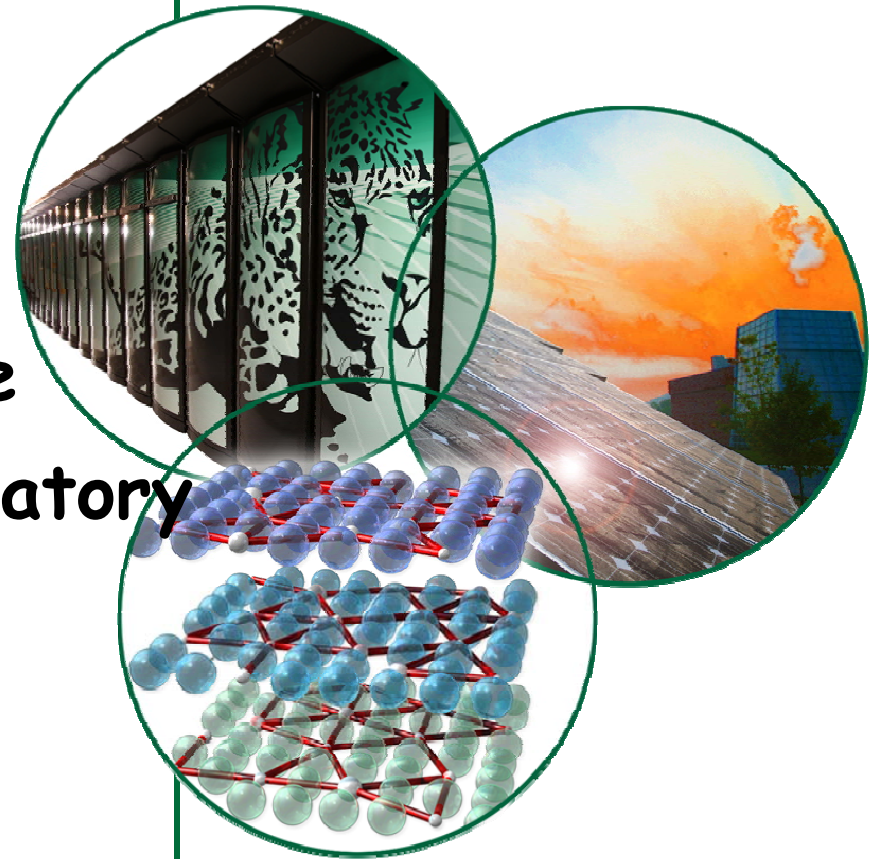


# Powder Diffraction

Ashfia Huq

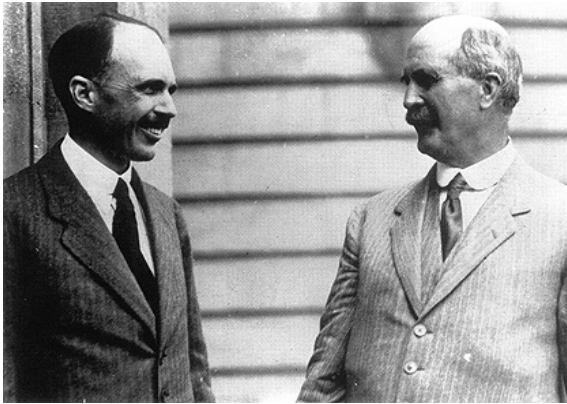
Spallation Neutron Source

Oak Ridge National Laboratory



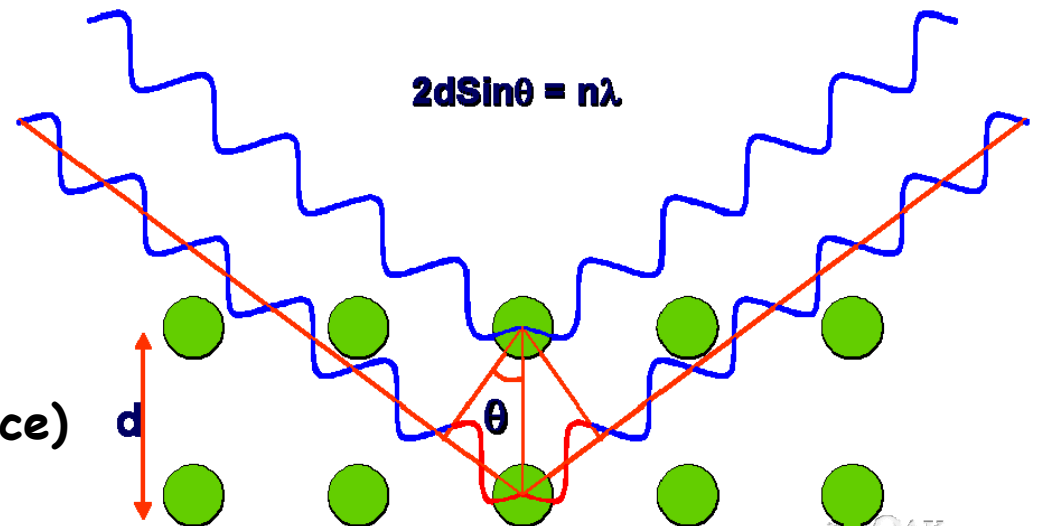
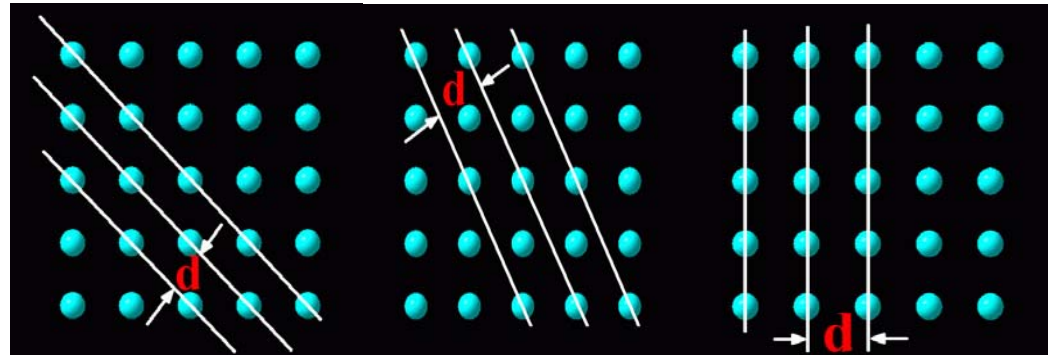
# Bragg's law

W.H. Bragg (1862-1942)  
W.L. Bragg (1890-1971)

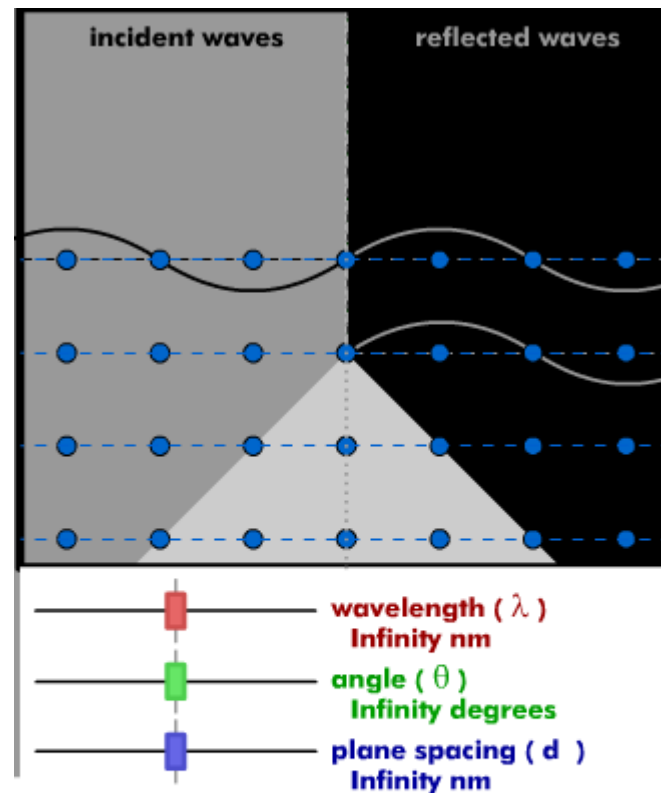


Shared 1915 Nobel Prize

- Zinc Blend (fcc not sc)
- NaCl (not molecular)
- Diamond (two overlapping fcc lattice)



# Bragg's law



Bragg's Law:

$$n \times \lambda = 2 \times d \times \sin(\theta)$$

**NaN x Infin = 2 x Infinix sin(nfini)**

**WAVES OUT OF PHASE**  
use the sliders to make **n** an integer

# Where are the atoms?

We need wavelength ( $\lambda$ )  $\sim$  Object size (for condensed matter that is  $\text{\AA}$ )



## X-ray:

( $\lambda$  :  $10^{-9}\text{m}$  -  $10^{-11}\text{m}$ )

$$\lambda[\text{\AA}] = 12.398/E_{\text{ph}}[\text{keV}]$$

### Source:

- Lab diffractometers
- Synchrotron Sources

## Neutron:

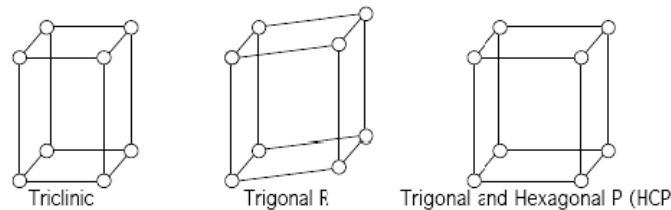
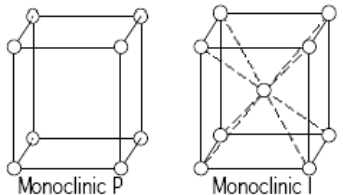
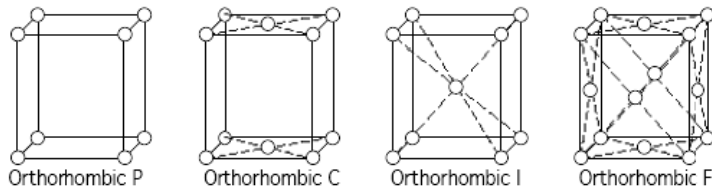
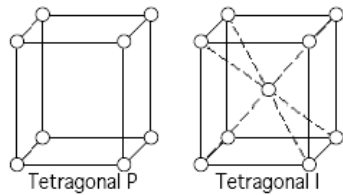
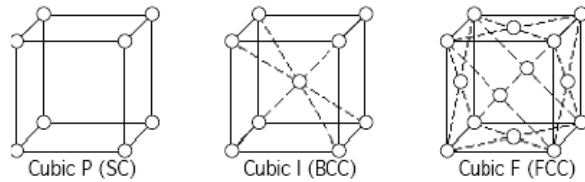
(thermal  $\lambda$  :  $1-4\text{\AA}$ )

$$E_n[\text{meV}] = 81.89/\lambda^2[\text{\AA}]$$

### Source:

- Reactors (fission)
- Spallation Source

# Crystal Structure = Basis + Lattice



Basis		Lattice
	$\otimes$	
System	Angles and Dimensions	Lattices in System
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma$	P (primitive)
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$	P (primitive) I (body centered)
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	P (primitive) C (base centered) I (body centered) F (face centered)
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	P (primitive) I (body centered)
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	P (primitive) I (body centered) F (face centered)
Trigonal	$a = b = c, 120^\circ > \alpha = \beta = \gamma \neq 90^\circ$	R (rhombohedral primitive)
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	R (rhombohedral primitive)

**3d Bravais Lattices:  
14 types in 7 classes**

# Bragg Scattering from a crystal

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

## Simple Example:

Simple cubic cell with one atom basis at (000)

$$F_{hkl} = f e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} = f$$

For bcc lattice : SC with  $(000, \frac{1}{2} \frac{1}{2} \frac{1}{2})$  basis

$$F_{hkl} = f [e^{2\pi i(h \cdot 0 + k \cdot 0 + l \cdot 0)} + e^{2\pi i(h + k + l) \cdot \frac{1}{2}}] = 2f \text{ for even } (h+k+l) \\ = 0 \text{ for odd } (h+k+l)$$

# Simple Example:

Rewrite Bragg's Law for cubic system:

$$\sin^2\theta = (\lambda/4a)^2(h^2+k^2+l^2)\dots\dots\dots(1)$$

$(h^2+k^2+l^2)$	0	1	2	3	4	5	6	8	9	10	11	12	13	14	16	17	18	19	20	21	22	24	
sc																							
bcc																							
fcc																							
diamond																							

In a powder diffraction measurement (Al powder), we measure Bragg angles  $\theta$  using  $\text{Cu K}_\alpha$  radiation. The Bragg angles are  $19.48^\circ, 22.64^\circ, 33.00^\circ, 39.68^\circ, 41.83^\circ, 50.35^\circ, 57.05^\circ, 59.42^\circ$ . Determine the type of lattice and the lattice parameter.

$\theta$	$\sin^2\theta$	$\sin^2\theta/\sin^2\theta_i$	$3*\sin^2\theta/\sin^2\theta_i$
19.48	0.111	1	3
22.64	0.148	1.333	4
33.00	0.297	2.676	8
39.68	0.408	3.675	11
41.83	0.445	4.009	12
50.35	0.593	5.340	16
57.05	0.704	6.342	19
59.42	0.741	6.676	20

We have indexed the cell to a fcc lattice.  $\lambda = 1.5417$ . Plug in any of these values to eqn (1) to find  $a = 4.004\text{\AA}$ .



# Things get a little more complex when you consider systems that are not orthogonal

## General Formula:

$$\frac{1}{d_{hkl}^2} = |H_{hkl}|^2 = (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)$$

recall (reciprocal lattice vector)

$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot \vec{a}_j \times \vec{a}_k}$$

$$\frac{1}{d_{hkl}^2} = \frac{1}{(1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma)} \times \left\{ \frac{h^2 \sin^2 \alpha}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2 \sin^2 \gamma}{c^2} + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) - \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) - \frac{2hk}{ab} (\cos \gamma \cos \alpha - \cos \beta) \right\}$$

# Space Groups

There are 7 crystal systems:

- ❖ **Triclinic**, all cases not satisfying the requirements of any other system. There is no necessary symmetry other than translational symmetry, although inversion is possible.
- ❖ **Monoclinic**, requires either 1 twofold axis of rotation or 1 mirror plane.
- ❖ **Orthorhombic**, requires either 3 twofold axes of rotation or 1 twofold axis of rotation and two mirror planes.
- ❖ **Tetragonal**, requires 1 fourfold axis of rotation.
- ❖ **Rhombohedral**, also called trigonal, requires 1 threefold axis of rotation.
- ❖ **Hexagonal**, requires 1 six fold axis of rotation.
- ❖ **Isometric or cubic**, requires 4 threefold axes of rotation.

Crystal system	No. of <u>point groups</u>	No. of <u>bravais lattices</u>	No. of <u>space groups</u>
<u>Triclinic</u>	2	1	2
<u>Monoclinic</u>	3	2	13
<u>Orthorhombic</u>	3	4	59
<u>Tetragonal</u>	7	2	68
<u>Rhombohedral</u>	5	1	25
<u>Hexagonal</u>	7	1	27
<u>Cubic</u>	5	3	36
<b>Total</b>	<b>32</b>	<b>14</b>	<b>230</b>

# Space Groups

International Tables for Crystallography (2006). Vol. A, Space group 35, pp. 238–239.

***Cmm2***

No. 35

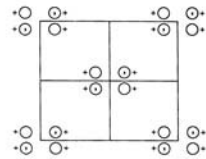
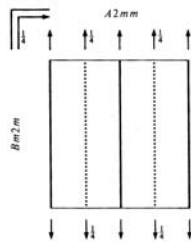
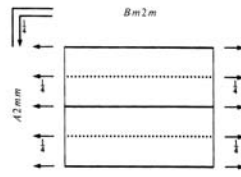
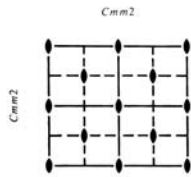
$C_{2v}^{11}$

***Cmm2***

***mm2***

Orthorhombic

Patterson symmetry ***Cmmm***



Origin on *mm2*

Asymmetric unit  $0 \leq x \leq \frac{1}{2}; 0 \leq y \leq \frac{1}{2}; 0 \leq z \leq 1$

Symmetry operations

For (0,0,0)+ set

(1) 1 (2) 2 0,0,z (3) *m* x,0,z (4) *m* 0,y,z

For  $(\frac{1}{2}, \frac{1}{2}, 0)$ + set

(1)  $t(\frac{1}{2}, \frac{1}{2}, 0)$  (2) 2  $\frac{1}{2}, \frac{1}{2}, z$  (3) *a* x,  $\frac{1}{2}, z$  (4) *b*  $\frac{1}{2}, y, z$

CONTINUED

No. 35

***Cmm2***

Generators selected (1);  $t(1, 0, 0)$ ;  $t(0, 1, 0)$ ;  $t(0, 0, 1)$ ;  $t(\frac{1}{2}, \frac{1}{2}, 0)$ ; (2); (3)

Positions

Multiplicity,  
Wyckoff letter,  
Site symmetry

Coordinates  
(0,0,0)+  $(\frac{1}{2}, \frac{1}{2}, 0)$ +

Reflection conditions

General:

$hkl : h + k = 2n$

$0kl : k = 2n$

$h0l : h = 2n$

$hkl : h + k = 2n$

$h00 : h = 2n$

$0k0 : k = 2n$

Special: as above, plus

no extra conditions

no extra conditions

$hkl : h = 2n$

no extra conditions

no extra conditions

8 *f* 1 (1) x,y,z (2) x,y,z (3) x,y,z (4) x,y,z

4 *e* *m*.. 0,y,z 0,y,z

4 *d* .*m*. x,0,z x,0,z

4 *c* ..2  $\frac{1}{2}, \frac{1}{2}, z$   $\frac{1}{2}, \frac{1}{2}, z$

2 *b* *m**m*2 0, $\frac{1}{2}$ ,z

2 *a* *m**m*2 0,0,z

Symmetry of special projections

Along [001] *c*2*mm*

$a' = a$   $b' = b$

Origin at 0,0,z

Along [100] *p*1*m*1

$a' = \frac{1}{2}b$   $b' = c$

Origin at x,0,0

Along [010] *p*1*l**m*

$a' = c$   $b' = \frac{1}{2}a$

Origin at 0,y,0

Maximal non-isomorphic subgroups

**I** [2] *C*1*m*1 (*C**m*, 8) (1; 3)+

[2] *C*m11 (*C**m*, 8) (1; 4)+

[2] *C*112 (*P*2, 3) (1; 2)+

**IIa** [2] *P**b**a*2 (32) 1; 2; (3; 4) +  $(\frac{1}{2}, \frac{1}{2}, 0)$

[2] *P**b**m*2 (*P**m**a*2, 28) 1; 3; (2; 4) +  $(\frac{1}{2}, \frac{1}{2}, 0)$

[2] *P**m**a*2 (28) 1; 4; (2; 3) +  $(\frac{1}{2}, \frac{1}{2}, 0)$

[2] *P**m**m*2 (25) 1; 2; 3; 4

**IIIb** [2] *I**m**a*2 ( $c' = 2c$ ) (46); [2] *I**b**m*2 ( $c' = 2c$ ) (*I**m**a*2, 46); [2] *I**b**a*2 ( $c' = 2c$ ) (45); [2] *I**m**m*2 ( $c' = 2c$ ) (44); [2] *C**c**c*2 ( $c' = 2c$ ) (37);

[2] *C**m**c*2 ( $c' = 2c$ ) (36); [2] *C**c**m*2 ( $c' = 2c$ ) (*C**m**c*2, 36)

Maximal isomorphic subgroups of lowest index

**IIc** [2] *C**m**m*2 ( $c' = 2c$ ) (35); [3] *C**m**m*2 ( $a' = 3a$  or  $b' = 3b$ ) (35)

Minimal non-isomorphic supergroups

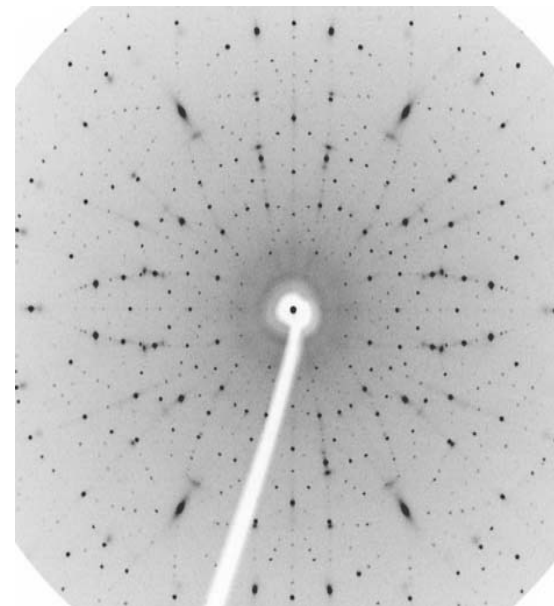
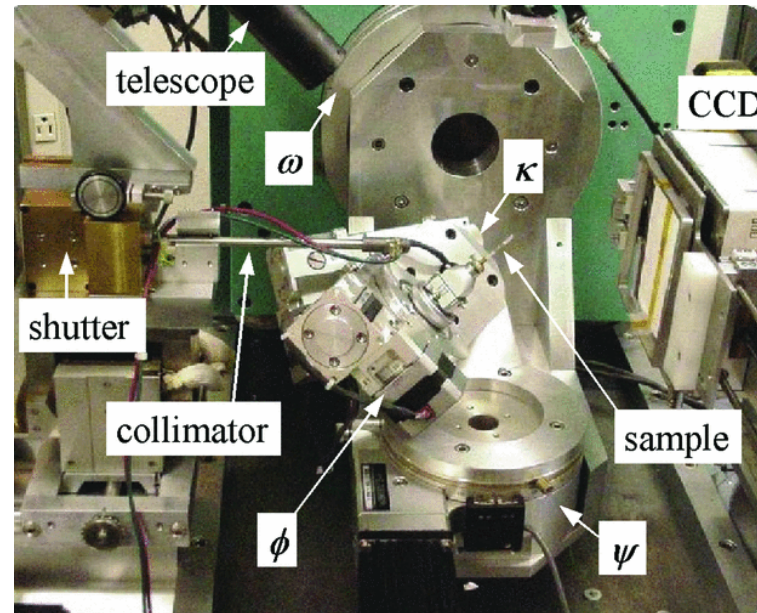
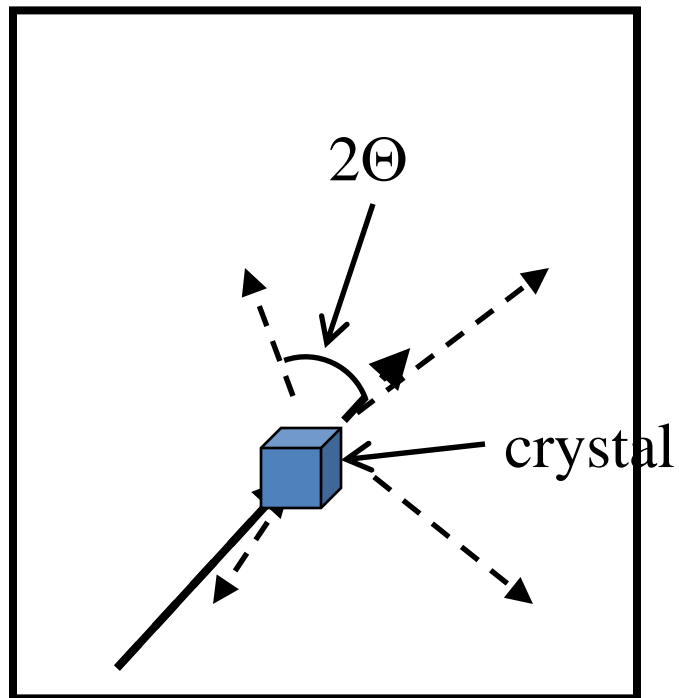
**I** [2] *C**m**m**m* (65); [2] *C**m**m**c* (67); [2] *P*4*m**m* (99); [2] *P*4*b**m* (100); [2] *P*4,*c**m* (101); [2] *P*4,*n**m* (102); [2] *P*42*m* (111);

[2] *P*42,*m* (113); [3] *P*6*m**m* (183)

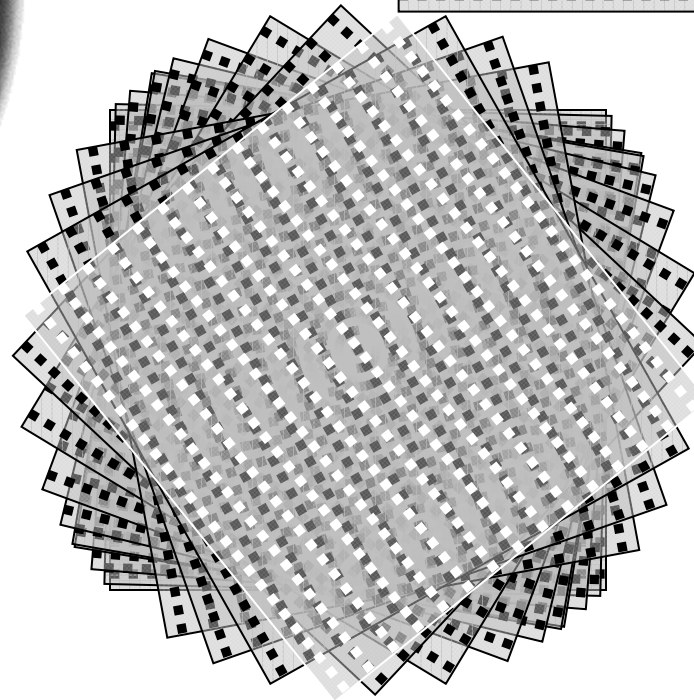
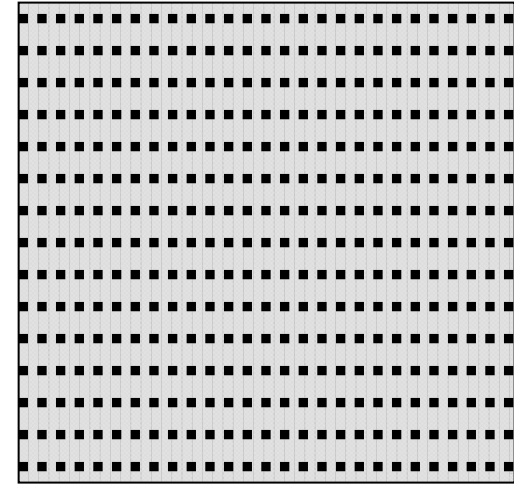
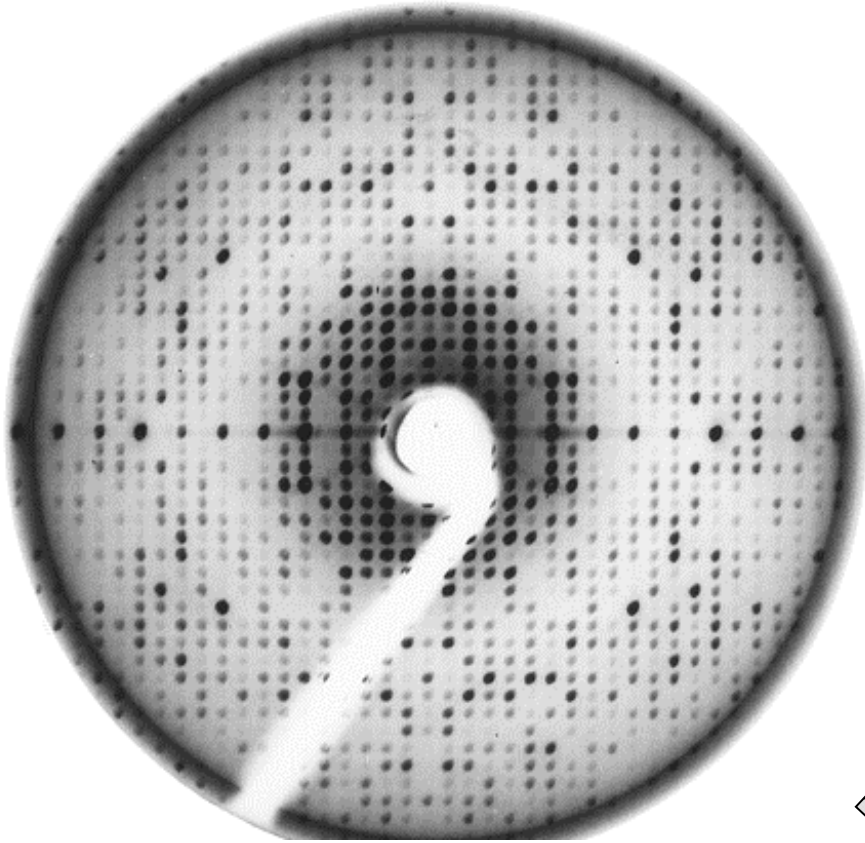
**II** [2] *F**m**m*2 (42); [2] *P**m**m*2 ( $a' = \frac{1}{2}a, b' = \frac{1}{2}b$ ) (25)

# Single Crystals:

Sample must be correctly oriented in space with respect to the chosen reflection plane.



# What if you don't have a single crystal?

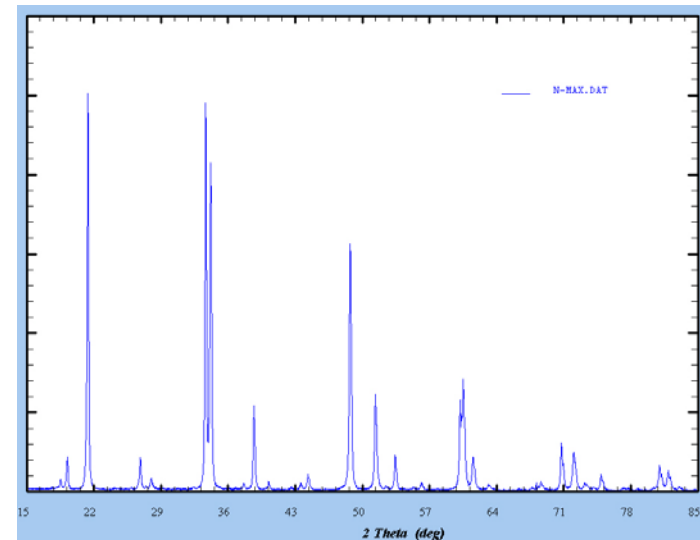
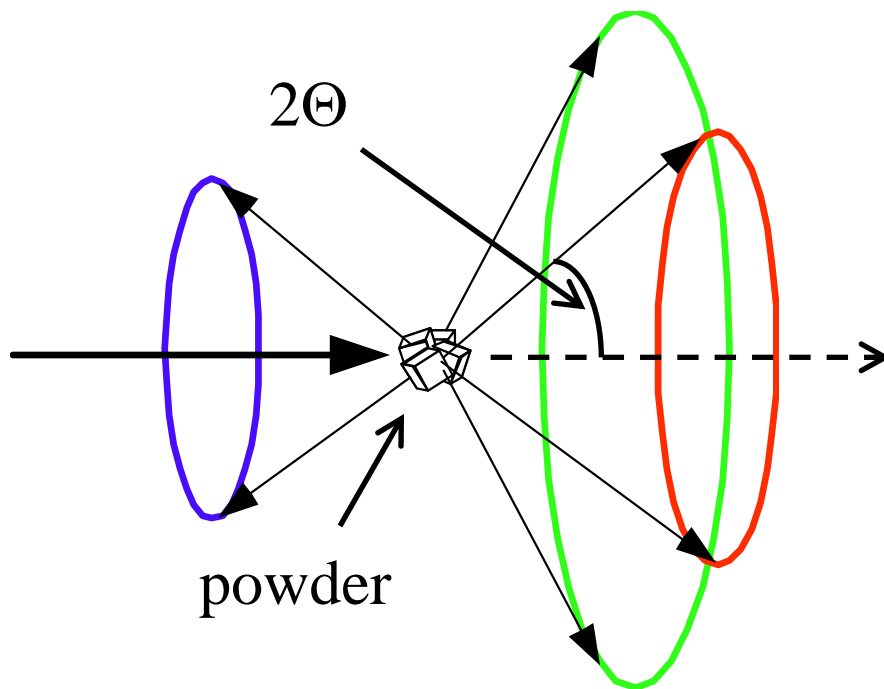


R.J. Cernik, summer school, Chester 2004

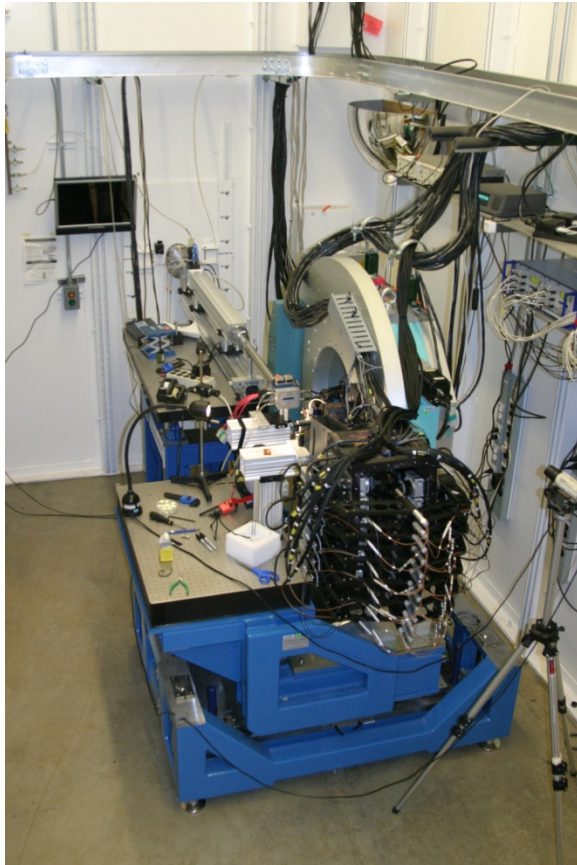
# Powder Diffraction

## ❖ Powder

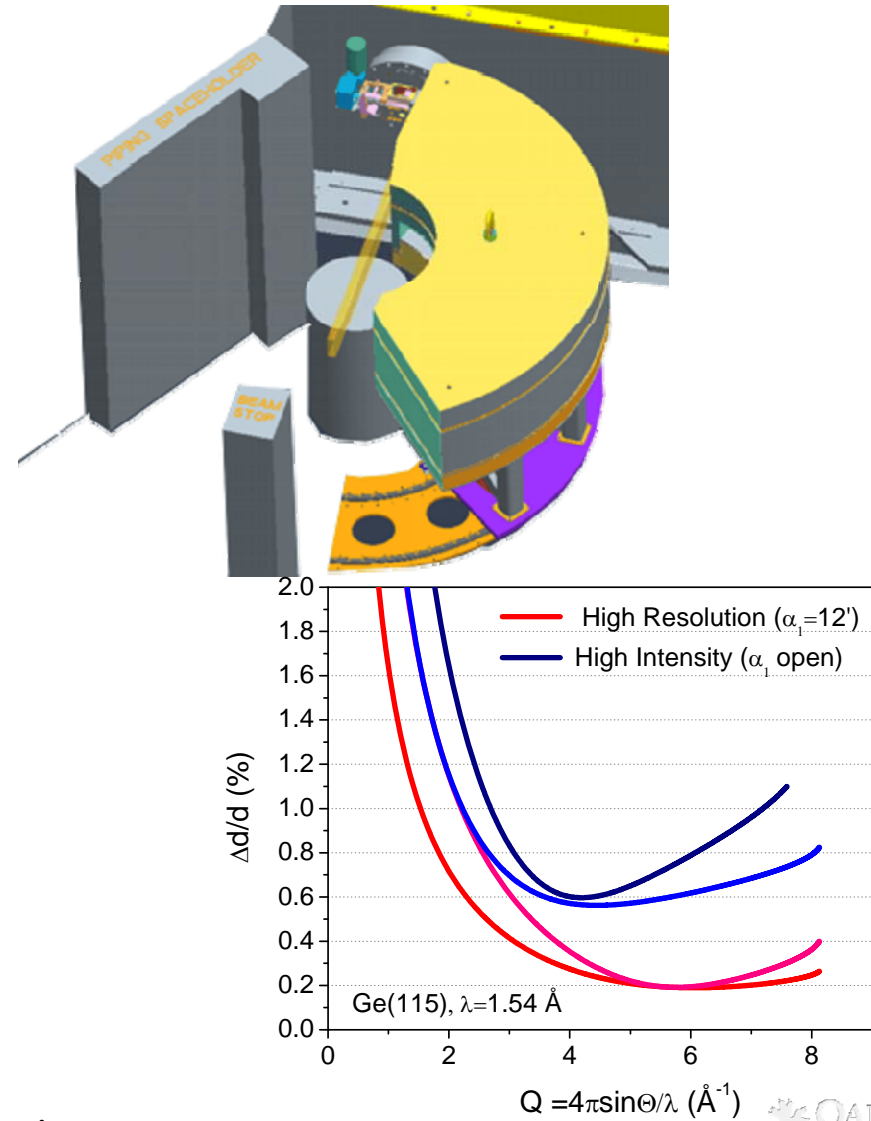
- ❖ Sizable samples have billions of crystals
- ❖ In the absence of texture, all crystal orientations are equally represented



# Powder Instruments at user facilities



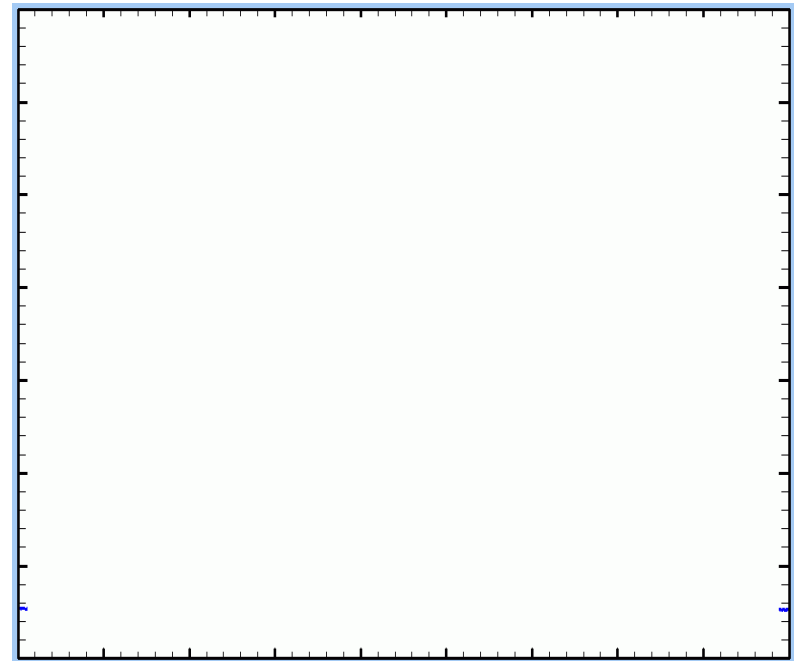
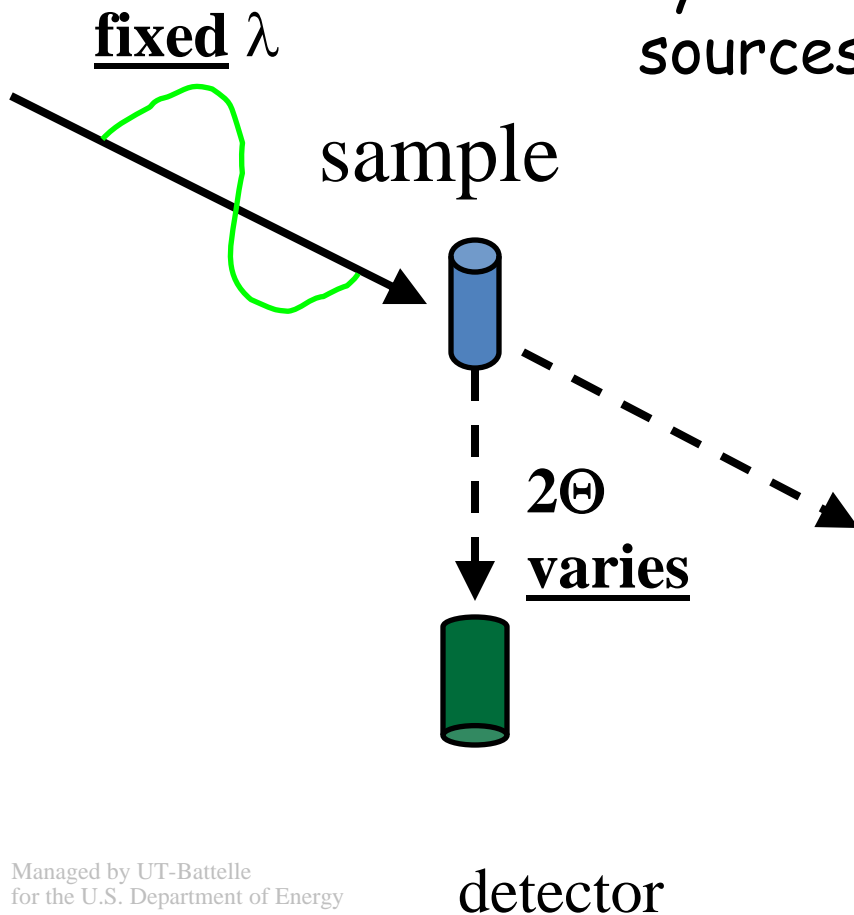
beamline 11BM at APS



beamline HB2a at HFIR

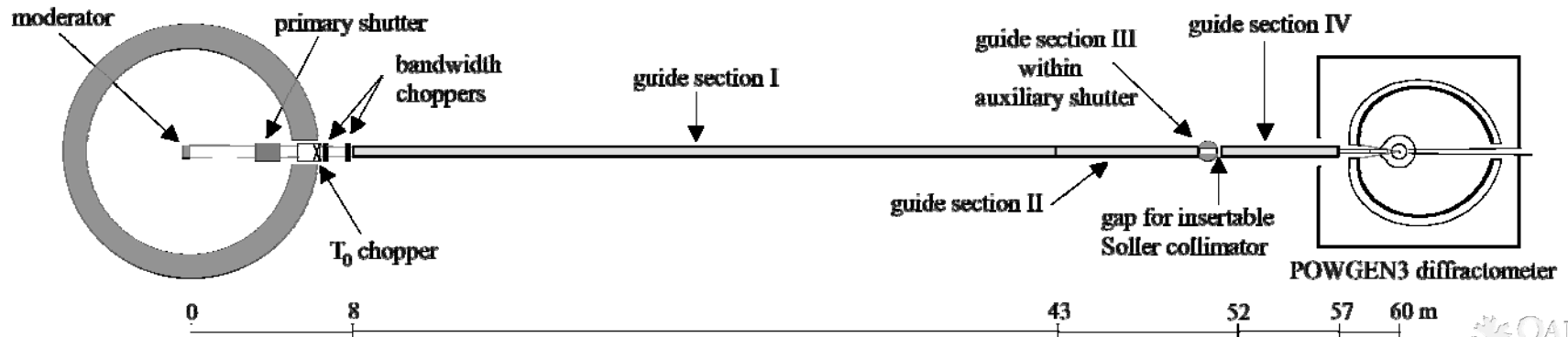
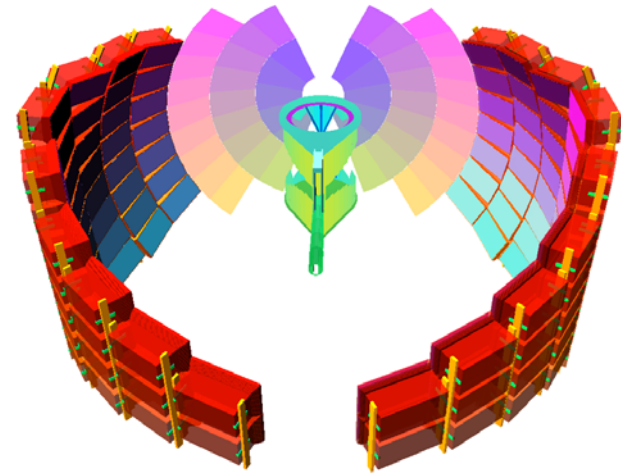
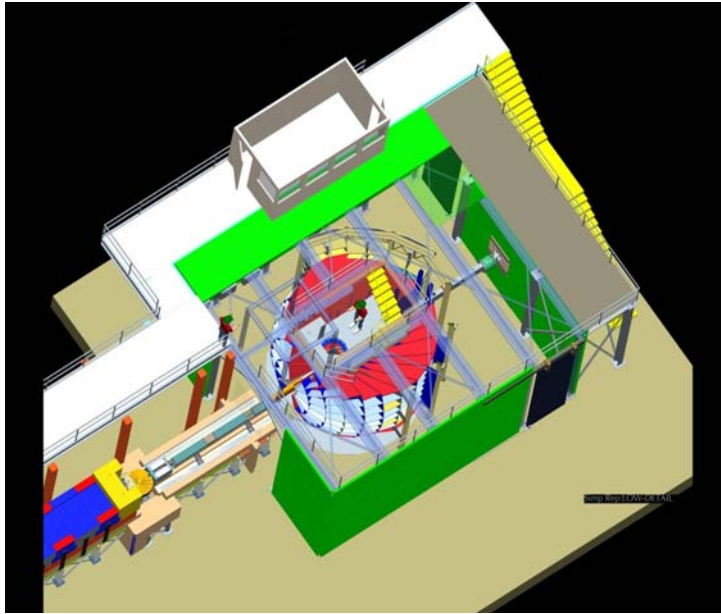
# Constant wavelength ( $2d\sin\Theta = \lambda$ )

(X-ray tubes and monochromated synchrotron or steady neutron sources)

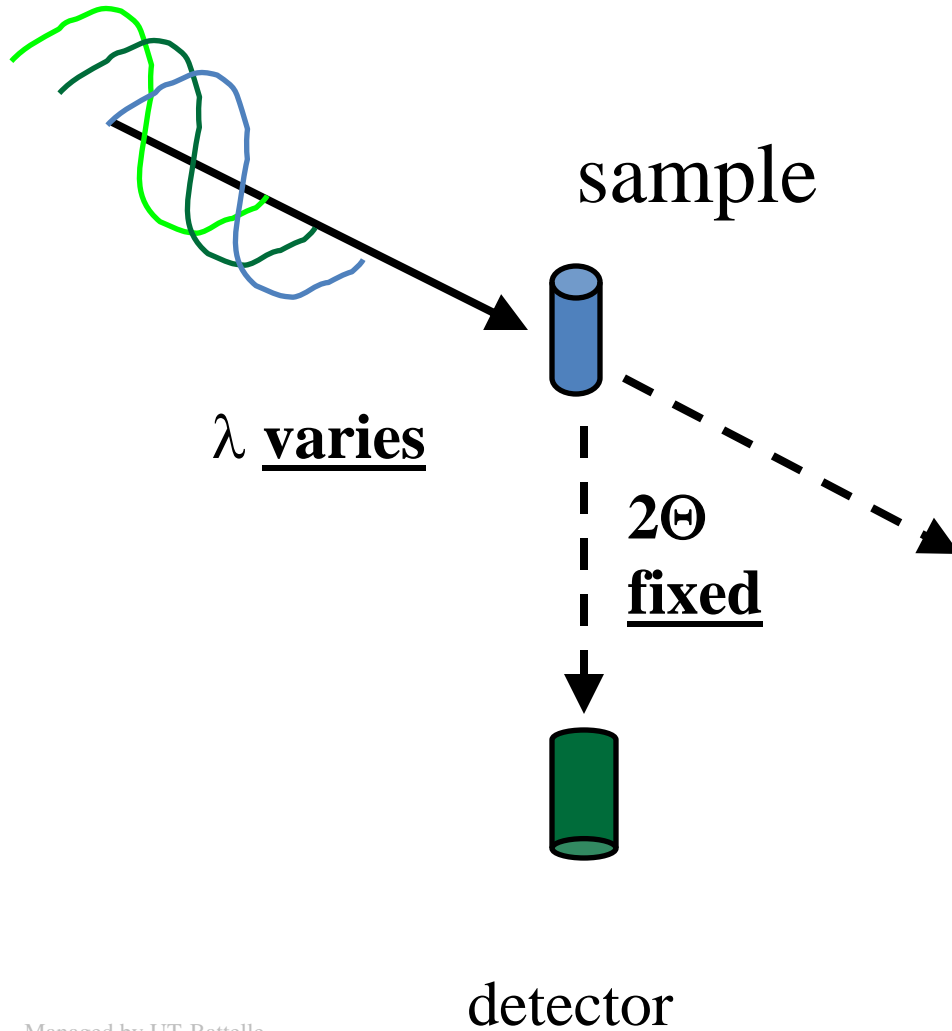




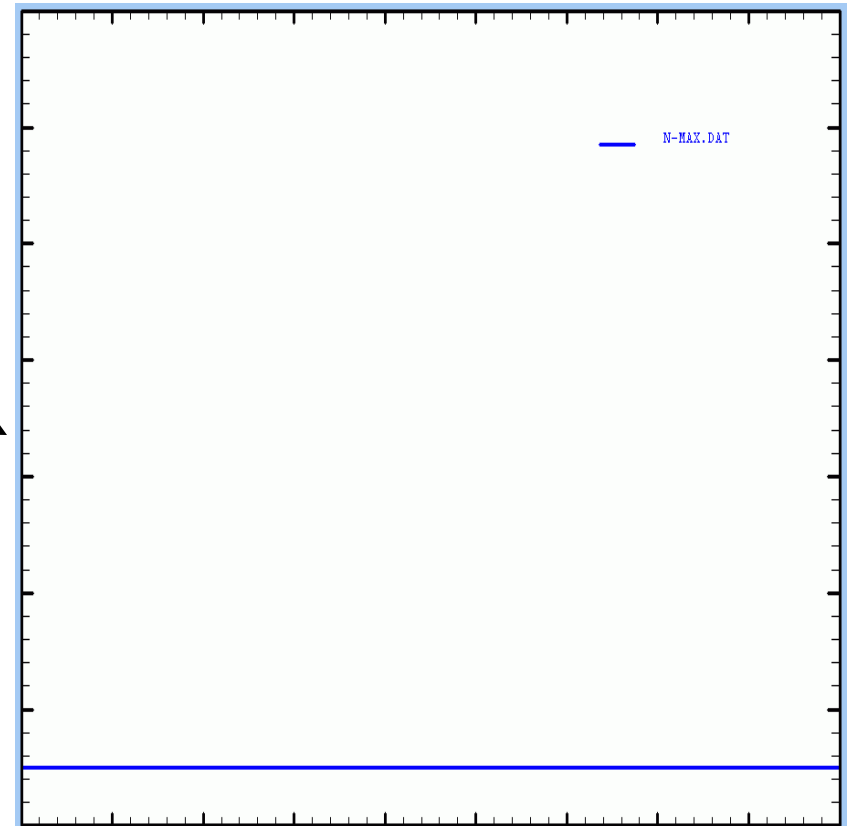
# Time of flight instrument (POWGEN)



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



(Pulsed sources: e.g. SNS)



# Time of Flight method

de Broglies relationship:

$$\lambda = h/mv = ht/mL$$

Combine with Bragg to get

$$2d\sin\theta = ht/mL \Rightarrow t = 2d\sin\theta \cdot mL/h$$

$$t_{hkl} = 505.5569 L d_{hkl} \sin\theta$$

Resolution:

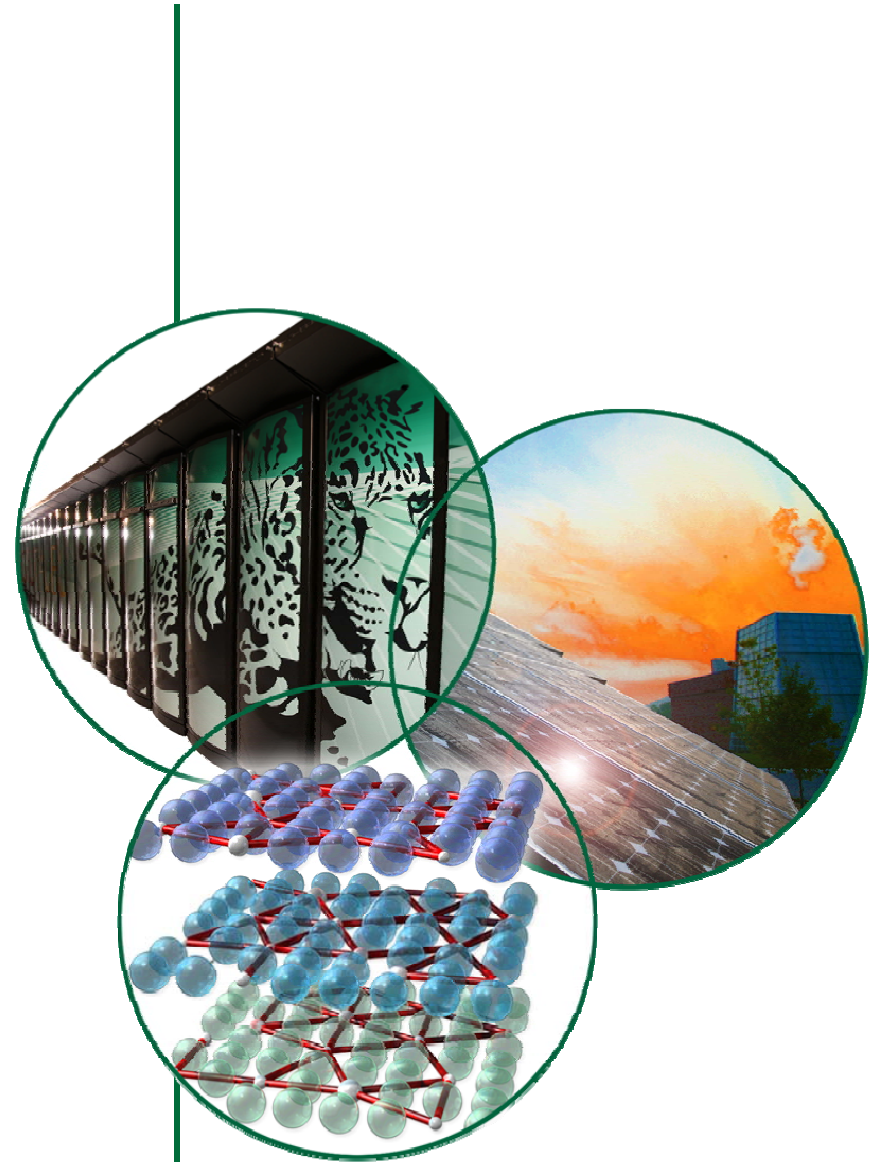
$$R(d) = \Delta d/d = [(\Delta t/t)^2 + (\Delta L/L)^2 + (\Delta\theta)^2 \cot^2\theta]^{1/2}$$

Bragg Intensity:

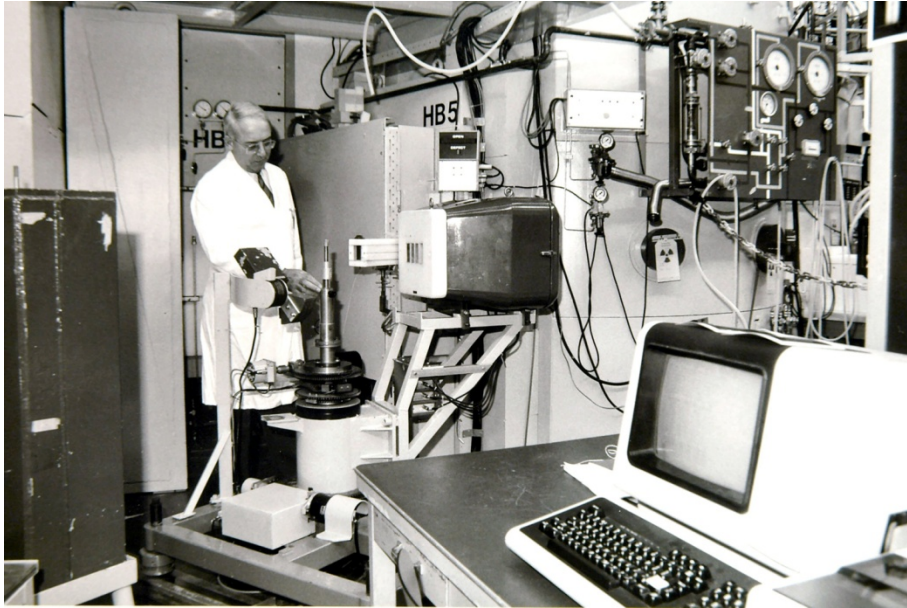
$$Y_{ph} = F_{ph}^2 H(T - T_{ph}) K_{ph} \text{ where } K_{ph} = E_{ph} A_h O_{ph} M_p L / V_p$$

$$y_{\tau}(i) = D_{\text{expt}} \{H(t)w(i)\} f_{DS} I_L(\lambda) \varepsilon(\lambda) N_s \frac{\lambda^4 \cos\theta \cdot \Delta\theta}{4v_{uc} \sin^2\theta} A_{\tau}(\lambda) E_{\tau}(\lambda) j_{\tau} |F_{\tau}|^2$$

# Rietveld Refinement



# Hugo Rietveld

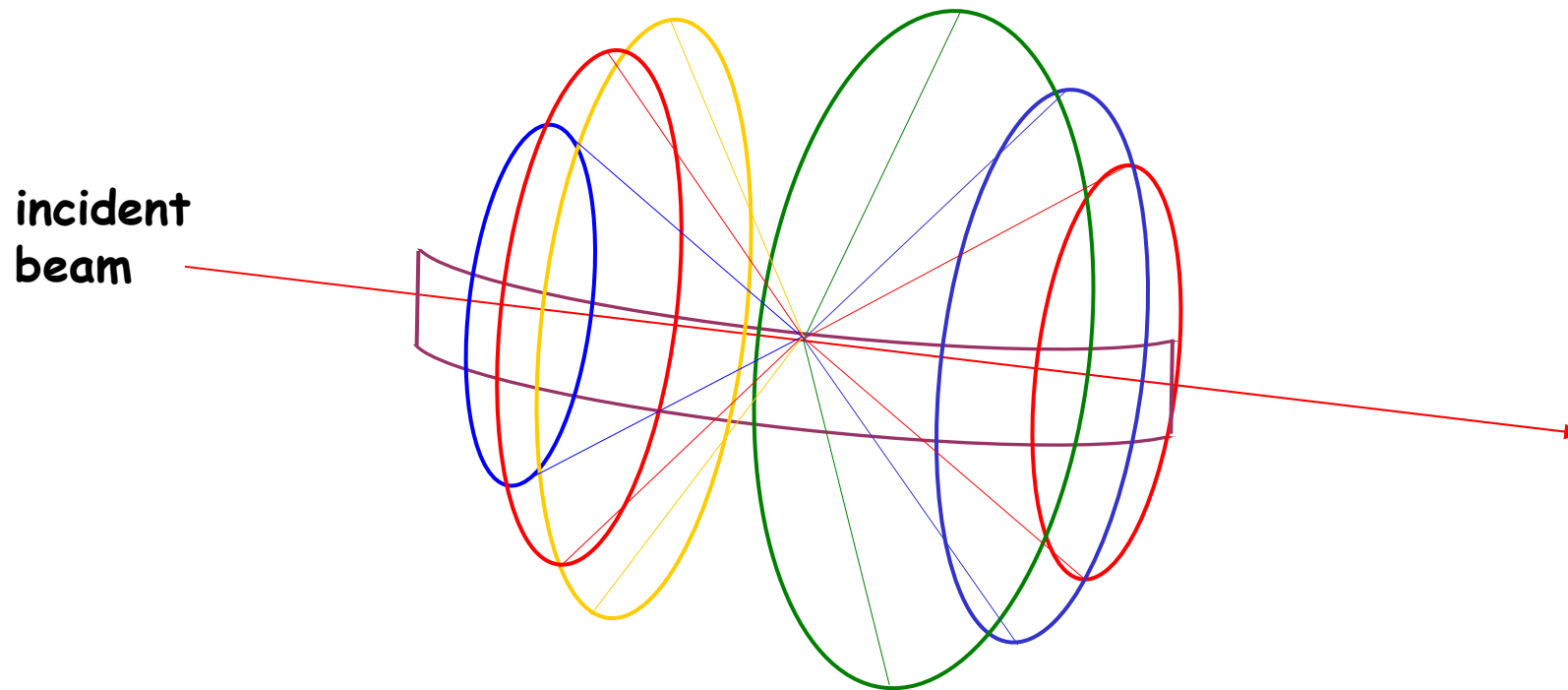


**Dr. Rietveld at the neutron powder diffractometer at the High Flux Reactor of the Energy Research Foundation ECN in Petten, The Netherlands. (1987)**

*J. Appl. Cryst.* **2**, 65, 1969

“A structure refinement method is described which does not use integrated neutron powder intensities, single or overlapping, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram. Nuclear as well as magnetic structures can be refined, the latter only when their magnetic unit cell is equal to, or a multiple of, the nuclear cell. The least-squares refinement procedure allows, with a simple code, the introduction of linear or quadratic constraints between the parameters.”

# Rietveld Refinement (Powder Diffraction)



In a diffraction experiment if the sample is a powder, there will be many grains aligned to diffract the incident beam of neutrons/x-rays. 3D information is reduced to 1D, makes analysis harder than single crystal experiments.

# Rietveld Refinement Least Square Method

**Model that describes the structure**

**Profile parameters**

(lattice, line-shape, background etc.)

**Atomic information**

(fractional co-ordinates, thermal parameters  
fractional occupancy etc.)

No effort is made in advance to allocate observed intensity to particular Bragg reflections nor to resolve overlapped reflections. Consequently, a reasonably good starting model is needed. The method is a structure refinement method and not a structure solution method.

## Rietveld Refinement (cont'd)

The contribution of an atom at  $r_j$  in real space to a reflection  $K = (hkl)$  is given by the structure factor of that reflection

$$F_{hkl} = \sum_j N_j b_j e^{2\pi i K \cdot r_j} e^{-M_j}$$

( $M_j$  = Debye-Waller factor,  $M_j = 8\pi^2 \overline{u_s^2} \sin^2 \theta / \lambda^2$ )

$N_j$  = site occupancy

$b_j$  = scattering length)

Rietveld refinement models the **entire pattern** as calculate intensities:

$$y_{oi} = s \sum_K L_K |F_K|^2 f(t_i - t_K) + y_{bi}$$

( $s$  = scale factor,  $L_K$  = instrumental and sample factors,  $f$  = profile function,  $y_{ci}$  = background)



## Rietveld Refinement (cont'd)

The Least Square refinement then adjusts the refinable parameters to minimize the residuals until the best fit is obtained.

$$\chi^2 = \frac{\sum_{i=1}^{N_{\text{obs}}} w_i (\mathbf{I}_{\text{oi}} - \mathbf{I}_{\text{ci}})^2}{(N_{\text{obs}} - N_{\text{var}})}$$

Here  $w_i = 1/\sigma_i^2$ , is the statistical weight of the  $i$ th profile observation which is the inverse of the variance of the  $i$ th observation.  $\mathbf{I}_{\text{oi}}$  and  $\mathbf{I}_{\text{ci}}$  are observed and calculated intensities.

From a purely mathematical point of view,  $R_{\text{wp}}$  is the most meaningful R factor because the numerator is the residual being minimized. So this is the best indicator of the progress of the refinement.

$$R_{\text{wp}}^2 = \frac{\sum_{i=1}^{N_{\text{obs}}} w_i (\mathbf{I}_{\text{oi}} - \mathbf{I}_{\text{ci}})^2}{w_i (\mathbf{I}_{\text{oi}})^2}$$

While numerical criteria are important it is also imperative to use graphical criteria of fit like difference plots.

# Typical Rietveld Refinement

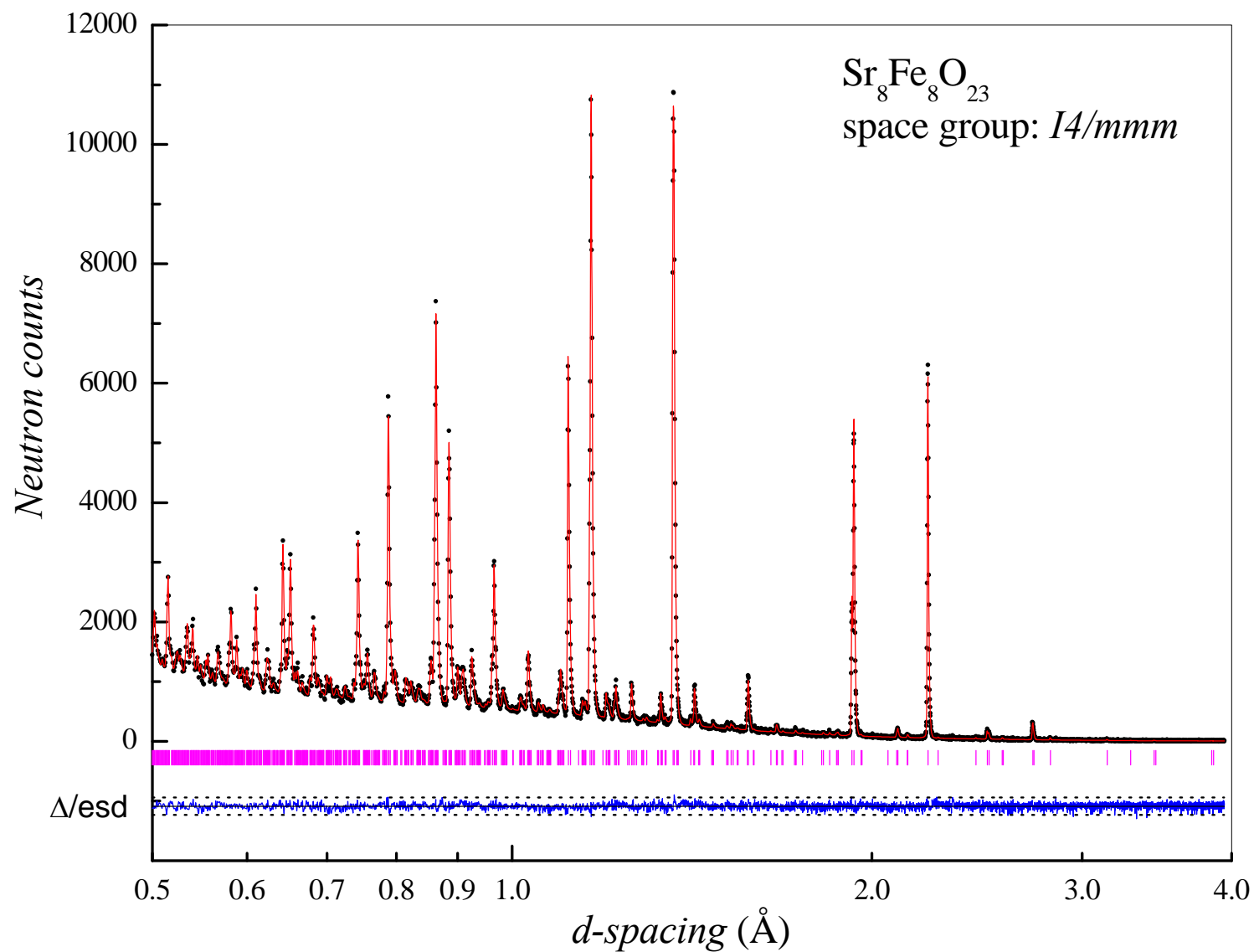


Fig. 5  
Hodges et al. J. Solid State Chem. 151, 190(2000)  
for the U.S. Department of Energy

# Peak Profiles:

## CW peak shapes

Convolution of pseudo-Voigt with result of considering the intersection of the Debye Scherrer diffraction cone that is at the scattering angle of  $2\Theta$  and a finite height slit positioned below  $2\Theta$  by  $\tau$

$$H(\Delta T) = \int P(\Delta T - \tau) D(\tau) d\tau$$

$$\sigma = [ U \tan^2\Theta + V \tan\Theta + W + P/\cos^2\Theta ]^{1/2}$$

(Gaussian variance)

$$\gamma = (X + X_{e/s} \cos\phi) / \cos\Theta + (Y + Y_e \cos\phi + g_L d^2) \tan\Theta$$

(Lorentzian, size broadening due to stacking fault)

TOF diffractometers that use cryogenic moderators have more complex behavior for a b and peak position.

# Peak Profiles:

## TOF peak shapes

Convolution of rising and falling (back to back) exponentials with pseudo-Voigt (a linear combination of Lorentzian and a Gaussian)

$$H(\Delta T) = \int E(\Delta T - t)P(t)dt$$

moderator introduces fast and slow decay constants ( $\alpha$ ,  $\beta$ )

$$\alpha = \alpha_1 / d$$

(rising exponential)

$$\beta = \beta_0 + \beta_1 / d^4$$

(falling exponential)

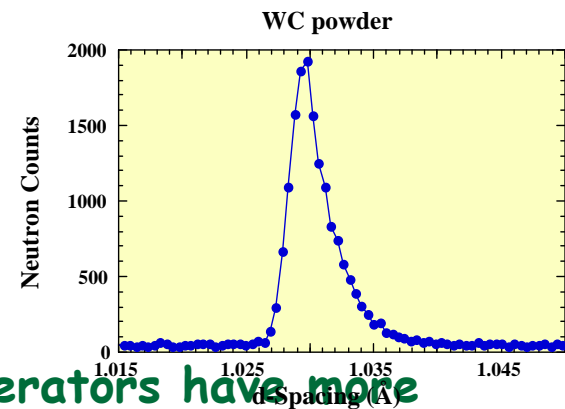
$$\sigma = [ \sigma_0^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 ]^{1/2}$$

(Gaussian)

$$\gamma = [ \gamma_2 d^2 + \gamma_{2e/2s} d^2 \cos\phi + \gamma_s^2 d^3 ]$$

(Lorentzian)

TOF diffractometers that use cryogenic moderators have more complex behavior for a b and peak position.



# Information obtained from Rietveld Refinement:

## Phase Fractions

Scale factors relate the weight fractions of  $p_{th}$  phase :

$$W_p = \frac{S_{ph} m_p}{\sum_{p=1}^{N_p} S_{ph} m_p}$$

( $m_p$  = unit cell mass for phase  $p$ ,  $S_{ph}$  = Rietveld scale factor)

## Sample Broadening

Only affects the Gaussian component of the peak width; contributions from strain  $S$  and particle size broadening  $P$  can be separated:

$$S = (1/C)[8\ln 2(\sigma_1^2 - \sigma_{1i}^2)]^{1/2} 100\%$$

( $\sigma_{1i}$  = strain-free value for  $\sigma_1$ )

$$P = (CK)/[8\ln 2\sigma_2]^{1/2} \text{ \AA}$$

( $K$  = Scherrer constant)

## Other things to be keep in mind

Recall  $K_{ph} = E_{ph} A_h O_{ph} M_p L / V_p$

$E_{ph}$ : Extinction correction

$A_h$ : Absorption correction

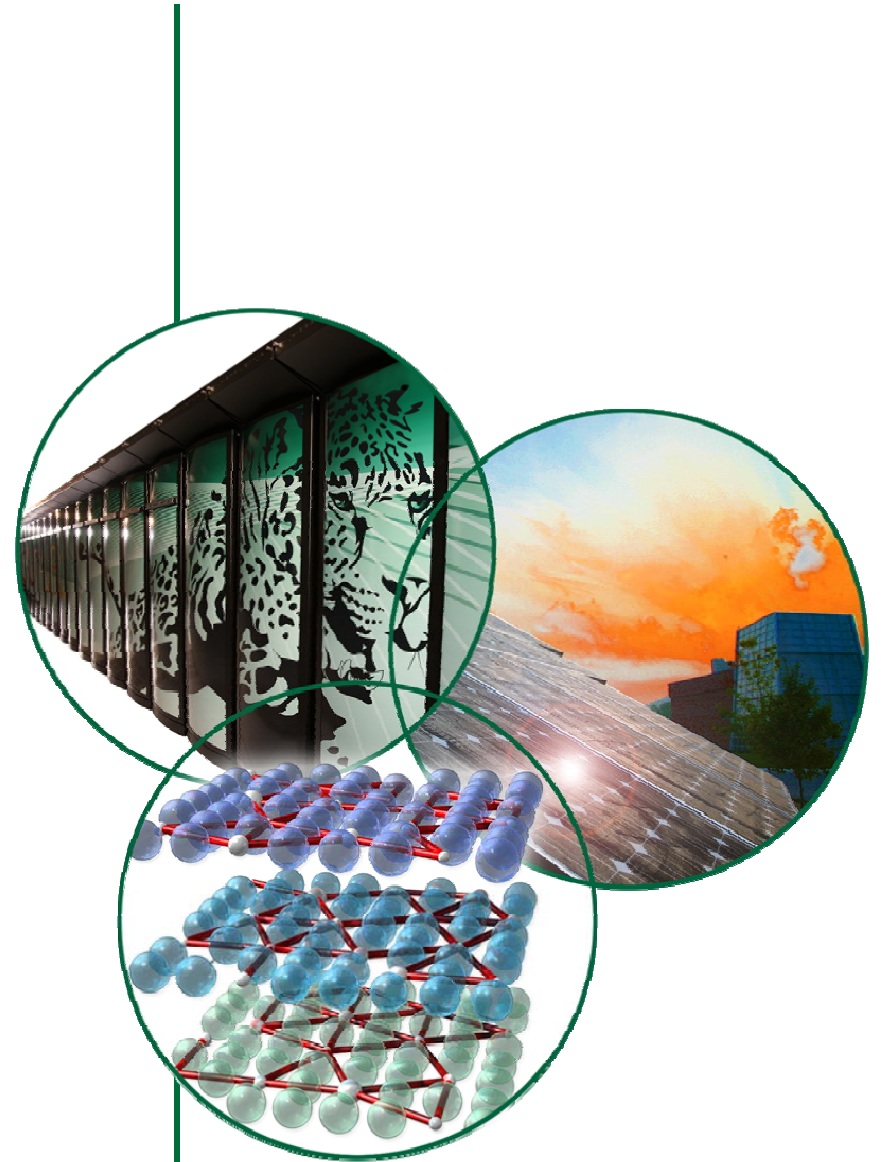
$O_{ph}$ : Preferred orientation correction

$M_p$ : Reflection multiplicity

$L$ : Angle dependent correction (Lorentz-polarization)

$V_p$ : Unit cell volume for the phase

# Ab-initio Structure Solution from Powder Diffraction?



U.S. DEPARTMENT OF  
**ENERGY**



**OAK RIDGE NATIONAL LABORATORY**

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

**“Powder diffraction is of minimal value in crystal structure analysis and is not discussed in this book.”**

Ladd and Palmer in  
'Structure determination by X-ray crystallography' Plenum Press

**but here are some other wise words**

➤ **“Heavier-than-air flying machines are impossible”**

**Lord Kelvin, president, Royal Society (1895)**

➤ **“I think there is a world market for about five computers.”**

**Thomas J. Watson, chairman of the board of IBM(1943)**

➤ **“640K ought to be enough for anybody.”**

**Bill Gates, 1981**

Bill David, PSI Powder Diffraction Workshop June 2008



## Structure solution from powder data:

Given atom positions, it is straightforward to compute the diffraction pattern

$$I_{hkl} = \left| \sum_{\text{atoms } j} f_j \exp(i\vec{Q}_{hkl} \cdot \vec{R}_j) \right|^2$$

Solve a new structure from powder data

1. Get data
2. Find the lattice
3. Space group (internal symmetries) systematic absences, density, guess, luck
4. Extract intensities of each individual ( $hkl$ ) peak
5. Solve structure
6. Refine

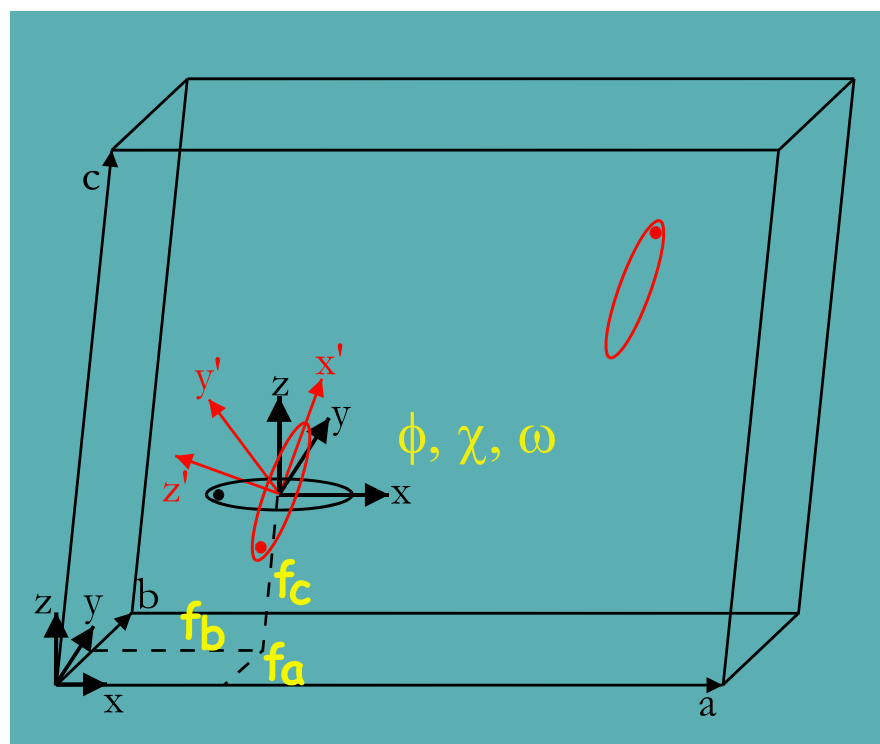
## Methods of Solution:

- Adaptation of standard single crystal techniques
- direct space methods based on prior chemical knowledge
- A combination of the two
- Global optimization: simulated annealing, genetic algorithm
- Charge flipping algorithm

Solution of structures of organic molecules from powder data:

Difficulties: generally weak scatterers, serious overlap for  $d < 2A$ , patterns weak at high angles.

Use of known molecular geometry is helpful -- make a model, put it into the lattice, and test it against the data.



## Using simulated annealing to search this large space.

### Comparing proposed solution with data

### Ideas borrowed from simulations of spin glasses:

1. Metropolis algorithm to generate ensemble of configurations representative of a given temperature
2. Gradually lower temperature to find lowest energy states

### Measure agreement of proposed solution with data:

### R-factor $\leftrightarrow$ energy

1. Always accept a move that leads to a better fit to the data
2. don't reject all moves that lead to a poorer fit, accept poorer fits with Boltzmann probability

$$\exp[-(\chi_{\text{new}}^2 - \chi_{\text{old}}^2)/T]$$

# Software and other resources:

<http://www.ccp14.ac.uk/>

## Indexing:

- Crysfire: <http://www.ccp14.ac.uk/tutorial/crys/>

## Rietveld:

- GSAS: <http://www.ccp14.ac.uk/solution/gsas/>
- Fullprof: <http://www.ccp14.ac.uk/ccp/web-mirrors/fullprof/>
- Rietan, Topas, Expo, JANA, Jade etc.

## Structure Solution:

- DASH: [http://www.ccdc.cam.ac.uk/products/powder\\_diffraction/dash/](http://www.ccdc.cam.ac.uk/products/powder_diffraction/dash/)
- FOX: <http://vincefn.net/Fox/>
- PSSP:
- Topas: [http://www.dur.ac.uk/john.evans/topas\\_academic/topas\\_main.htm](http://www.dur.ac.uk/john.evans/topas_academic/topas_main.htm)

# Reference material

- ❑ Elements of X-ray diffraction (B.D. Cullity)
- ❑ Introduction to X-ray Powder Diffractometry (R. Jenkins & R.L. Snyder)
- ❑ Modern Powder Diffraction (edited by Bish & Post)
- ❑ The Rietveld Method (edited by R.A. Young)
- ❑ Neutron Diffraction (G.E. Bacon)
- ❑ Theory of neutron scattering from condensed matter (S.W. Lovesey)
- ❑ Structure determination from powder diffraction data (Edited by W.I.F. David, K. Shankland, L.B. McCusker and Ch. Baerlocher)