

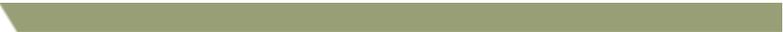
# A Very Abbreviated Introduction to Powder Diffraction

Brian H. Toby

# Outline

- Stuff you should know:
  - Diffraction from single crystals
  - X-rays vs Neutrons; Types of scattering
- Diffraction from powders
- Why do we use powder diffraction?
- Instruments for powder diffraction collection
- Materials effects in powder diffraction
- Crystallographic analysis of powder diffraction data
- Appendices:
  - More on peak shapes
  - More on crystallography
  - Where to go for more information





# Single Crystal Diffraction Review



# Single crystal diffraction: the movie

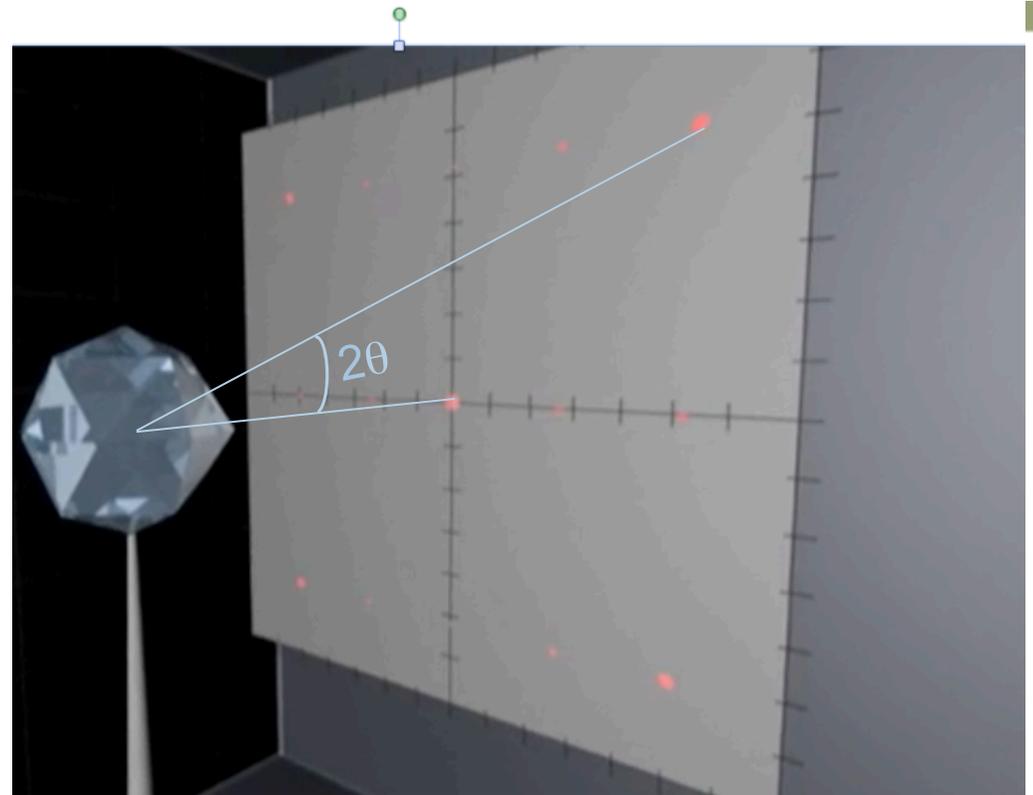
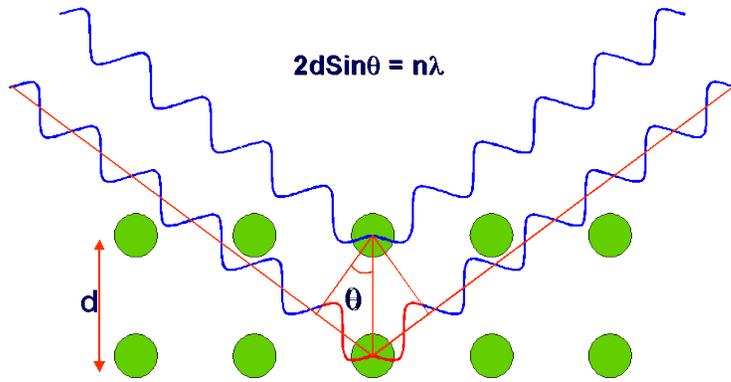


Video from Diamond synchrotron (U.K.)



# Bragg scattering in single crystals

- Reflection positions (Bragg's law)



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

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

$$F_{hkl} \propto \sum_j f_j \exp[2\pi i(\underline{h}x_j + \underline{k}y_j + \underline{l}z_j)] \exp(-U_j Q^2/2) \text{ sum over all atoms in the crystal (or unit cell).}$$

$x_j, y_j, z_j$ : position of atom in unit cell

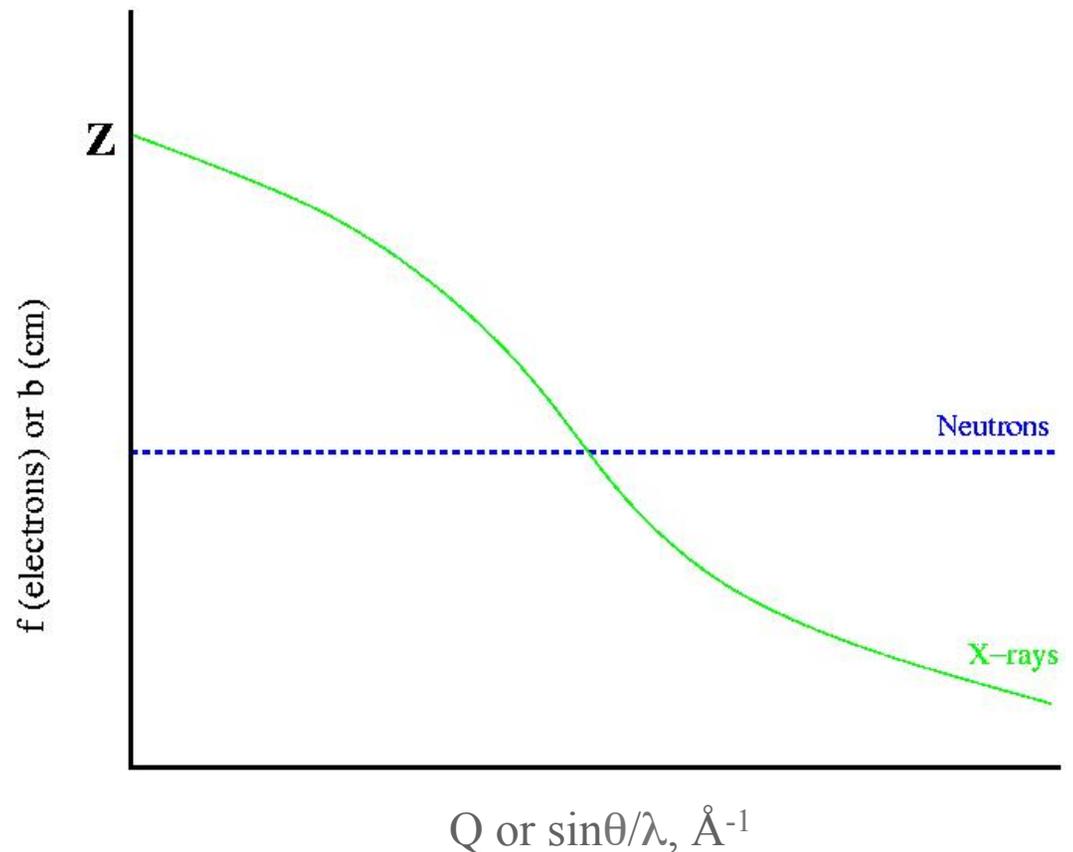
$U_j$ : atom displacements

$f_j$  (or  $b_j$ ): scattering power of atom

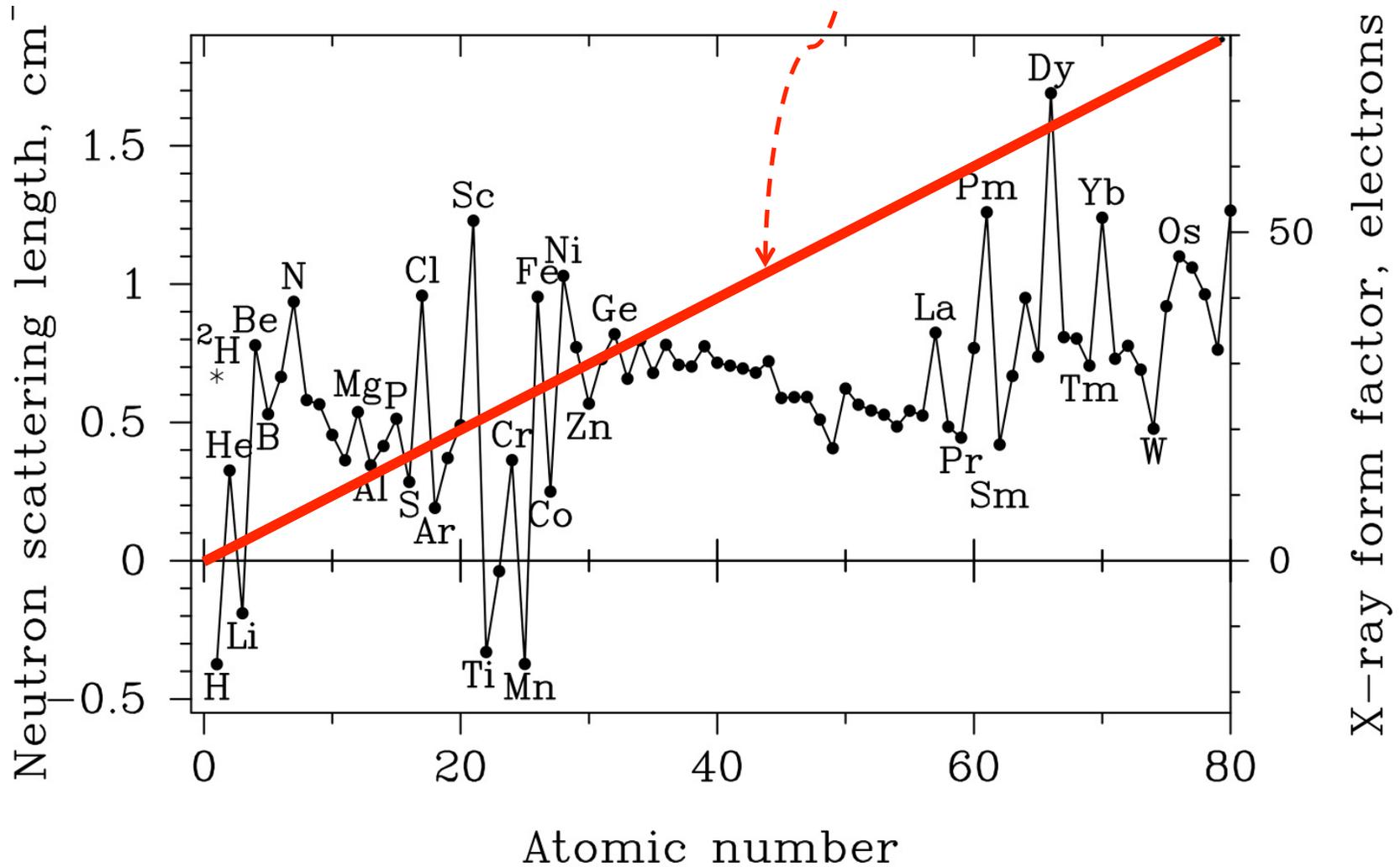
# Coherent Atomic Scattering Power (diffraction)

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

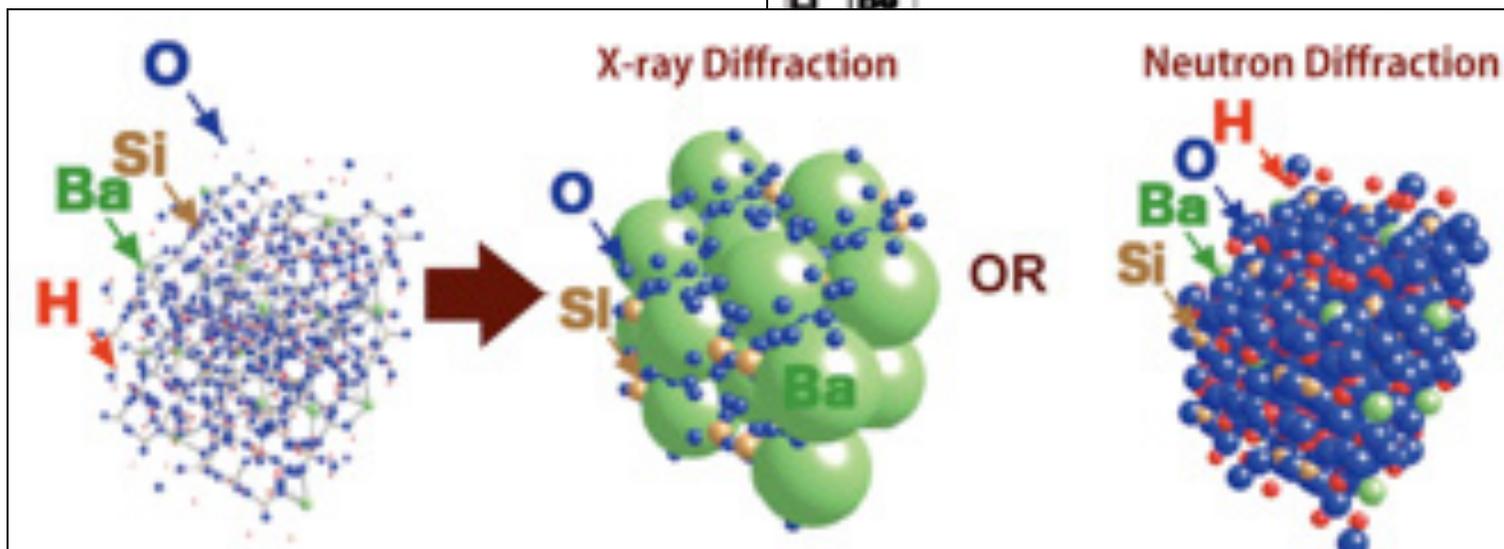
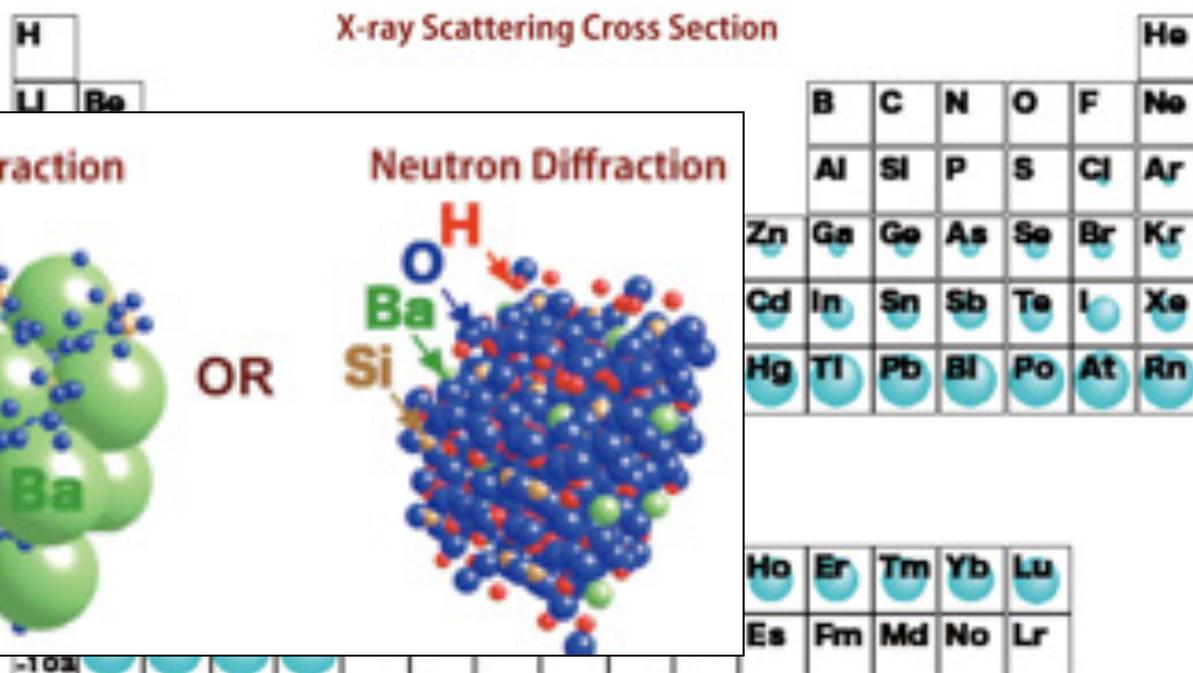
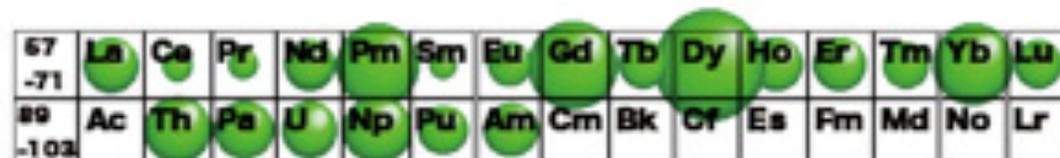
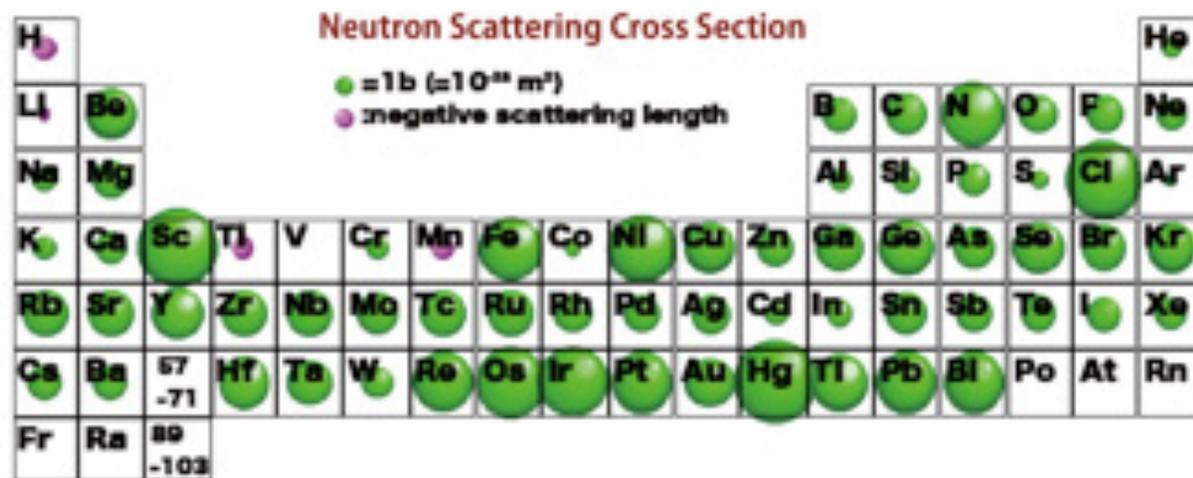
- **X-rays:** The scattering power (form factor,  $f_i$ ) of an atom depends on the number of electrons in the atom and  $Q$  ( $Q \propto \sin\theta/\lambda$ )
  - X-ray scattering changes near absorption edges
- **Neutrons:** The scattering power (scattering length,  $b_i$ ) of an atom depends on the 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



# Neutrons and x-rays “see” atoms differently



# 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.

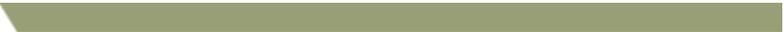
## Neutrons

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 had to analyze



# Types of scattering



# Coherent vs Incoherent Scattering

- Coherent scattering -- since phase is retained, scattering occurs with interference between nearby atoms
  - atom-atom correlation info obtained: diffraction
- Incoherent scattering – probe phase is randomized, no interference
  - self-correlation (simpler analysis): spectroscopy

# Elastic vs Inelastic Scattering

- Elastic scattering – No transfer of energy between atoms and probe, only momentum
- Inelastic scattering – probe loses energy to atoms (for neutrons also possible to gain energy)



# Types of neutron scattering measurements

	<i>Elastic Scattering</i>	<i>Inelastic Scattering</i>
<i>Coherent Scattering</i>	Diffraction (structural studies)	Phonons, magnons... (collective excitations)
<i>Incoherent Scattering</i>	QENS (diffusion, low barrier motion)	Neutron Spectroscopies (atomic vibrations)



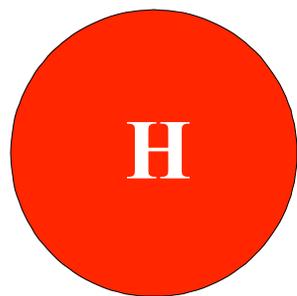
# Incoherent and inelastic scattering

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



# Powder Diffraction

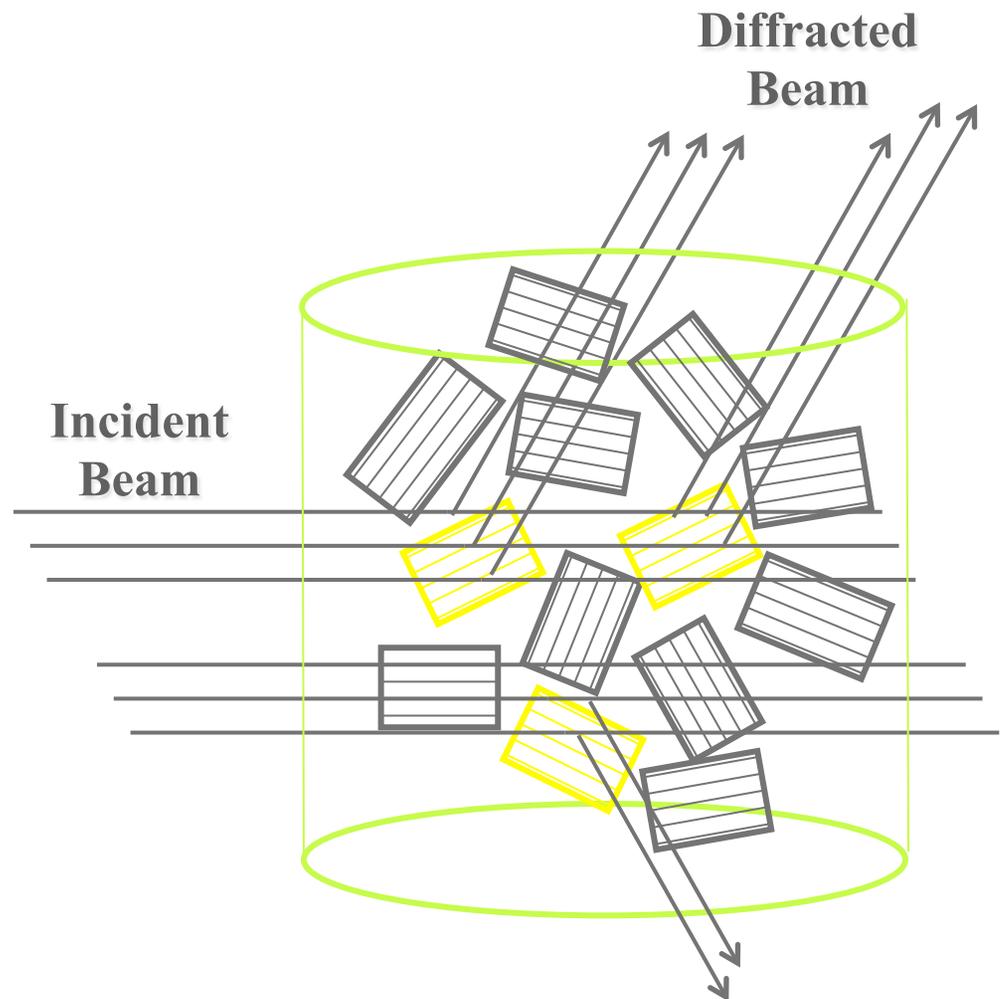


# Diffraction from random polycrystalline material

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

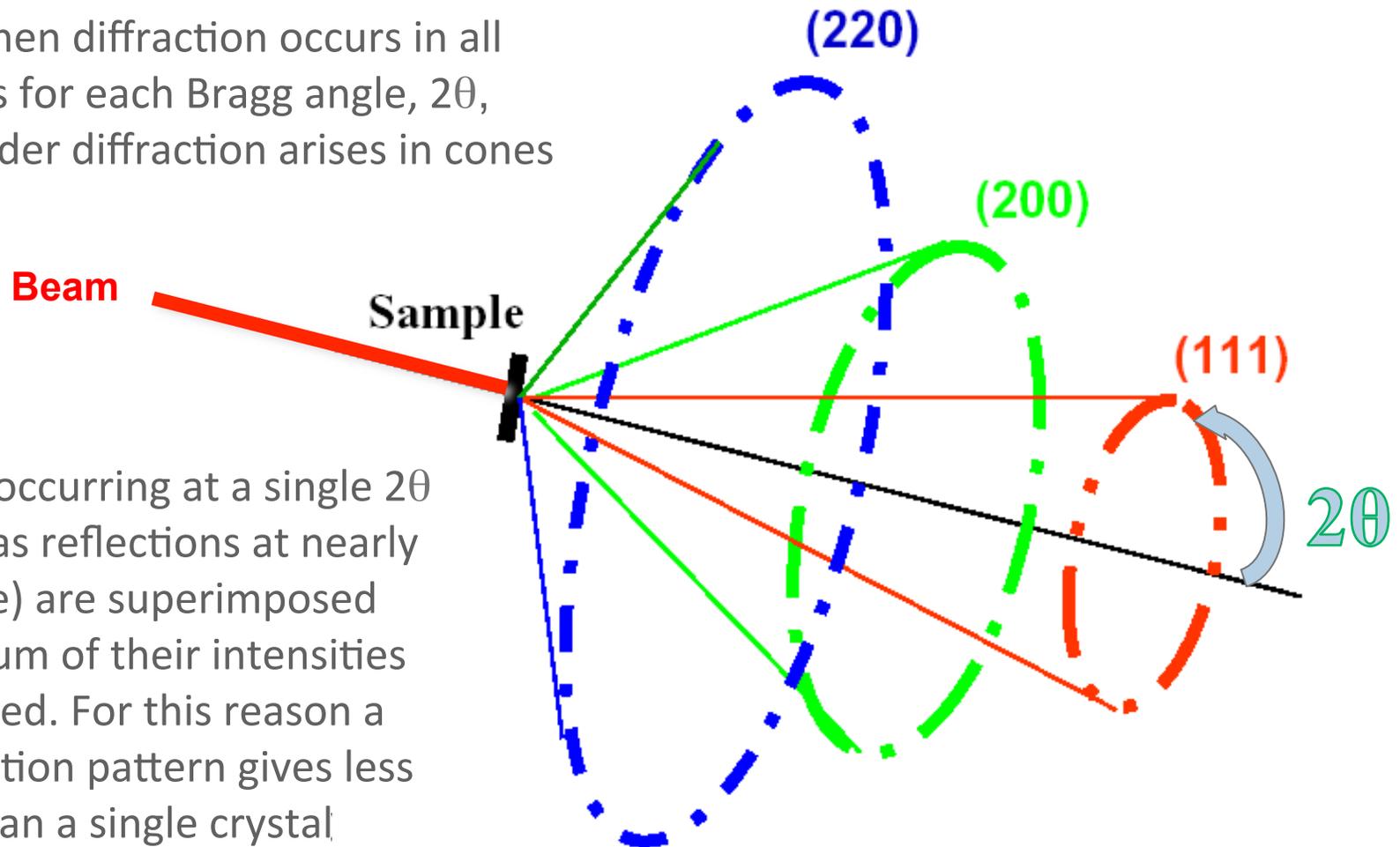
A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction

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



# 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



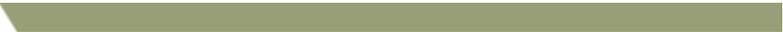
All reflections occurring at a single  $2\theta$  value (as well as reflections at nearly the same value) are superimposed and only the sum of their intensities can be measured. For this reason a powder diffraction pattern gives less information than a single crystal measurement



# 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)



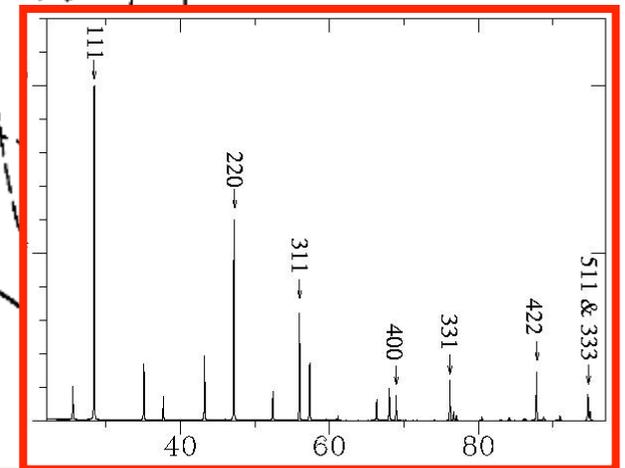
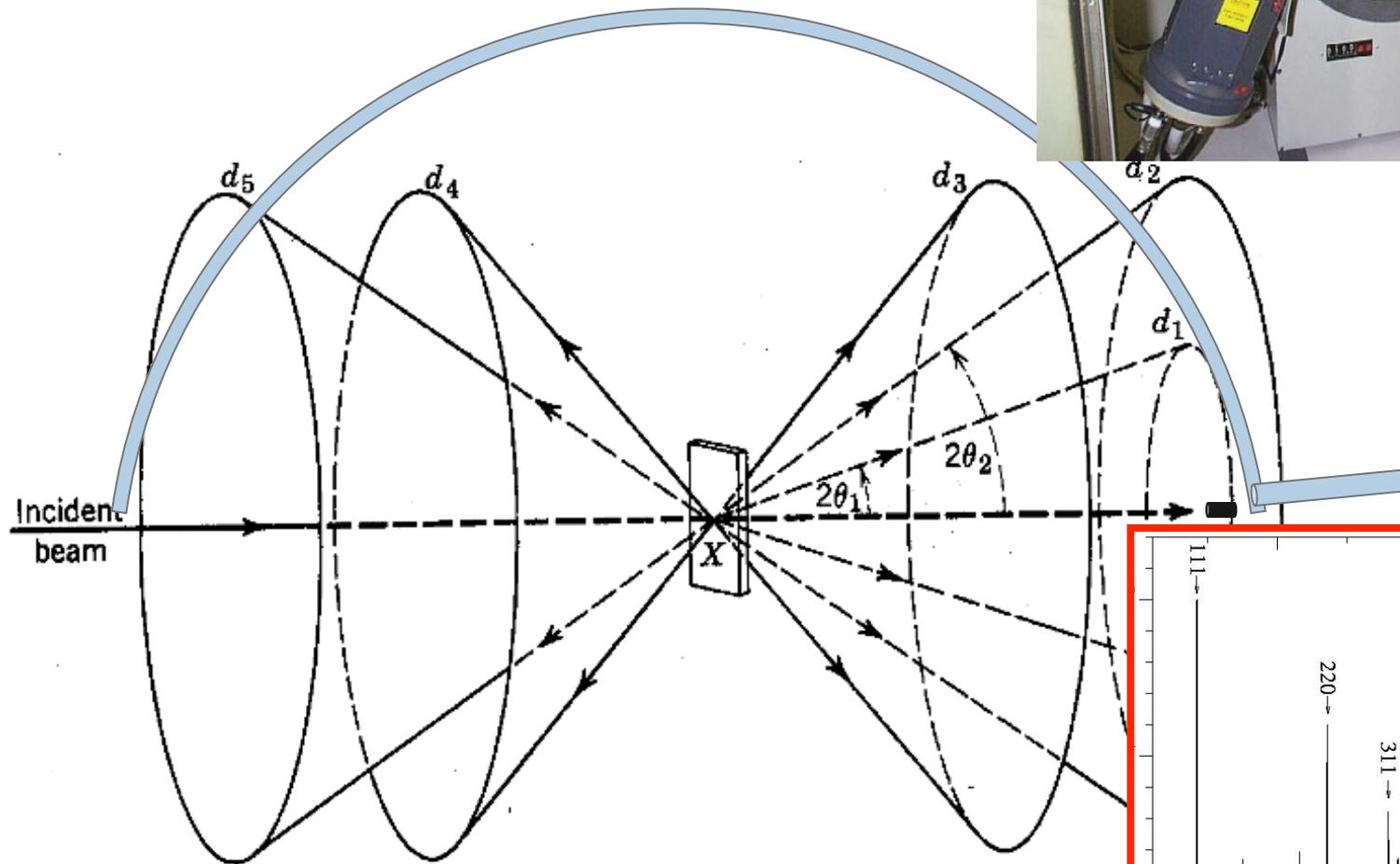


# **Types of Powder Diffraction Measurements**



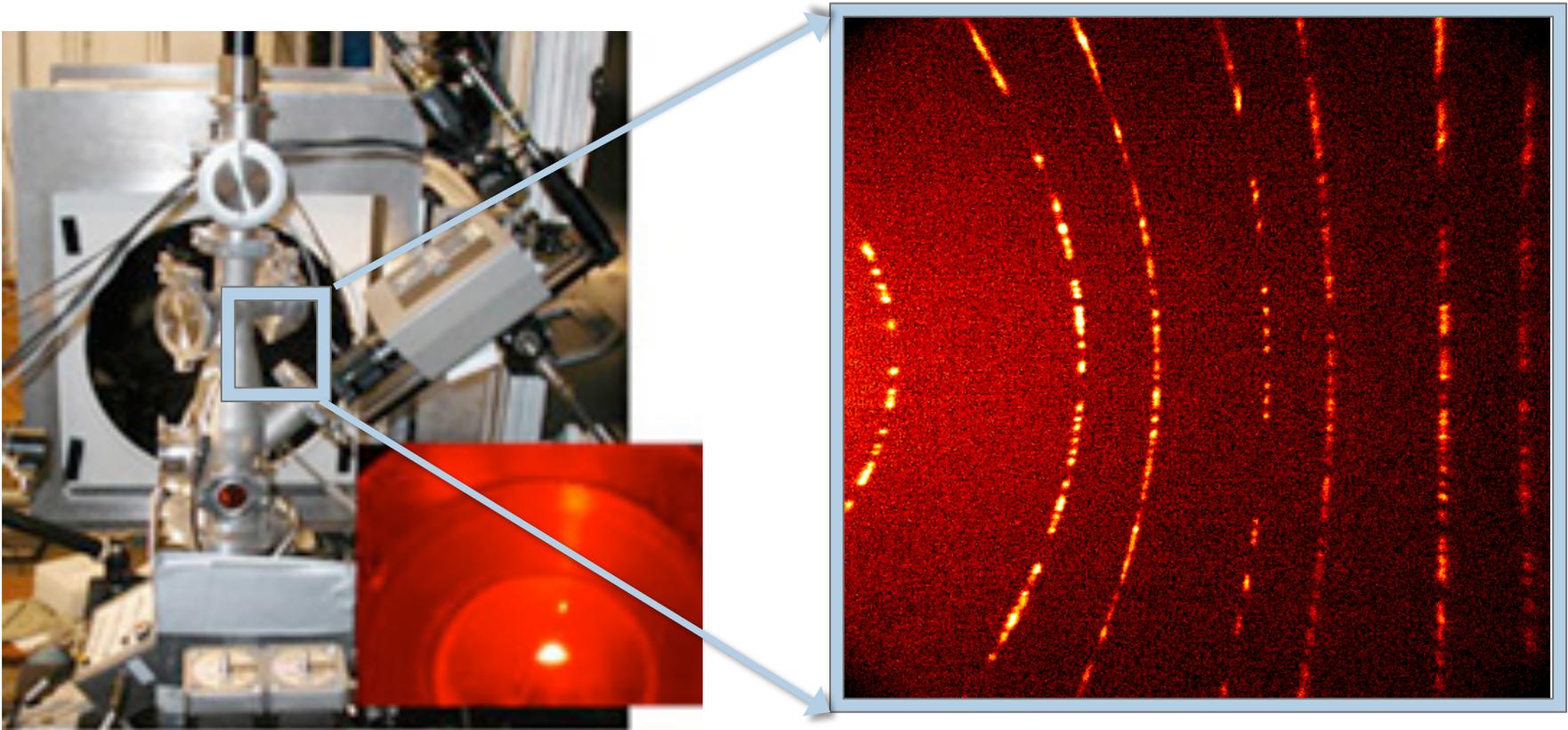
# Measuring powder diffraction

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



# 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



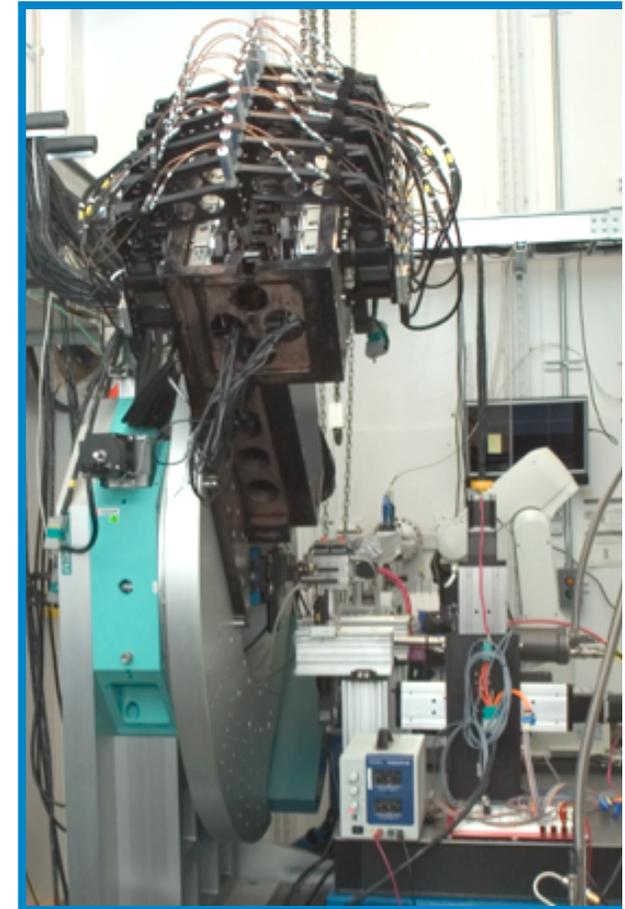
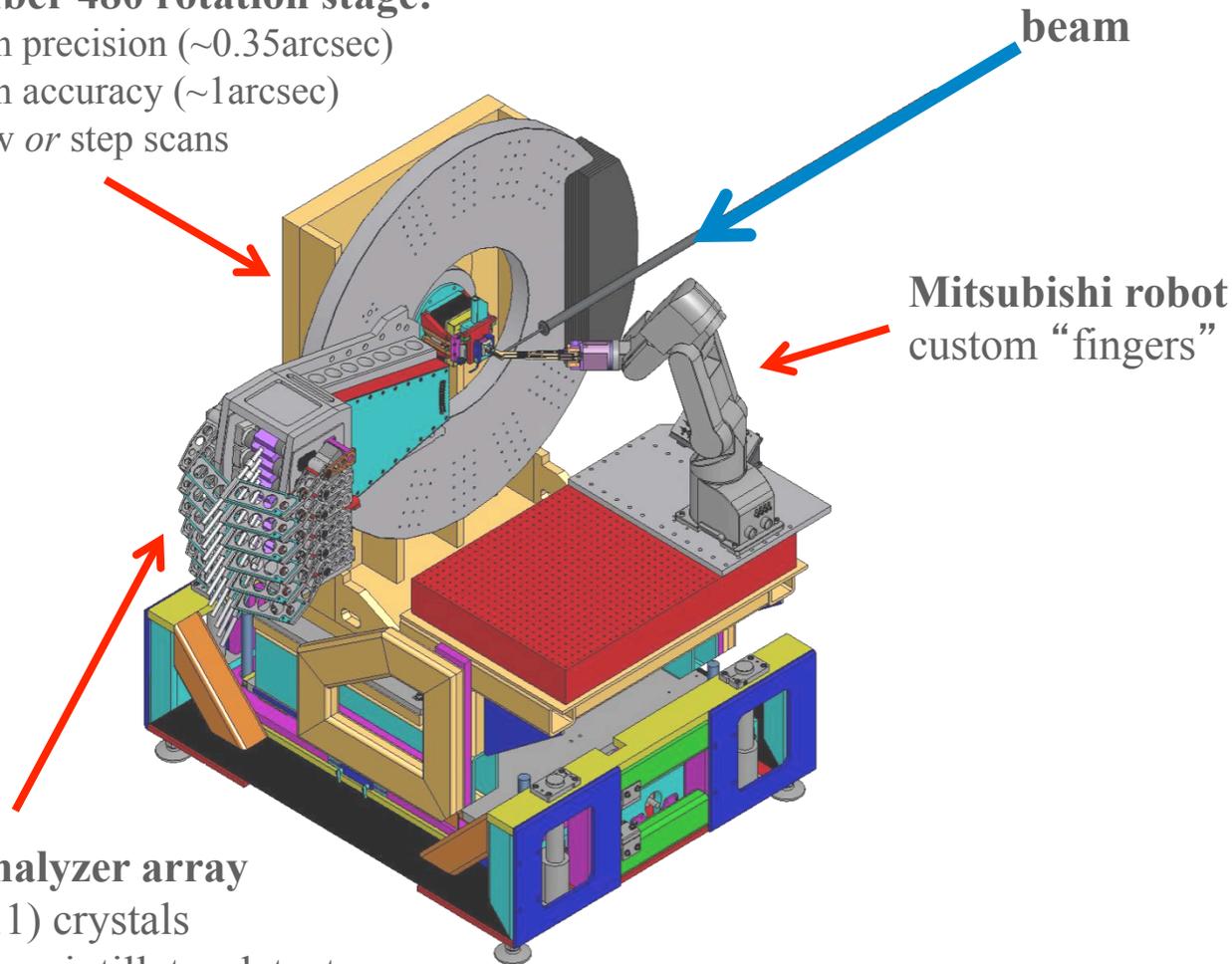
# *Highest resolution requires high collimation. Optimal is a crystal analyzer between the sample and detector: 11-BM Diffractometer*

## **Huber 480 rotation stage:**

high precision ( $\sim 0.35$ arcsec)

high accuracy ( $\sim 1$ arcsec)

slew *or* step scans



**Complete pattern is  
measured in <1 hour**



# 11-BM Robotic Data Collection

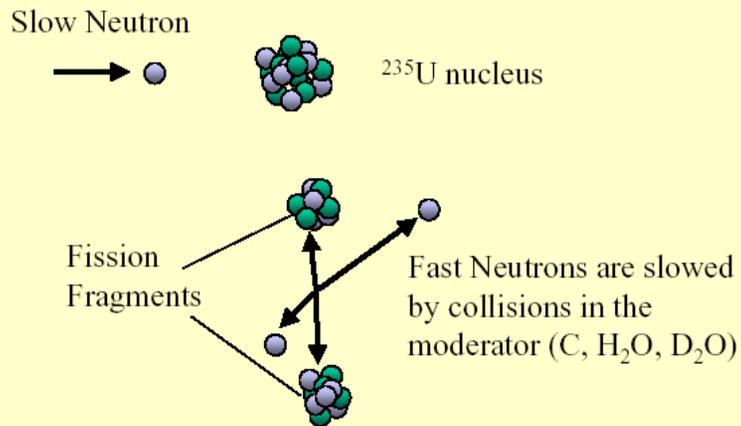


(Matt Suchomel: <http://youtu.be/sowojskY7c4> or search APS 11-BM on YouTube)

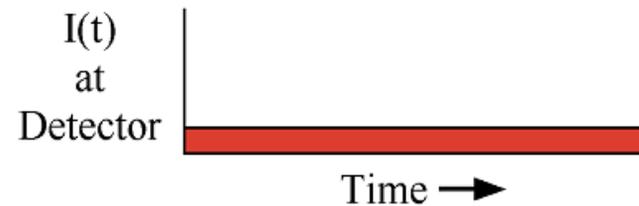
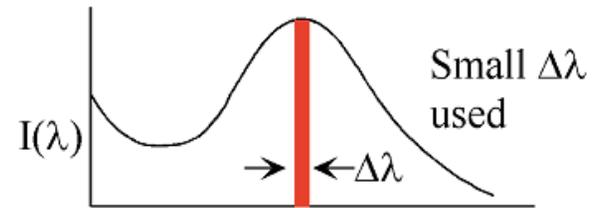
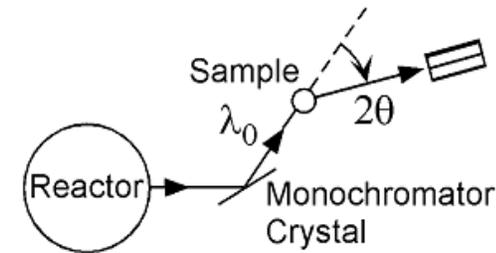


# Reactor Source Neutron Diffraction

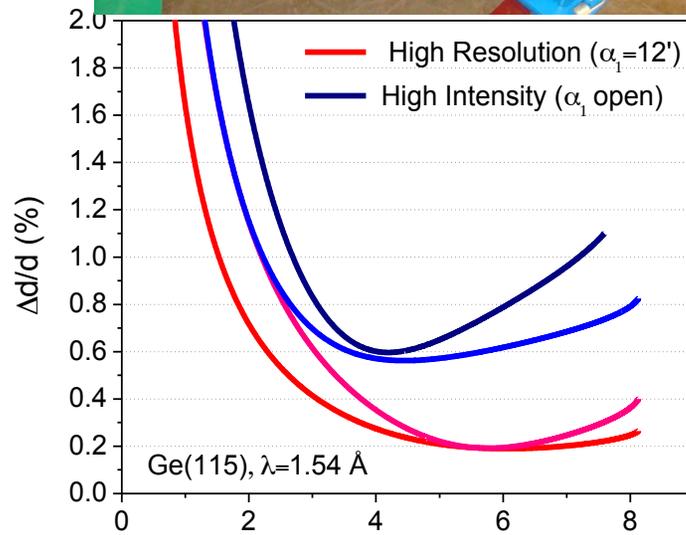
## Producing neutrons by fission



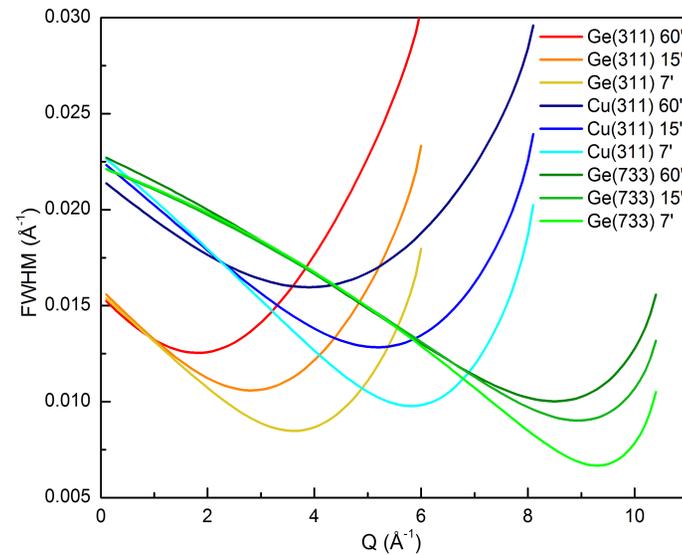
## STEADY STATE TECHNIQUE



# Powder Instruments: Constant Wavelength



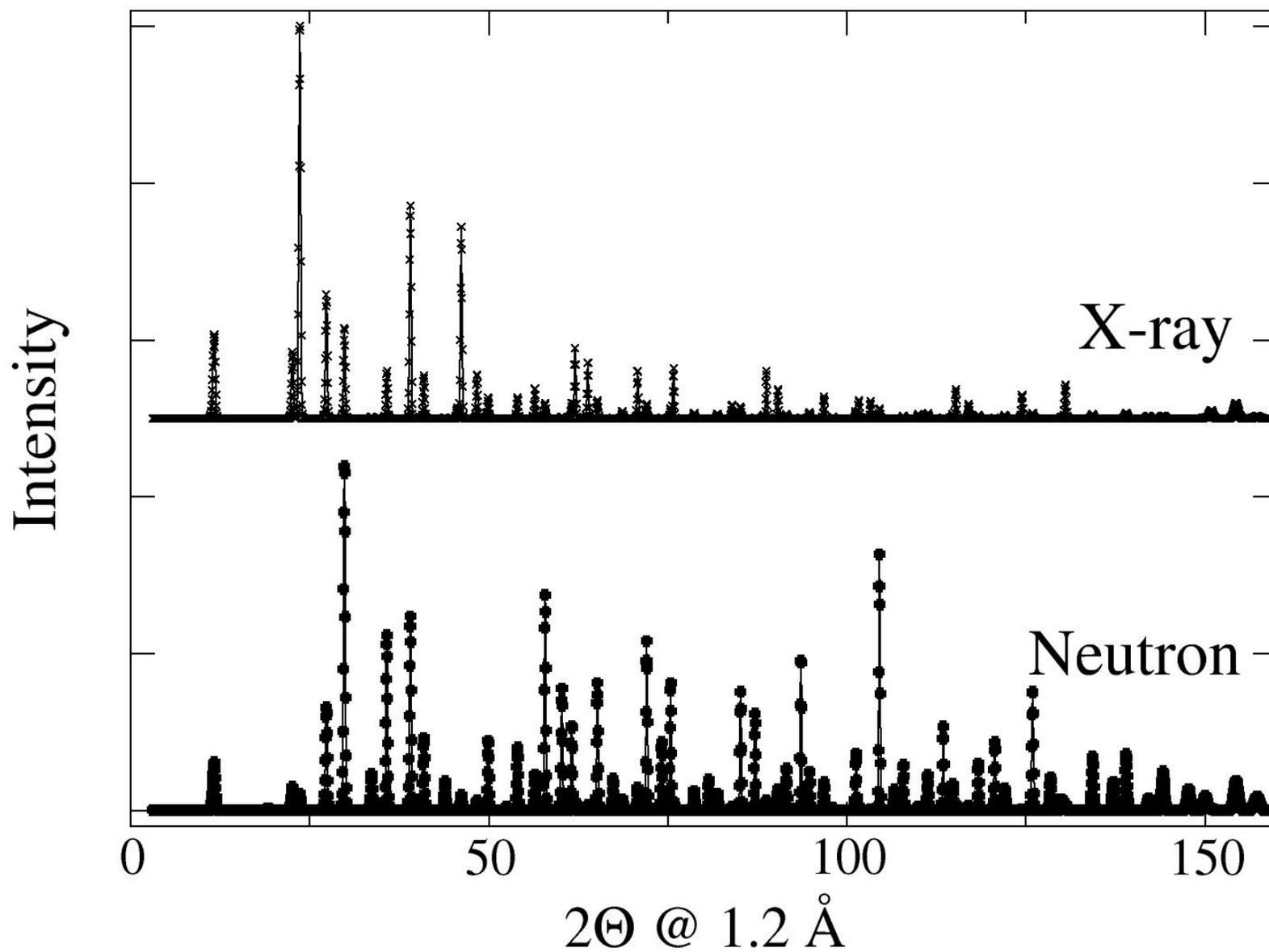
beamline HB2a at HFIR



beamline BT1 at NIST (NCNR)



# Comparison of $\text{Tb}_2\text{TiO}_7$ with x-rays & neutrons



# Spallation Sources

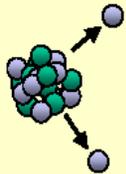
A pulse of protons impacting the target produces a shower of fast neutrons that are slowed down in a moderator. A new pulse is created  $\sim 30$  times/sec

## Producing neutrons by spallation

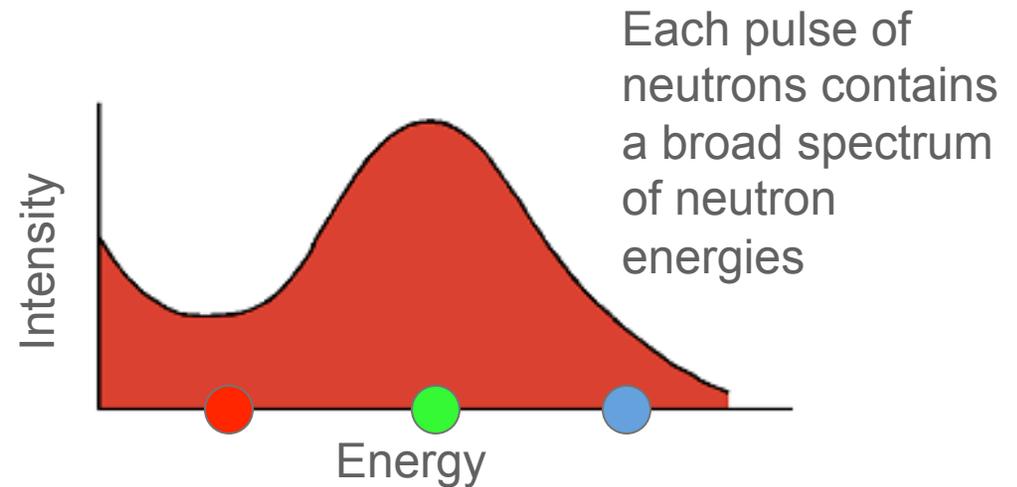
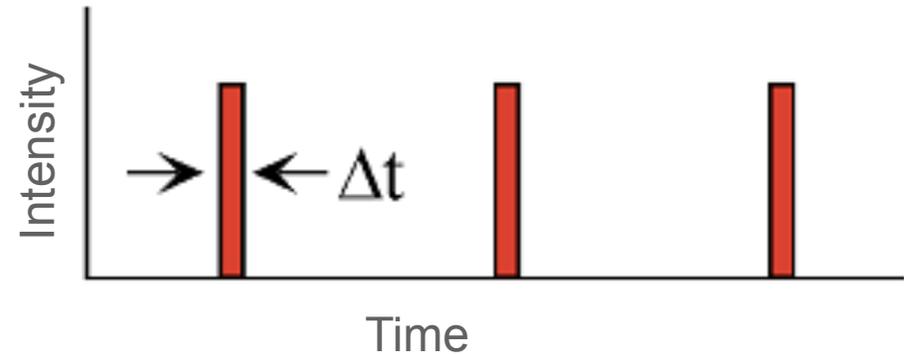
Fast proton



Heavy nucleus (Ta, U, Hg)

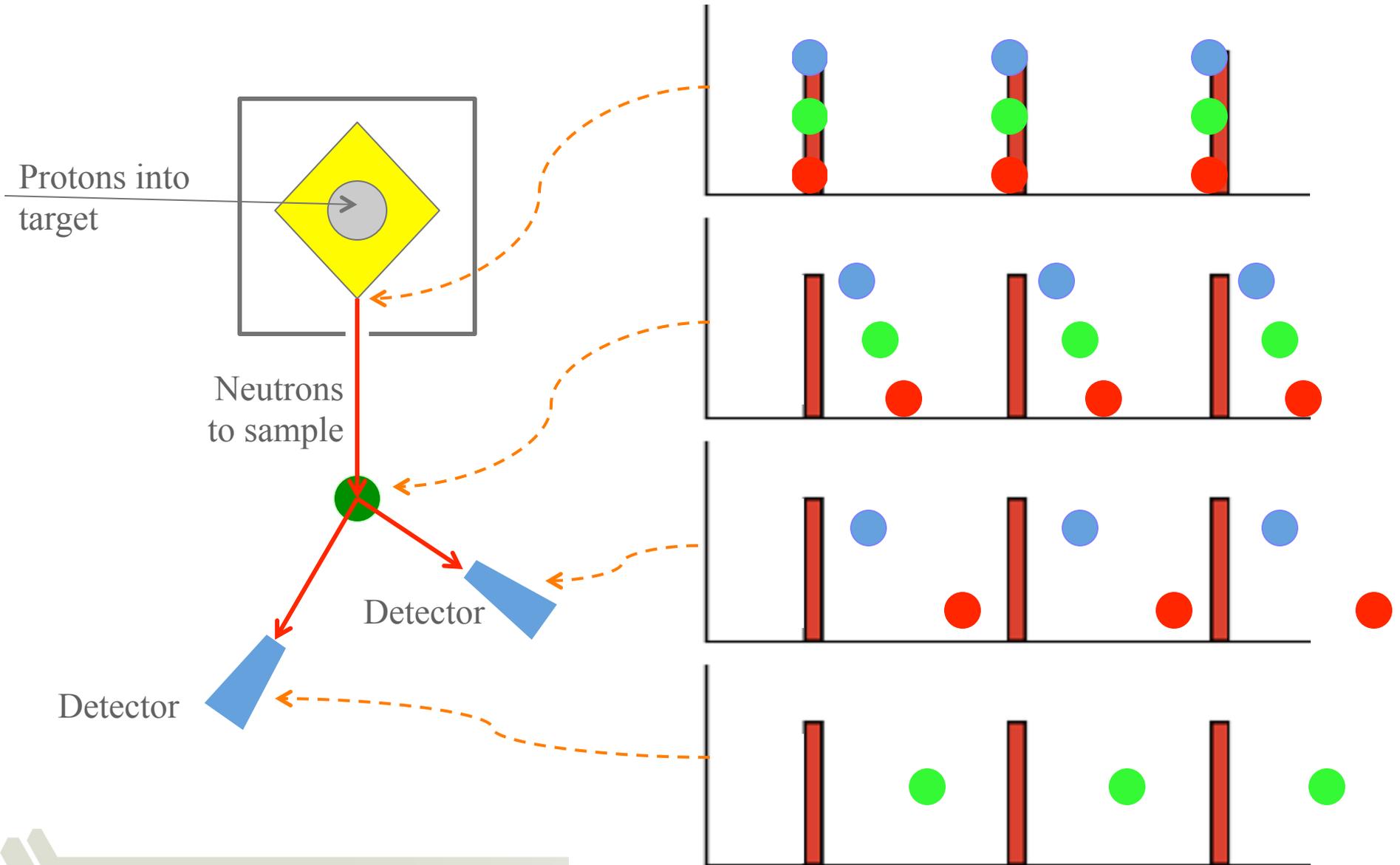


Fast Neutrons are slowed by collisions in a moderator (CH<sub>4</sub>, H<sub>2</sub>O, D<sub>2</sub>O)



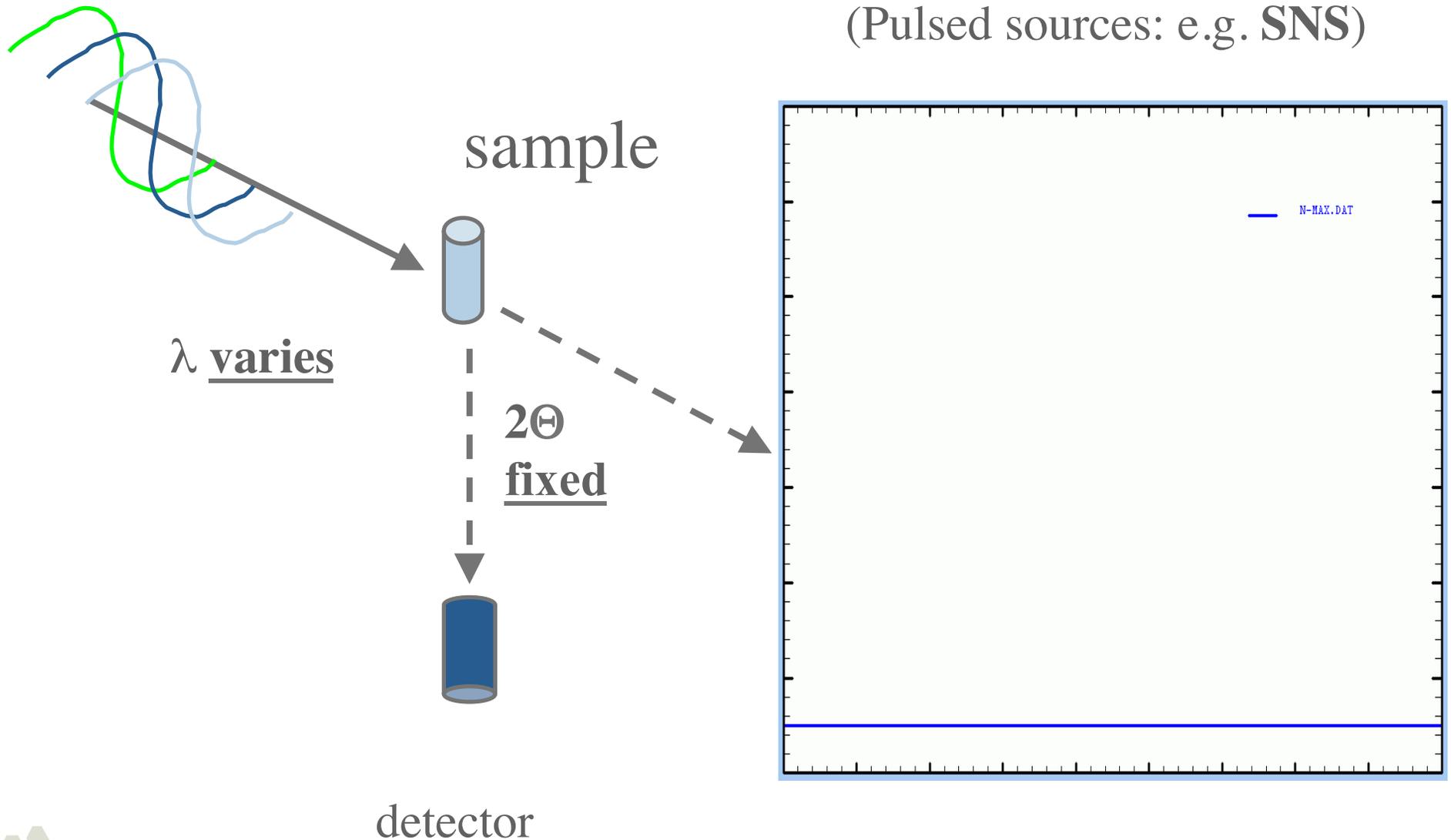
# Time of Flight Diffraction

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



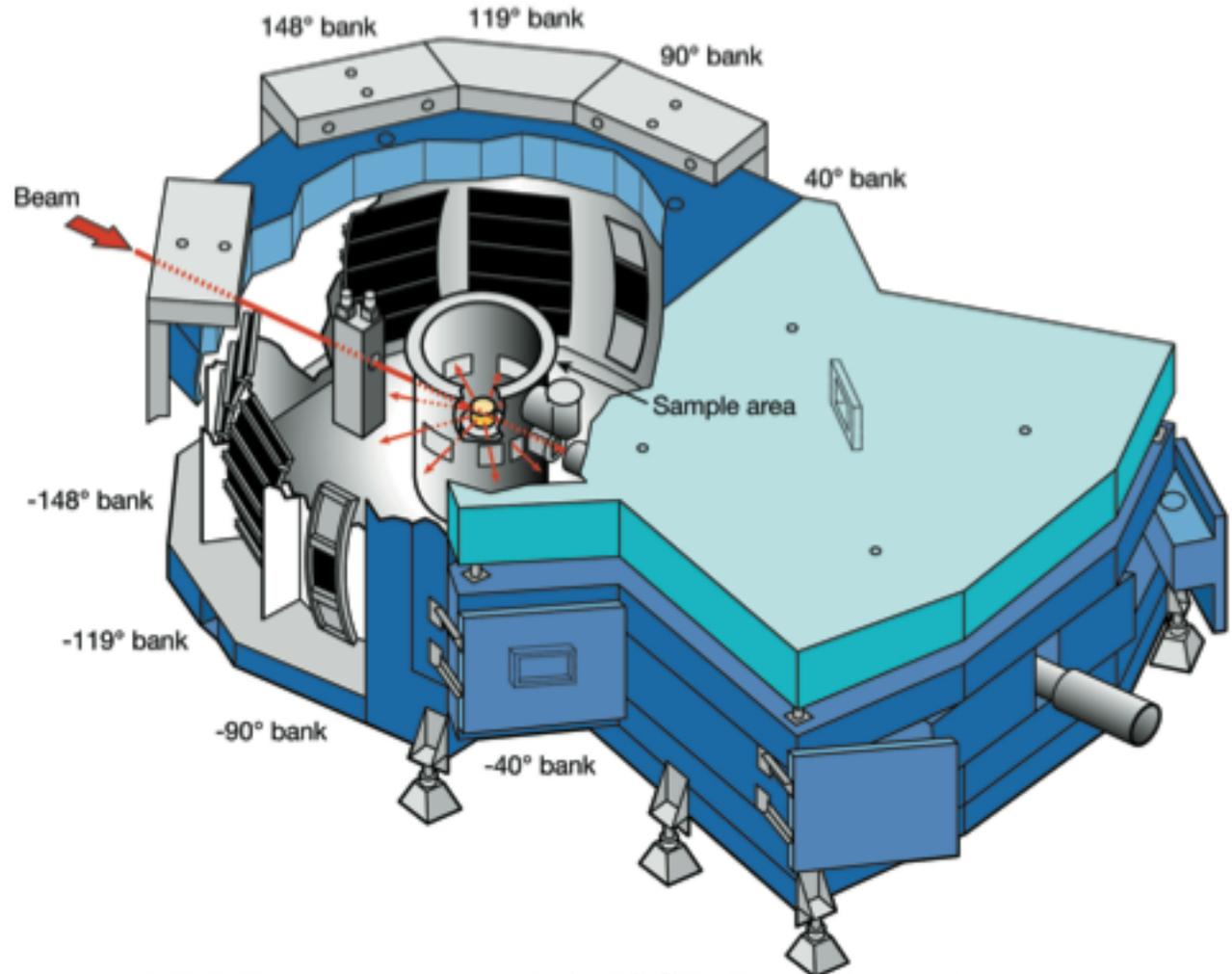
# Time-of-flight ( $2d\sin\Theta=\lambda$ )

(Pulsed sources: e.g. SNS)



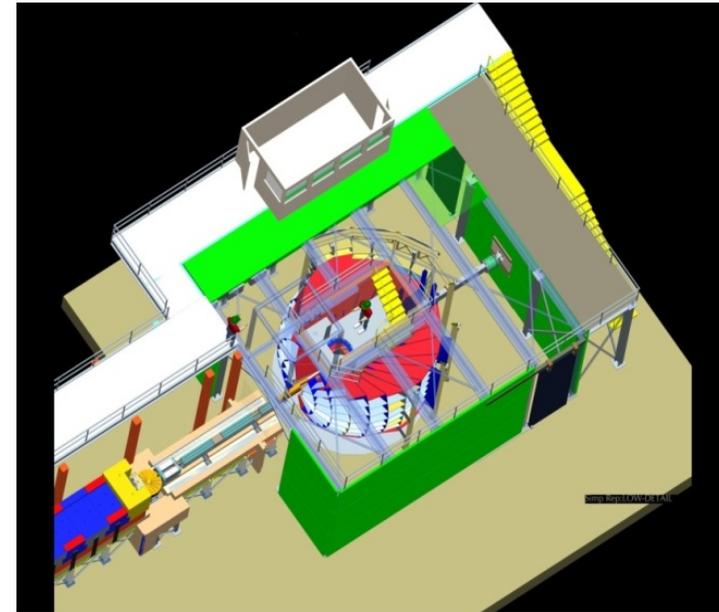
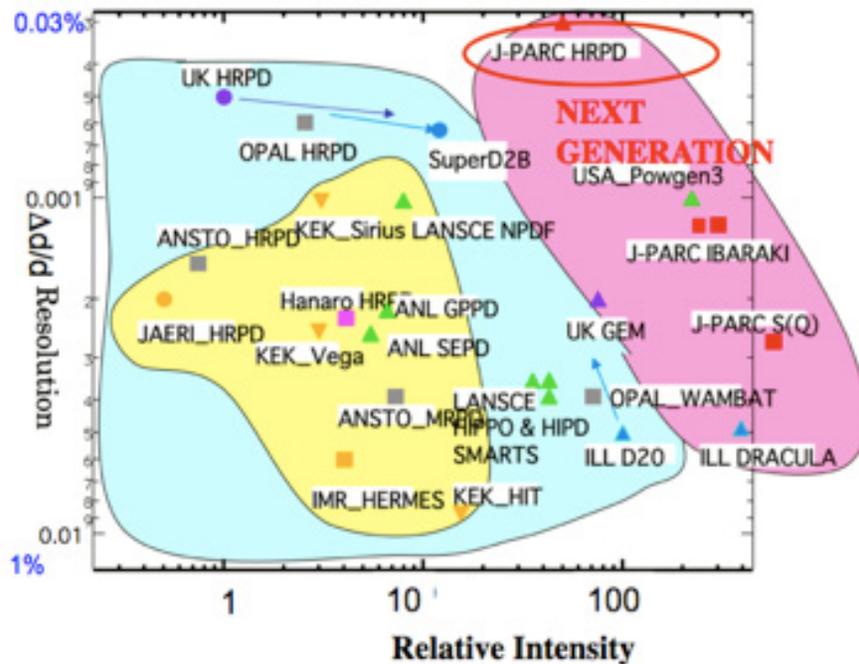
# Neutron Powder Diffraction with Spallation Source

- 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<sup>rd</sup> Generation TOF Instruments: High Intensity and High Resolution

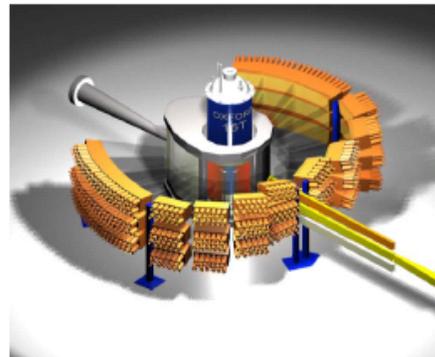


SNS: POWGEN[-3]

GEM (ISIS TS-I)

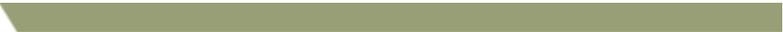


WISH  
A high-resolution magnetic diffractometer for TS-II



Super HRPD (JSNS)





# **Understanding Materials Effects in Powder Diffraction**



# Materials effects on Powder Diffraction

Peak broadening:

- Crystallite size:
  - What happens when crystals become small?
- Residual Stress (Strain)
  - What happens if matrix effects do not allow crystallites to equilibrate lattice parameters?

*Note that these effects can vary in different crystallographic directions:  
anisotropic peak broadening (best handled in GSAS-II)*



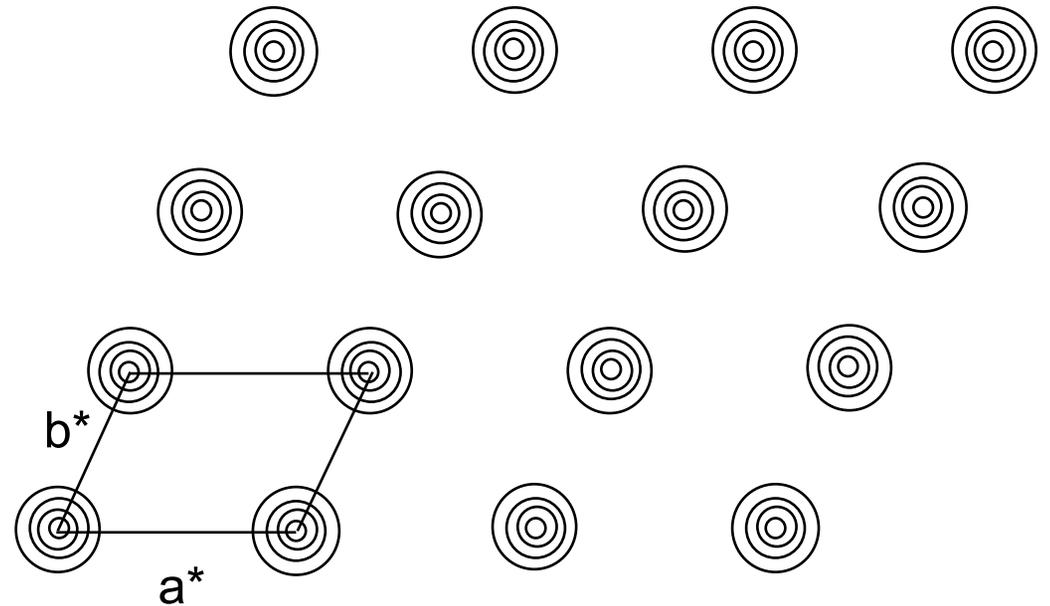
# Crystallite Size Broadening

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

The FT from a finite length array is broadened.

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

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



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

# Crystallite Size Broadening

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

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

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

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

See GSAS Manual, pp 158-167.

GSAS fits crystallite broadening with two profile terms:

- LX -> Lorentzian
- GP -> Gaussian

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

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

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

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

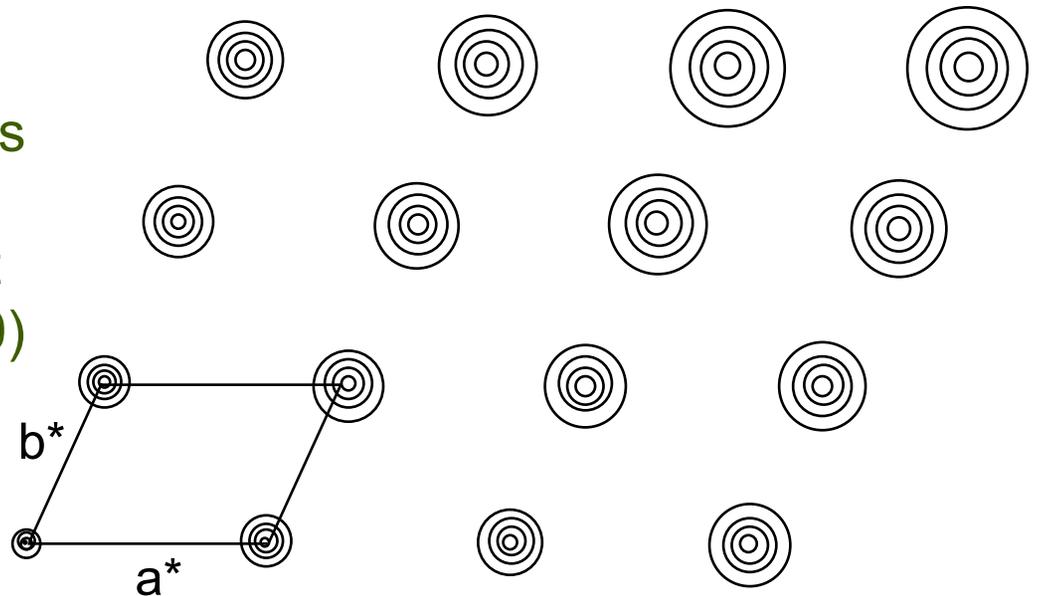


# Microstrain Broadening

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

This leads to a range of lattice constants.

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



# Microstrain Broadening

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

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

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

See GSAS Manual, pp 158-167.

GSAS fits strain broadening with two profile terms:

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

*(note that GU also has an instrumental contribution)*

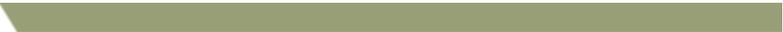
*Relation between strain (as percentage) and GSAS terms:*

$$S = 100\% \frac{\pi}{18000} LY$$

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

*where  $GU_I$  accounts for the instrumental contribution*





# **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

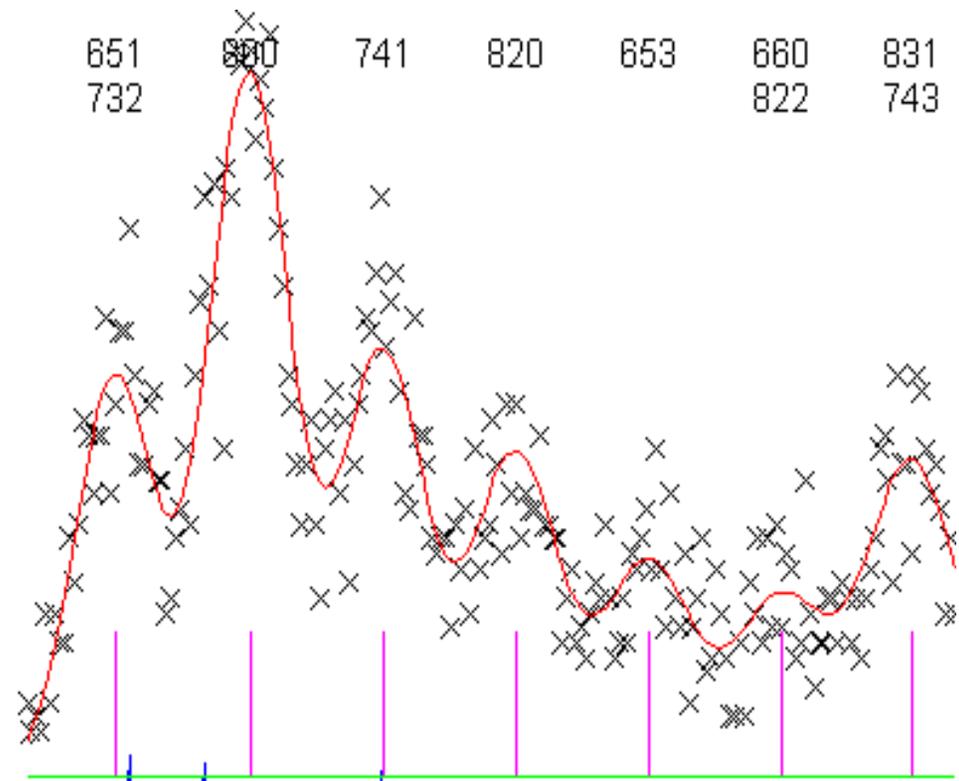
- Qualitative reasoning: similarities in patterns implied similar structures
- Visual comparison between computed and observed structure verifies approximate model
- Fits, where accurate (& precise) models were rarely obtained

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



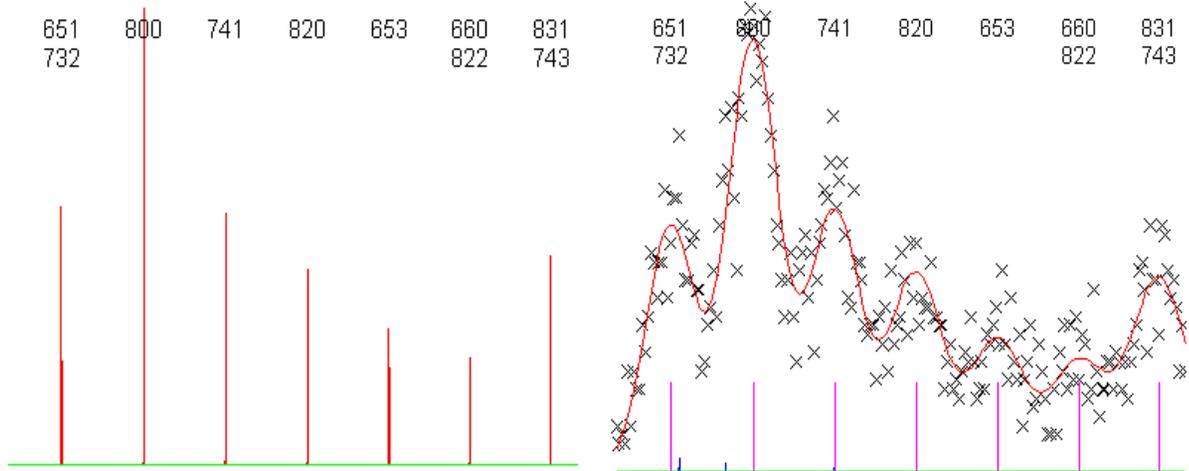
# Hugo Rietveld's technique

- 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

# Powder data fitting

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

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

$y_i$  = observed powder diffraction intensities

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

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

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

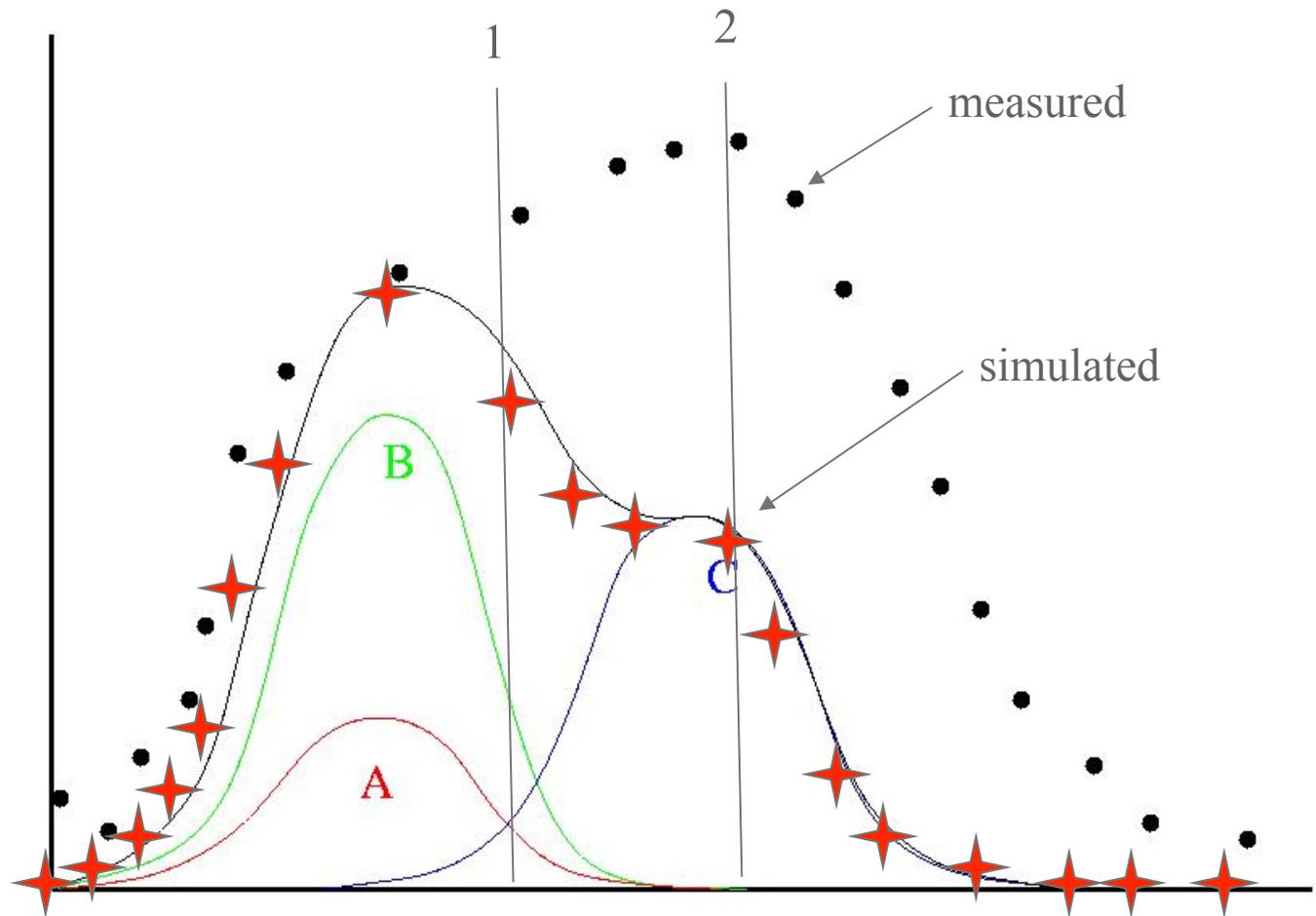
+ lattice parameters  
+ “experimental” parameters for peak shapes, background...

# 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)

# The physics that determine peak profiles

## Common factors

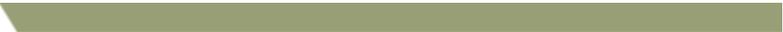
- Instrumental Resolution
  - Axial Divergence (Low Angle Asymmetry)
  - Sample placement/transparency
  - Crystallite Broadening\*
  - Strain Broadening\*
- \* Note that these effects can vary for different classes of reflections (anisotropic peak broadening)

## Less common factors

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

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





## 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*

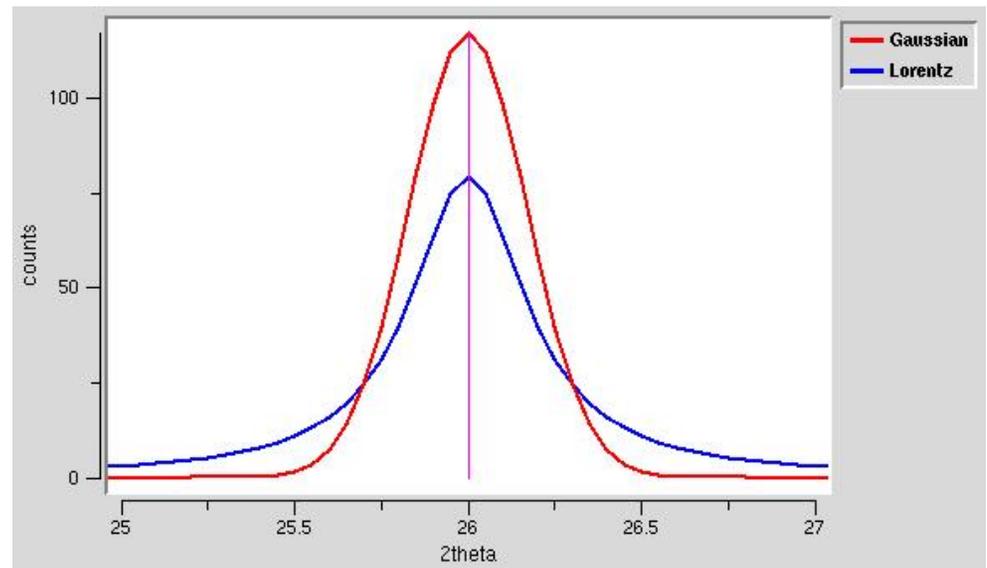
## Normalized Gaussian

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

## 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  $\Gamma_G$  and  $\gamma_L$  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 ( $\eta$ ) in GSAS manual,  $\eta=0$  is Gaussian,  $\eta=1$  is Lorentzian]



# CW: Variation of FWHM with Q

## Gaussian

- U, V & W are Cagliotti terms, derived as instrument response function for CW neutron diffraction. Incomplete for x-rays.
- P is a crystallite broadening contribution

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

## Lorentzian

- X is crystallite broadening
- Y is strain broadening

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

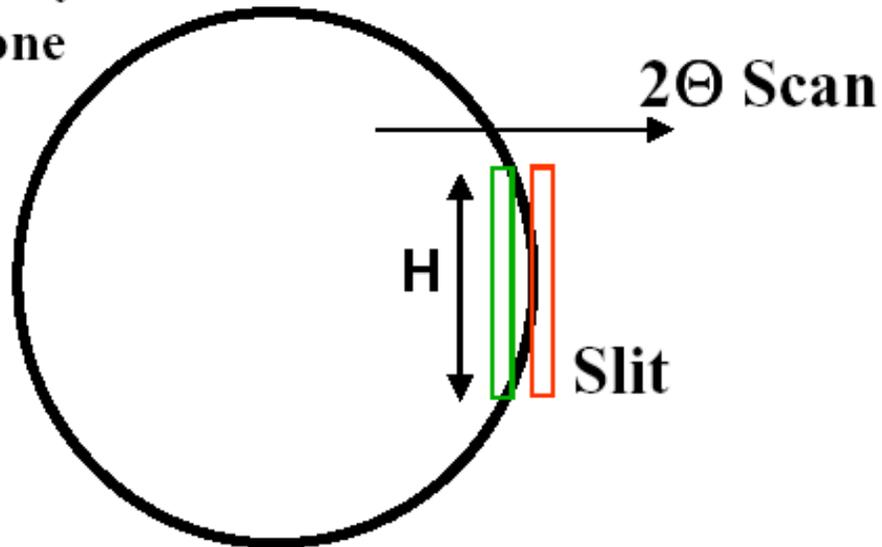
*N.B. no instrumental broadening term*



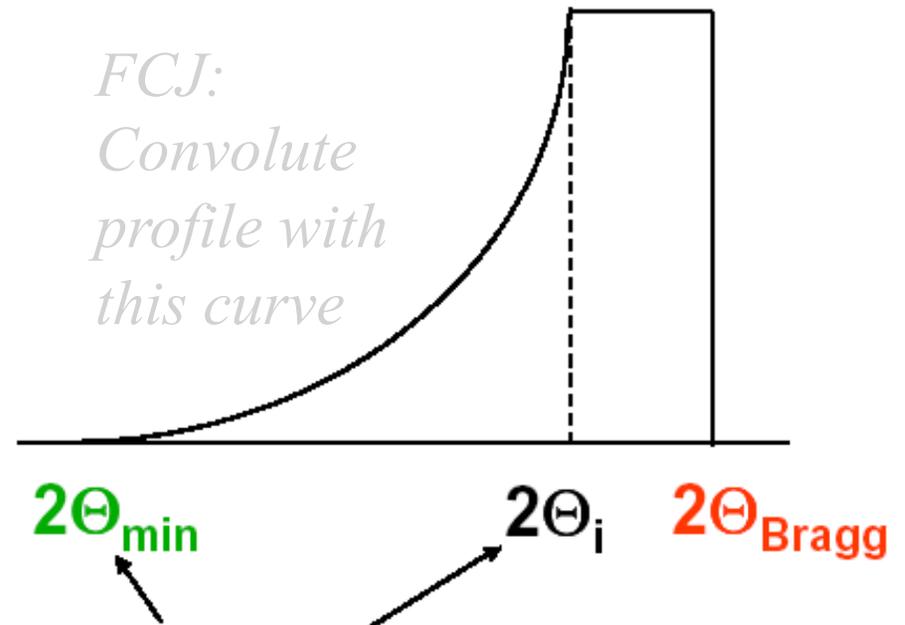
# Axial Divergence (Low Angle Asymmetry)

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

Debye-Scherrer  
cone



*FCJ:  
Convolute  
profile with  
this curve*



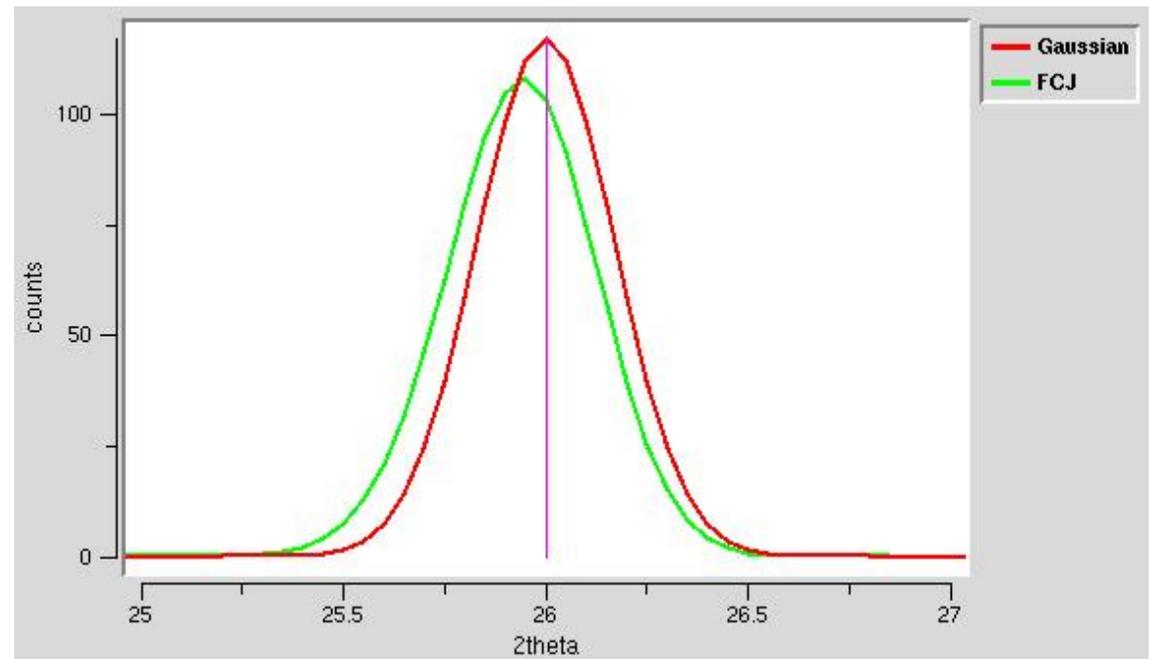
Depend on slit & sample “heights” wrt diffr. radius  
 $H/L$  &  $S/L$  - parameters in function  
(typically 0.005 - 0.020)



# 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),  $T_s$

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

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

*R is diffractometer radius*

*These corrections correlate very highly with the zero correction for  $2\theta$ , 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  $2\theta$ ).



## 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

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

## 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

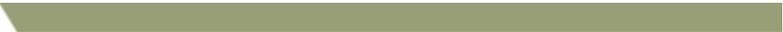
$$\sigma^2(M_{hkl}) = S_{400}(h^4 + k^4) + S_{004}l^4 + 3S_{220}h^2k^2 + 3S_{202}(h^2l^2 + k^2l^2)$$

### 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





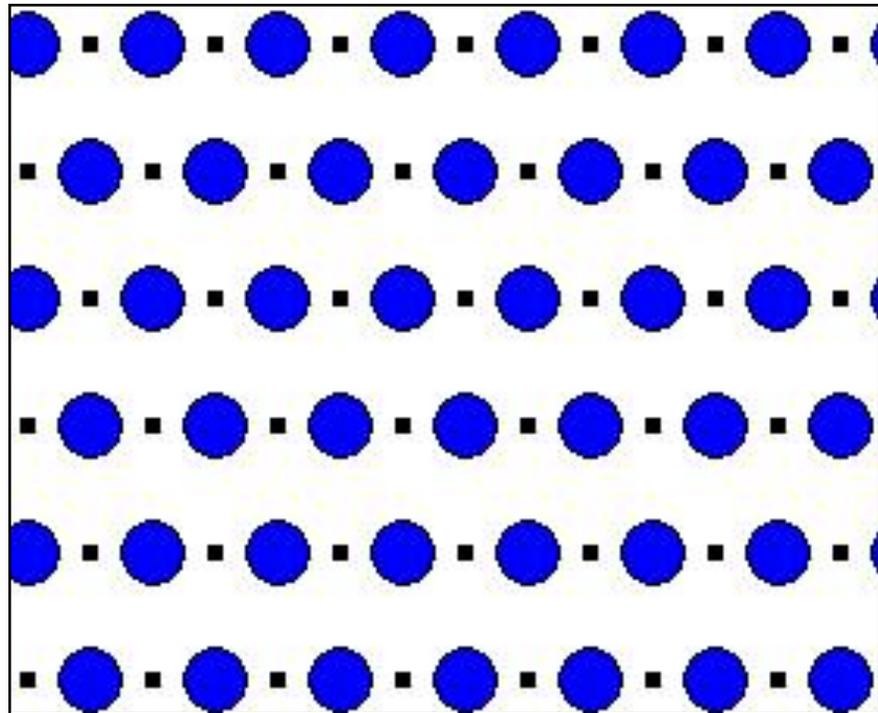
## Appendix 2: more on crystallography



# The Lattice

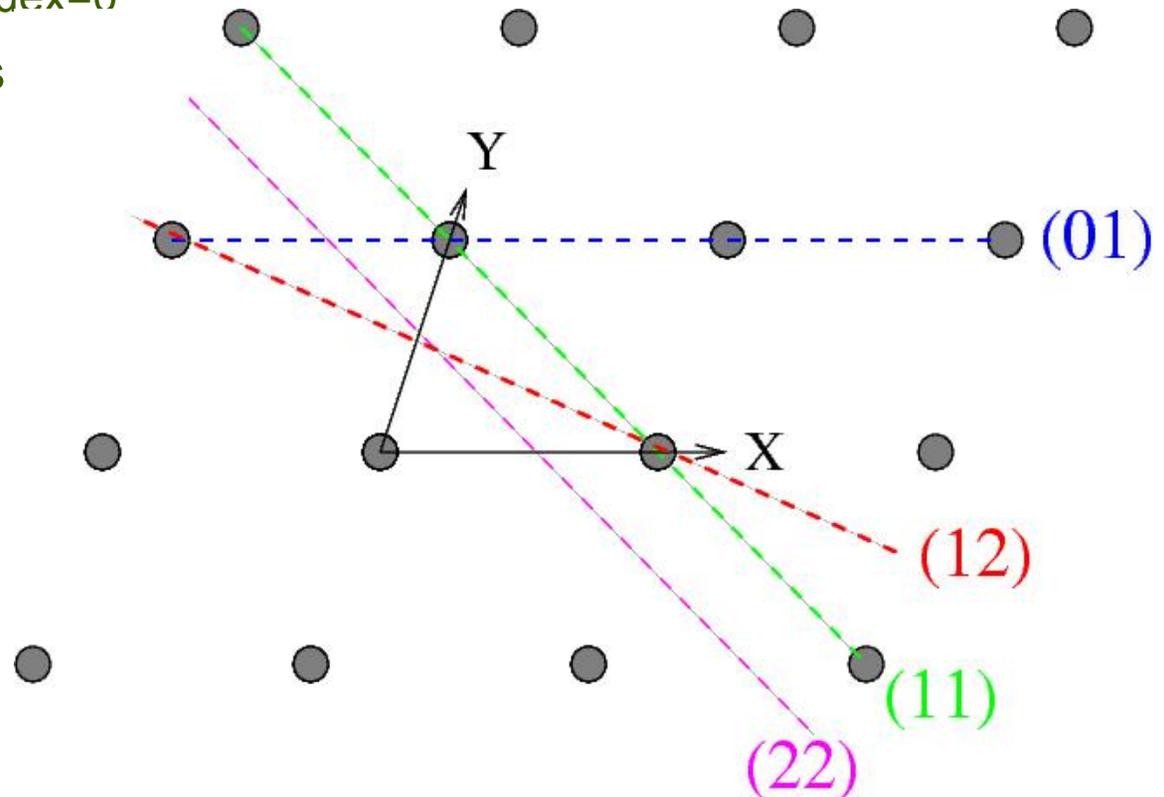
- Crystals are constructed from repeated arrangements of atoms.
- Crystalline structure can be described as set of “identical boxes” stacked in 3D; the contents of each box is identical (exception: quasicrystals)
  - ***A lattice*** is a mathematical concept where each lattice point describes an identical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



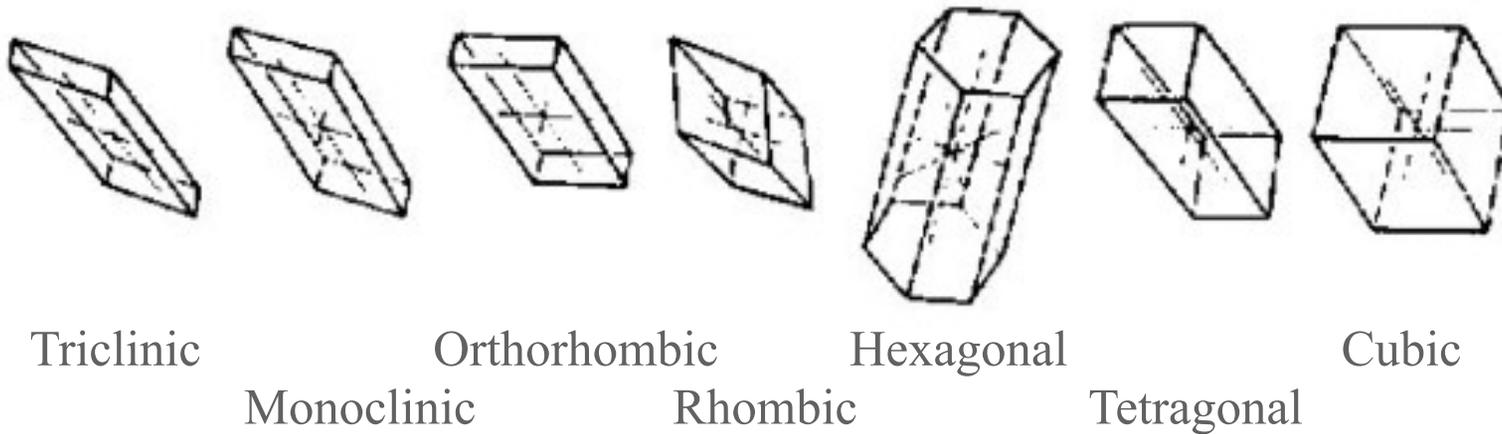
# Lattice planes

- General Indices: lattice planes are indexed by the inverse of where they cut each axis:
  - Intercept of 0.5  $\rightarrow$  index=2
  - Intercept of  $\infty$  ( $\parallel$  to axis)  $\rightarrow$  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***

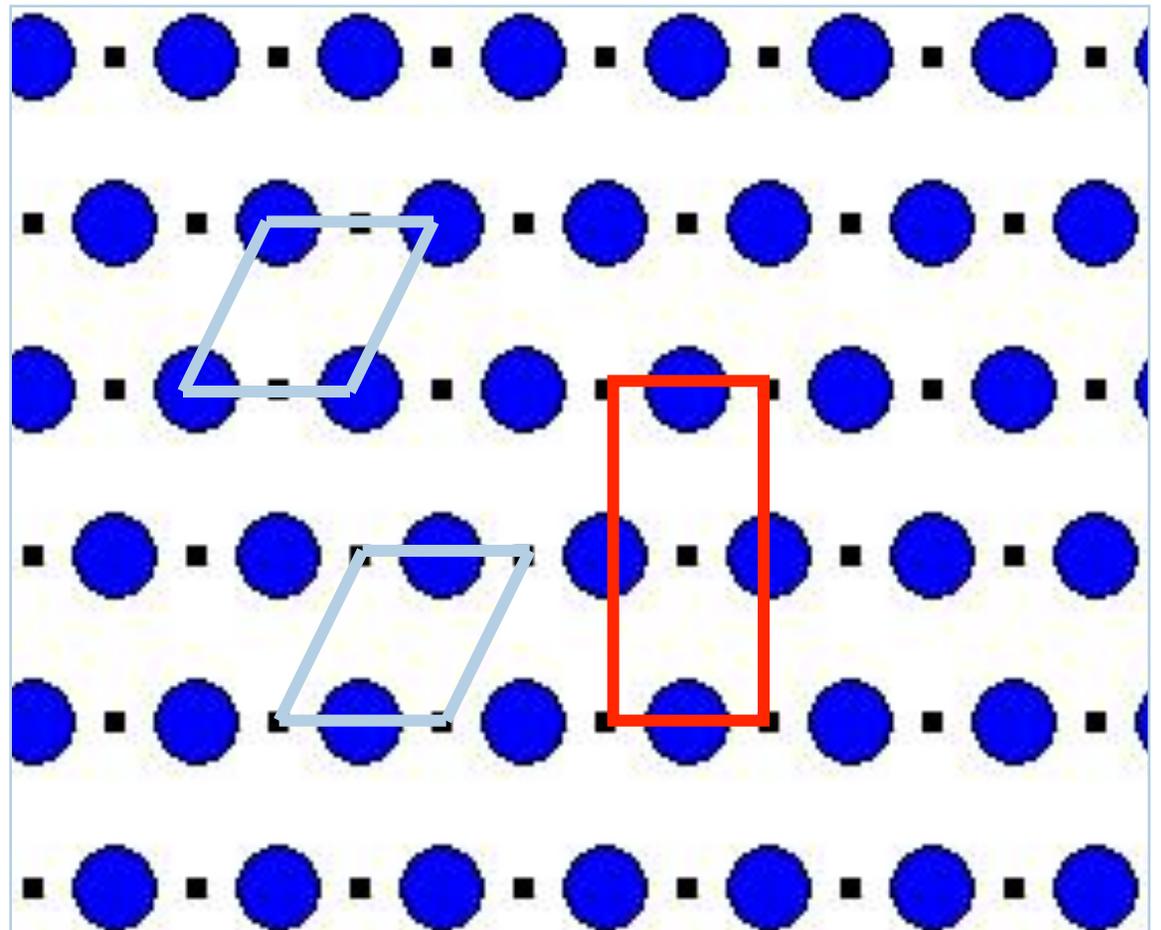


(Image from <http://pasadena.wr.usgs.gov/office/given/geo1/lecturenotes/SevenCrystalSystems.html>)



# 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

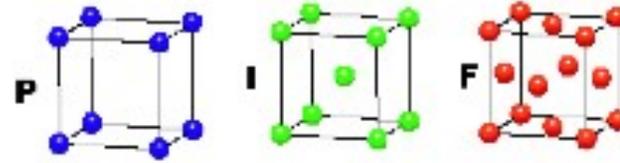
Centering causes lattice points to be placed inside units cells (**body center**, **face centers**) giving rise the **14 Bravais lattices** (1848)

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

## CUBIC

$$a = b = c$$

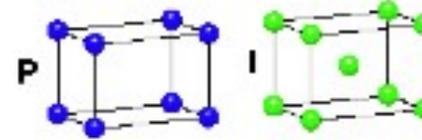
$$\alpha = \beta = \gamma = 90^\circ$$



## TETRAGONAL

$$a = b \neq c$$

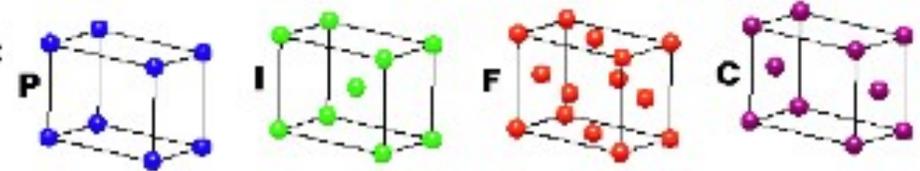
$$\alpha = \beta = \gamma = 90^\circ$$



## ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

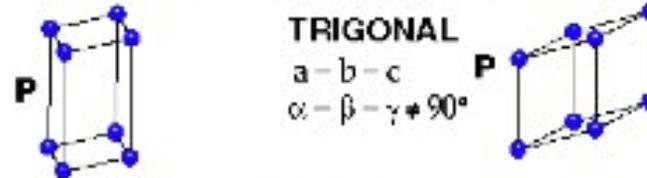


## HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

$$\gamma = 120^\circ$$

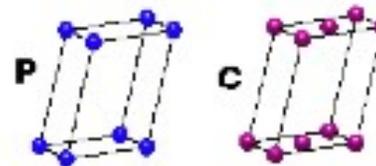


## MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

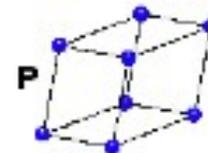
$$\beta \neq 120^\circ$$



## TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



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

(Figure from [http://www.chemsoc.org/exemplarchem/entries/2003/bristol\\_cook/latticetypes.htm](http://www.chemsoc.org/exemplarchem/entries/2003/bristol_cook/latticetypes.htm))



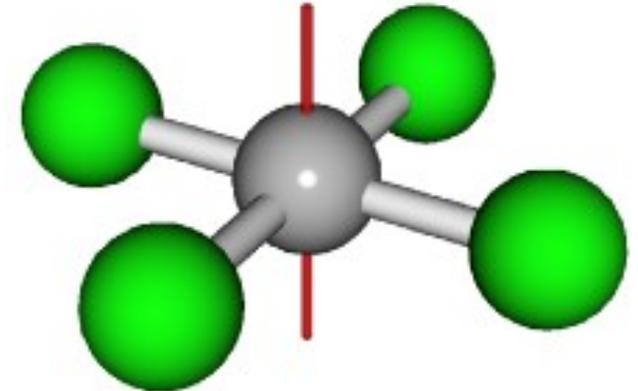
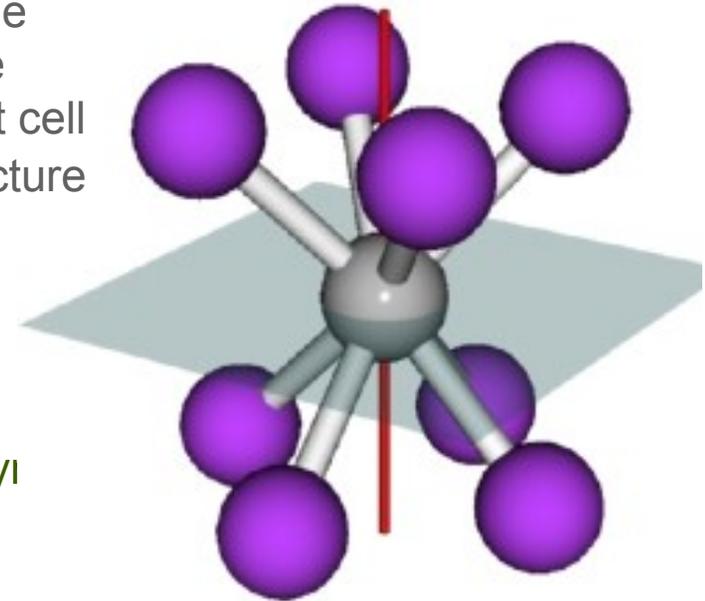
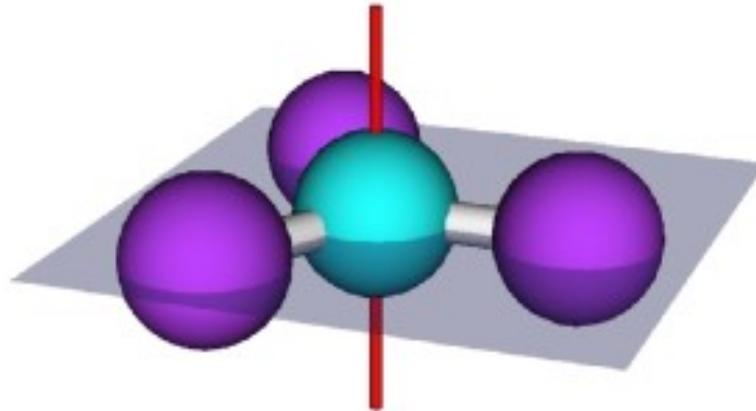
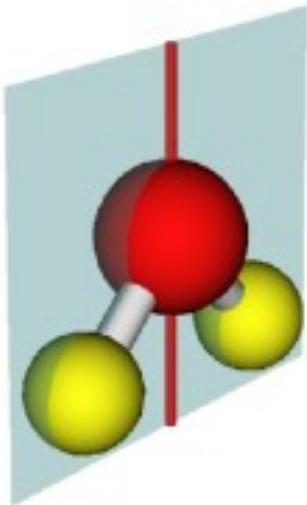
# Symmetry

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

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

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

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

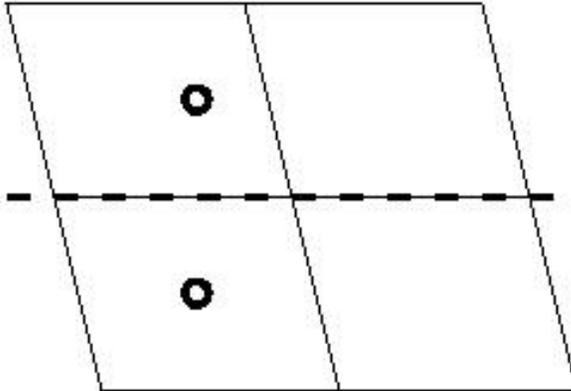


(Images from <http://members.tripod.com/~EppE/302rev2.htm>)

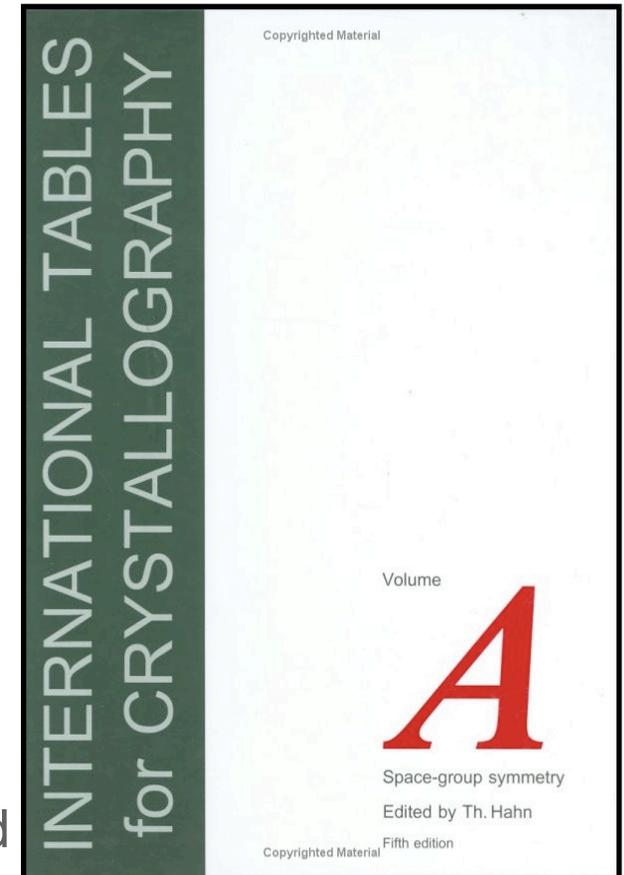


# Space Groups

- Not all combinations of symmetry and lattice types are compatible
  - Example: mirror plane perpendicular to a non-orthogonal pair of axes – 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** recommend **Space Groups for Solid State Scientists** by G. Burns and A. M. Glazer as a good place to learn about space groups and s.g. properties



# 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.*

# Fractional coordinates

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

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

- △ This notation allows for simple description of symmetry operations:

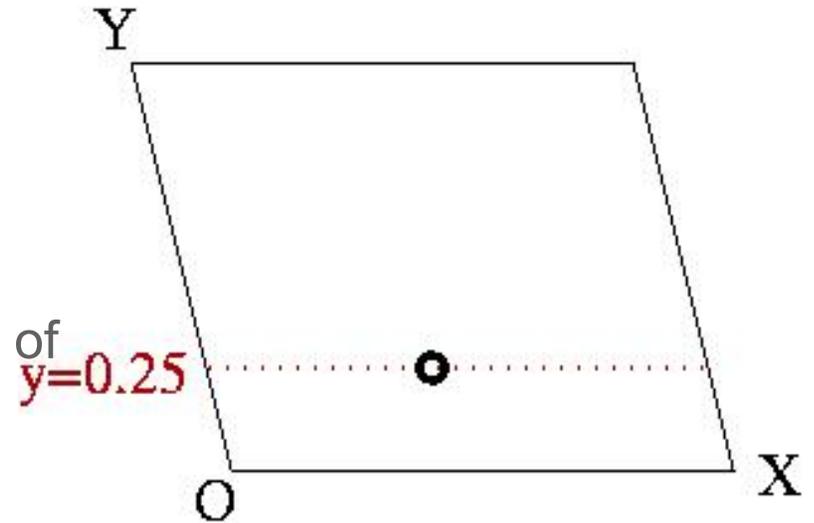
- $(x,y,z) \rightarrow (1+x, y, z)$  [translation on x]

- $(x,y,z) \rightarrow (1/2+x, 1/2+y, 1/2+z)$  [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 ( $\pm 2\sigma$ )



# 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:

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

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

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

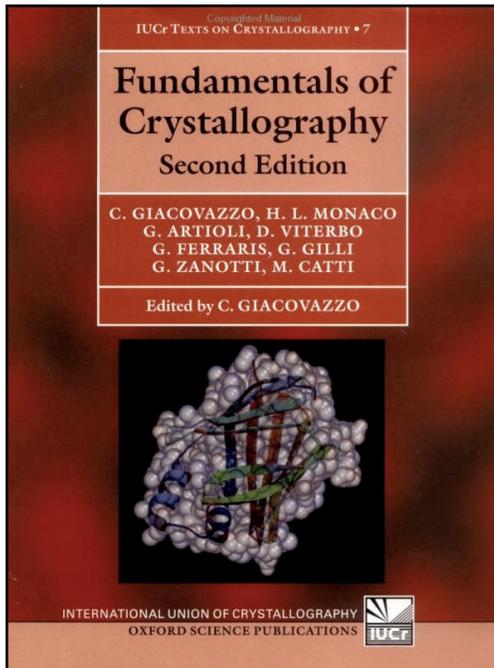
*Use of the reciprocal lattice makes computation of the Fourier transform of the atomic positions straightforward.*

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



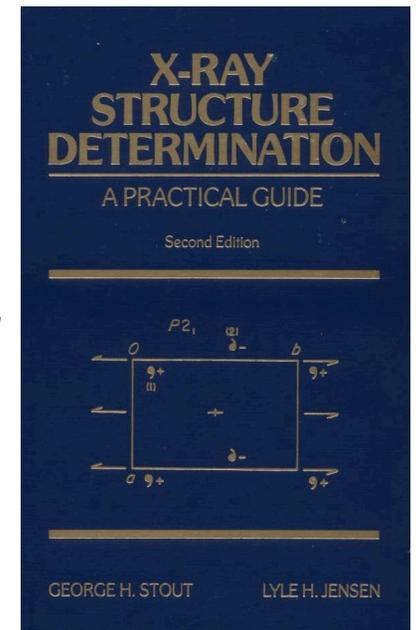
# Where to go for more...

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. 1<sup>st</sup> book for many in field.*]



## APS Web lectures on powder diffraction crystallography:

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

([http://www.aps.anl.gov/Xray\\_Science\\_Division/Powder\\_Diffraction\\_Crystallography](http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography))

*Intended to introduce Rietveld refinement techniques with GSAS & EXPGUI*

