spherical shells





- 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





Bragg-Brentano Diffractometer

- The Bragg-Brentano diffractometer is the dominant geometry found in most laboratories. Typically operates in a θ-2θ geometry, but can operate in θ:θ geometry
- The relationship between θ (the angle between the specimen surface and the incident X-ray beam) and 2θ (the angle between the incident beam and the receiving slit-detector) is maintained throughout the analysis.
- • r1 and r2 are fixed and equal and define a diffractometer circle in which the specimen is always at the centre.



Debye-Scherrer Geometry





My Other 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



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 $\lambda/2$ 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 I mixed



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



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



Atom	Site	X	У	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



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.



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 kth Bragg reflection,
- k₁ ... k₂ are the reflections contributing intensity to point i,
- the superscript p corresponds to the possible phases present in the sample.

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

Peak Shapes

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



 The width of peaks is usually not constant.

 $H^2 = Utan^2\theta + Vtan\theta + W$



Peak Asymmetry

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



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 onFrom E. Bozin BNLShort-range order

Bragg intensity \rightarrow long range order (Å⁻¹) Diffuse intensity \rightarrow short range order ŝ 10 Q (Å⁻¹) 15 20 $G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$

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.

Absorption

Plot illustrating how sample absorption (MuR) can impact data quality



To decrease the mu×r of a highly absorbing sample, one must lower its effective packed density or reduce its radius. One trick is to mix the powder of your absorbing sample with a low density and amorphous material such as silica (SiO₂ glass) powder or amorphous boron.

For a good discussion see http://11bm.xray.aps.anl.gov/absorption.html

relative intensity (patterns not on same scale)

X-rays and Neutrons, Same Same but Different

S-XRD



Neutron

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

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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

