



Argonne  
NATIONAL LABORATORY

## A Very Abbreviated Introduction to Powder Diffraction

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ENERGY

### Outline

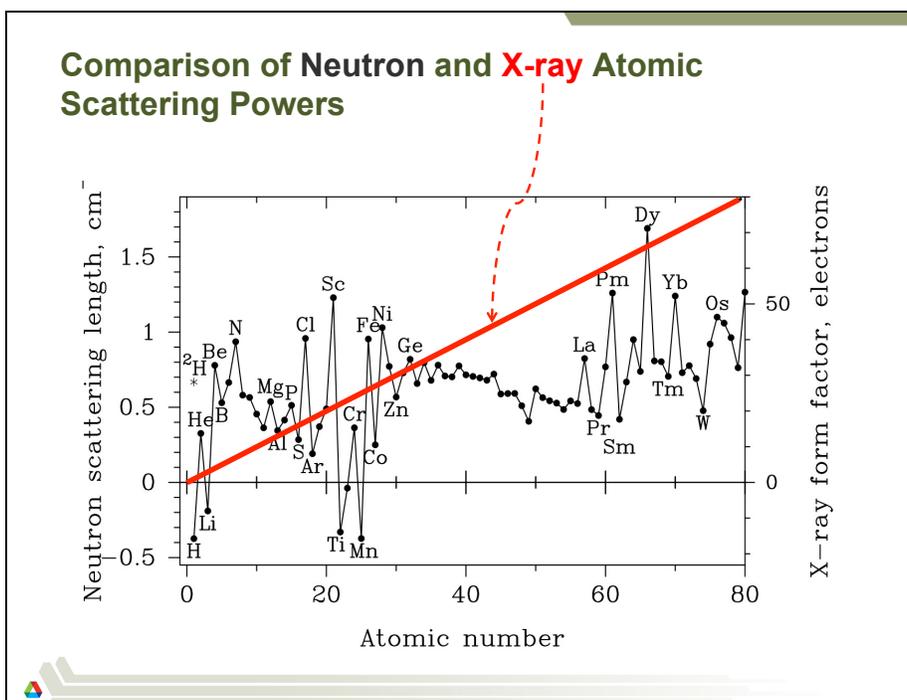
- Diffraction properties of atoms with x-rays and neutrons
- Diffraction from single-crystals vs. powders
- Why do we use powder diffraction?
- Materials effects in powder diffraction
- Instruments for powder diffraction collection
- Crystallographic analysis of powder diffraction data
- Appendices: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

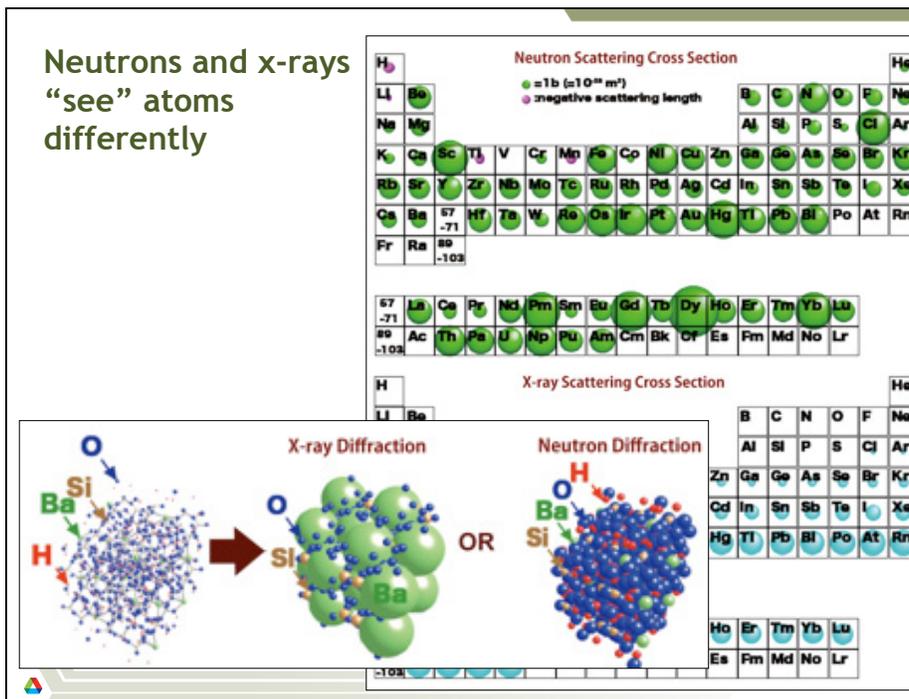


### Coherent Atomic Scattering Power (diffraction)

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





## 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 ( $\sim 80$  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

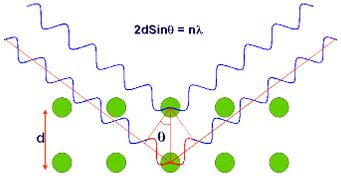


Video from Diamond synchrotron (U.K.)

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### Bragg scattering in single crystals

- Reflection positions (Bragg's law)
 

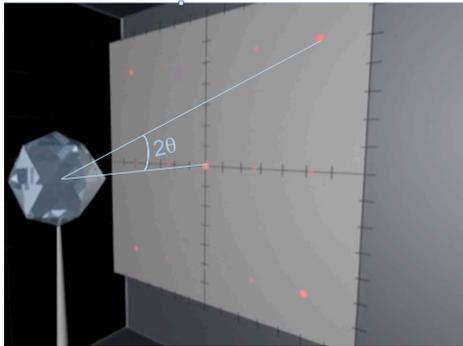


Note that  $d$  above is a reciprocal space quantity (actually  $d = 1/d^*$ ),  $|\mathbf{d}^*| = |h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*|$ ,  
 better:  $\lambda = 4 \pi \sin\theta / Q$

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

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

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



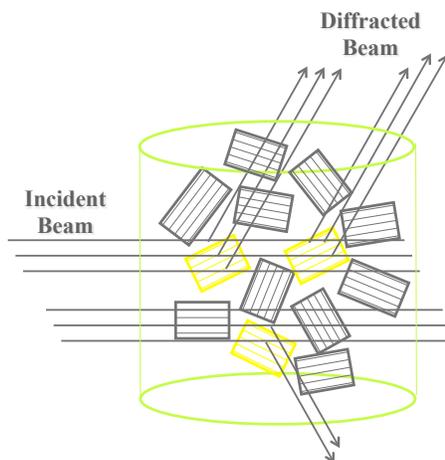
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### Diffraction from random polycrystalline material

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

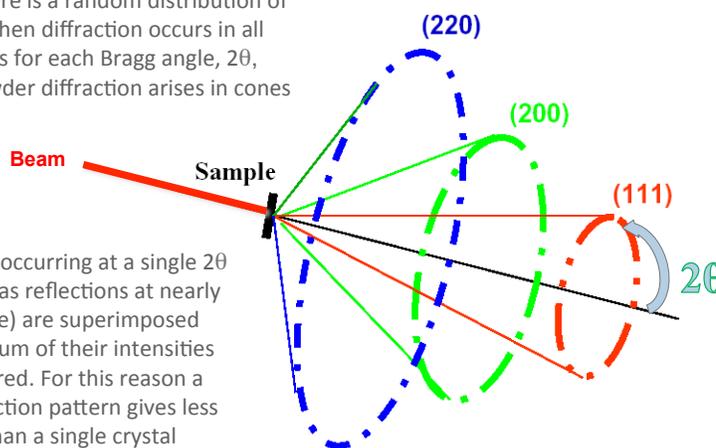
Diffraction occurs only at specific angles, those where Bragg's Law is satisfied.

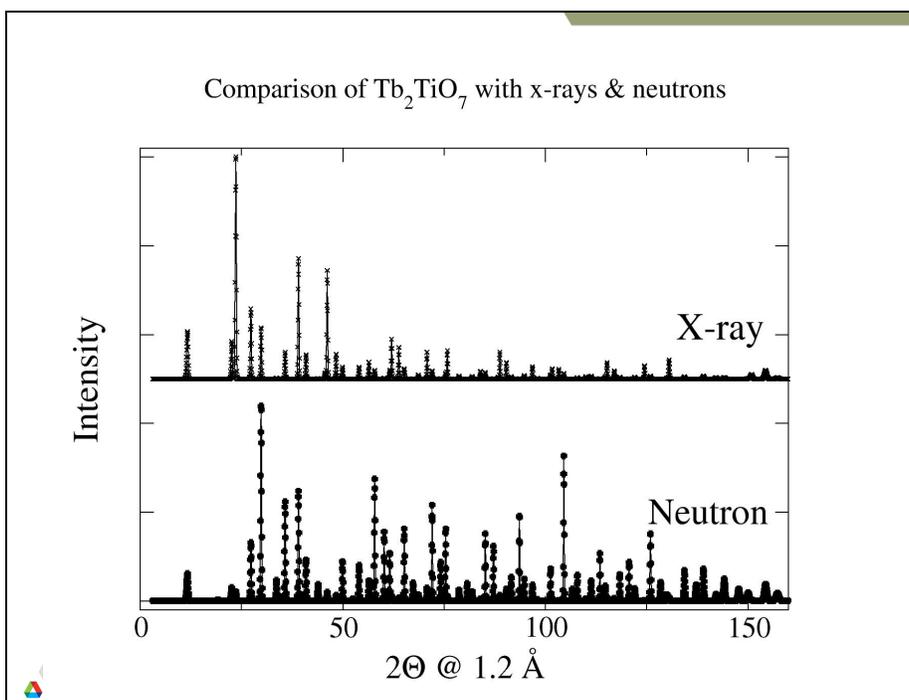
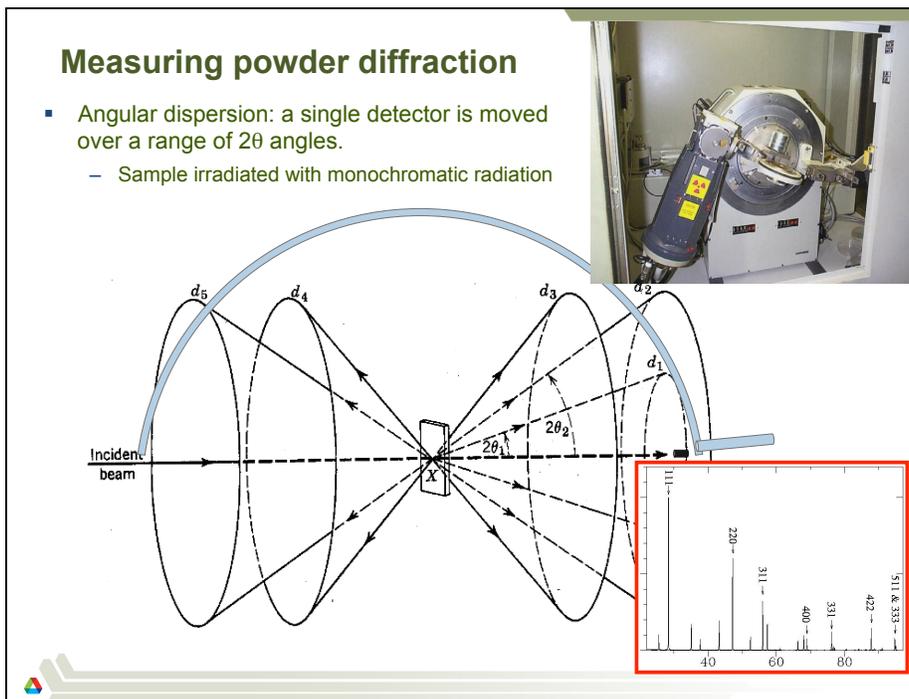


### Bragg cones in powder diffraction

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

All reflections occurring at a single  $2\theta$  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:

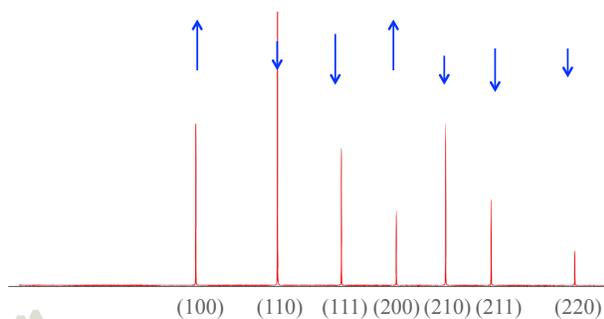
- How the crystallites are oriented, if not random (texture)
- The average sizes of the crystallites (peak broadening)
- Residual stress (peak broadening)

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

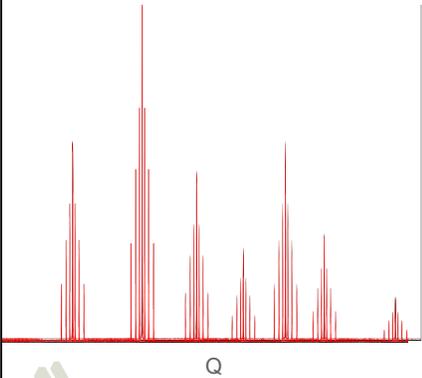
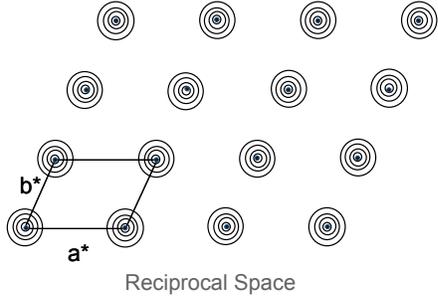


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### Crystallite (size) broadening

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).

Reciprocal Space

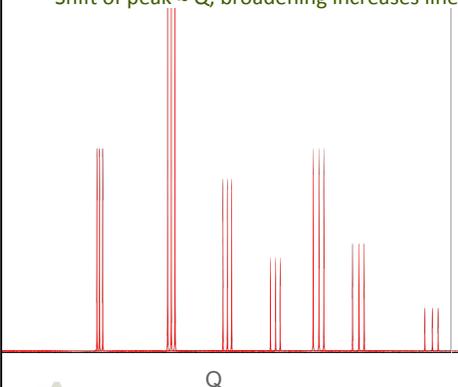
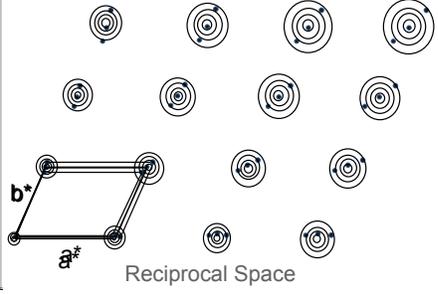
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### Microstrain (residual stress) broadening

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)

Reciprocal Space

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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

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

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

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

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

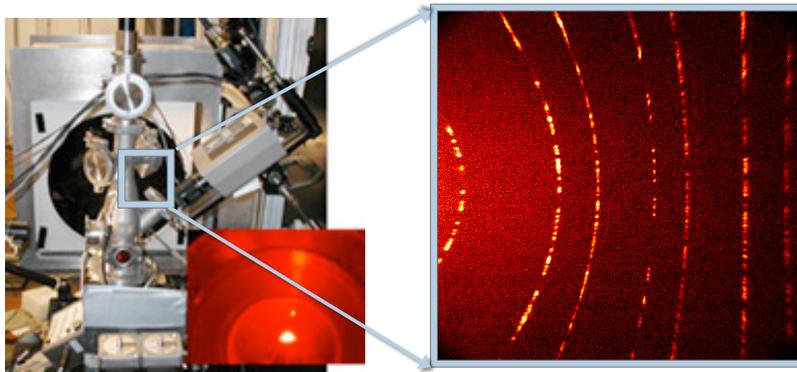
See GSAS Manual, pp 158-167.

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## Types of Powder Diffraction Measurements

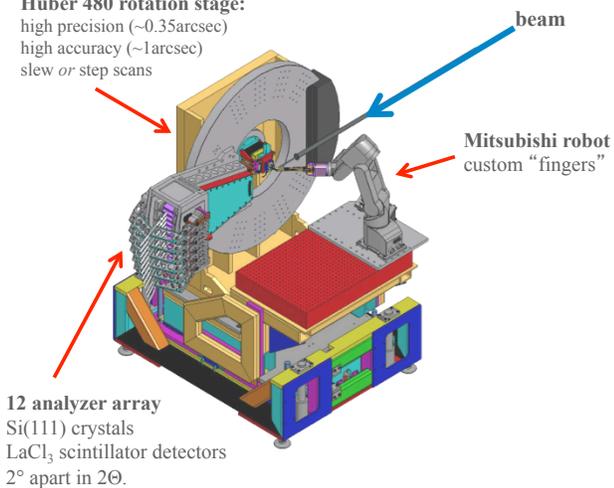
### Area Detection

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



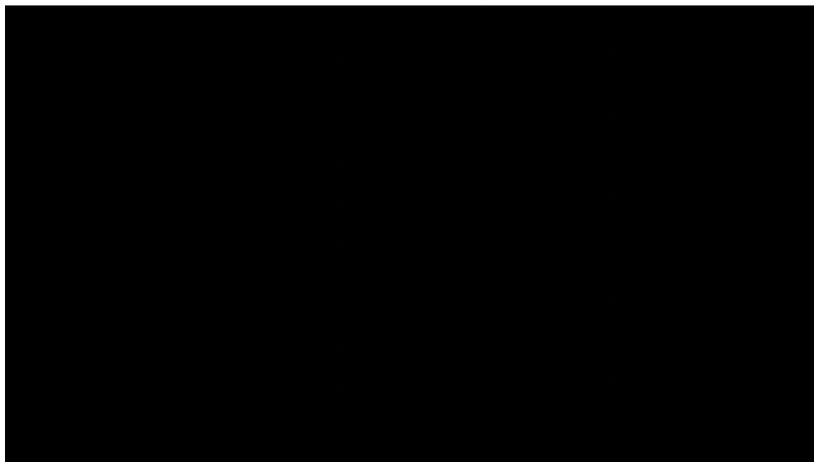
### *Highest resolution requires high collimation. Optimal is a crystal analyzer between the sample and detector: 11-BM Diffractometer*

**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

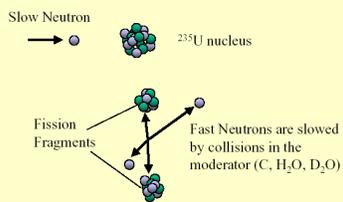


(Matt Suchoel: <http://youtu.be/sowojskY7c4> or search APS 11-BM on YouTube)

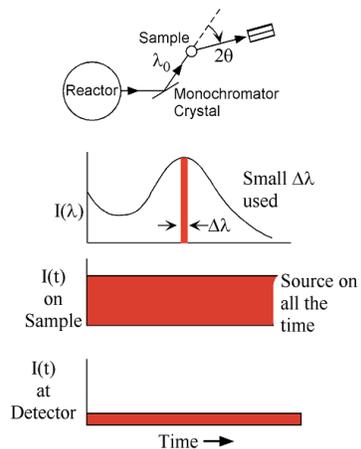
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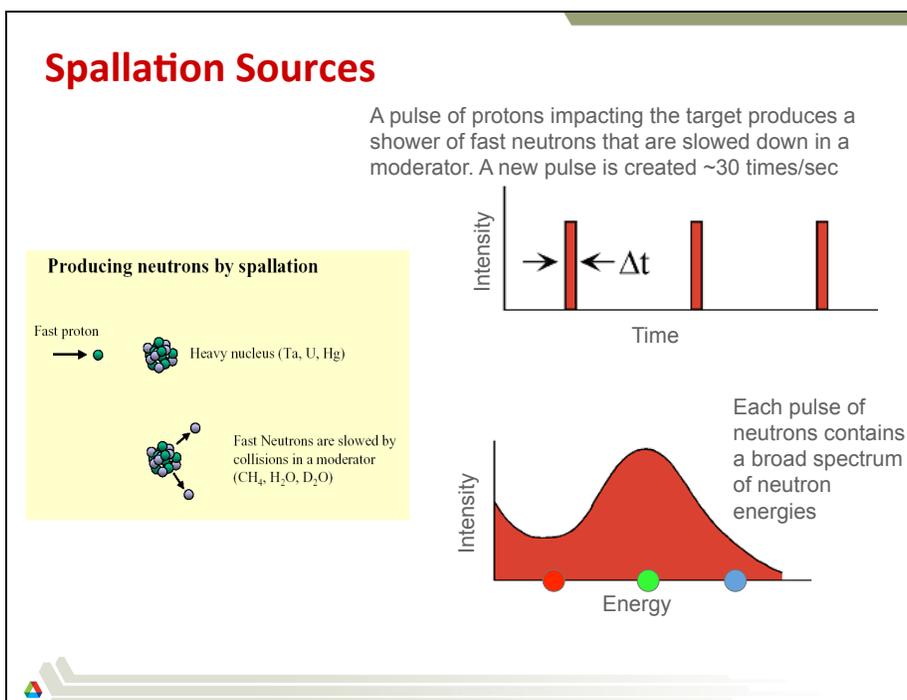
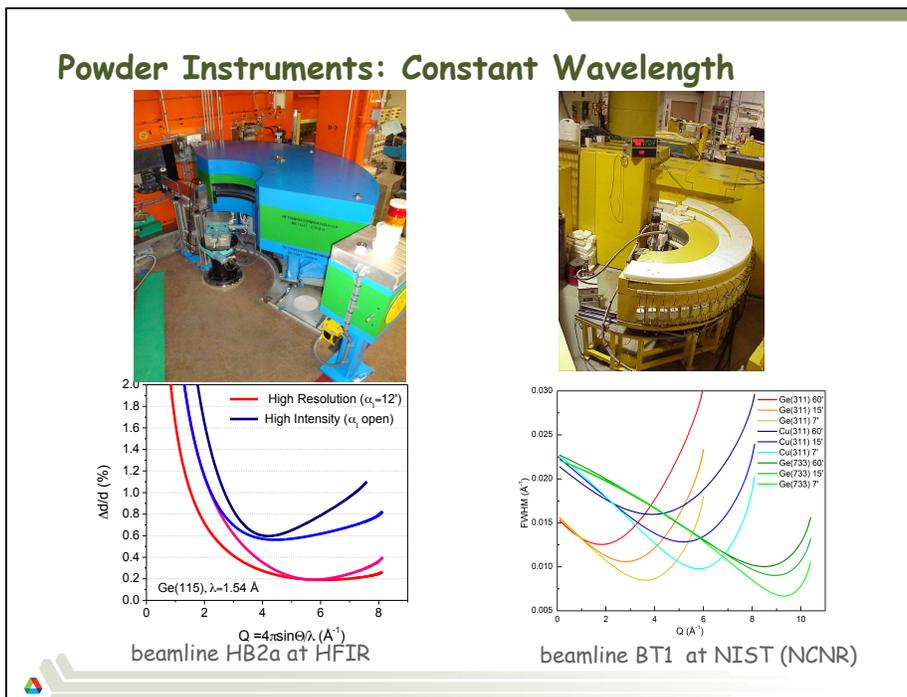
## Reactor Source Neutron Diffraction

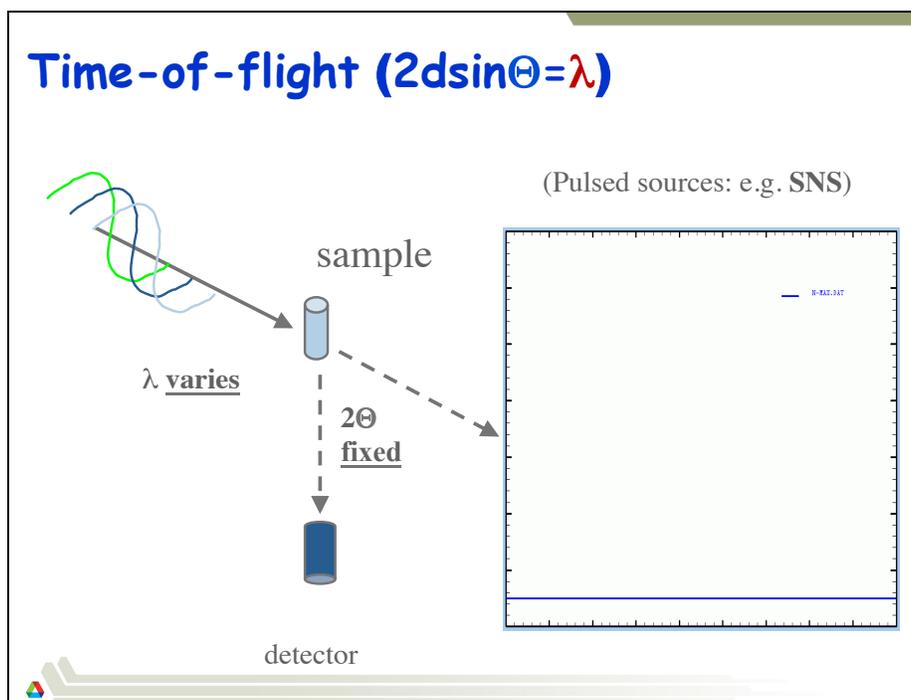
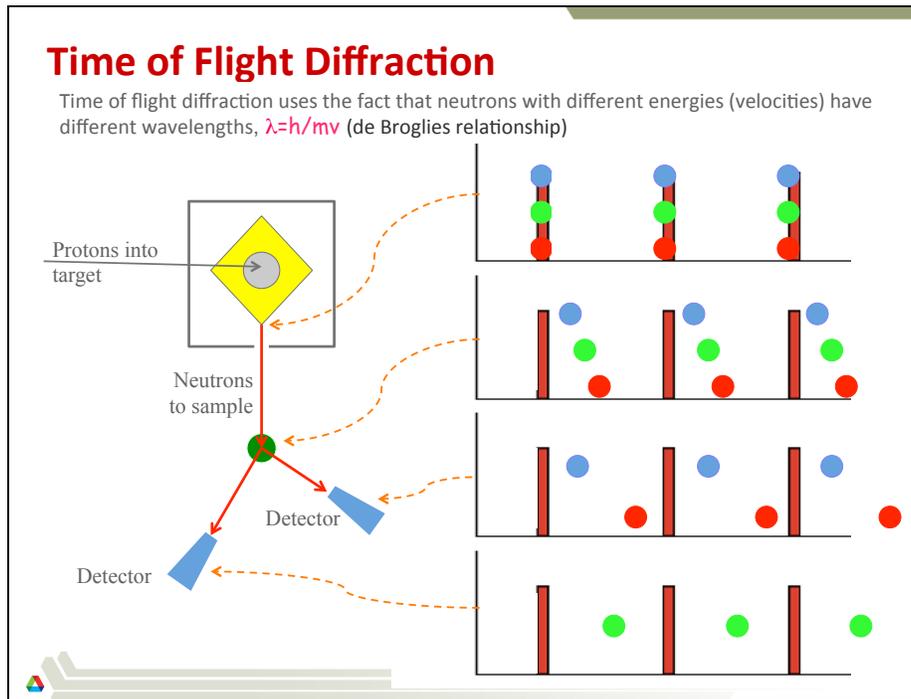
### Producing neutrons by fission



### STEADY STATE TECHNIQUE

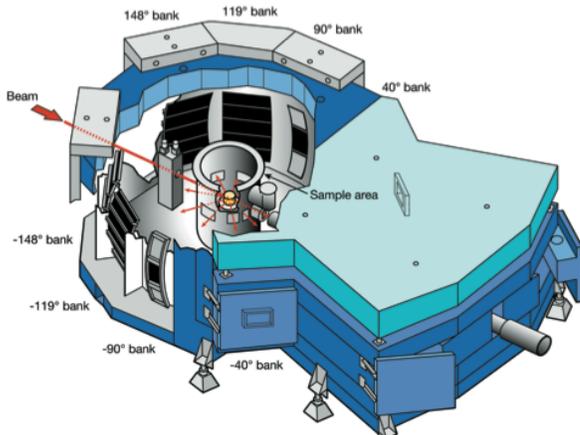






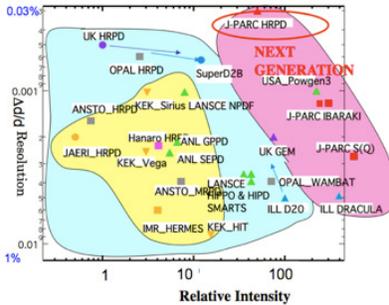
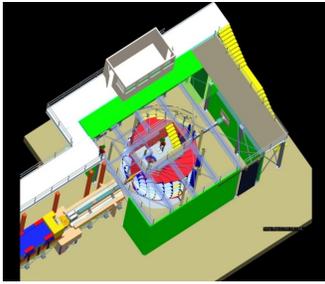
### Neutron Powder Diffraction with Spallation Source

- 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

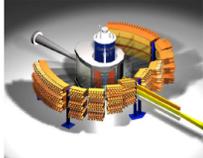



SNS: POWGEN[-3]

**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

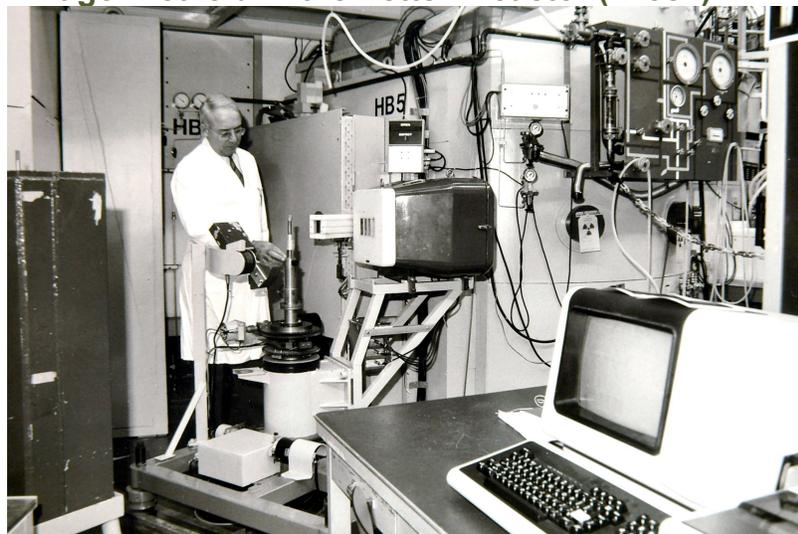
- Hugo Rietveld realized that if a pattern could be modeled, the fit between a computed pattern and observed data could be optimized.
  - Similar to single-crystal diffraction, except that now “experiment dependent parameters” must now be fit as well.
    - Background
    - Peak broadening
    - Lattice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

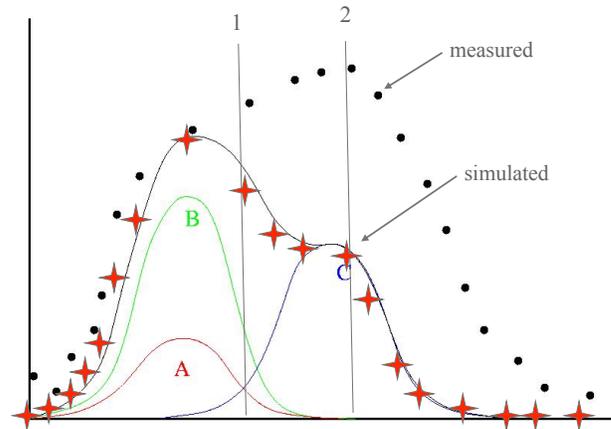
+ lattice parameters  
+ “experimental” parameters for peak shapes, background...

## 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)

