

Getting Started with Rietveld



Getting Started with Rietveld

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Outline

- △ Why is crystallography unique?
- △ Crystallographic Literacy
- △ Diffraction from single crystals
- △ Diffraction from powders
- △ Powder Diffraction crystallography before Rietveld
- △ Hugo Rietveld's technique
- △ Rietveld Applications
- △ Requirements & Limitations

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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 overcomes 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!

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Crystallographic literacy

- △ The power of crystallography is such that its results are used in almost all areas of the physical and biological sciences; scientists need to understand the language of crystallography to utilize the literature.
- △ Rietveld analysis is a sophisticated form of crystallographic modeling that requires a strong understanding of these concepts

Subsequent sections of this talk will list (but not teach) key fundamental concepts in crystallography

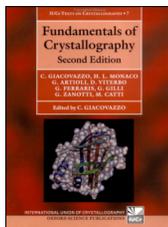
- My recommendation: **be sure that you understand these concepts before trying to do Rietveld analysis**

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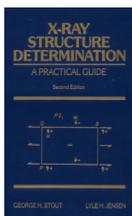
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Where to go for more...

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.]



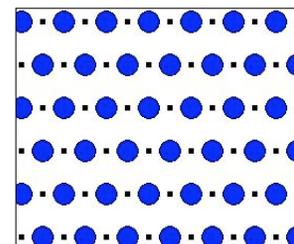
X-Ray Structure Determination: A Practical Guide (2nd Ed.), G. H. Stout, & L. H. Jensen (Wiley, 1989, ~\$150) [Focused on small-molecule single crystal techniques, dated, but very easy to read; very good explanations of fundamentals. Favorite of many in field, who started with this book.]

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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."

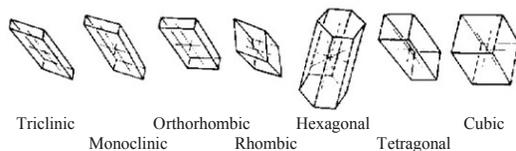
Commonly used phrases such as "lattice compound" or "interstitials in the lattice" misuse the concept of a lattice.



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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>)

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Lattice Types

- △ Lattice points may also be placed inside units cells (**body center**, **face centers**) giving rise the **14 Bravais lattices** (1848)

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 $a=b \neq c$ $\alpha=\beta=90^\circ$ $\gamma=120^\circ$	
MONOCLINIC $a \neq b \neq c$ $\alpha=\gamma=90^\circ$ $\beta \neq 90^\circ$	
TRICLINIC $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	

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

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

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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

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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 amongst the atoms inside a unit cell

- This allows the unit cell (and thus the entire structure) to be built from just a section of the unit cell
- The minimal section representative of the entire structure is called the **asymmetric unit**

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Types of Symmetry

△ 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>)

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Space Groups

△ Not all combinations of symmetry and lattice types are compatible

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

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

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

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For more information on space groups...

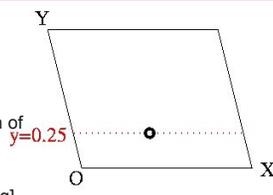
Δ I recommend *Space Groups for Solid State Scientists* by G. Burns and A. M. Glazer (Academic Press, New York, 1990).

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Fractional coordinates

Δ 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 ($\pm 2\sigma$)

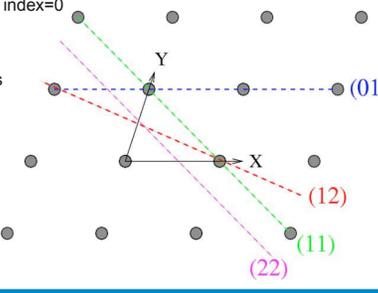
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Lattice planes

Δ General Indices: lattice planes are indexed by the inverse of where they cut each axis:
 - Intercept of 0.5 \rightarrow index=2
 - Intercept of ∞ (|| to axis) \rightarrow index=0

Δ Related concept: Miller indices
 - used for crystal faces
 - Contain no common factors

Δ Notation: [] defines a direction
 - [100] is along a axis



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Reciprocal Lattice

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

Δ This means that if we have two vectors:
 $\mathbf{r} = xa + yb + zc$ and $\mathbf{d}^* = ha^* + kb^* + lc^*$
 Then no cross-terms are needed for the dot product:
 $\mathbf{r} \cdot \mathbf{d}^* = hx + ky + lz$

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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Diffraction from single crystals

Δ 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:

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

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

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

Δ 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

Also, since $e^{i\phi} = i \sin\phi + \cos\phi$

- $F_{hkl} \propto \sum f_i [i \sin[2\pi(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2) + \sum f_i \cos[2\pi(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2)]$
- f_i represents the scattering power of an atom
- U_i represents the average displacement of an atom from its ideal site

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Atomic Scattering Power

Δ The scattering power (form factor, f) of an atom for X-rays depends on the number of electrons in the atom and Q

Δ The scattering power (scattering length, b) of an atom for neutrons depends on the isotope and is independent of Q

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Comparison of Neutron and X-ray Atomic Scattering

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Centrosymmetric Single Crystal Diffraction Intensities

- △ When all atoms are in pairs where x,y,z and -x,-y,-z (centrosymmetric with a center of symmetry at the origin)
- △ noting that
 - $e^{i\phi} = i \sin\phi + \cos\phi$ and
 - Also $\cos(-\phi) = \cos\phi$ while $\sin\phi = -\sin\phi$
 - This means $e^{i\phi} + e^{-i\phi} = 2 \cos\phi$
- △ This allows the simplification:
 - $F_{hkl} \propto \sum f_i \cos[2\pi(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2)$

Where now the sum only includes one atom in each pair

For this reason, crystallographic programs always want the center of symmetry at the origin for centrosymmetric space groups (Origin 2)

X-ray Structure Factors are the Fourier Transform of the Electron Density in a Crystal

- △ Electron density: $\rho(x,y,z)$ (probability of finding an electron at location x,y,z)

$$\rho(x,y,z) \propto \sum F_{hkl} \exp[-2\pi i(hx_i + ky_i + lz_i)]$$
- △ $\rho(x,y,z)$ and F_{hkl} are Fourier conjugates:

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

For neutrons $\rho(x,y,z)$ becomes a function of nuclear density weighted by the scattering lengths of the individual atoms

The Crystallographic Phase problem: we measure $|F_{hkl}|^2$ and do not know the phase. This limits our ability to use this relationship

Single crystal intensities are collected by orienting the crystal in multiple orientations with a detector to measure scattered intensities

How are Single-Crystal data used?

1. Collect $|F_{hkl}|$ for many reflections
2. Use Direct Methods or a Patterson map to come up with an approximate structure
3. Use Fourier computations to look for missing atoms.
 - △ Fourier uses phases computed from approximate structure
4. Optimize the model by minimizing the differences between the observed $|F_{hkl}|$ and values for F_{hkl} computed from the structural model

Repeat steps 3 & 4 as needed.

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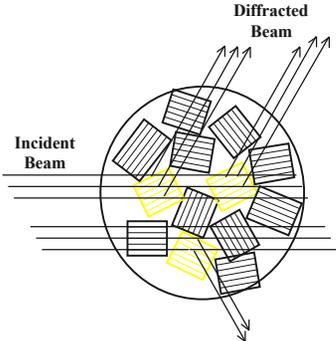
What if two materials are present?

- △ When a sample is composed of two or more crystalline phases the powder diffraction contains the weighted sum of the diffraction patterns from each phase
- △ Mixtures can be identified
- △ Peak areas allow amounts of each phase to be quantified

Diffraction from random polycrystalline material

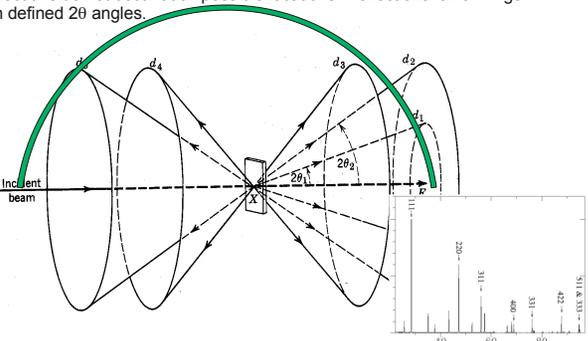
In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder), there are a large number of small crystallites.

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



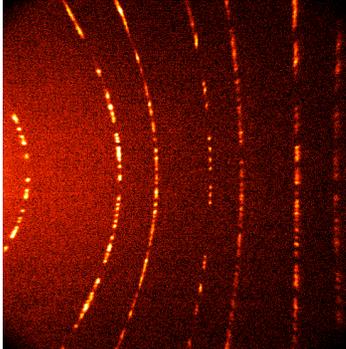
Bragg rings in powder diffraction

△ Reflections do not occur at all possible locations. Reflections fall on rings with defined 2θ angles.



What if we don't have an infinite number of crystals?

- △ When number of crystals is too small, the pattern becomes "grainy" -- diffraction from individual crystals dominates
- △ Diffraction intensities become unreliable
 - Increase sample size
 - Grind the sample to decrease domain size
 - Oscillate or rotate the sample
 - *Spinning does not help much*
 - Use area detection & integrate the entire ring.



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What if the crystals do not have random orientation?

If some crystal orientations are over- or under-represented, the intensities of lines will be increased or decreased

- in extreme cases, classes of lines can disappear

△ Preferred orientation

- Can be desired for engineering properties
- Occasionally beneficial for structure solution
- Usually problematic for Rietveld & quantitation

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Avoiding preferred orientation

- △ Grind samples
- △ Use rotating capillaries (synchrotron)
 - Bragg-Brentano spinning does not help at all!
- △ Do not smooth flat plate specimens
- △ Consult literature: (~5 decades worth)

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What about "bad crystals"?

- △ Crystals smaller than $\ll 1 \mu\text{m}$ can show broadening
- △ Twinning: not a problem
- △ Stacking faults: can add intensity in weird ways (see Diffax program)
- △ Poorly ordered materials: intensity falls off quickly (~ like extra-large Debye-Waller)

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What did people do before Rietveld?

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

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

Computation of powder diffraction data was commonly done; patterns could be used to verify a model was correct by seeing similarities

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Hugo Rietveld's technique

△ Hugo Rietveld realized that if a pattern could be modeled, the fit between these data and the a computed pattern 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
- Fewer data are available (usually)

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Graphical Rietveld Example

hkl	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 $|F_{hkl}|^2 * \text{multiplicity}$
- 4) Convolute peaks & add background
- 5) Optimize model, peak widths, etc. to improve fit

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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

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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

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Disadvantage of Rietveld: Many parameters need to be fit

- | | |
|----------------------------|----------------------------|
| △ Background | △ Scaling |
| – fixed | – Phase fractions |
| – functions | △ Structural parameters |
| △ Peak shape | – atom positions |
| – “fundamental parameters” | – occupancies |
| – functions | – displacement parameters |
| △ Lattice constants | △ Preferential Orientation |
| – zero correction | △ Absorption |
| – flat plate terms | |

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

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