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Introduction to Powder Diffraction

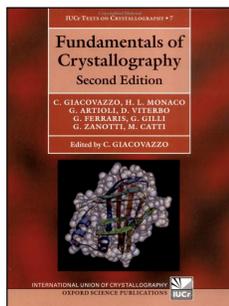
Brian H. Toby

Outline

- § Where to go for more information
- § Some background on crystallography
- § Diffraction from single crystals
- § Diffraction from powders
- § Instruments for powder diffraction collection
- § Materials effects in powder diffraction
- § Crystallographic analysis of powder diffraction data
- § (Total scattering/PDF analysis)

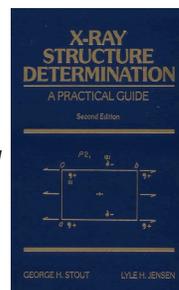
Where to go for more...

There are many texts available. My favorites:



Fundamentals of Crystallography (2nd Ed.), Carmelo Giacovazzo, et al. (Oxford, 2002, ~\$90) [Modern & very comprehensive, quite reasonable price considering quality, size & scope.]

X-Ray Structure Determination: A Practical Guide (2nd Ed.), G. H. Stout, & L. H. Jensen (Wiley, 1989, ~\$150) [Focused on small-molecule single crystal techniques, dated, but very easy to read; very good explanations of fundamentals. 1st book for many in field.]



APS Web lectures on powder diffraction crystallography:

www.aps.anl.gov: look for Education/Schools/Powder Diffraction Crystallography (http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography)

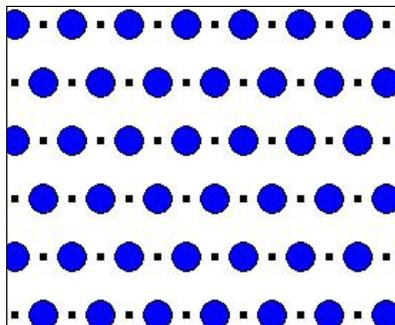
Intended to introduce Rietveld refinement techniques with GSAS & EXPGUI



The Lattice

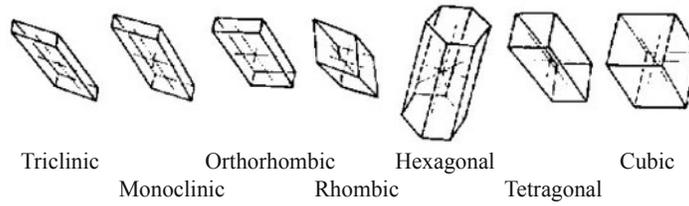
- § Crystals are constructed from repeated arrangements of atoms.
- § Crystalline structure can be described as set of “identical boxes” stacked in 3D; the contents of each box is identical (exception: quasicrystals)
 - **A lattice** is a mathematical concept where each lattice point describes an identical environment; lattice points are the corners of the “identical boxes.”

Commonly used phrases such as “lattice compound” or “interstitials in the lattice” misuse the concept of a lattice.



The Unit Cell

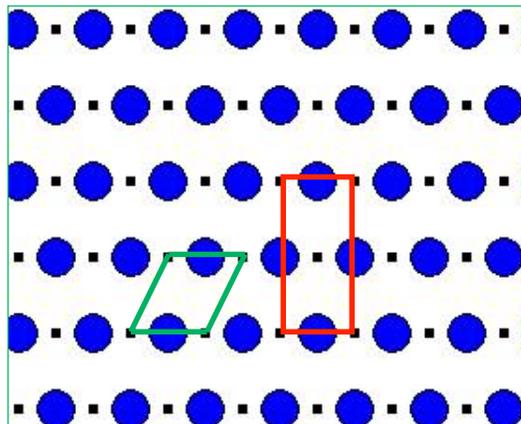
- § The **unit cell** describes at least one repeating unit that can be used to construct the structure
- § There are 7 types of unit cells corresponding to the **7 crystal systems**



(Image from <http://pasadena.wr.usgs.gov/office/given/geo1/lecturenotes/SevenCrystalSystems.html>)

Centering is used to increase symmetry

- § The green (primitive) unit cell does not demonstrate two-fold symmetry that can be seen in the red (centered) cell



Lattice Types

Centering causes lattice points to be placed inside units cells (**body center**, **face centers**) giving rise the **14 Bravais lattices** (1848)

Have non-perpendicular axes: (non-orthogonal coordinate systems)

CUBIC $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	
TETRAGONAL $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
ORTHORHOMBIC $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
HEXAGONAL $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
TRIGONAL $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	
MONOCLINIC $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 120^\circ$	
TRICLINIC $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	

4 Types of Unit Cell
 P = Primitive
 I = Body-Centred
 F = Face-Centred
 C = Side-Centred
 +
 7 Crystal Classes
 → 14 Bravais Lattices

(Figure from http://www.chemsoc.org/exemplarchem/entries/2003/bristol_cook/latticetypes.htm)

Symmetry

The construction of a crystal from the unit cell requires repeated translation of the "building block" in all three directions: **lattice symmetry**

§ Additional symmetry is almost always present between the atoms in a unit cell. This means the unit cell (and thus the entire structure) can be built from just a section of the unit cell

- The minimal section representative of the entire structure is called the **asymmetric unit**

§ Types of symmetry elements in crystals

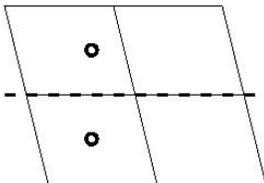
- Lattice translations (includes lattice centering)
- Mirror planes
- Proper/improper Rotation axes (includes center of symmetry)
- Screw Axes
- Glide Planes

(Images from <http://members.tripod.com/~EppE/302rev2.htm>)

Space Groups

§ Not all combinations of symmetry and lattice types are compatible

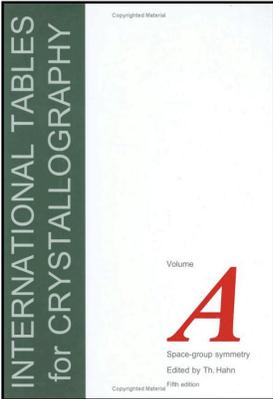
- Example: mirror plane perpendicular to a non-orthogonal pair of axes



Δ There are only 230 unique ways to combine symmetry elements for a 3D lattice: **230 space groups**

Δ Space groups are tabulated in ***The International Tables of Crystallography, Volume A***

Δ I recommend ***Space Groups for Solid State Scientists*** by G. Burns and A. M. Glazer as a good place to learn about space groups and s.g. properties



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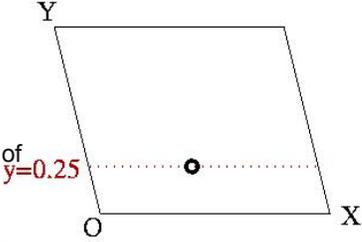
Fractional coordinates

§ Atom locations are measured in fractions of the unit cell edges

- Note atom is at $x=0.45, y=0.25$

Δ This notation allows for simple description of symmetry operations:

- $(x,y,z) \rightarrow (1+x, y, z)$ [translation on x]
- $(x,y,z) \rightarrow (1/2+x, 1/2+y, 1/2+z)$ [centering]
- $(x,y,z) \rightarrow (-x, -y, -z)$ [center of symmetry @ origin]



In crystallographic notation $x=0.45(3)$ means that there is a standard uncertainty of 0.03 on the value for x of 0.45

Equivalently, there is a 95% chance that x is between 0.39 and 0.51 ($\pm 2\sigma$)

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Lattice planes

§ General Indices: lattice planes are indexed by the inverse of where they cut each axis:

- Intercept of 0.5 → index=2
- Intercept of ∞ (|| to axis) → index=0

§ Related concept: Miller indices

- used for crystal faces
- Contain no common factors

§ Notation: [] defines a direction

- [100] is along a axis

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Reciprocal Lattice

§ To simplify math when working with non-orthogonal coordinate systems, we use a construct called the **reciprocal lattice** (indicated by star) where each reciprocal axis is perpendicular to two “real space” axes:

- $a^* \cdot a = 1; a^* \cdot b = 0; a^* \cdot c = 0$
- $b^* \cdot a = 0; b^* \cdot b = 1; b^* \cdot c = 0$
- $c^* \cdot a = 0; c^* \cdot b = 0; c^* \cdot c = 1$

§ This means that if we have two vectors:

$$\underline{r} = xa + yb + zc \quad \text{and} \quad \underline{d}^* = ha^* + kb^* + lc^*$$

Then no cross-terms are needed for the dot product:

$$\underline{r} \cdot \underline{d}^* = hx + ky + lz$$

Use of the reciprocal lattice makes computation of the Fourier transform of the atomic positions straightforward.

Historical note: the value of the reciprocal lattice for working with non-orthogonal coordinate systems was first recognized by J. Willard Gibbs (1881)

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Single Crystal Diffraction

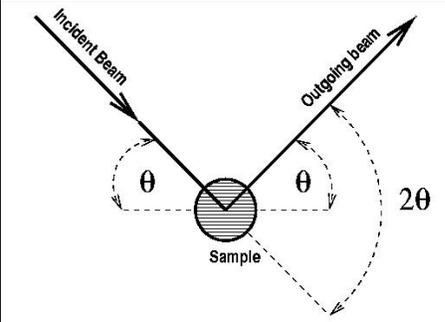


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Diffraction from single crystals

§ Diffraction occurs when the *reciprocal lattice planes* of a crystal are aligned at an angle θ with respect to the beam and the wavelength of an incident beam satisfies:

- $n\lambda = 2 d \sin\theta$ (or better, $\lambda = 4 \pi \sin\theta / Q$) [Bragg's Law]
- $d = 1/|\underline{d}^*| = 1/|ha^* + kb^* + lc^*|$



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Single Crystal Diffraction Intensities

§ The Intensity of a diffracted beam, I_{hkl} is related to a imaginary number called the **structure factor**, F_{hkl}

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

§ The structure factor is determined by summing over all atoms in the crystal:

- $F_{hkl} \propto \sum f_i \exp[2\pi i(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2)$

Since adding 1 to x_i, y_i or z_i does not change the above this can be simplified to sum over the atoms of one unit cell

- f_i represents the scattering power of an atom
- U_i represents the average displacement of an atom from its ideal site

Powder Diffraction

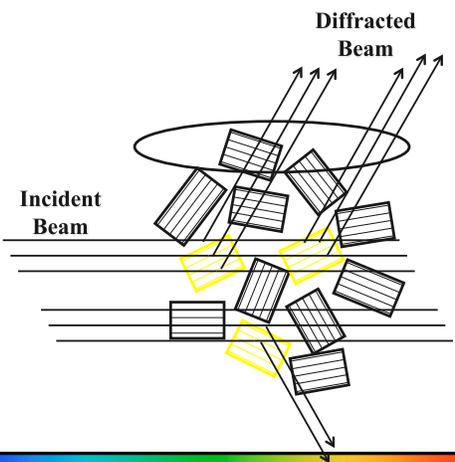
Diffraction from random polycrystalline material

In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder), there are a large number of small crystallites.

A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction

Diffraction occurs only at angles where Bragg's Law is satisfied:

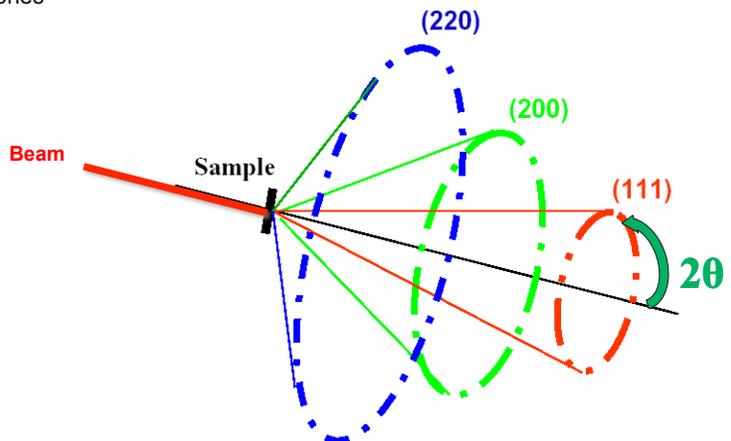
$$\lambda = 4 \pi \sin\theta / Q$$



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Bragg cones in powder diffraction

Diffraction in all directions, thus powder diffraction occurs in cones



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X-rays vs Neutrons (why not both?)

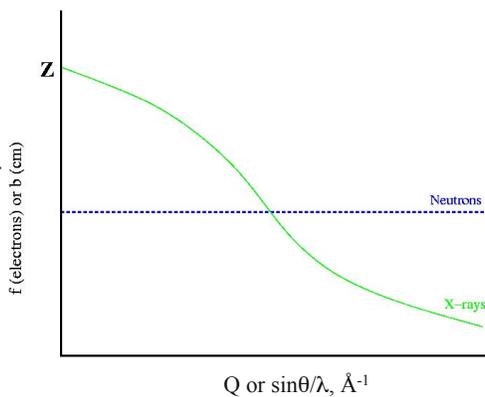
Coherent Atomic Scattering Power (diffraction)

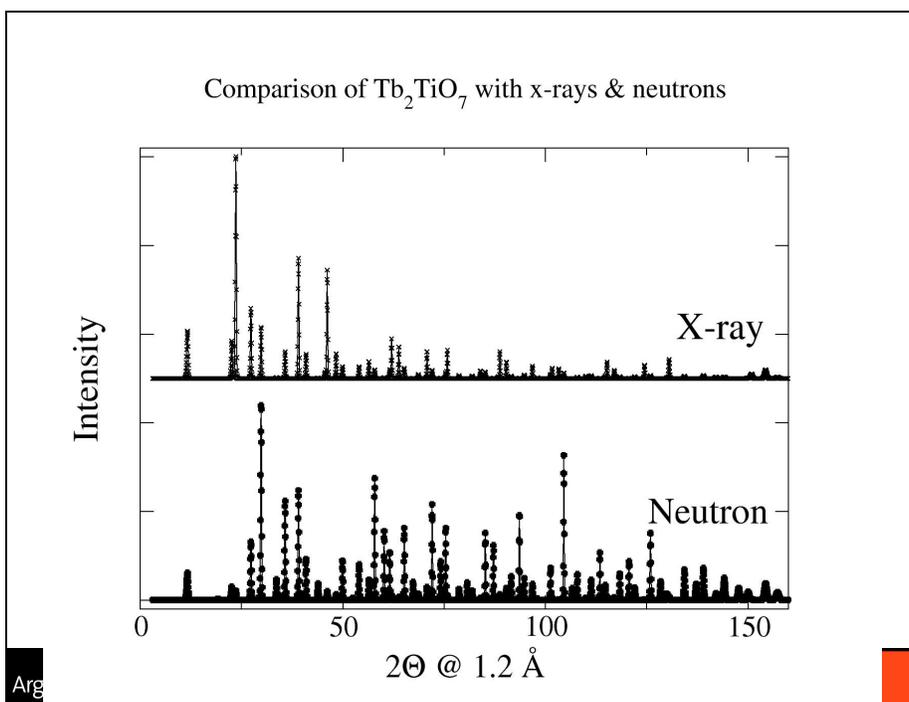
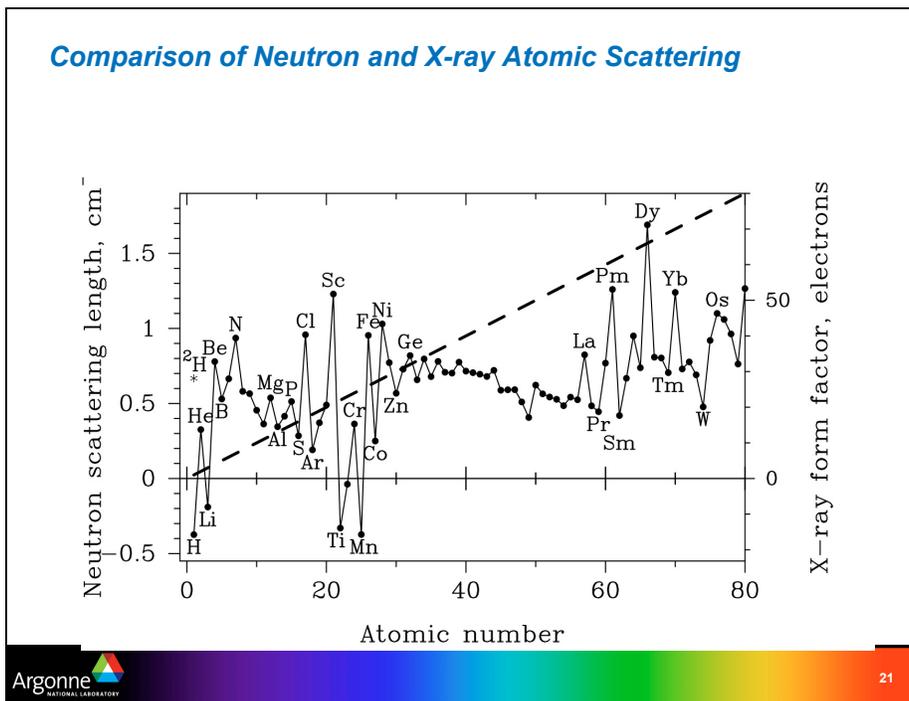
Structure factors: $F_{hkl} = n \sum f_i \exp[2\pi i(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2)$
Diffraction Intensity: $I_{hkl} \propto |F_{hkl}|^2$

§ **X-rays:** The scattering power (form factor, f) of an atom depends on the number of electrons in the atom and Q ($Q \propto \sin\theta/\lambda$)

§ **Neutrons:** The scattering power (scattering length, b) of an atom depends on the isotope and is independent of Q

- A few isotopes scatter with opposite phase to most, for these we write $f(b)$ as negative





Powder Diffraction Measurements

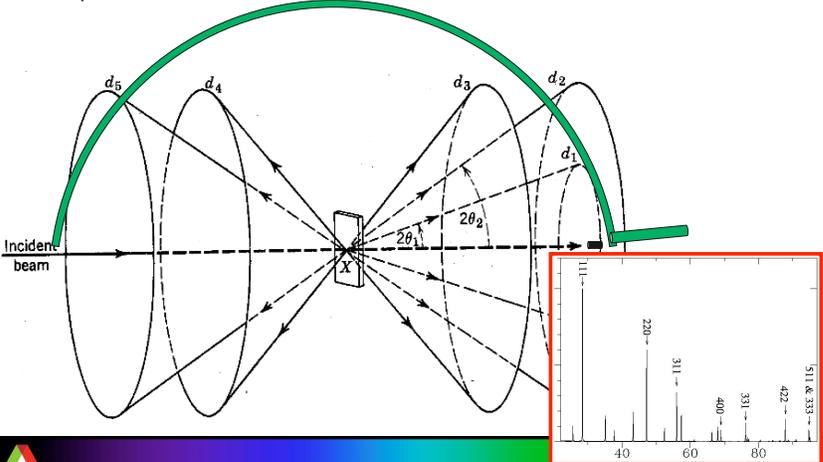


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Measuring powder diffraction

§ In the simplest experiment, a single detector is moved over a range of 2θ angles.

- Sample irradiated with monochromatic radiation



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Synchrotron powder diffraction

§ With an area detector, a complete powder diffraction pattern can be collected in a fraction of a second.

- Fast
- Medium resolution
- High background

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Highest resolution requires high collimation. Optimal is a crystal analyzer between the sample and detector: 11-BM Diffractometer

Huber 480 rotation stage:
 high precision (~0.35arcsec)
 high accuracy (~1arcsec)
 slew or step scans

beam

Mitsubishi robot
 custom "fingers"

Sample X,Y,Z stage
Sample spinner
 (1,000-10,000 rpm)

12 analyzer array
 Si(111) crystals
 LaCl₃ scintillator detectors
 2° apart in 2θ.

Sample environment
 Cryostream (80-500 K)
future environments ..

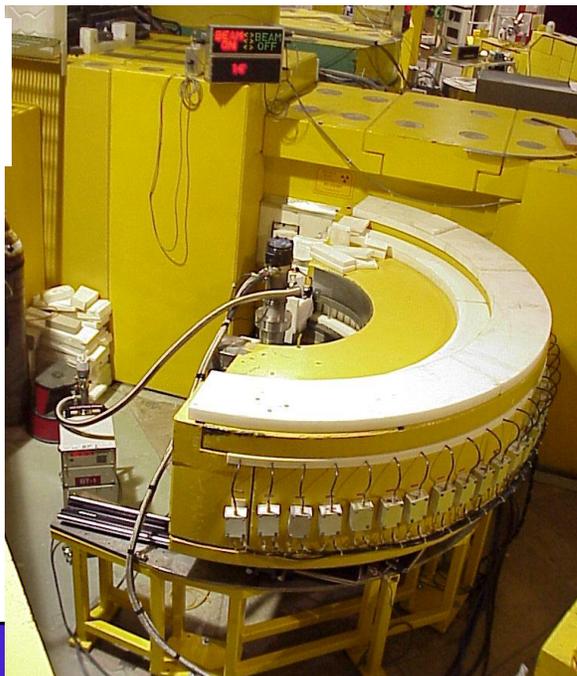
Complete pattern is measured in <1 hour

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Neutron Powder Diffraction: Constant Wavelength

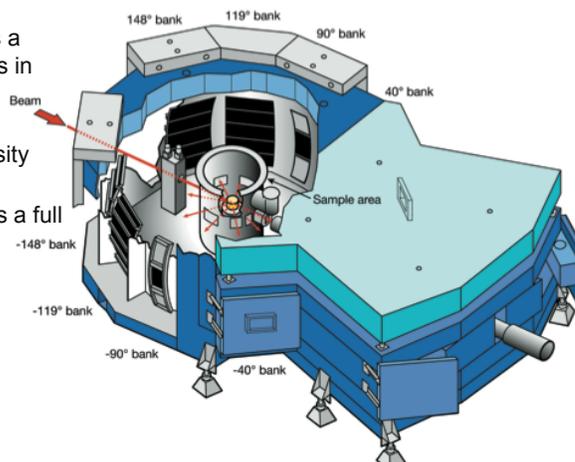
BT-1 @ NIST

- § 32 Detectors with 5° spacing cover a 160° range
- § Complete pattern is measured with a 5° scan (typically a 2-10 hours)



Neutron Powder Diffraction with Spallation Source

- § Spallation source provides a broad band of wavelengths in sharp pulses
 - TOF detection allows measurement of intensity versus wavelength
 - Each detector provides a full diffraction pattern
 - Data collection times:
 - *Seconds to hours*



NPDF instrument at LANSCE (Los Alamos)



Materials Effects in Powder Diffraction

Materials effects on Powder Diffraction

Peak broadening:

§ Crystallite size:

- What happens when crystals become small?

§ Residual Stress (Strain)

- What happens if matrix effects do not allow crystallites to equilibrate lattice parameters?

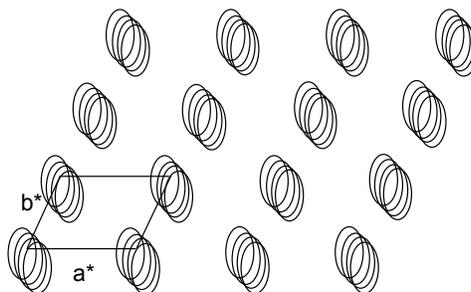
Crystallite Size Broadening

The Fourier transform (FT) from an infinite array of regularly spaced objects is an array of delta functions.

The FT from a finite length array is broadened.

The finite sizes of crystallites will broaden all orders of reflections equally in units of Q ($\propto d^*$)

- differing reciprocal space directions may have differing amounts of broadening, if crystallites dimensions are not isotropic on average



Crystallite Size Broadening can produce Lorentzian peak shapes (common) or Gaussian peak shapes (uncommon) or a combination of both.



Crystallite Size Broadening

$\Delta d^* = \text{constant}$

$$\Delta d^* = \frac{\Delta d}{d^2} = \frac{\Delta \theta \cot \theta}{d}$$

$$= \frac{\Delta 2\theta \cot \theta \sin \theta}{\lambda}$$

$$\Delta 2\theta = \frac{\lambda \Delta d}{d^2 \cos \theta}$$

See GSAS Manual, pp 158-167.

GSAS fits crystallite broadening with two profile terms:

- LX -> Lorentzian
- GP -> Gaussian

Relation between avg. size (p) and GSAS terms:

$$p = \frac{18000K\lambda}{\pi LX} \quad p = \frac{18000K\lambda}{\pi \sqrt{GP}}$$

$K \approx 1$ (Scherrer constant, related to crystal shape)

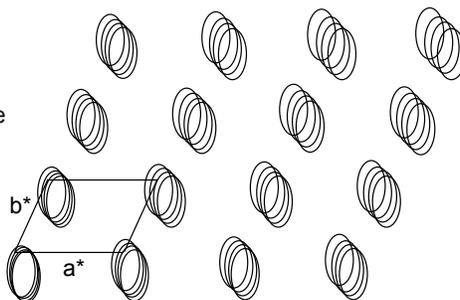


Microstrain Broadening

When a material has residual stresses present, some crystallites are compressed. This must be balanced by other crystallites that are stretched (because $\sum F=ma=0$)

This leads to a range of lattice constants.

The spread between diffraction locations for the maximum and minimum lattice constant increases linearly with Q ($\Delta Q/Q$ or $\Delta d/d = \text{constant}$)



Microstrain Broadening

$$\frac{\Delta d}{d} = \text{constant}$$

$$\frac{\Delta d}{d} = \frac{\Delta d^*}{d^*} = \Delta\theta \cot\theta$$

$$\Delta 2\theta = \frac{2\Delta d}{d} \tan\theta$$

GSAS fits strain broadening with two profile terms:

- LY -> Lorentzian (most common)
- GU -> Gaussian

(note that GU also has an instrumental contribution)

See GSAS Manual, pp 158-167.

Relation between strain (as percentage) and GSAS terms:

$$S = 100\% \frac{\pi}{18000} LY \quad S = 100\% \frac{\pi}{18000} \sqrt{GU - GU_I}$$

where GU_I accounts for the instrumental contribution

**Where Strain Differs by Reflection Class:
“Anisotropic peak broadening”**

Strain may be anisotropic

- think of a layered material where the layers can be pulled apart without much effort, but the layers themselves are quite “hard” (resistant to applied forces).
- Such a material will be “squishy” in the layer direction and rigid in the other two (more broadening in the squishy direction.)

Canonical anisotropic strain model: P. W. Stephens, *Journal of Applied Crystallography* **32**, 281 (1999).

- Restricts strain components in terms of 1st & 2nd-order terms allowed by lattice symmetry

Anisotropic strain broadening terms

Broadening – as variance

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L, H + K + L = 4$$

General expression – triclinic – 15 terms

$$\begin{aligned} \sigma^2(M_{hkl}) = & S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2) + \\ & 2(S_{310}h^3k + S_{103}hl^3 + S_{031}k^3l + S_{130}hk^3 + S_{301}h^3l + S_{013}kl^3) + \\ & 4(S_{211}h^2kl + S_{121}hk^2l + S_{112}hkl^2) \end{aligned}$$

Symmetry effects – monoclinic (b unique) – 9 terms

$$\begin{aligned} \sigma^2(M_{hkl}) = & S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3S_{202}h^2l^2 + 3(S_{220}h^2k^2 + S_{022}k^2l^2) + \\ & 2(S_{301}h^3l + S_{103}hk^3) + 4S_{121}hk^2l \end{aligned}$$

Anisotropic strain broadening terms

Symmetry effects – orthorhombic - mmm – 6 terms

$$\sigma^2(M_{hkl}) = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2)$$

Tetragonal – 4/mmm – 4 terms

$$\sigma^2(M_{hkl}) = S_{400}(h^4 + k^4) + S_{004}l^4 + 3S_{220}h^2k^2 + 3S_{202}(h^2l^2 + k^2l^2)$$

Cubic – m3m – 2 terms

$$\sigma^2(M_{hkl}) = S_{400}(h^4 + k^4 + l^4) + 3S_{220}(h^2k^2 + h^2l^2 + k^2l^2)$$

Trigonal, Rhombohedral & Hexagonal – it depends – 3 or 4 terms

Crystallographic Modeling

Why did Crystallography Revolutionize Science?

1. Crystallography was the first scientific technique that provided *direct* information about molecular structure
 - Early work was intuitive: structures assigned based on patterns and symmetry (some results predate X-rays!)
2. X-ray and neutron diffraction observations can be modeled very accurately directly when the molecular structure is known
3. Diffraction can provide a very large number of independent observations
 - probability of finding an incorrect structure model that is both plausible and is in good agreement with the diffraction observations is very small (but not zero!)
4. Computer-assisted least-squares optimization allows structural models to be improved, limited only by the quality of the data
5. Statistical and brute-force techniques overcome the incomplete nature of diffraction observations (direct methods vs. “the phase problem”).

100+ years later, no other technique offers as much power for learning about molecular structure!

Fitting crystallographic data -- what is it all about?

- § We perform an experiment:
 - Get lots of intensity and position measurements in a diffraction measurement: what do they tell us?
- § Obtain an unit cell that fits the diffraction positions (indexing)
- § “Solve the structure”: determine an approximate model to match the intensities
- § Add/modify the structure for completeness & chemical sense
- § Optimize the structure (model) to obtain the best fit to the observed data
 - This is usually done with Gauss-Newton least-squares fitting
 - Parameters to be fit are structural and may account for other experimental effects
- § Least Squares gives us a Hessian matrix; inverse is variance-covariance matrix which gives uncertainties in the parameters

Crystallography from powder diffraction: before Rietveld

How did crystallographers use powder diffraction data?

- § Avoided powder diffraction
- § Manually integrate intensities
 - discard peaks with overlapped reflections
- Or
 - rewrote single-crystal software to refine using sums of overlapped reflections

Simulation of powder diffraction data was commonly done

- § Qualitative reasoning: similarities in patterns implied similar structures
- § Visual comparison between computed and observed structure verifies approximate model
- § Fits, where accurate (& precise) models were rarely obtained

Error propagation was difficult to do correctly (but not impossible)

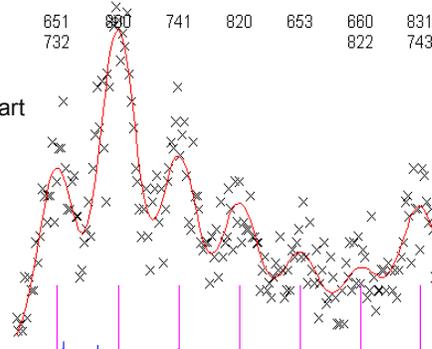
Hugo Rietveld's technique

§ Hugo Rietveld realized that if a pattern could be modeled, the fit between a computed pattern and observed data could be optimized.

- Similar to single-crystal diffraction, except that now “experiment dependent parameters” must now be fit as well.

- Background
- Peak broadening
- Lattice constants

- Must have approximate model to start
- Fewer data are available (usually)



Calculation of Powder Diffraction: Graphical Example

<i>hkl</i>	mult	D-space	F_{hkl}	phase
6,5,1	48	1.548	0.29	0
7,3,2	48	1.548	1.709	180
8,0,0	6	1.5236	29.45	0
7,4,1	48	1.5004	2.327	0
8,2,0	24	1.4781	3.703	0
6,5,3	48	1.4569	1.27	0
6,6,0	12	1.4365	0.242	180
8,2,2	24	1.4365	2.086	0
8,3,1	48	1.417	0.22	180
7,4,3	48	1.417	1.827	180

1) Generate reflection list

2) Compute F_{hkl} from model

3) Peak heights are generated from $|F_{hkl}|^2 \cdot \text{multiplicity}$

4) Convolute peaks & add background

5) Optimize model, peak widths, etc. to improve fit

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Hugo Rietveld in the Petten Reactor (~1987)

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<i>Single crystal fitting</i>	<i>Powder data fitting</i>
Minimize equation $\sum w_i [y_i - Y(x_i, \mathbf{p})]^2$ where	
Data: $y_i = F_{hkl}(\text{obs})$	y_i = observed powder diffraction intensities
Model: $Y(x_i, \mathbf{p}) = F_{hkl}(\text{calc})$	$Y(x_i, \mathbf{p})$ = computed diffraction intensities from ($F_{hkl}(\text{calc})$), background model, profile convolution, preferred orientation correction...
Parameters ($p_1, p_2, p_3 \dots p_m$): atomic coordinates, displacement (T) factors	+ lattice parameters + “experimental” parameters for peak shapes, background...

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Hugo Rietveld's other breakthrough

§ Based on intensities from the model, estimates for F_{hkl} can be made, even when reflections are completely overlapped:

Location 1:
20% to A
40% to B
40% to C

Location 2:
100% to C

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Rietveld Applications

- § Crystallographic structure determination
- § Quantify amounts of crystalline phases
 - (Amorphous content too, with neutrons)
- § Engineering properties
 - Residual stress
 - Preferred orientation
- § Lattice constant determination

What sort of data are needed for Rietveld Analysis?

- § Must be possible to fit peak shapes
- § Q range and resolution demands dictated by structural complexity
- § Data from lab instruments should be used *with caution* for structure determination
- § Neutron data are usually necessary for occupancy determination

***Disadvantage of Rietveld:
Many non-structural parameters need to be fit***

- § Background
 - fixed
 - functions
- § Peak shape
 - "fundamental parameters"
 - functions
- § Lattice constants
 - zero correction
 - flat plate terms
- § Scaling
 - Phase fractions
- § Structural parameters
 - atom positions
 - occupancies
 - displacement parameters
- § Preferential Orientation
- § Absorption

Powder diffraction offers fewer observations and worse peak-to-background than single crystal diffraction

Limitations of Rietveld

- § Rietveld can only discern parameters that have effects on the powder diffraction pattern
 - Cannot separate some effects ever
 - *Absolute configuration*
 - *Magnetic moment directions unless they break symmetry*
- § If two parameters have approximately the same effect on the powder diffraction pattern, they correlate and they cannot be differentiated (e.g. occupancies & displacement parameters)

The physics that determine peak profiles

Common factors

- § Instrumental Resolution
 - § Axial Divergence (Low Angle Asymmetry)
 - § Sample placement/transparency
 - § Crystallite Broadening*
 - § Strain Broadening*
- * Note that these effects can vary for different classes of reflections (anisotropic peak broadening)

Less common factors

- § Stacking faults*
 - § Modulated Structures*
 - § Coherence differing by atom type*
 - § Compositional inhomogeneity!
- * Hard to model
! Sometimes impossible to model

Results of these factors are convoluted to produce the observed peak shape.

Approaches to Profile Models

Three different approaches to reproducing peak shapes have been used:

- § Empirical functions
Functions are chosen simply because they are computationally simple and fit peaks well. The parameters cannot be interpreted because they have no relationship to the underlying physics of diffraction.
- § Physically-based parameters
Functions are based on the physical phenomena. Parameters are usually found empirically, but often have a physical meaning.
- § "Fundamental Parameters"
Functions and where possible parameter values are determined from diffraction physics. The only adjustable parameters are those related to sample properties.

Lorentz (Cauchy) and Gaussian Broadening Functions

Most instrument & sample broadening contributions are Lorentzian or Gaussian

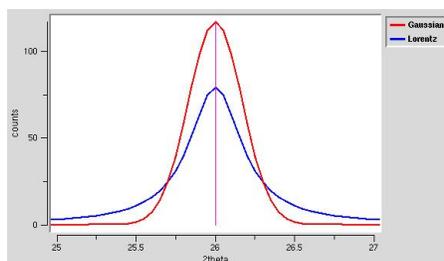
Normalized Gaussian

$$G(\Delta T, \Gamma_G) = \frac{1}{\sqrt{\pi} \Gamma_G} \exp \left[-\frac{4 \ln 2 (\Delta T)^2}{\Gamma_G^2} \right]$$

Normalized Lorentzian

$$L(\Delta T, \gamma_L) = \frac{2}{\pi \gamma_L} \frac{1}{1 + \left(\frac{2 \Delta T}{\gamma_L} \right)^2}$$

Note that peak widths vary so Γ_G and γ_L are both functions of Q



Gaussian & Lorentzian functions compared. Both curves have same FWHM & area, but note the much longer tails for the Lorentzian.

Voigt vs. Pseudo-Voigt

A Gaussian convoluted with a Lorentzian function is a Voigt function, however the Voigt is slow to compute and the derivatives are messy. Few Rietveld programs implement a Voigt.

The "pseudo-Voigt" is the weighted sum of a Gaussian & Lorentzian function – approximation is normally pretty good

Fractions of each function depend on the relative widths of each [see mixing factor (η) in GSAS manual, $\eta=0$ is Gaussian, $\eta=1$ is Lorentzian]

CW: Variation of FWHM with Q

Gaussian

§ U, V & W are Cagliotti terms, derived as instrument response function for CW neutron diffraction. Incomplete for x-rays.

§ P is a crystallite broadening contribution

Lorentzian

§ X is crystallite broadening

§ Y is strain broadening

$$\gamma = \frac{X}{\cos \Theta} + Y \tan \Theta$$

N.B. no instrumental broadening term

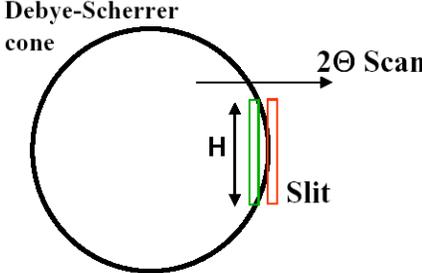
$$\Gamma_g^2 = U \tan^2 \Theta + V \tan \Theta + W + \frac{P}{\cos^2 \Theta}$$


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Axial Divergence (Low Angle Asymmetry)

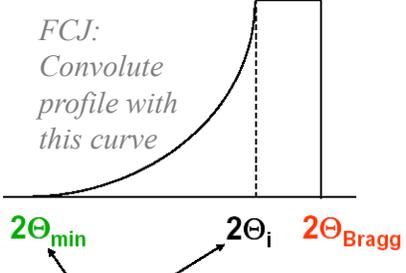
Work of Finger, Cox & Jephcoat, based on derivations by van Laar & Yelon

Debye-Scherrer cone



Depend on slit & sample "heights" wrt diffr. radius
H/L & S/L - parameters in function
 (typically 0.005 - 0.020)

FCJ: Convolute profile with this curve

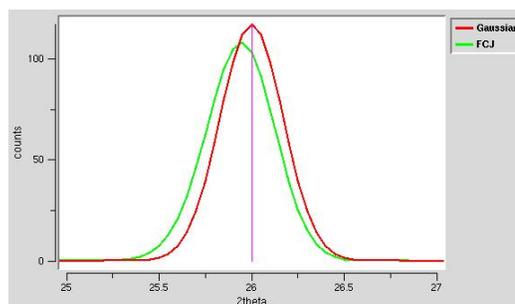



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F-C-J: Example

§ The Finger-Cox-Jephcoat correctly models the effective shift of the peak due to axial divergence.

Note: the “competition,” the split Pearson VII (empirical), does not model this effect at all!



Sample Displacement & Transparency

In **Bragg-Brentano geometry**, samples are ideally placed exactly at rotation axis and all diffraction occurs from sample surface (highly absorbing sample). Neither is commonly true.

§ Peak centers are shifted by

- Sample Displacement (SHFT), S_s
- Sample transparency (TRNS), T_s

$$\Delta T' = \Delta T + S_s \cos \Theta + T_s \sin 2\Theta$$

$$\text{displacement} = \frac{-\pi R S_s}{36000} \quad \mu_{\text{eff}} = \frac{-9000}{\pi R T_s}$$

R is diffractometer radius

*These corrections correlate very highly with the zero correction for 2θ , ZERO. **Do not refine this too.***

Parallel-Beam instruments (neutron or synchrotron) are very tolerant of displacement and transparency. Never refine SHFT or TRNS, but do refine ZERO (correction to 2θ).