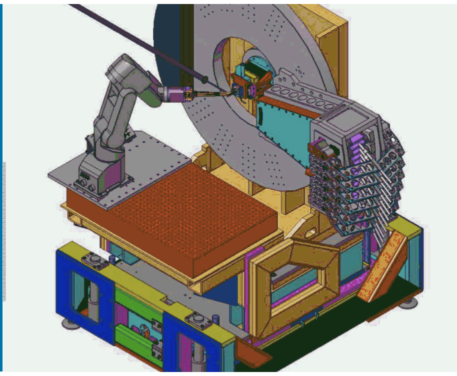
A VERY ABBREVIATED INTRODUCTION TO POWDER DIFFRACTION



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2018 NX School

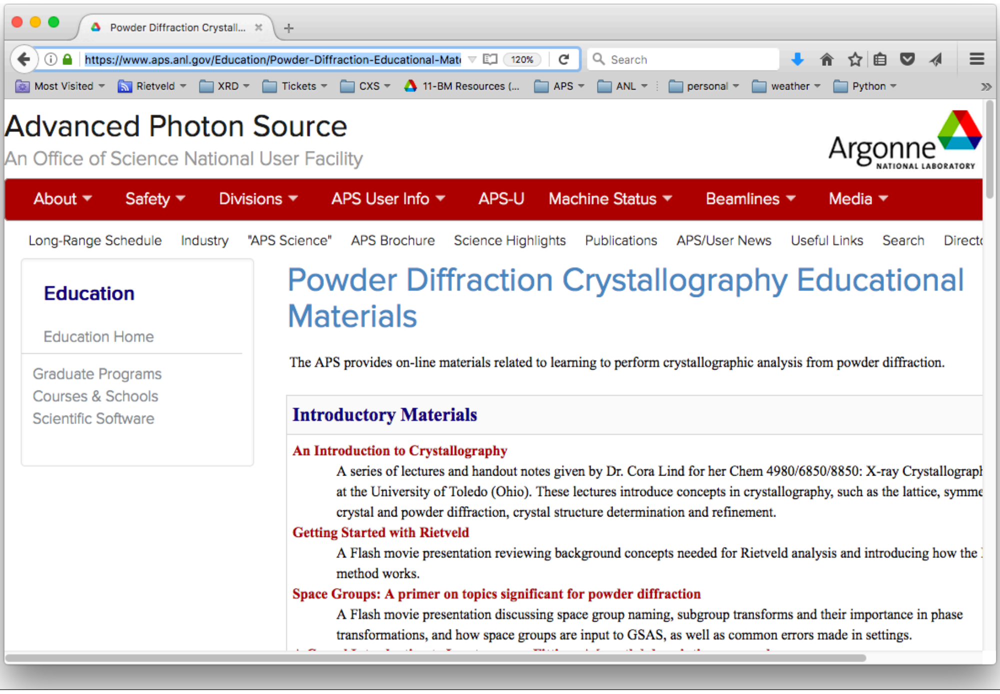
OUTLINE

- 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

LOTS OF MATERIAL ON WEB (SOME DATED)

Argonne's contribution: http://bit.ly/RietveldEd

https://www.aps.anl.gov/Education/Powder-Diffraction-Educational-Materials



Powder Diffraction Crystallography Educational Materials

The APS provides on-line materials related to learning to perform crystallographic analysis from powder diffraction.

Introductory Materials

An Introduction to Crystallography
A series of lectures and handout notes given by Dr. Cora Lind for her Chem 4980/6850/8850: X-ray Crystallograp at the University of Toledo (Ohio). These lectures introduce concepts in crystallography, such as the lattice, symme crystal and powder diffraction, crystal structure determination and refinement.

Getting Started with Rietveld
A Flash movie presentation reviewing background concepts needed for Rietveld analysis and introducing how the method works.

Space Groups: A primer on topics significant for powder diffraction
A Flash movie presentation discussing space group naming, subgroup transforms and their importance in phase transformations, and how space groups are input to GSAS, as well as common errors made in settings.

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!

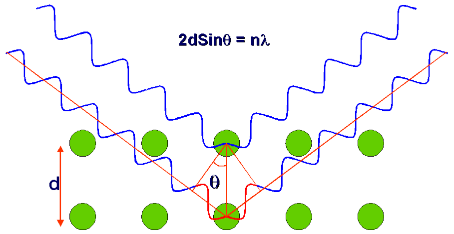
PHYSICS OF DIFFRACTION

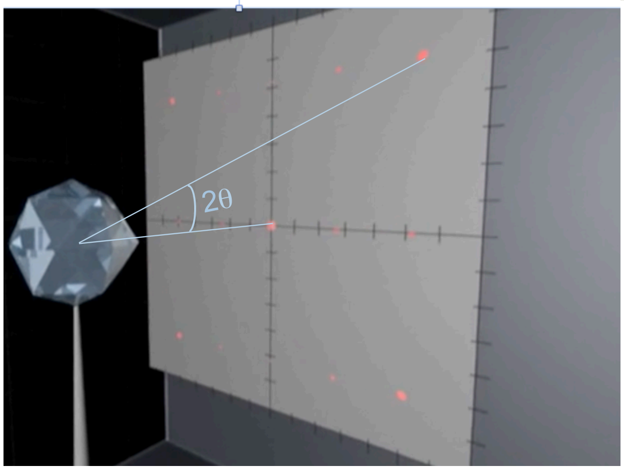
SINGLE CRYSTAL DIFFRACTION: THE MOVIE

Video from Diamond synchrotron (U.K.)

Bragg scattering in single crystals:
1) Reflection positions

Bragg's law:





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

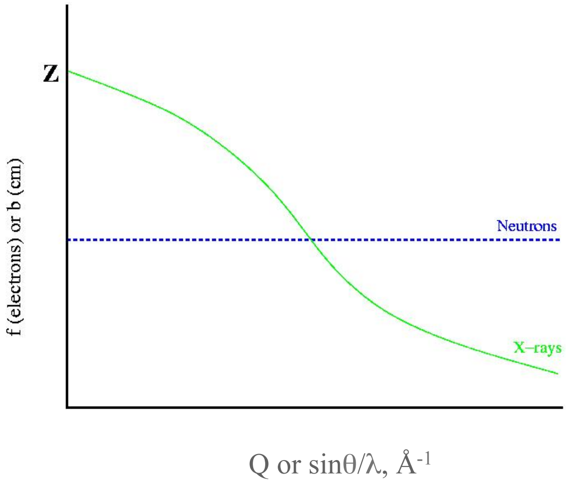
Note that d really should be considered a reciprocal space quantity ($d = 1/d^*$), $\underline{\mathbf{d^*}} = h\underline{a^*} + k\underline{b^*} + \ell\underline{c^*}$

Better (IMHO): $\lambda = 4\ \pi\ \sin\theta\ /\ Q$

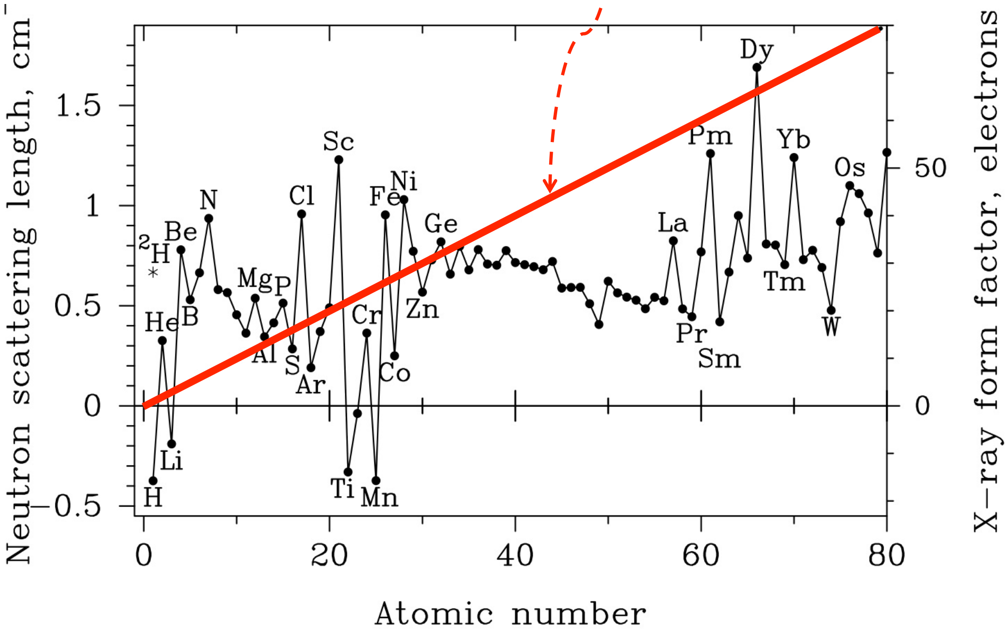
Bragg scattering in single crystals:
2) Reflection Intensities

Structure factors: $F_{hkl} = n\sum_i f_i \exp[2\pi i(hx_i + ky_i + \ell z_i)]\ \exp(-U_iQ^2/2)$

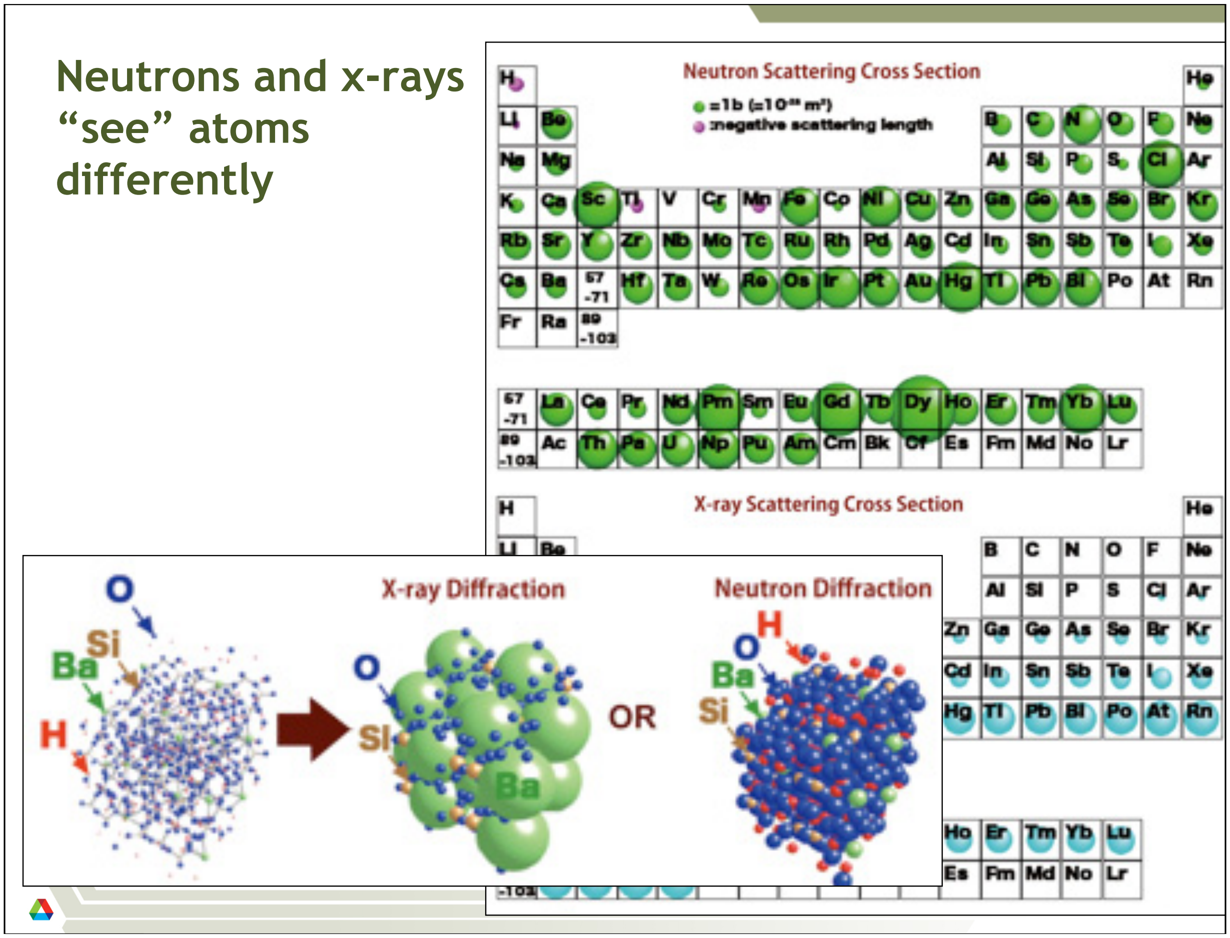
- **X-rays**: The scattering power (form factor, f_i) of an atom depends on the number of electrons in the atom and Q ($Q \propto \sin\theta/\lambda$)
  - X-ray scattering changes near absorption edges
- **Neutrons**: The scattering power (scattering length, b_i) of an atom depends on the isotope and 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 valence electrons; $f_M(Q)$ similar to x-rays, except fall-off is faster



Comparison of Neutron and X-ray Atomic Scattering Powers



Neutrons and x-rays “see” atoms differently



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.

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’(λ) + i f”(λ)**
  - 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 had to analyze

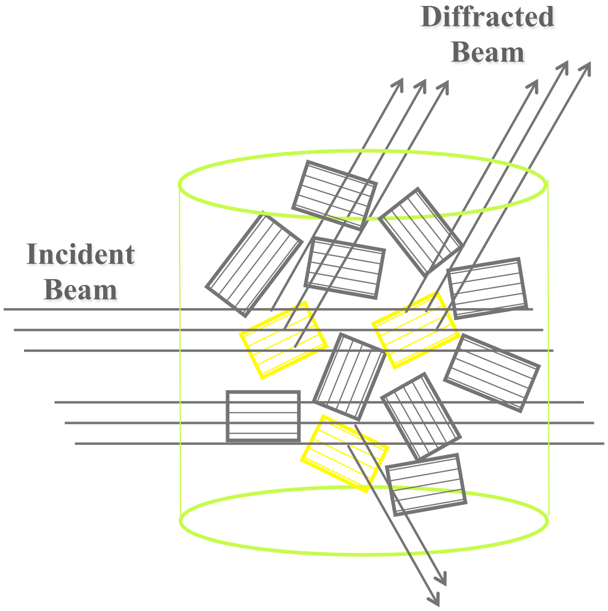
SINGLE-CRYSTAL VS. POWDER DIFFRACTION

Diffraction from random polycrystalline material

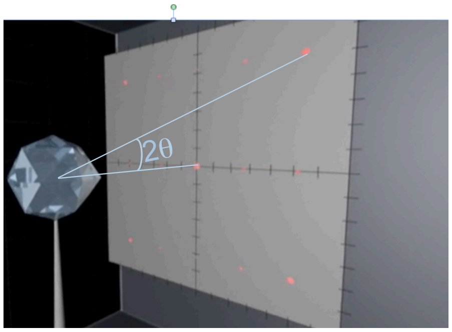
In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder) contains a very large number of crystallites.

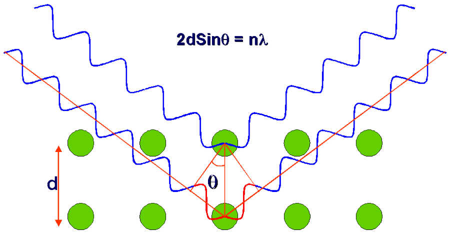
A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction

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



In both single crystal & powder diffraction diffraction positions and intensities can be treated separately





Reflection Positions: $\lambda = 4\pi \sin\theta / Q$

Reflection positions are determined by the lattice

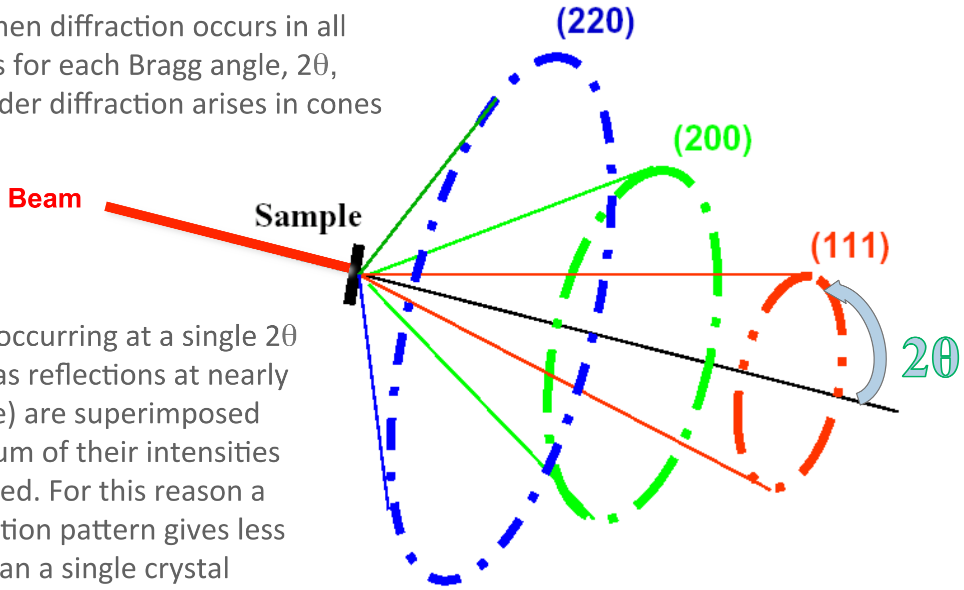
Reflection Intensities: $F_{hkl} = n\sum f_i \exp[2\pi i(hx_i + ky_i + \ell z_i)] \exp(-U_i Q^2/2)$

Reflection intensities are determined by the atom positions

This will be on the quiz!

Bragg cones in powder diffraction

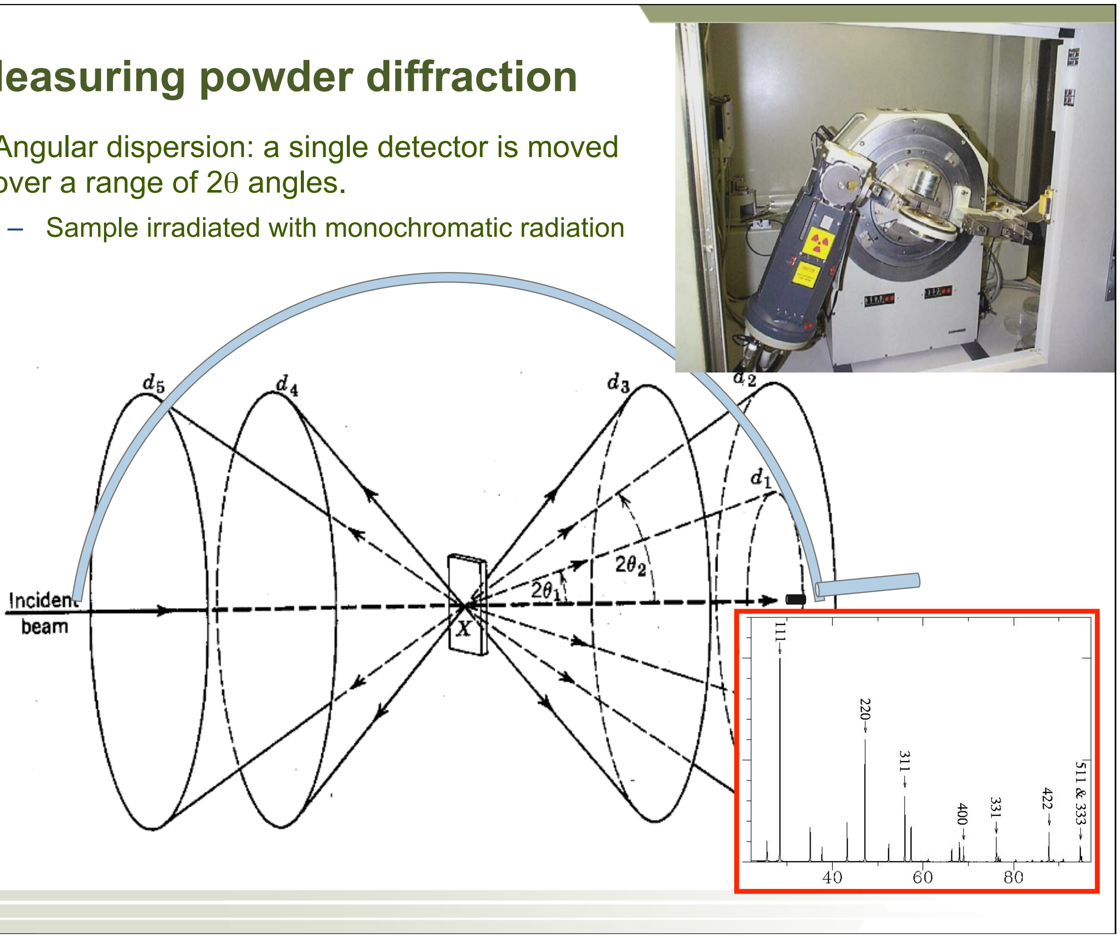
Since there is a random distribution of crystals then diffraction occurs in all directions for each Bragg angle, 2θ, thus powder diffraction arises in cones



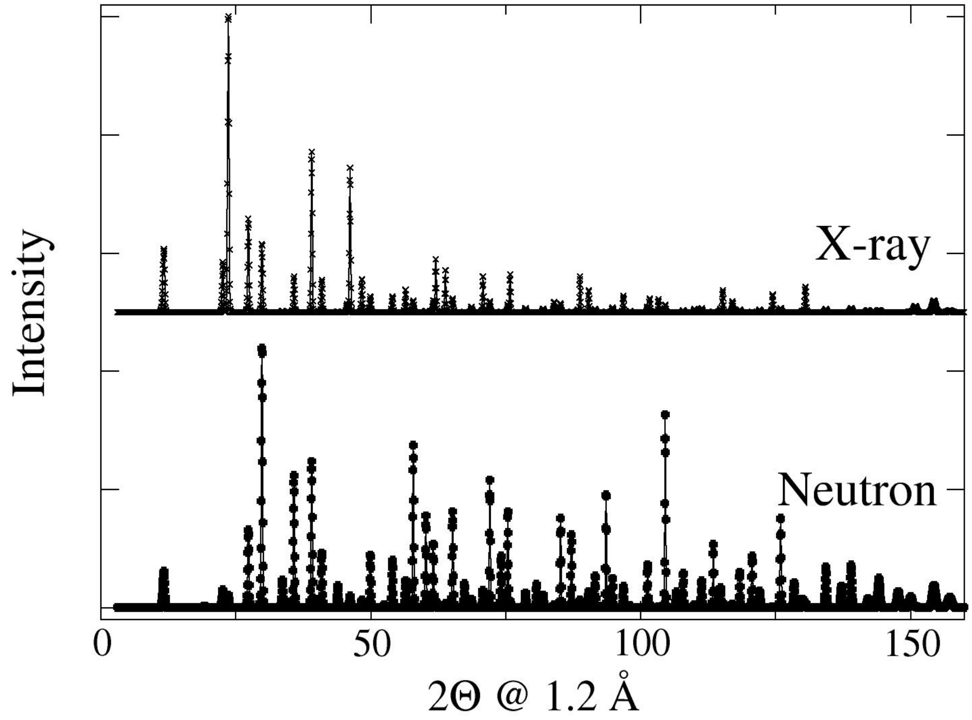
All reflections occurring at a single 2θ value (as well as reflections at nearly the same value) are superimposed and only the sum of their intensities can be measured. For this reason a powder diffraction pattern gives less information than a single crystal measurement

Measuring powder diffraction

- Angular dispersion: a single detector is moved over a range of 2θ angles.
  - Sample irradiated with monochromatic radiation



Comparison of Tb_2TiO_7 with x-rays & neutrons



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)

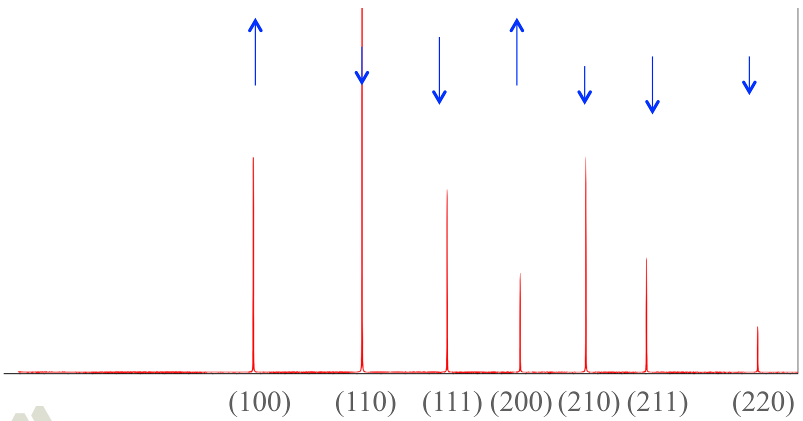
Less commonly:

- 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



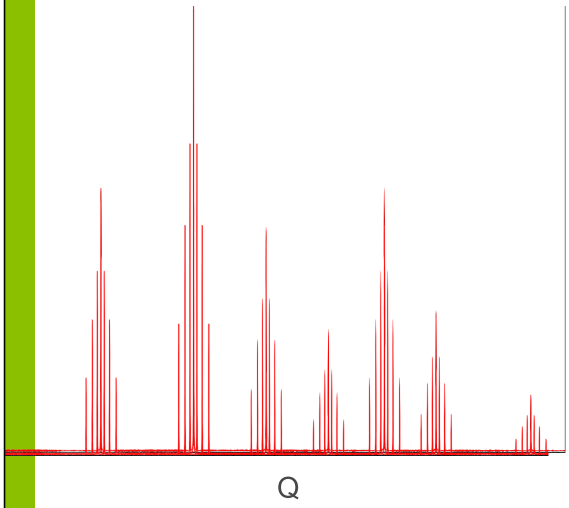
Texture can be measured directly in a specialized measurement (pole figure)

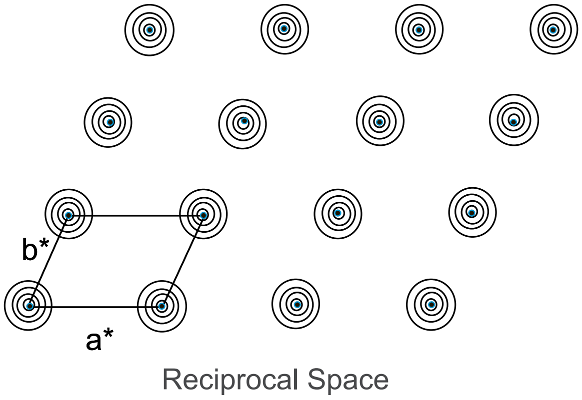
To model texture we use two approaches: March-Dollase model or Orientation Distribution Function (spherical harmonics)

UNDERSTANDING SAMPLE EFFECTS (I): 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).



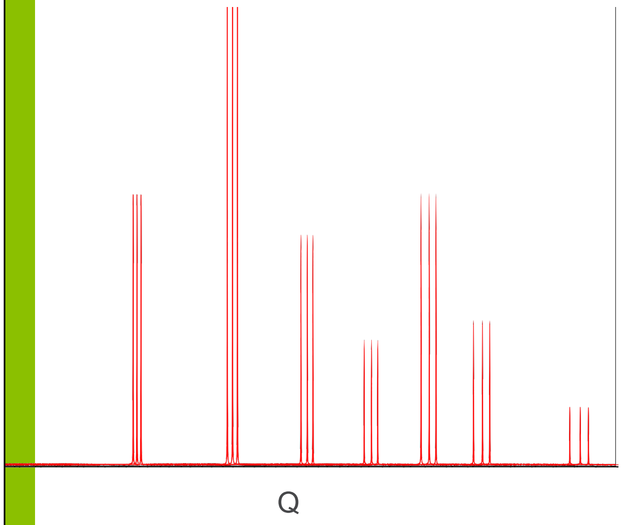


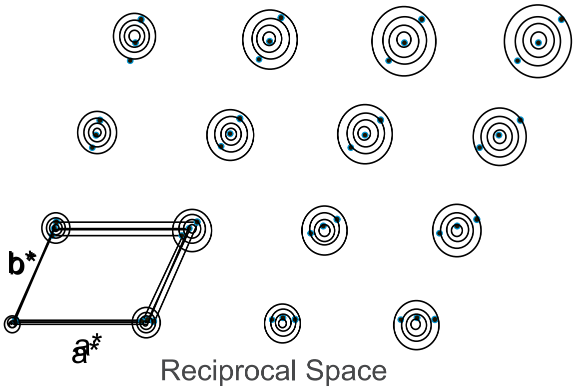
UNDERSTANDING SAMPLE EFFECTS (II): MICROSTRAIN (RESIDUAL STRESS) BROADENING

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 ≈ Q, broadening increases linearly with Q (ΔQ/Q or Δd/d constant)





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

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

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

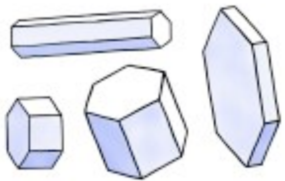
$$\Delta 2\Theta = \frac{2\Delta d}{d} \tan\Theta$$

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

See GSAS Manual, pp 158-167.

ANISOTROPIC BROADENING: BROADENING CAN BE DIRECTION-DEPENDENT

Crystallite broadening will vary with *hkl* when crystallites have smaller average dimensions in certain crystallographic directions, broadening reflections by class



www.its.caltech.edu/~atomic/snowcrystals

Microstrain broadening will vary with *hkl* if a material is more stiff (harder) in some crystallographic directions than others, again broadening reflections by class

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

Cubic – m3m – 2 terms

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

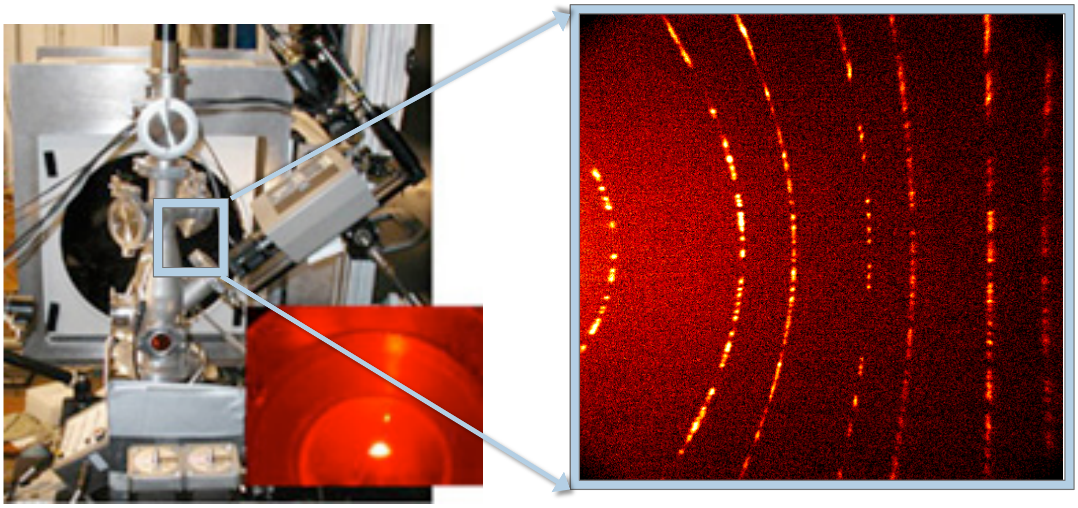
General expression – triclinic – 15 terms

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

TYPES OF POWDER DIFFRACTION MEASUREMENTS

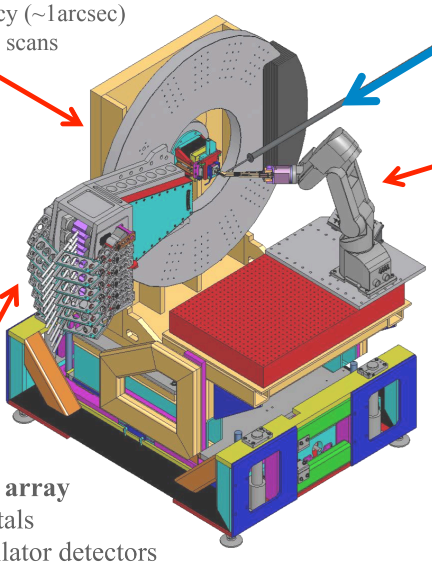
Area Detection

- 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

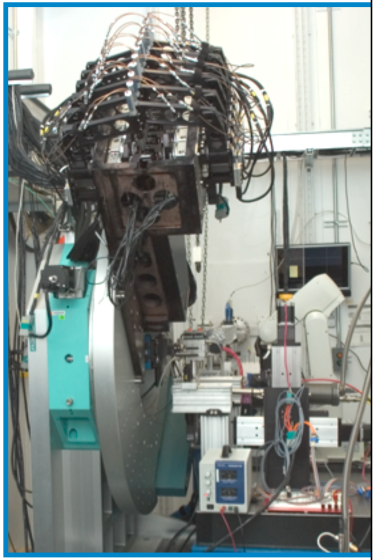
Huber 480 rotation stage:
high precision (~0.35arcsec)
high accuracy (~1arcsec)
slew *or* step scans



beam

Mitsubishi robot
custom "fingers"

12 analyzer array
Si(111) crystals
LaCl$_3$ scintillator detectors
2° apart in 2Θ.

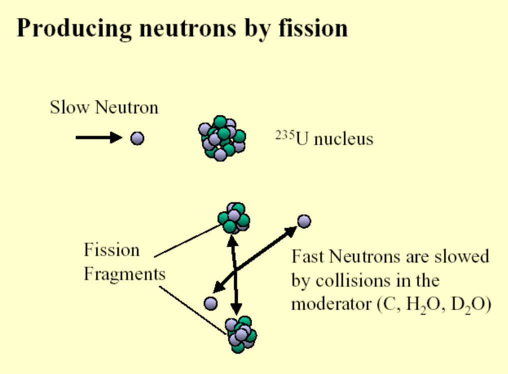


Complete pattern is measured in <1 hour

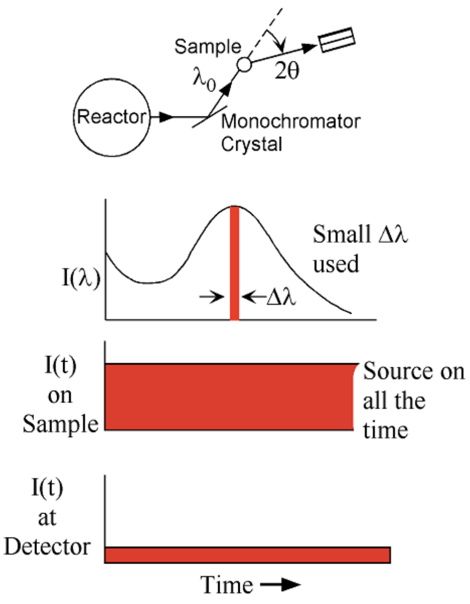
11-BM Robotic Data Collection

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

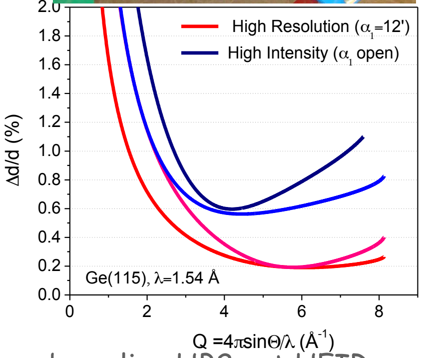
Reactor Source Neutron Diffraction


Producing neutrons by fission

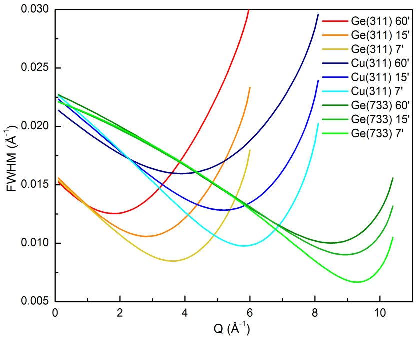
STEADY STATE TECHNIQUE



Powder Instruments: Constant Wavelength



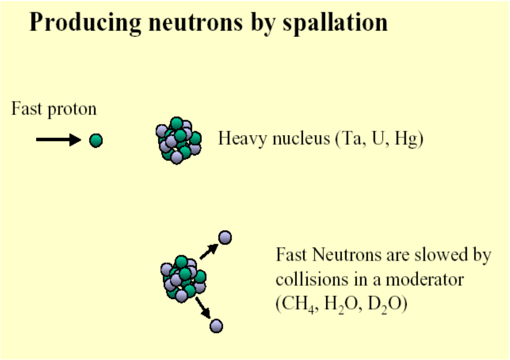
beamline HB2a at HFIR

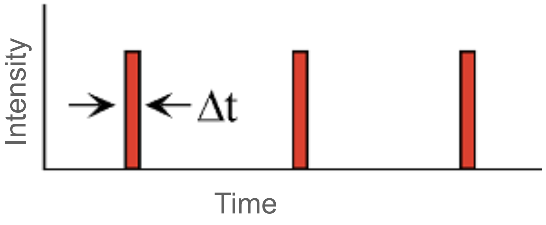


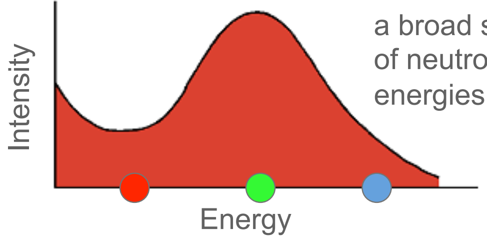
beamline BT1 at NIST (NCNR)

Spallation Sources

A pulse of protons impacting the target produces a shower of fast neutrons that are slowed down in a moderator. A new pulse is created ~30 times/sec


Producing neutrons by spallation





Each pulse of neutrons contains a broad spectrum of neutron energies

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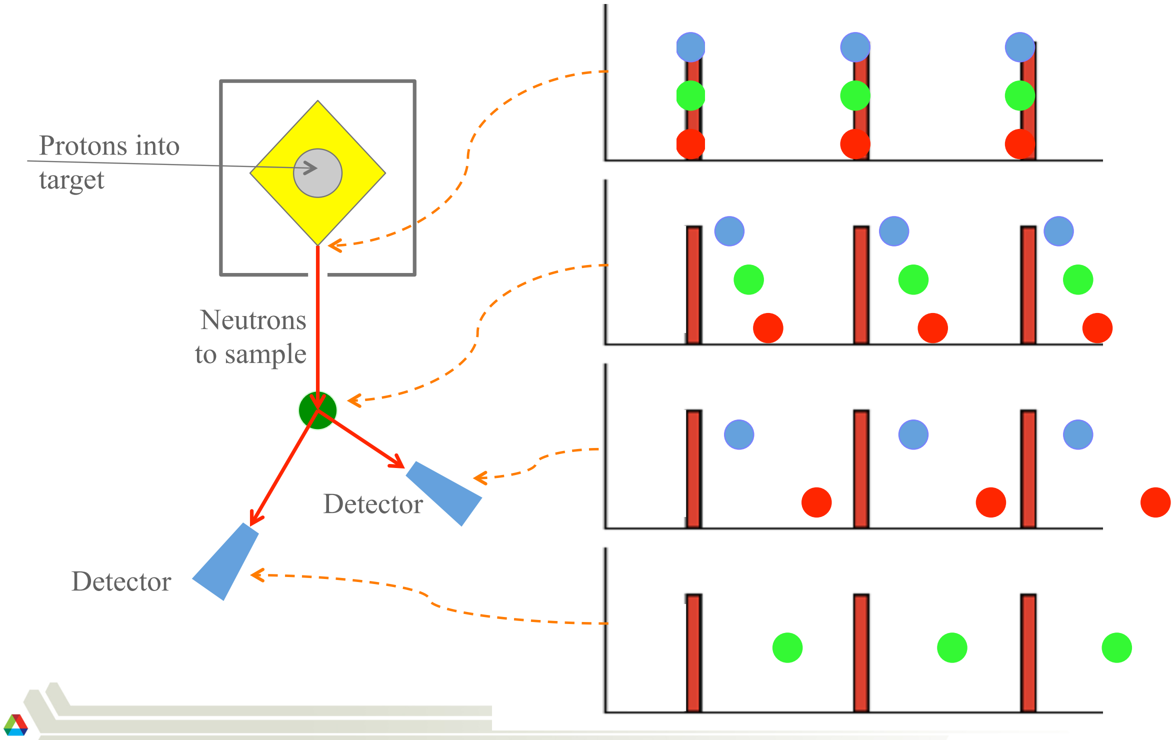
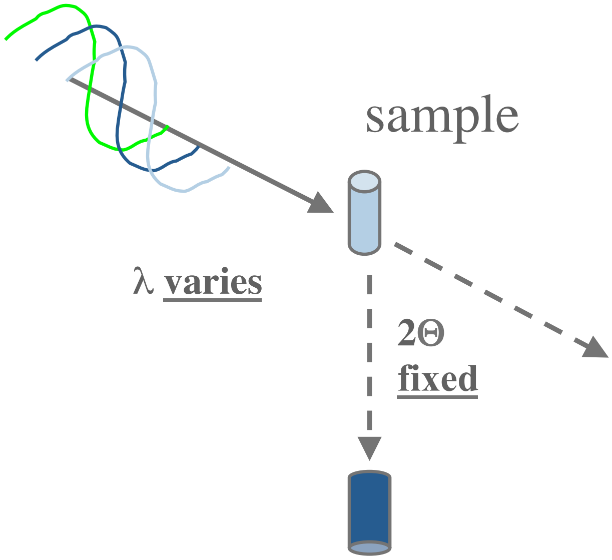
Time of Flight Diffraction

Time of flight diffraction uses the fact that neutrons with different energies (velocities) have different wavelengths, λ=h/mv (de Broglies relationship)



Time-of-flight (2dsinΘ=λ)

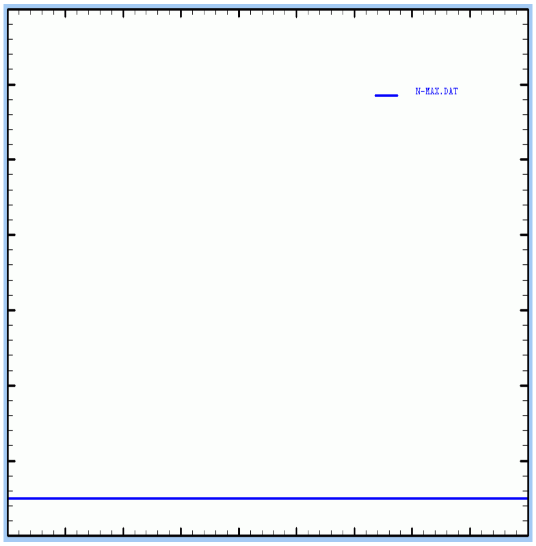
(Pulsed sources: e.g. **SNS**)



sample

λ **varies**

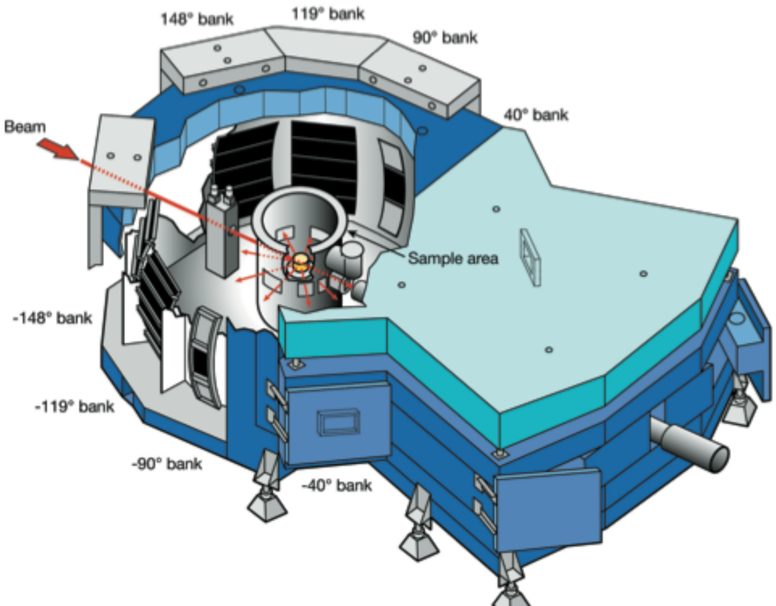
2Θ
fixed



detector

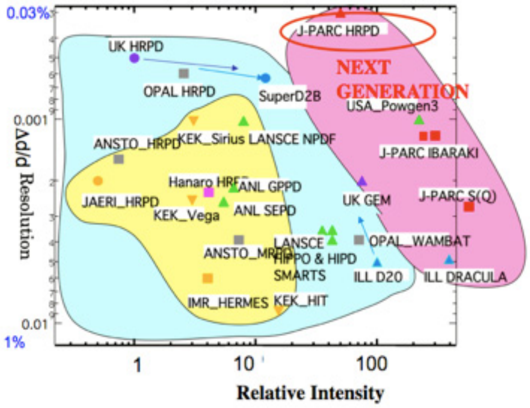
Neutron Powder Diffraction with Spallation Source

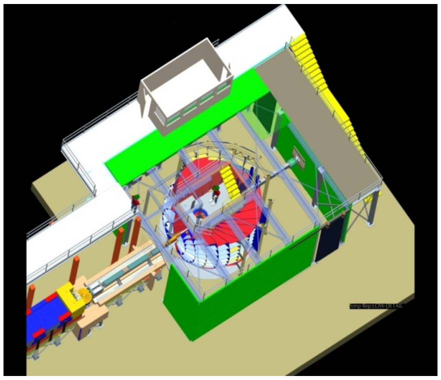
- Spallation source provides a broad band of wavelengths in sharp pulses
  - TOF detection allows measurement of intensity versus wavelength
  - Each detector provides a full diffraction pattern
  - Data collection times:
    - Seconds to hours



NPDF instrument at LANSCE (Los Alamos)

3^{rd} Generation TOF Instruments: High Intensity and High Resolution

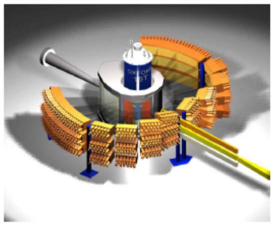




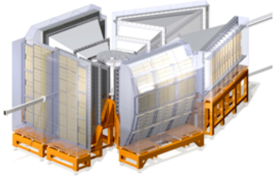
SNS: POWGEN[-3]

GEM (ISIS TS-I)

WISH
A high-resolution magnetic diffractometer for TS-II



Super HRPD (JSNS)



FITTING OF POWDER DIFFRACTION DATA (RIETVELD ANALYSIS)

Fitting crystallographic data from powder diffraction -- 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

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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

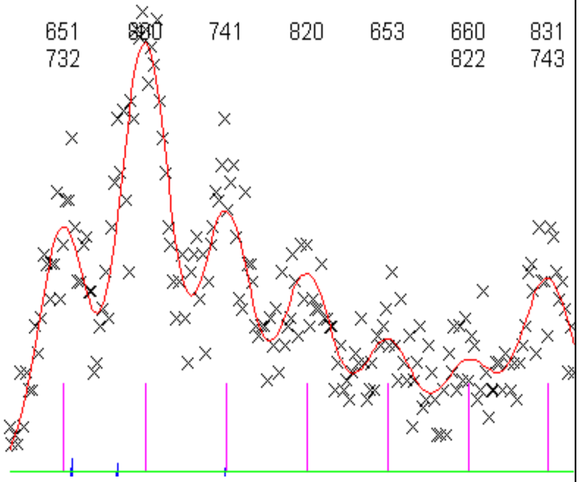
Simulation of powder diffraction data was commonly done

- 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)

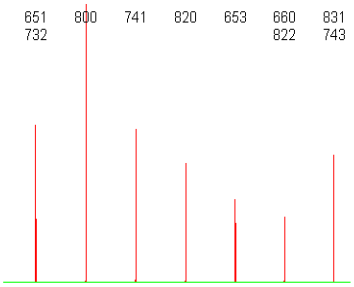
Hugo Rietveld's technique

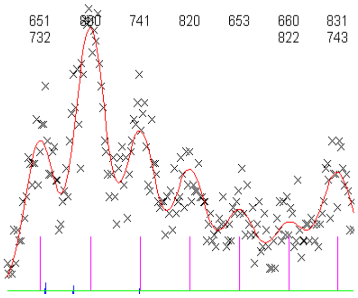
- Hugo Rietveld realized that if a pattern could be modeled, the fit between a computed pattern and observed data could be optimized.
  - Similar to single-crystal diffraction, except that now "experiment dependent parameters" must now be fit as well.
    - Background
    - Peak broadening
    - Lattice constants
  - Must have approximate model to start
  - Fewer data are available (usually)



Calculation of Powder Diffraction: Graphical Example

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

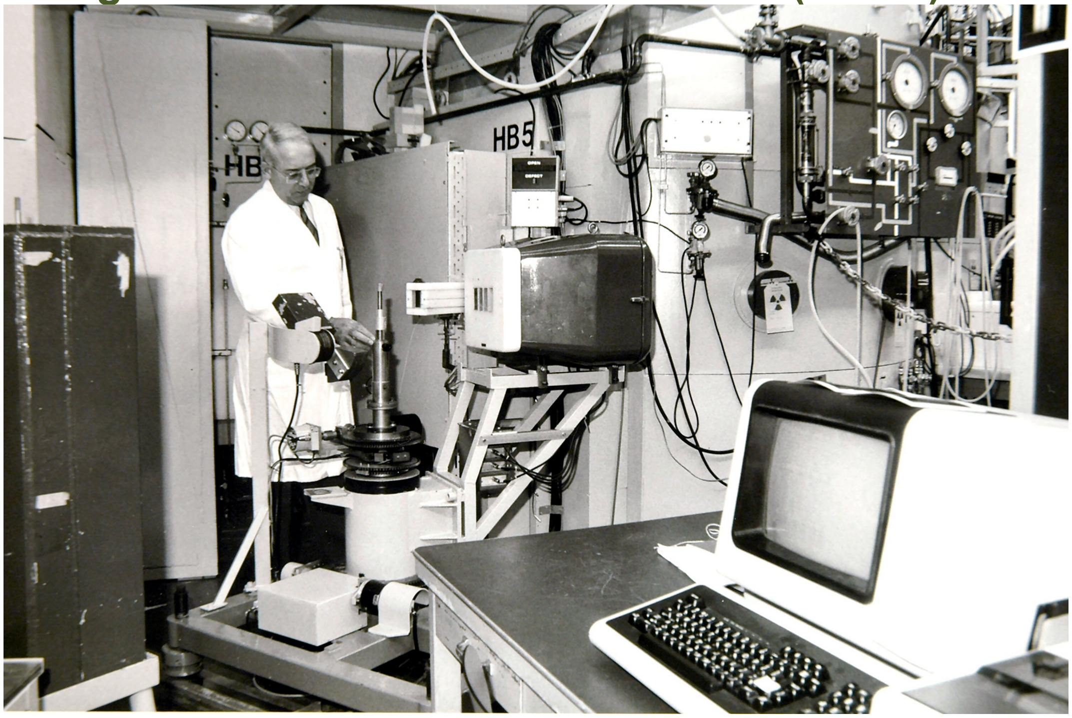
2) Compute F_{hkl} from model

3) Peak heights are generated from $|F_{hkl}|^2$*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

Powder data fitting

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

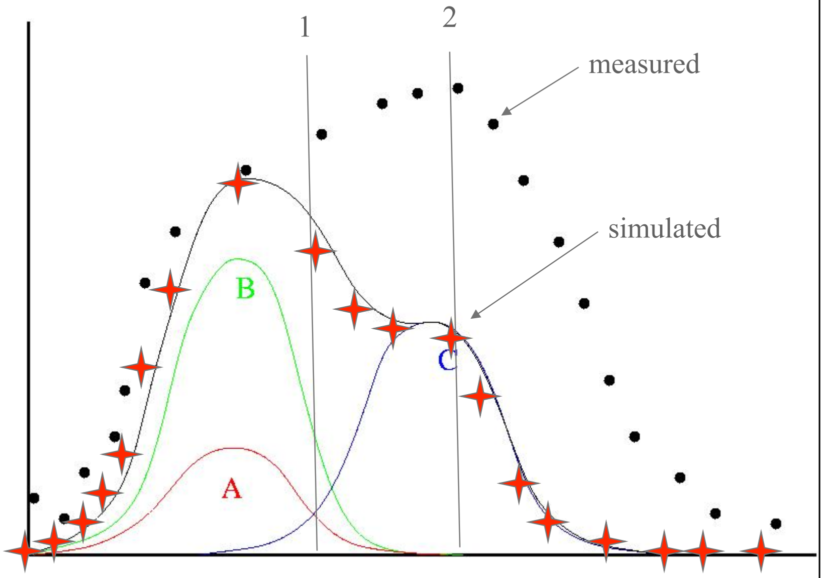
Data: $y_i = F_{hkl\ (obs)}$	y_i = observed powder diffraction intensities
Model: $Y(x_i,\mathbf{p}) = F_{hkl\ (calc)}$	$Y(x_i,\mathbf{p})$ = computed diffraction intensities from ($F_{hkl\ (calc)}$, background model, profile convolution, preferred orientation correction…
Parameters (p_1, p_2, p_3… p_m): atomic coordinates, displacement (T) factors	+ 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 (sometimes high-resolution x-ray data, *e.g.* 11-BM, is sufficient)

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)

SURVEY OF RIETVELD SOFTWARE

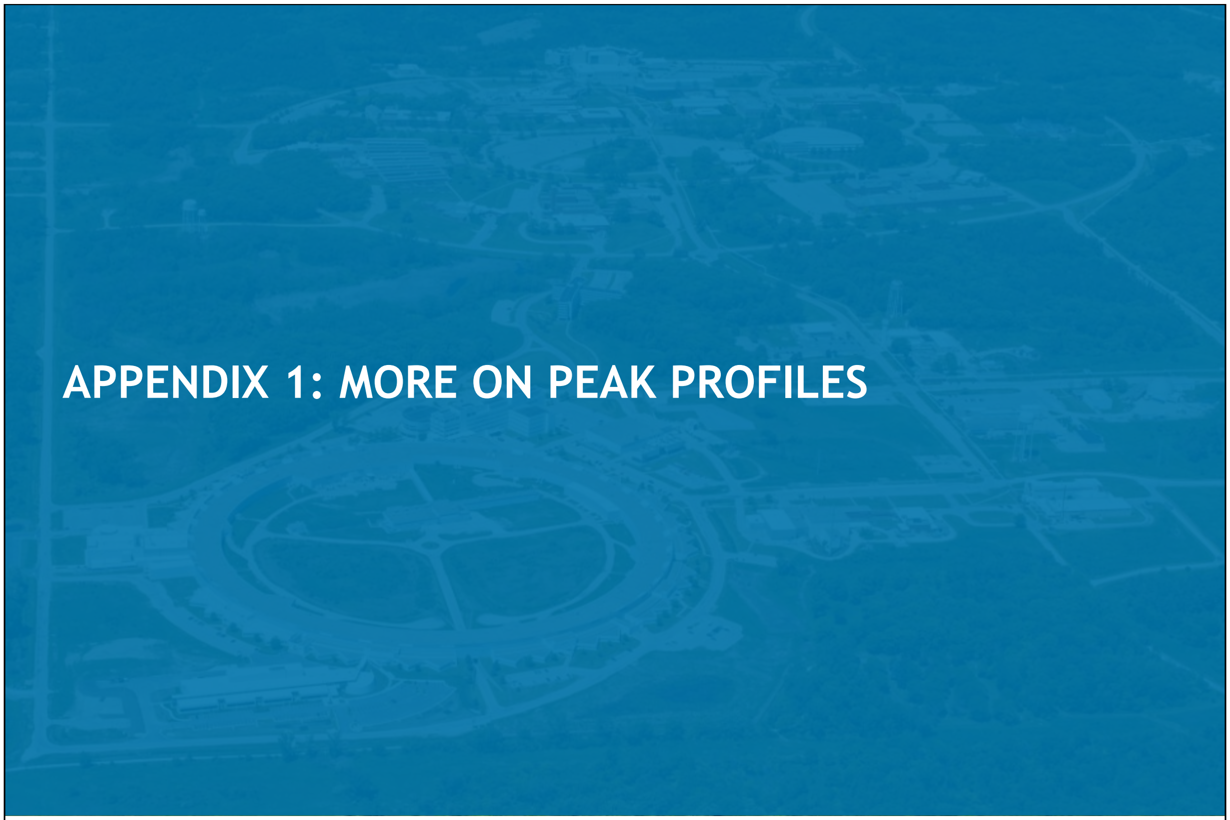
(There are a huge number of historical codes). These are the ones that are actively developed with wide use:

- FullProf: widely used, excellent support for magnetic scattering
- TOPAS: commercial; fundamental parameter peak shapes; very fast. Machine algebra allows arbitrary models
- MAUD: primarily for microscopic characterization (texture,…)
- JANA: primary focus modulated structures, excellent charge-flipping structure solution
- EXPO: primary focus direct-methods structure solution
- RIETAN: somewhat dated, widely used in Japan
- GSAS/EXPGUI: first comprehensive code; no longer supported (replaced by GSAS-II); limited magnetic scattering support
- GSAS-II: only code started in current decade; supports start-to-finish analysis process; sequential refinement mode for fitting large numbers of related patterns, still being completed

WHAT CAN YOU DO WITH GSAS-II?

GSAS-II does everything in GSAS/EXPGUI, and has extensive capabilities available only in very specialized programs

- Data reduction/initial processing
  - Image calibration
  - Image integration
  - Peak fitting/position determination
  - PDF computation (neutrons eventually)
  - TOF calibration
- Structure solution
  - Pattern
  - Charge flipping
  - Rigid body simulated annealing
- Crystallographic analysis
  - Powder diffraction
  - Single-crystal diffraction
  - Neutron and x-ray diffraction
  - Fitting of any of the above, combined
- Magnetic scattering (incommensurate, coming soon)
- Fitting of modulated (3+1) structural models
  - Neutron or x-ray
- Fitting of twinned single-crystal datasets
- Parametric structural analysis
  - Parametric equation fitting
- 2D dataset fitting:
  - Strain fitting
  - Texture fitting
- Stacking fault modeling (DIFFaX)
- Small-angle scattering analysis
- Reflectometry (CW)



APPENDIX 1: MORE ON PEAK PROFILES

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

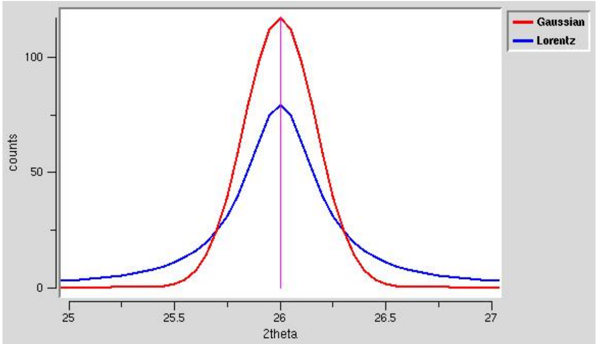
Normalized Gaussian

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

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, η=0 is Gaussian, η=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

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

Lorentzian

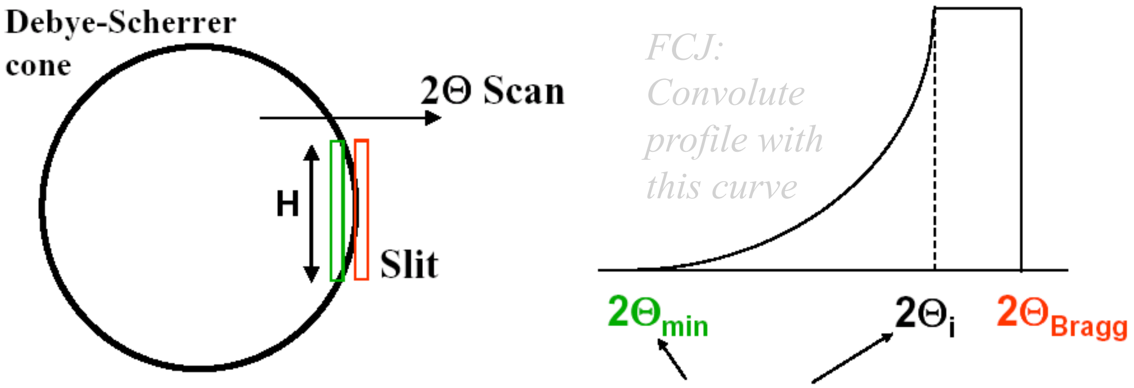
- X is crystallite broadening
- Y is strain broadening

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

N.B. no instrumental broadening term

Axial Divergence (Low Angle Asymmetry)

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



Debye-Scherrer cone

2Θ Scan

H

Slit

FCJ: Convolute profile with this curve

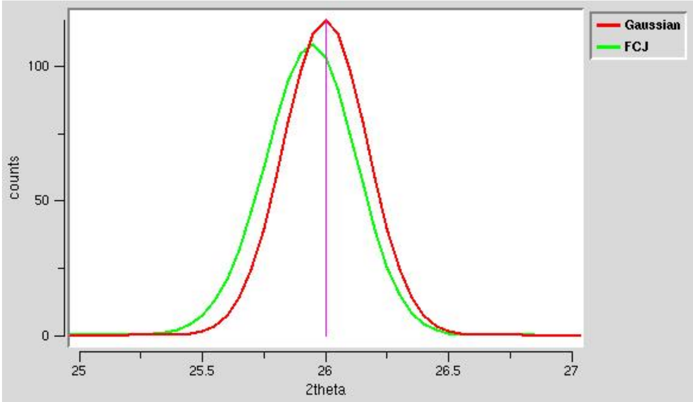
$2\Theta_{min}$ $2\Theta_i$ $2\Theta_{Bragg}$

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

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

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

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

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).

When 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

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

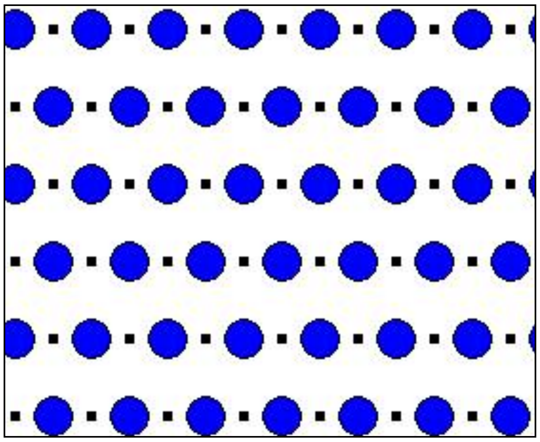
Trigonal, Rhombohedral & Hexagonal – it depends – 3 or 4 terms

APPENDIX 2: MORE ON CRYSTALLOGRAPHY

The Lattice

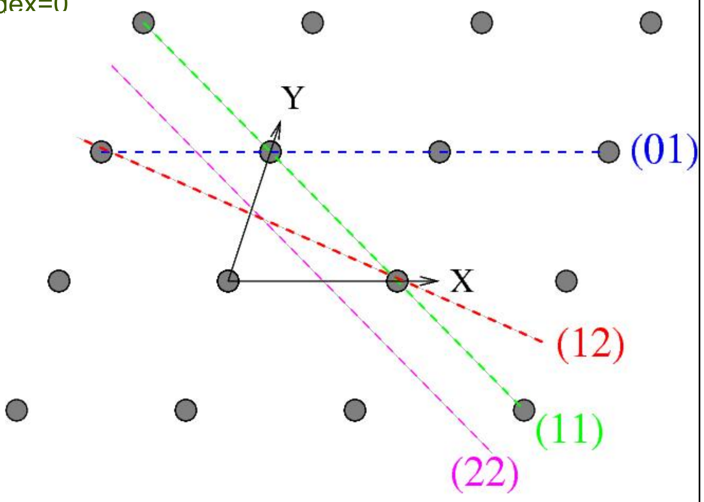
- Crystals are constructed from repeated arrangements of atoms.
- Crystalline structure can be described as set of "identical boxes" stacked in 3D; the contents of each box is identical (exception: quasicrystals)
  - ***A lattice*** is a mathematical concept where each lattice point describes an identical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



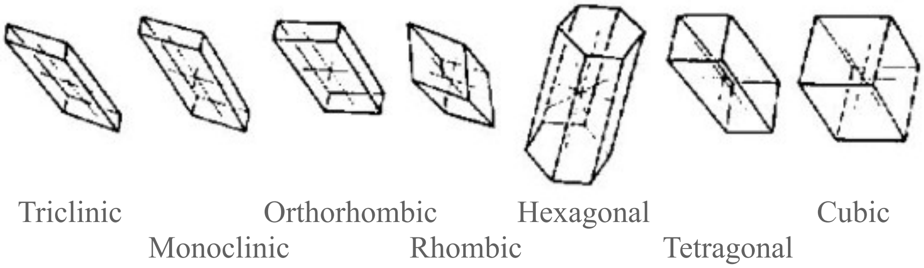
Lattice planes

- 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



The Unit Cell

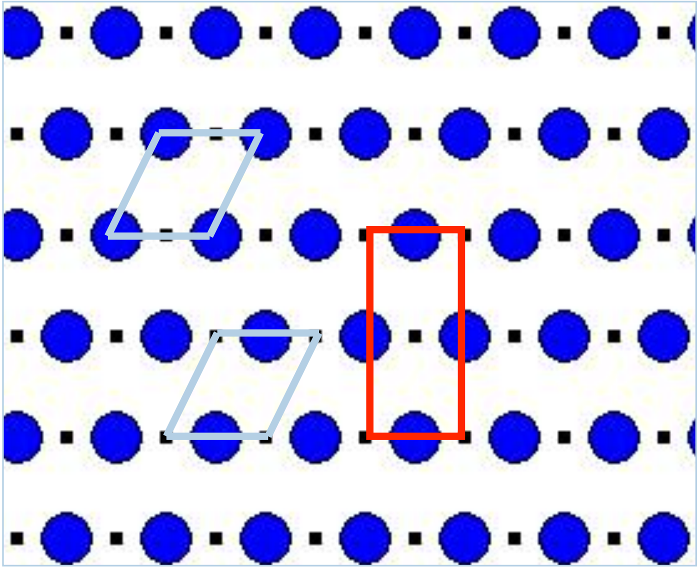
- The ***unit cell*** describes at least one repeating unit that can be used to construct the structure
- There are 7 types of unit cells corresponding to the ***7 crystal systems***



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

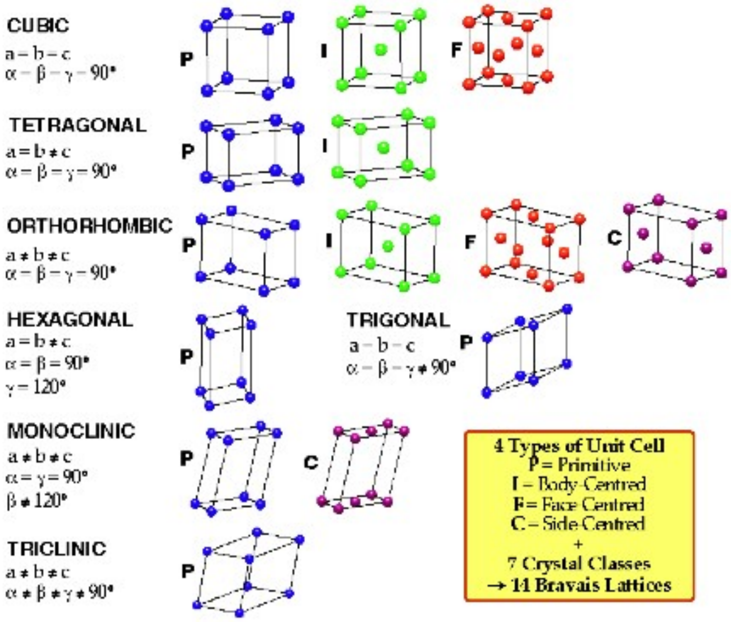
Centering is used to increase symmetry

- 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)



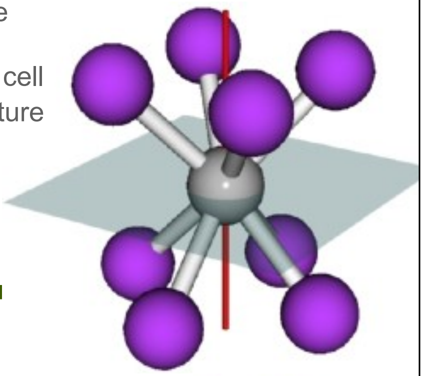
Have non-perpendicular axes: (non-orthogonal coordinate systems)

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

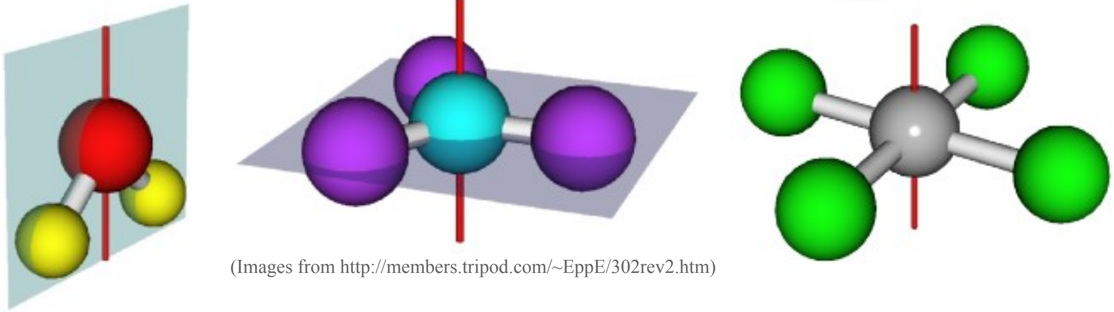
Symmetry

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***



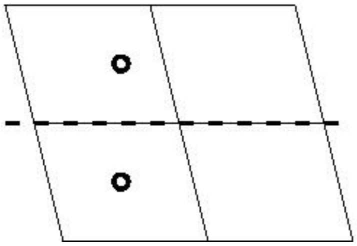
- Types of symmetry elements in crystals
  - Lattice translations (includes lattice centering)
  - Mirror planes
  - Proper/improper Rotation axes (includes center of sy
  - Screw Axes
  - Glide Planes



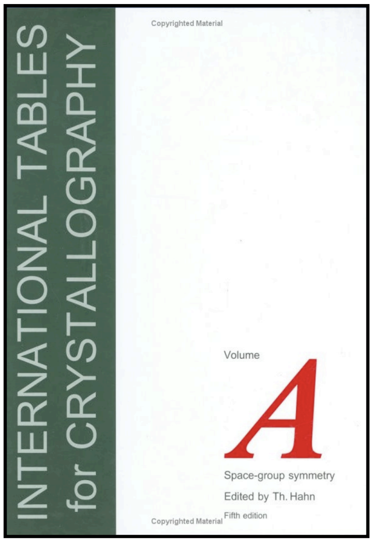
(Images from http://members.tripod.com/~EppE/302rev2.htm)

Space Groups

- Not all combinations of symmetry and lattice types are compatible
  - Example: mirror plane perpendicular to a non-orthogonal pair of axes – is not possible



- 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***
- 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 their properties



INTERNATIONAL TABLES for CRYSTALLOGRAPHY

Copyrighted Material

Volume A

Space-group symmetry

Edited by Th. Hahn

Fifth edition

Copyrighted Material

Symmetry, Space groups

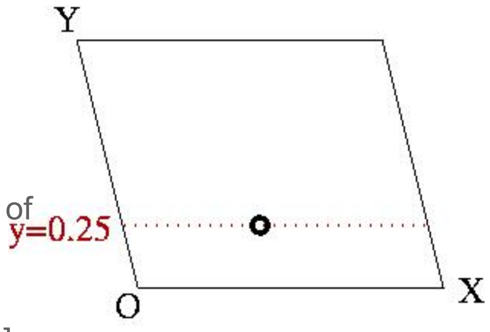
- Translational symmetry (centering, screw axes, glide planes) causes classes of reflections to have zero intensity: systematic extinctions
  - Non-translational symmetry (mirror planes, rotation axes, centers of symmetry) do not do this.
- Space groups describe the 230 (219 if chirality differences are ignored) ways that symmetry elements can be combined.
  - Symmetry provides the scaffolding that structures are built upon

I recommend Space Groups for Solid State Scientists *by* G. Burns and A. M. Glazer (Academic Press, New York, 1990*) to learn how to understand the International Tables.*

Alternate choice: Symmetry in Crystallography, Understanding the International Tables *by* Paolo Radaelli (IUCr, 2011)

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) --> (1+x, y, z) [translation on *x*]

(x,y,z) --> (1/2+x, 1/2+y, 1/2+z) [centering]

(x,y,z) --> (-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 (±2σ)

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:

$$\underline{\mathbf{r}} = xa + yb + zc \quad \text{and} \quad \underline{\mathbf{d^*}} = h a^* + k b^* + \ell c^*$$

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

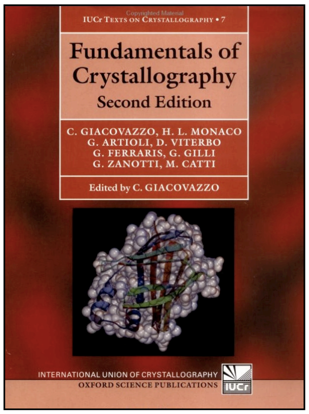
$$\underline{\mathbf{r}} \cdot \underline{\mathbf{d^*}} = hx + ky + \ell z$$

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)

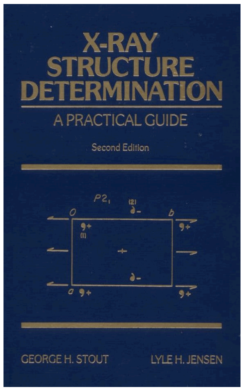
Where to go for more…

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