



Argonne
NATIONAL LABORATORY

A Very Abbreviated Introduction to Powder Diffraction

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ENERGY

Outline

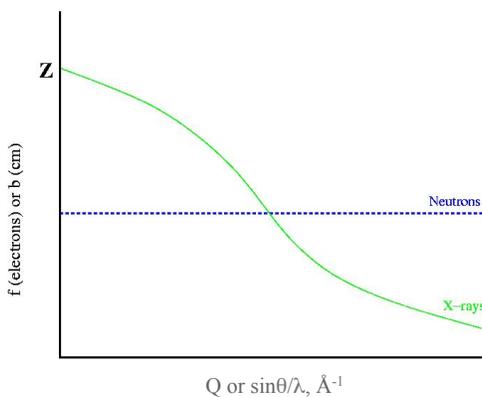
- Diffraction properties of atoms with x-rays and neutrons
- Diffraction from single-crystals vs. powders
- Why do we use powder diffraction?
- Materials effects in powder diffraction
- Instruments for powder diffraction collection
- Crystallographic analysis of powder diffraction data
- Appendices:
 - More on peak shapes
 - More on crystallography
 - Where to go for more information



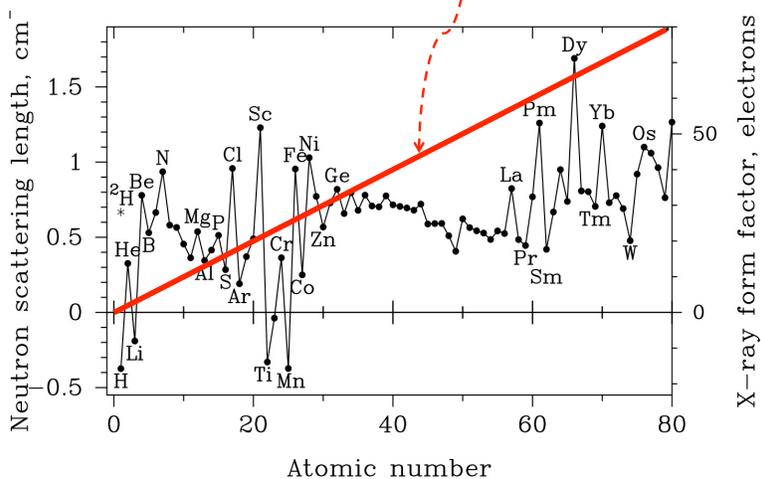
Coherent Atomic Scattering Power (diffraction)

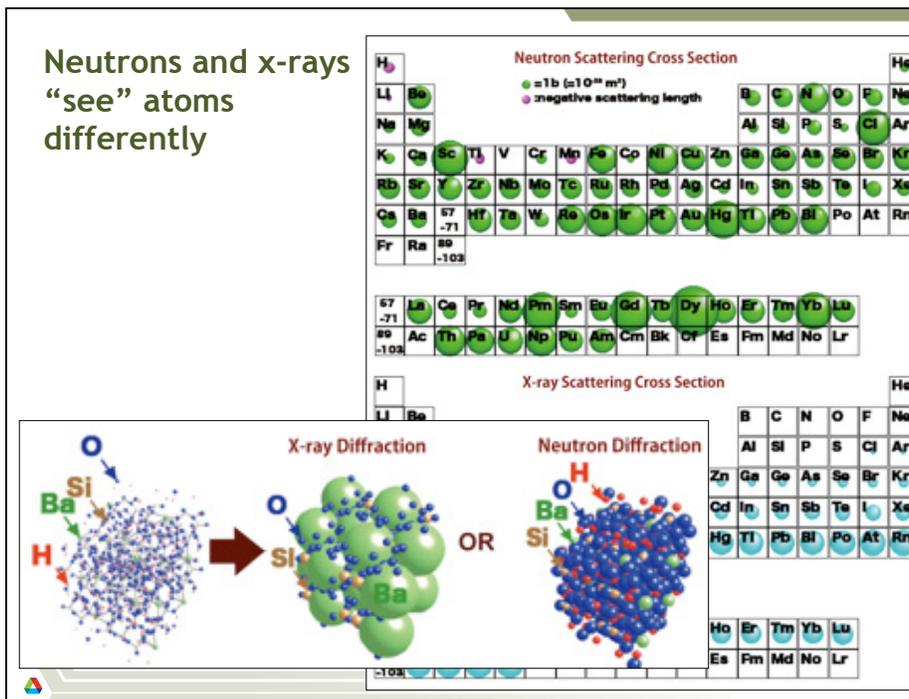
Structure factors: $F_{hkl} = n \sum f_i \exp[2\pi i(hx_i + ky_i + tz_i)] \exp(-U_i Q^2/2)$

- **X-rays:** The scattering power (form factor, f_i) of an atom depends on the number of electrons in the atom and Q ($Q \propto \sin\theta/\lambda$)
 - X-ray scattering changes near absorption edges
- **Neutrons:** The scattering power (scattering length, b_i) 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 b (f) as negative
 - Some isotopes atoms have neutron resonances (similar to x-rays)
 - Magnetic scattering is from electrons; $f_M(Q)$ similar to x-rays



Comparison of Neutron and X-ray Atomic Scattering Powers





Incoherent and inelastic scattering

Incoherent and inelastic scattering create background. *This is usually significant only with neutrons and most commonly for powder (less so single crystal) diffraction*

With neutrons, some type of atoms have large incoherent cross sections (phase is lost during the scattering).

Hydrogen (not deuterium) is the poster child for this: it has a huge incoherent scattering cross-section (~ 80 barns) that tends to overpower coherent scattering (typically < 1 barns for most atoms). Samples with more than a few atom % (not mass %) will have a significant background.

Hydrogen



Incoherent



Coherent

Deuterium



Incoherent



Coherent

Resonant scattering: scattering at a resonance edge causes atoms to “light up”

Experiments are sometimes performed at wavelengths close to absorption edges to enhance the scattering from particular elements

X-rays

The x-ray form factor has in fact three components:

- $f(Q) + f'(\lambda) + i f''(\lambda)$
 - f is determined by Q and the number of electrons in an atom and is independent of wavelength
 - f' and f'' are small except at wavelengths very close to an atom's absorption edge

At wavelengths close to an edge absorption becomes high; fluorescence occurs above the edge.

Neutrons

Scattering lengths for most atoms are wavelength-independent.

A similar “resonant scattering” type experiment can sometimes be performed comparing samples containing different isotopes (\$\$ to \$\$\$\$\$)

A few isotopes (mostly lanthanides and actinides) have adsorption edges at accessible wavelengths.

- This is usually a curse rather than a blessing: it makes TOF neutron scattering hard to analyze



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Single-crystal vs. Powder Diffraction



Single crystal diffraction: the movie

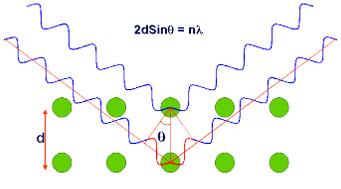


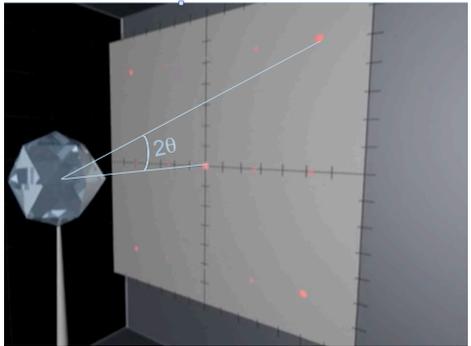
Video from Diamond synchrotron (U.K.)

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Bragg scattering in single crystals

- Reflection positions (Bragg's law)





Note that d above is a reciprocal space quantity (actually $d = 1/d^*$), $|\mathbf{d}^*| = |h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*|$,
 better: $\lambda = 4 \pi \sin\theta / Q$

- Reflection intensities are related to the square of "structure factor", F_{hkl}

$$F_{hkl} \propto \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \exp(-U_j Q^2/2)$$

sum over all atoms in the crystal (or unit cell).

x_j, y_j, z_j : position of atom in unit cell
 U_j : atom displacements
 f_j (or b_j): scattering power of atom

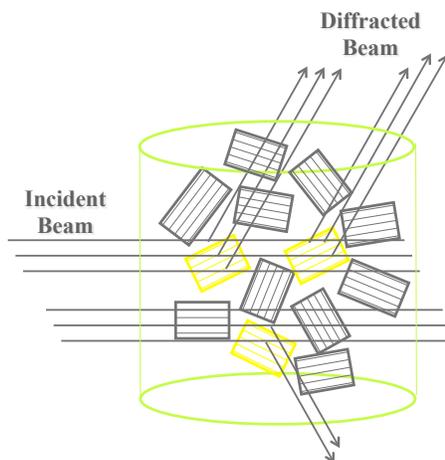
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Diffraction from random polycrystalline material

In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder) contains a very large number of crystallites.

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

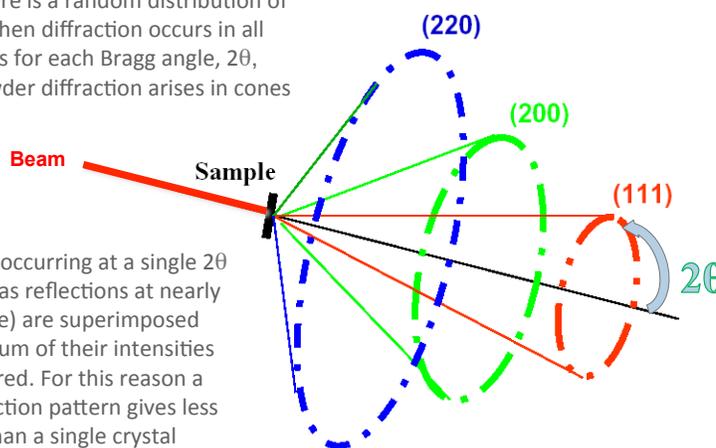
Diffraction occurs only at specific angles, those where Bragg's Law is satisfied.

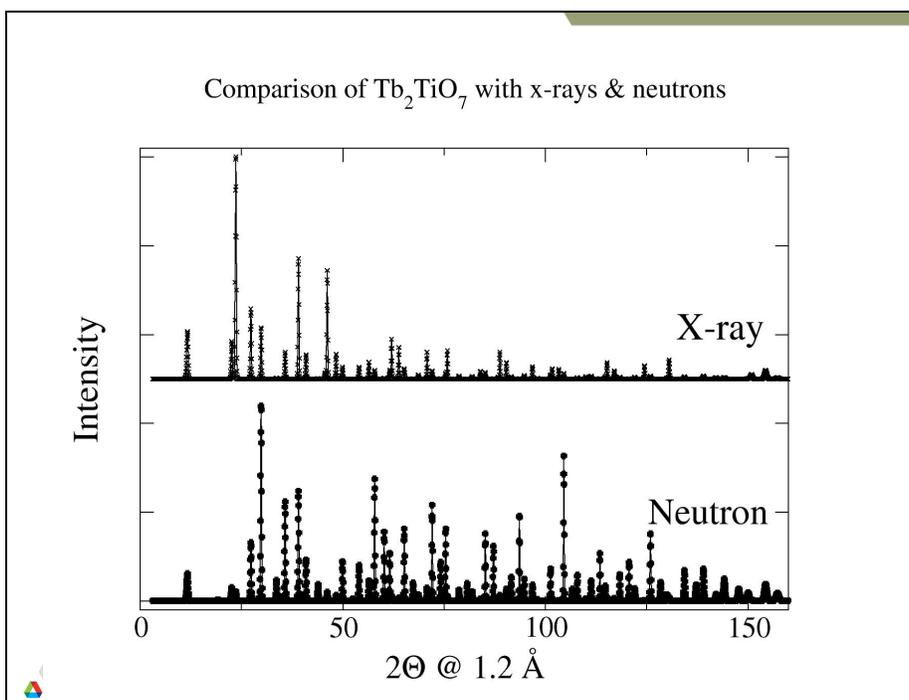
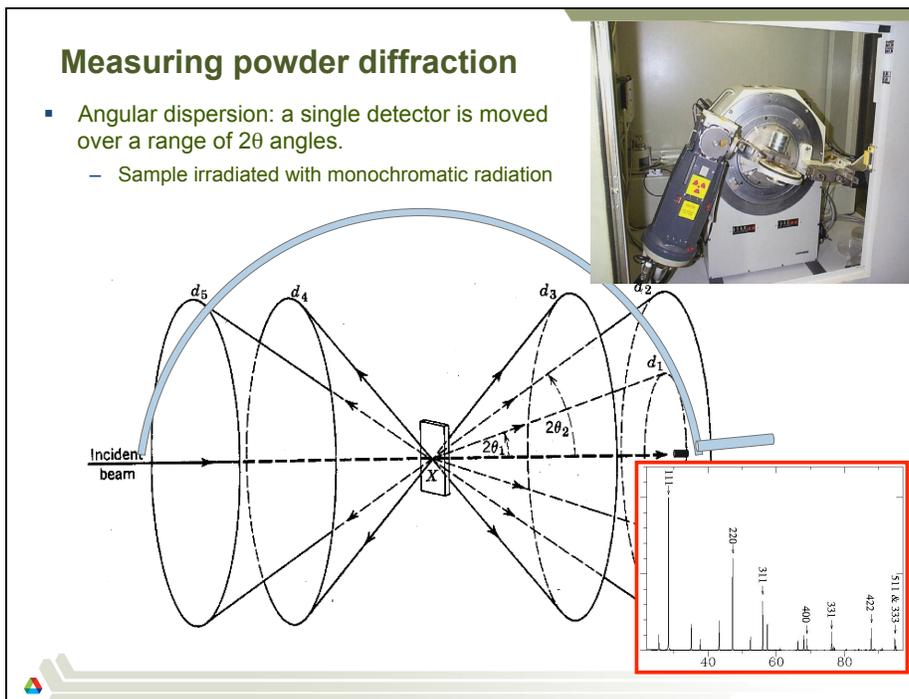


Bragg cones in powder diffraction

Since there is a random distribution of crystals then diffraction occurs in all directions for each Bragg angle, 2θ , thus powder diffraction arises in cones

All reflections occurring at a single 2θ value (as well as reflections at nearly the same value) are superimposed and only the sum of their intensities can be measured. For this reason a powder diffraction pattern gives less information than a single crystal measurement





Why do we do powder diffraction?

- Learn where the atoms are (single crystals, when available and appropriate, are better for this.)
- Determine the chemical phase(s) in a sample
- Measure lattice constants
- Quantify the components of a mixture
- Learn about physical specimen characteristics such as stress, preferred orientation or crystallite sizes
- Occupancies of elements amongst crystallographic sites (usually needs neutrons)

A Conceptual Basis for Understanding Materials Effects in Powder Diffraction

Materials effects on Powder Diffraction

For real materials, the powder diffraction pattern shows not only the crystal structure, but also shows microstructure details:

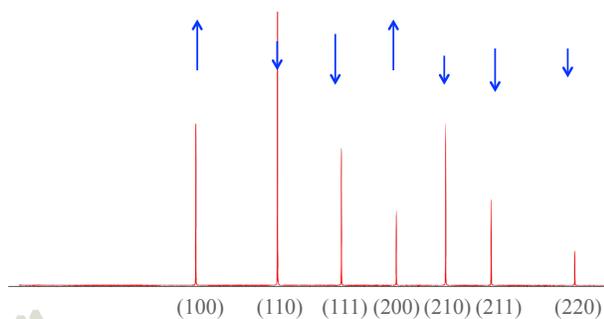
- How the crystallites are oriented, if not random (texture)
- The average sizes of the crystallites (peak broadening)
- Residual stress (peak broadening)

Less commonly:

- Stacking faults
- Modulated structures
- Extinction
- Compositional inhomogeneity
- Differences in ordering by atom type

Texture (non-random arrangement) affects reflection intensities

- Crystallite orientation will increase the intensity of reflections in orientations that are over-represented and will decrease other reflections
- If we have an overabundance of crystals aligned in along the (100) face, the reflections in that direction will have enhanced intensity

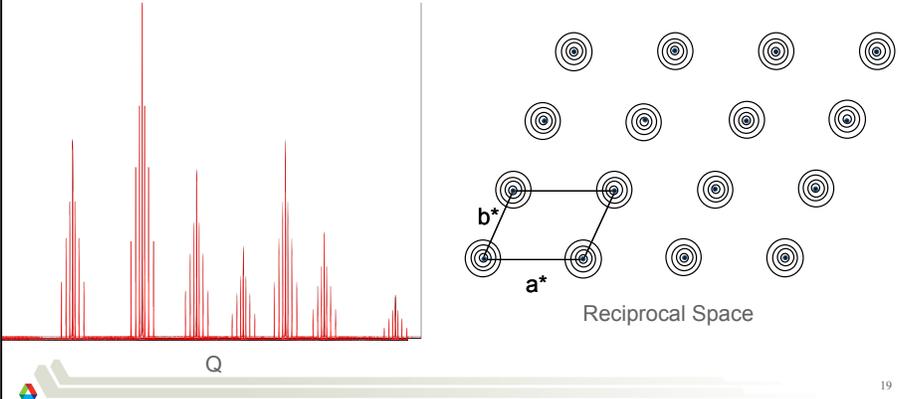


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Crystallite (size) broadening

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; all maxima are broadened equally in Q (or d).



The diagram illustrates the effect of finite crystallite size on diffraction. On the left, a plot shows a series of sharp peaks for an infinite array and broader peaks for a finite array. On the right, a reciprocal lattice is shown with a grid of points. For a finite array, each point is represented by a circular spot, indicating broadening in reciprocal space. The axes are labeled a^* and b^* .

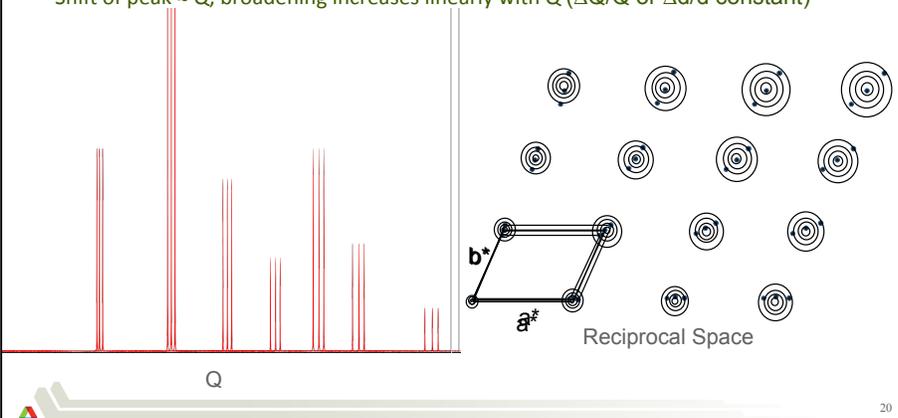
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Microstrain (residual stress) broadening

Strain & stress changes the lattice constants of a material

- In a material with residual stress
 - some crystallites are under tension,
 - others are compressed

Shift of peak $\approx Q$, broadening increases linearly with Q ($\Delta Q/Q$ or $\Delta d/d$ constant)



The diagram illustrates the effect of microstrain on diffraction. On the left, a plot shows a series of sharp peaks for a material with no strain and broader, shifted peaks for a material with residual stress. On the right, a reciprocal lattice is shown with a distorted grid of points, indicating broadening and shifting in reciprocal space. The axes are labeled a^* and b^* .

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Comparison of microstrain and crystallite broadening

Crystallite broadening

- $\Delta Q \approx \Delta d^* = \text{constant}$

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

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

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

Microstrain broadening

- $\Delta Q/Q \approx \Delta d^*/d^* = \text{constant}$

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

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

$$\Delta 2\Theta = k \tan \Theta$$

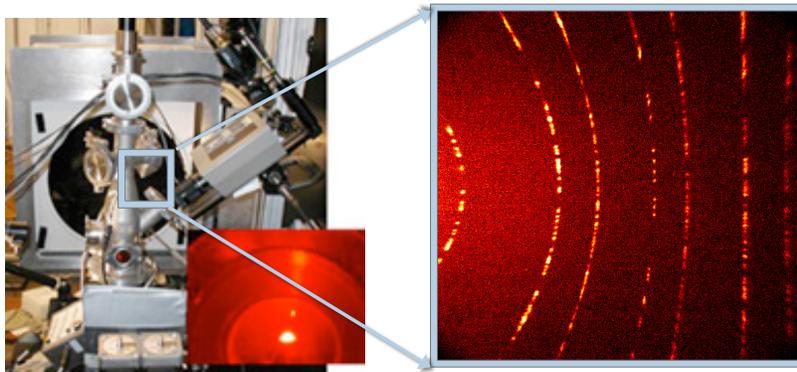
See GSAS Manual, pp 158-167.

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Types of Powder Diffraction Measurements

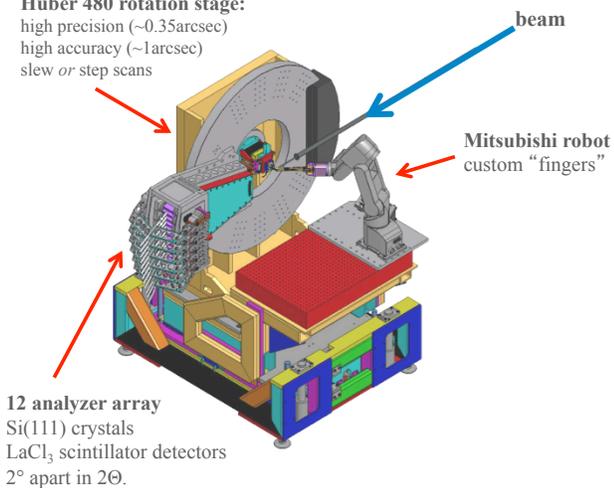
Area Detection

- With an area detector, a complete powder diffraction pattern can be collected in a fraction of a second.
 - Fast
 - Medium resolution
 - High background



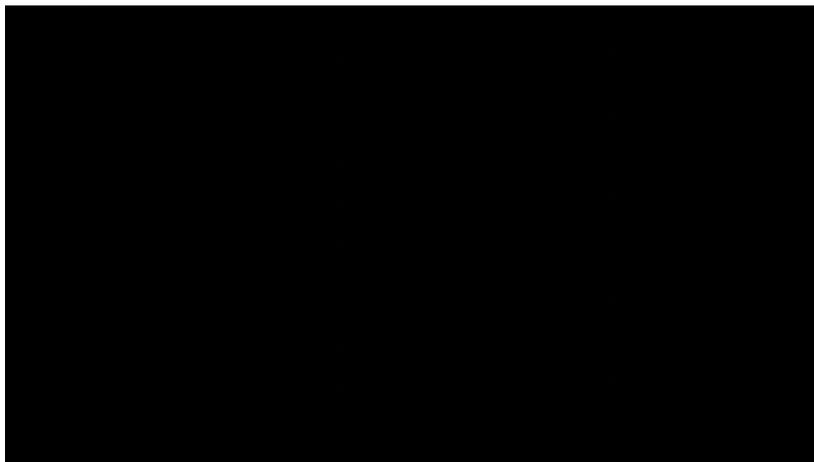
Highest resolution requires high collimation. Optimal is a crystal analyzer between the sample and detector: 11-BM Diffractometer

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



Complete pattern is measured in <1 hour

11-BM Robotic Data Collection

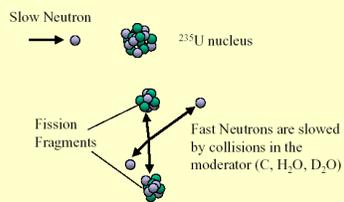


(Matt Suchoel: <http://youtu.be/sowojskY7c4> or search APS 11-BM on YouTube)

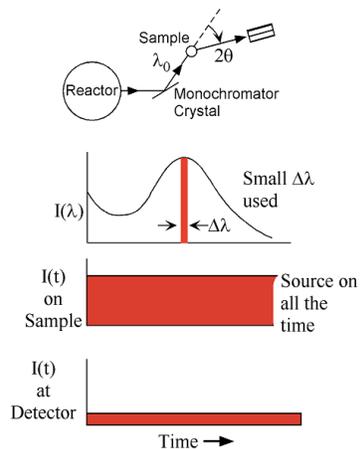
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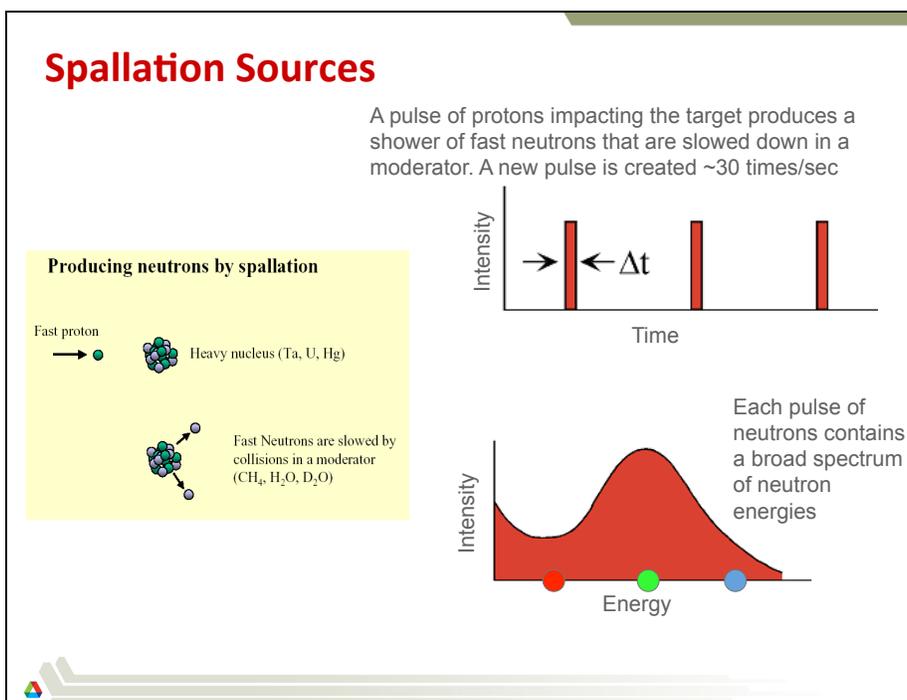
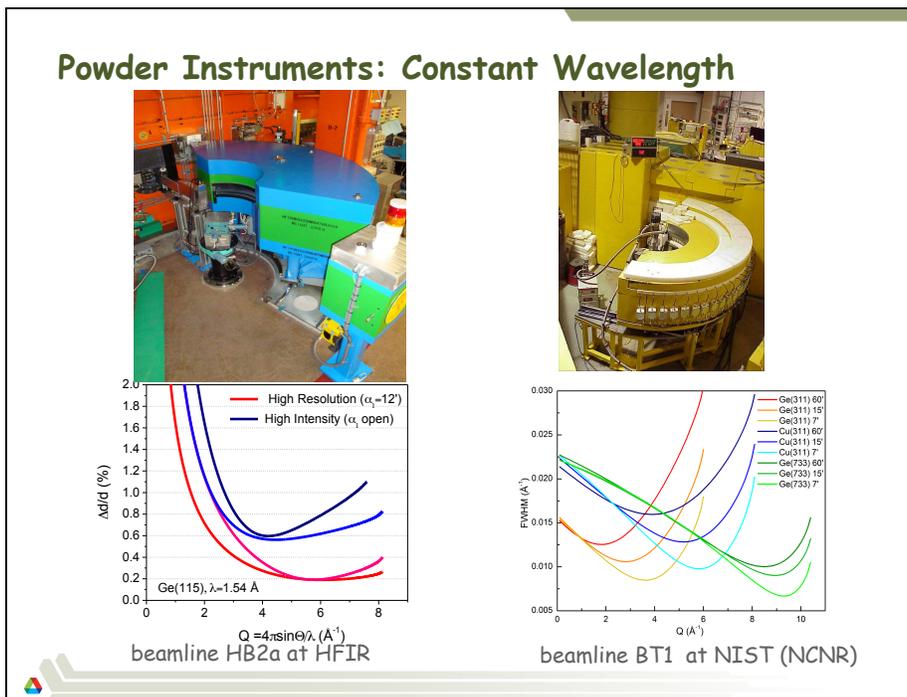
Reactor Source Neutron Diffraction

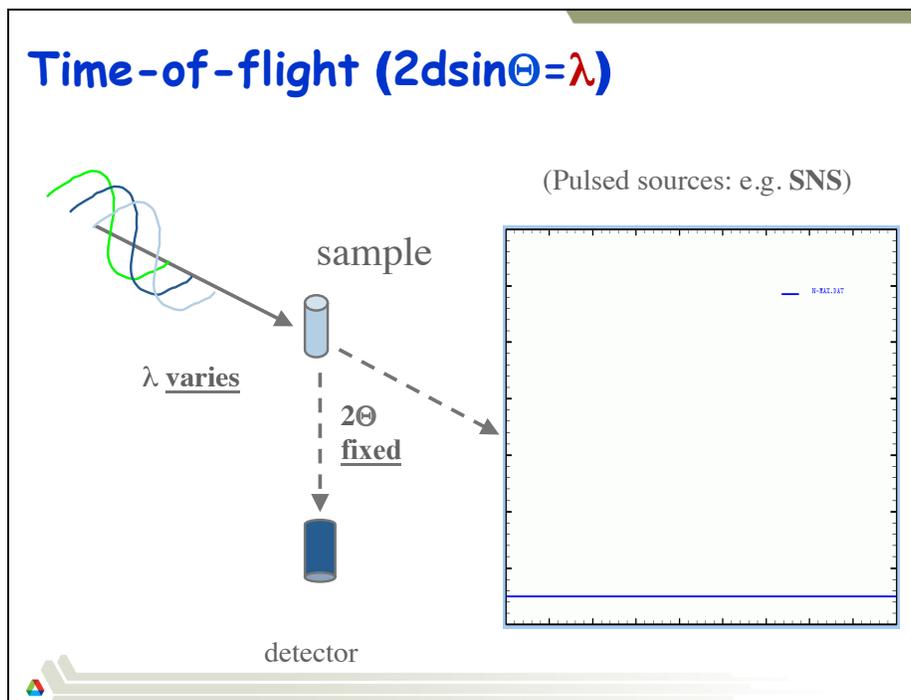
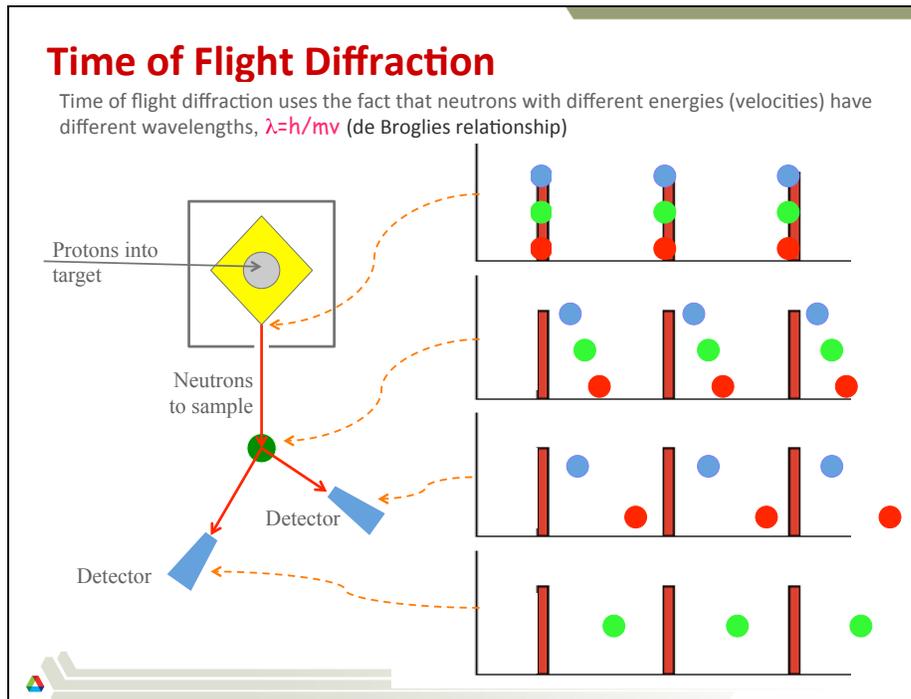
Producing neutrons by fission



STEADY STATE TECHNIQUE







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)

3rd Generation TOF Instruments: High Intensity and High Resolution

SNS: POWGEN[-3]

GEM (ISIS TS-I)

WISH
A high-resolution magnetic diffractometer for TS-II

Super HRPD (JSNS)

Fitting of Powder Diffraction Data (Rietveld Analysis)

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!

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

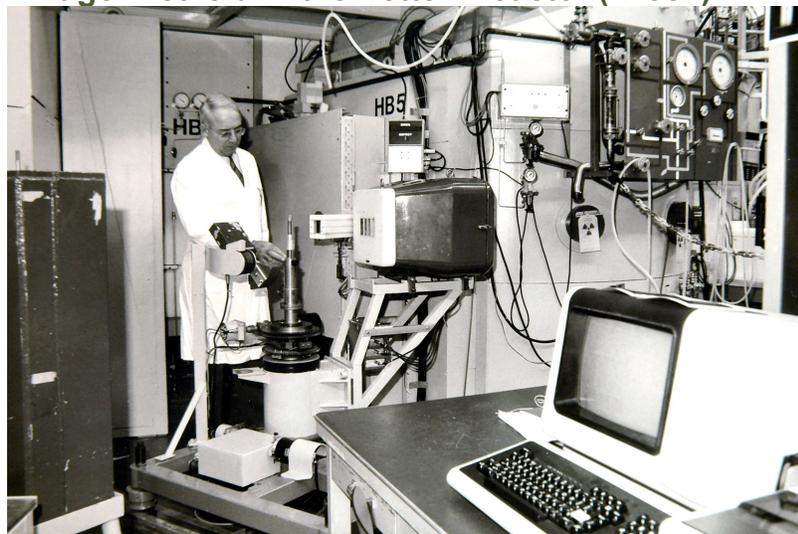
- Hugo Rietveld realized that if a pattern could be modeled, the fit between a computed pattern and observed data could be optimized.
 - Similar to single-crystal diffraction, except that now “experiment dependent parameters” must now be fit as well.
 - Background
 - Peak broadening
 - Lattice constants
 - 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

Hugo Rietveld in the Petten Reactor (~1987)



Single crystal fitting

Minimize equation $\sum w_i [y_i - Y(x_i, \mathbf{p})]^2$ where

Data: $y_i = F_{hkl}(\text{obs})$

Model: $Y(x_i, \mathbf{p}) = F_{hkl}(\text{calc})$

Parameters ($p_1, p_2, p_3 \dots p_m$):
atomic coordinates,
displacement (T) factors

Powder data fitting

y_i = observed powder diffraction intensities

$Y(x_i, \mathbf{p})$ = computed diffraction intensities from ($F_{hkl}(\text{calc})$), background model, profile convolution, preferred orientation correction...

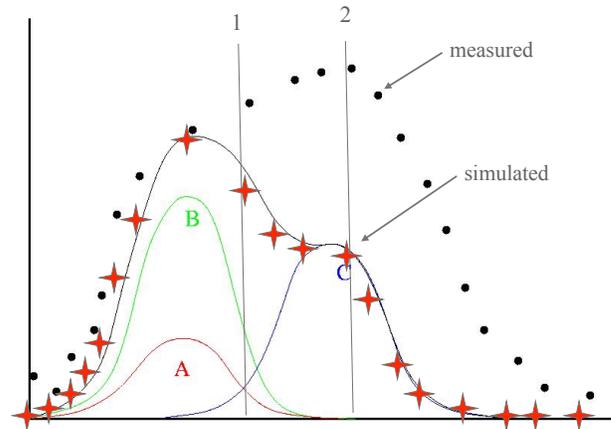
+ lattice parameters
+ "experimental" parameters for peak shapes, background...

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



Rietveld Applications

- Crystallographic structure determination
- Quantify amounts of crystalline phases
 - (Amorphous content possible indirectly)
- Engineering properties
 - Residual stress/Crystallite sizes
 - 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
 - Some things cannot ever be determined from powder diffraction:
 - Absolute configuration
 - “in symmetry plane” magnetic moment directions
- 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)

