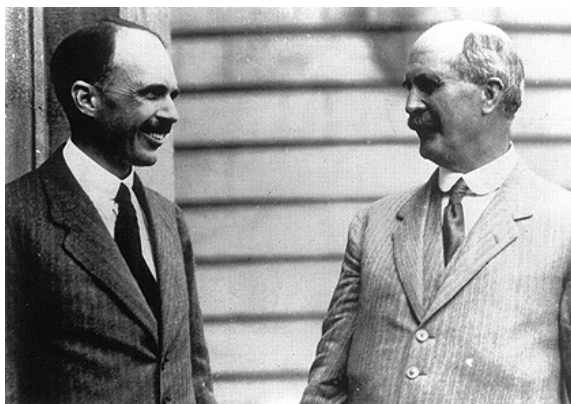


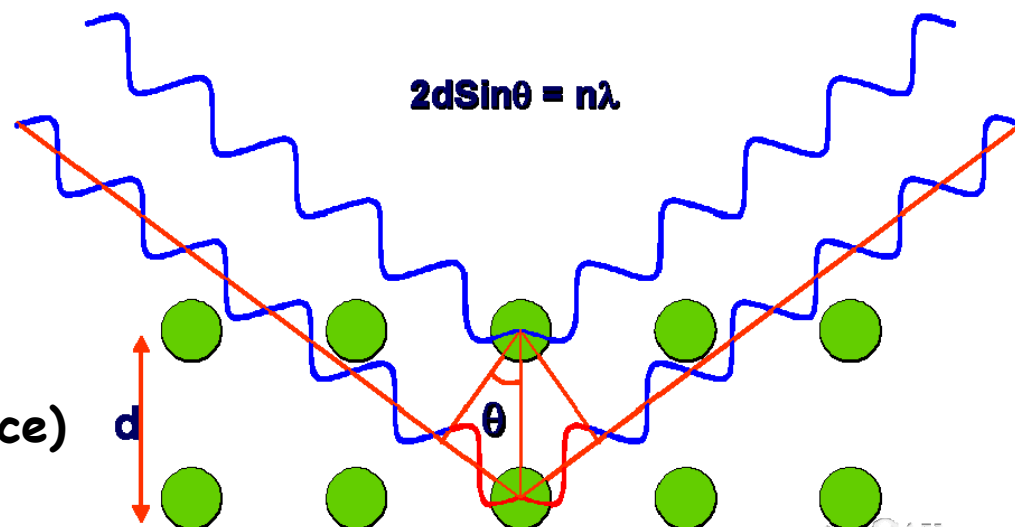
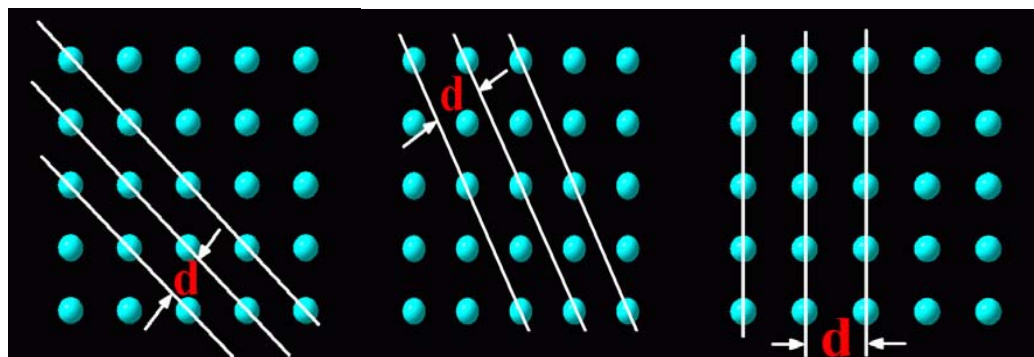
Bragg's law

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)



Where are the atoms?

We need wavelength (λ) \sim Object size (for condensed matter that is \AA)



X-ray:

(λ : 10^{-9}m - 10^{-11}m)

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

Source:

- Lab diffractometers
- Synchrotron Sources

Neutron:

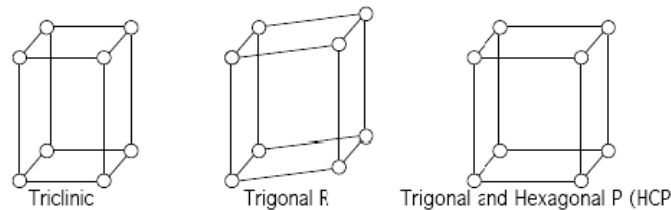
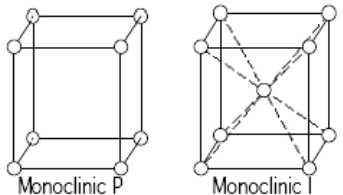
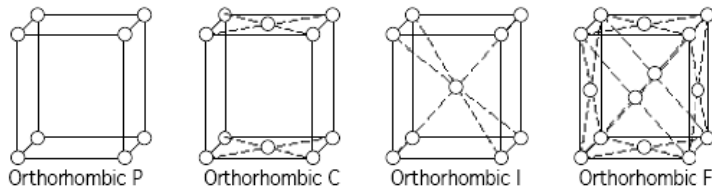
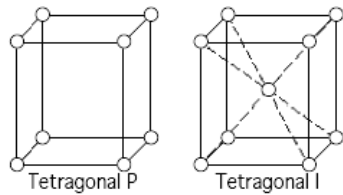
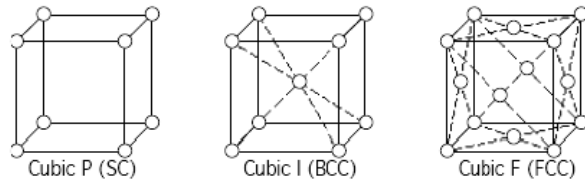
(thermal λ : $1-4\text{\AA}$)

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

Source:

- Reactors (fission)
- Spallation Source

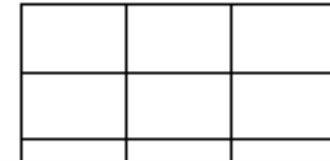
Crystal Structure = Basis + Lattice



Basis



Lattice



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

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

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
Total	32	14	230

Space Groups

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

Cmm2

No. 35

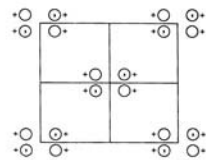
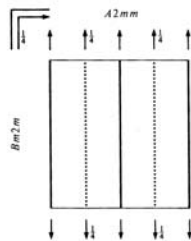
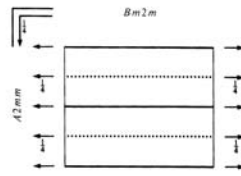
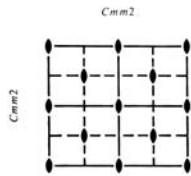
C_{2v}^{11}

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
8 <i>f</i> 1	(1) x,y,z (2) x,y,z (3) x,y,z (4) x,y,z

Reflection conditions

General:

hkl : $h + k = 2n$
0kl : $k = 2n$
h0l : $h = 2n$
hk0 : $h + k = 2n$
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

4 <i>e</i> <i>m</i> . .	0,y,z	0,y,z
4 <i>d</i> . <i>m</i> .	x,0,z	x,0,z
4 <i>c</i> . . 2	$\frac{1}{2}, \frac{1}{2}, z$	$\frac{1}{2}, \frac{1}{2}, z$
2 <i>b</i> <i>m</i> <i>m</i> 2	0, $\frac{1}{2}, z$	
2 <i>a</i> <i>m</i> <i>m</i> 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] <i>C</i> 1 <i>m</i> 1 (<i>C</i> <i>m</i> , 8)	(1; 3)+
	[2] <i>C</i> m11 (<i>C</i> <i>m</i> , 8)	(1; 4)+
	[2] <i>C</i> 112 (<i>P</i> 2, 3)	(1; 2)+
IIa	[2] <i>P</i> <i>b</i> <i>a</i> 2 (32)	1; 2; (3; 4) + $(\frac{1}{2}, \frac{1}{2}, 0)$
	[2] <i>P</i> <i>b</i> <i>m</i> 2 (<i>P</i> <i>m</i> <i>a</i> 2, 28)	1; 3; (2; 4) + $(\frac{1}{2}, \frac{1}{2}, 0)$
	[2] <i>P</i> <i>m</i> <i>a</i> 2 (28)	1; 4; (2; 3) + $(\frac{1}{2}, \frac{1}{2}, 0)$
	[2] <i>P</i> <i>m</i> <i>m</i> 2 (25)	1; 2; 3; 4
IIIb	[2] <i>I</i> <i>m</i> <i>a</i> 2 ($c' = 2c$) (46); [2] <i>I</i> <i>b</i> <i>m</i> 2 ($c' = 2c$) (<i>I</i> <i>m</i> <i>a</i> 2, 46); [2] <i>I</i> <i>b</i> <i>a</i> 2 ($c' = 2c$) (45); [2] <i>I</i> <i>m</i> <i>m</i> 2 ($c' = 2c$) (44); [2] <i>C</i> <i>c</i> <i>c</i> 2 ($c' = 2c$) (37); [2] <i>C</i> <i>m</i> <i>c</i> 2 ($c' = 2c$) (36); [2] <i>C</i> <i>c</i> <i>m</i> 2 ($c' = 2c$) (<i>C</i> <i>m</i> <i>c</i> 2, 36)	

Maximal isomorphic subgroups of lowest index

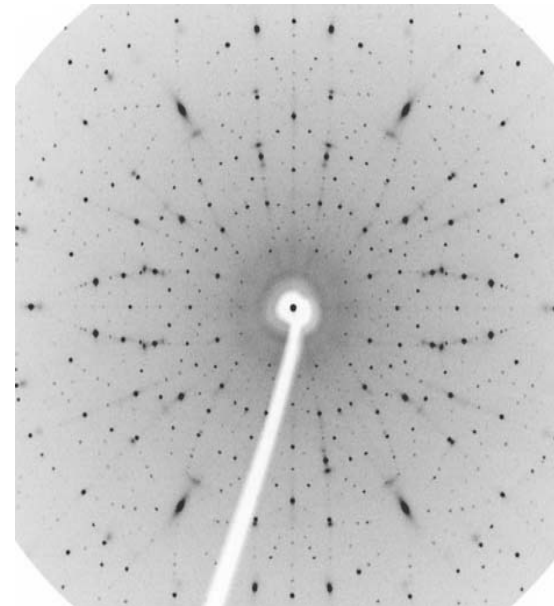
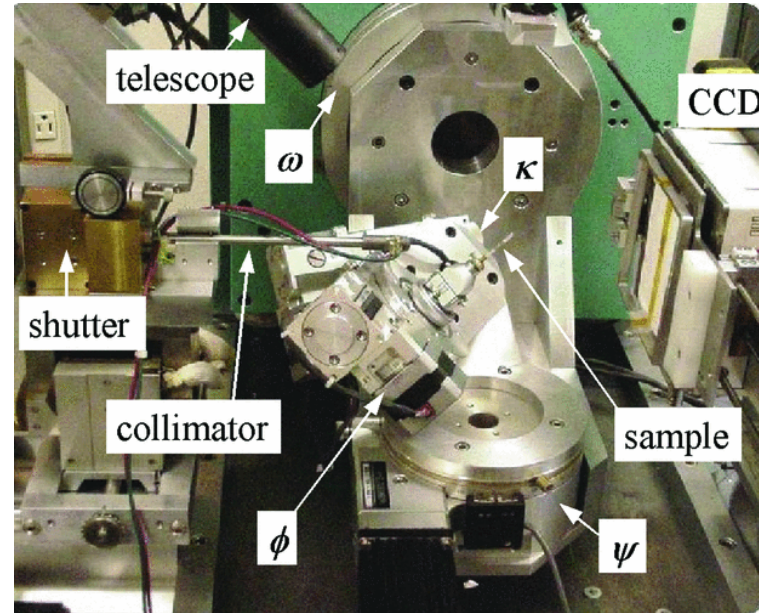
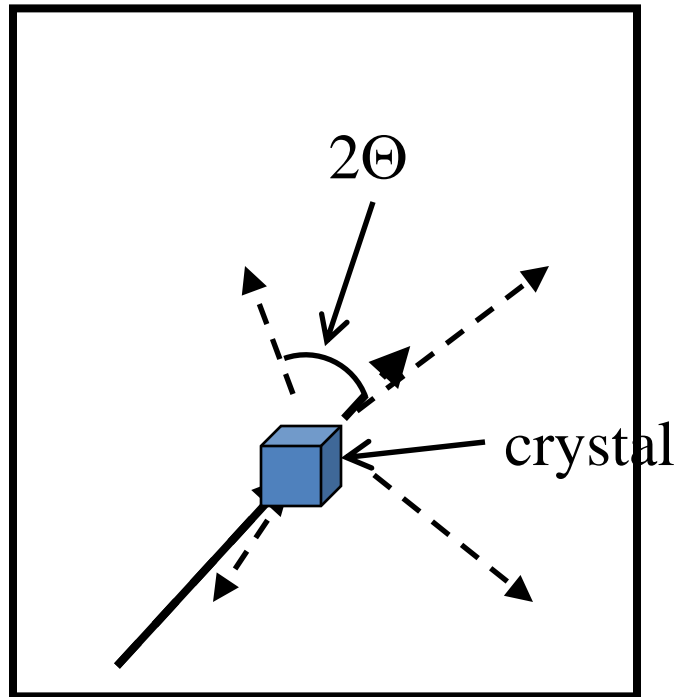
IIc [2] *Cmm2* ($c' = 2c$) (35); [3] *Cmm2* ($a' = 3a$ or $b' = 3b$) (35)

Minimal non-isomorphic supergroups

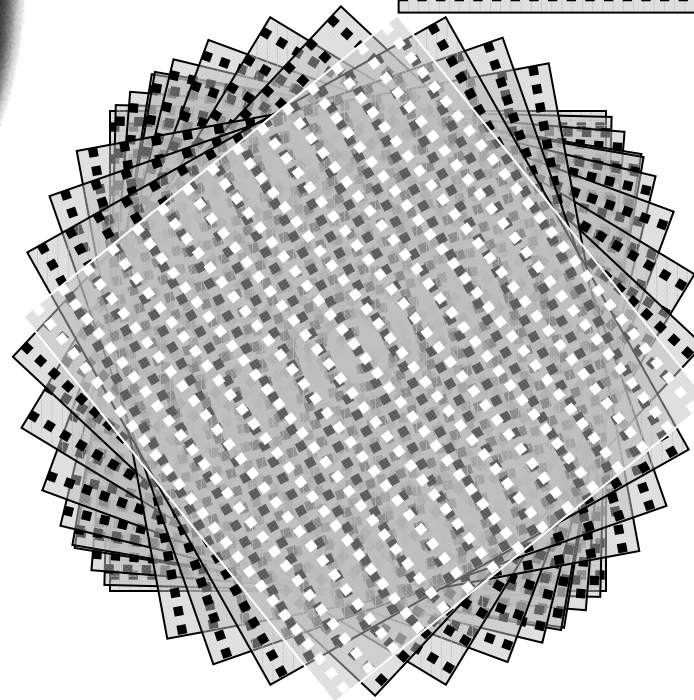
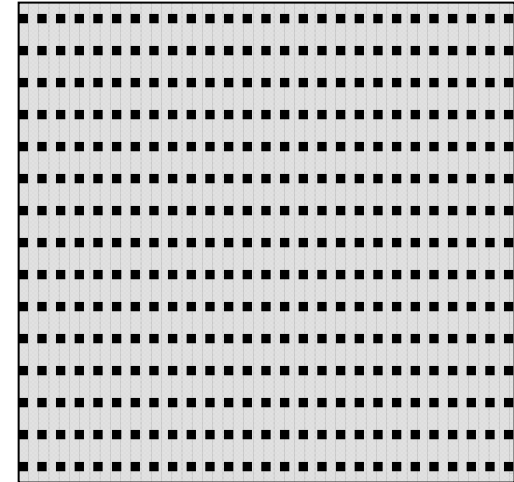
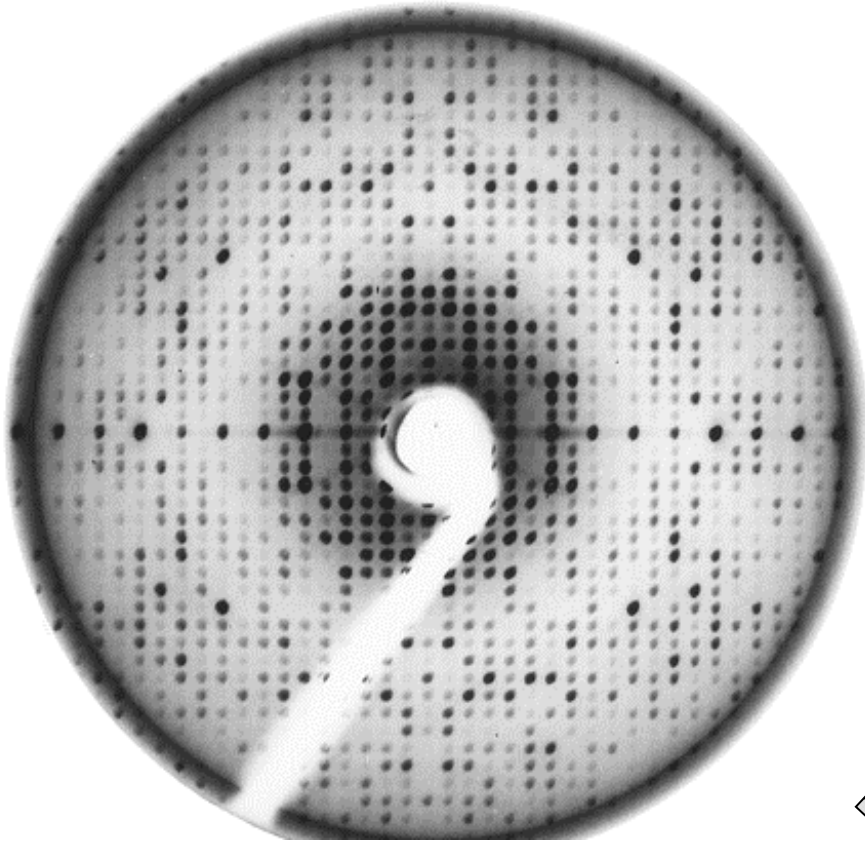
I	[2] <i>C</i> <i>m</i> <i>m</i> <i>m</i> (65); [2] <i>C</i> <i>m</i> <i>m</i> <i>c</i> (67); [2] <i>P</i> 4 <i>m</i> <i>m</i> (99); [2] <i>P</i> 4 <i>b</i> <i>m</i> (100); [2] <i>P</i> 4, <i>c</i> <i>m</i> (101); [2] <i>P</i> 4, <i>n</i> <i>m</i> (102); [2] <i>P</i> 42 <i>m</i> (111); [2] <i>P</i> 42, <i>m</i> (113); [3] <i>P</i> 6 <i>m</i> <i>m</i> (183)
II	[2] <i>F</i> <i>m</i> <i>m</i> 2 (42); [2] <i>P</i> <i>m</i> <i>m</i> 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?

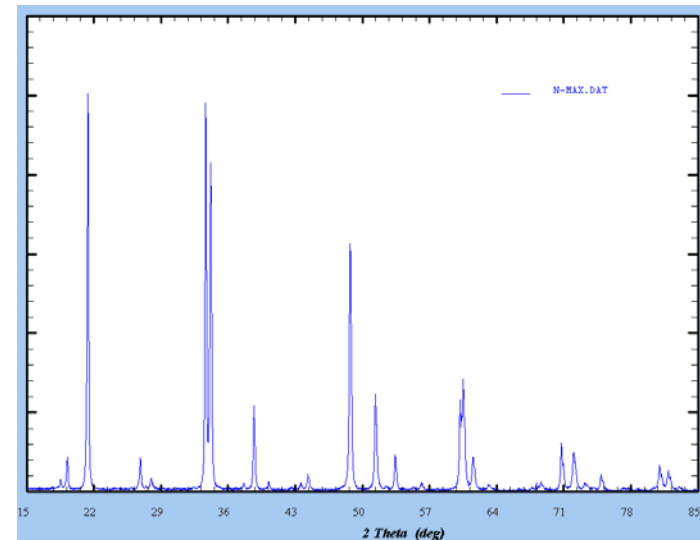
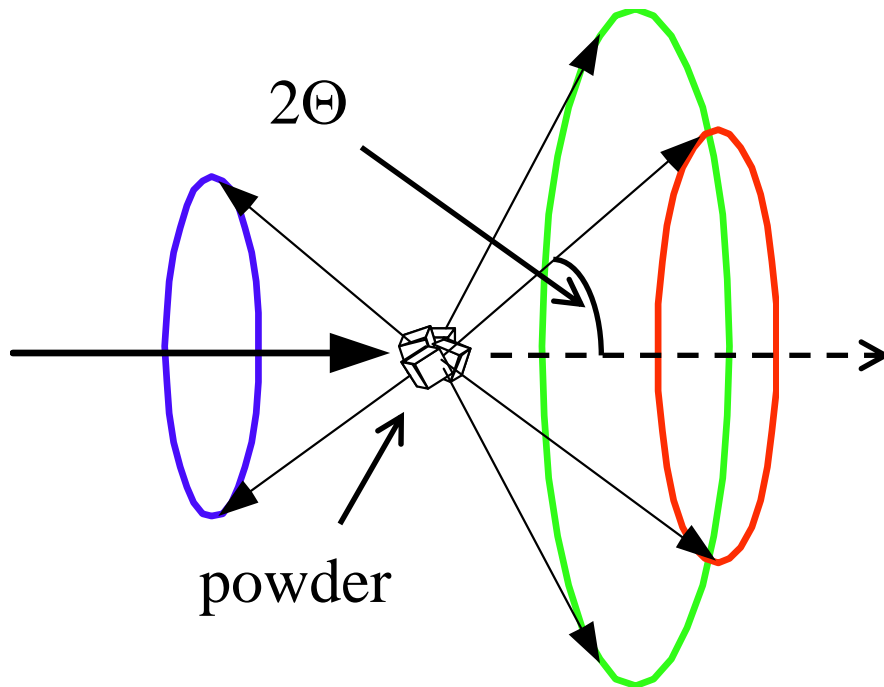


R.J. Cernik, summer school, Chester 2004

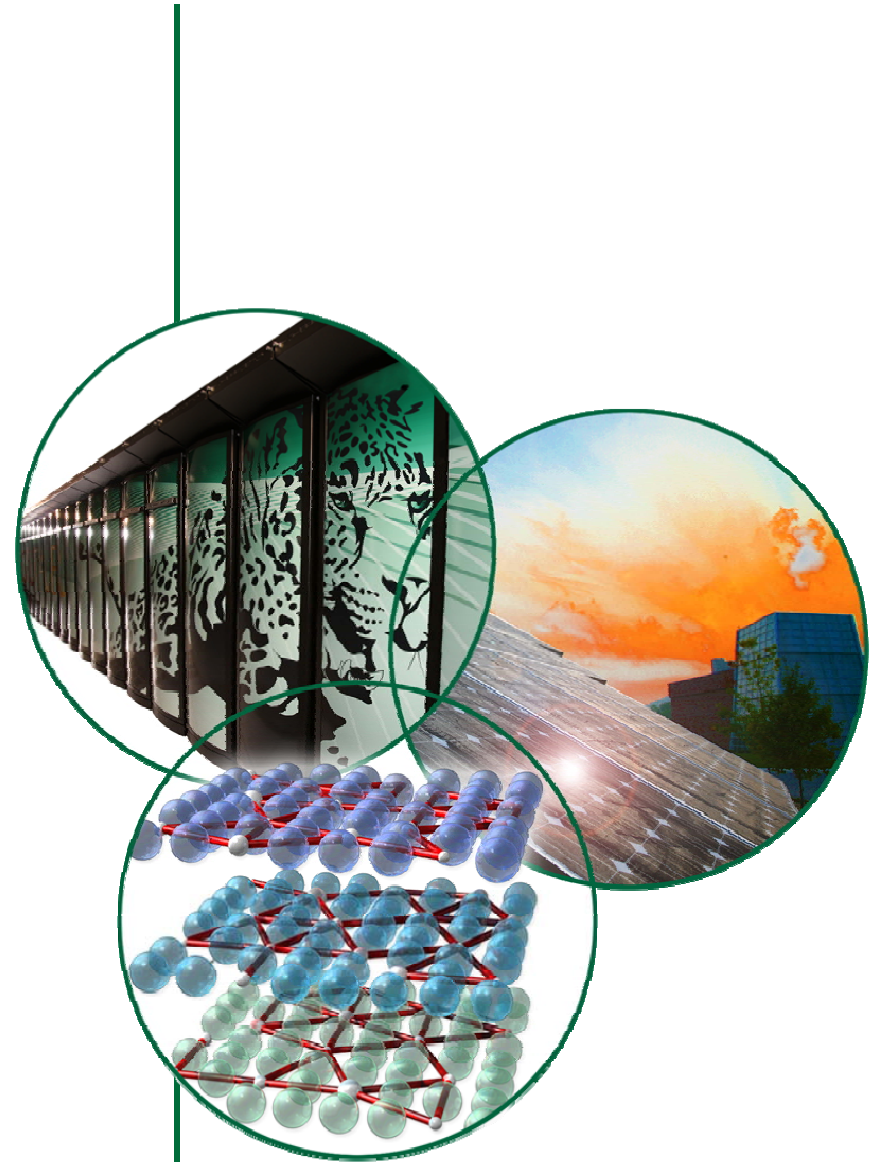
Powder Diffraction

❖ Powder

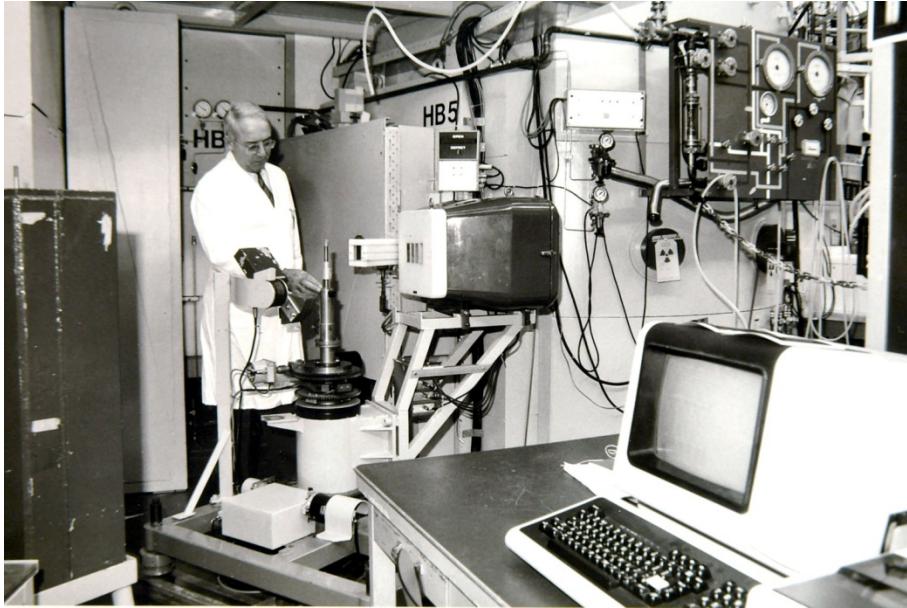
- ❖ Sizable samples have billions of crystals
- ❖ In the absence of texture, all crystal orientations are equally represented



Rietveld Refinement



Hugo Rietveld

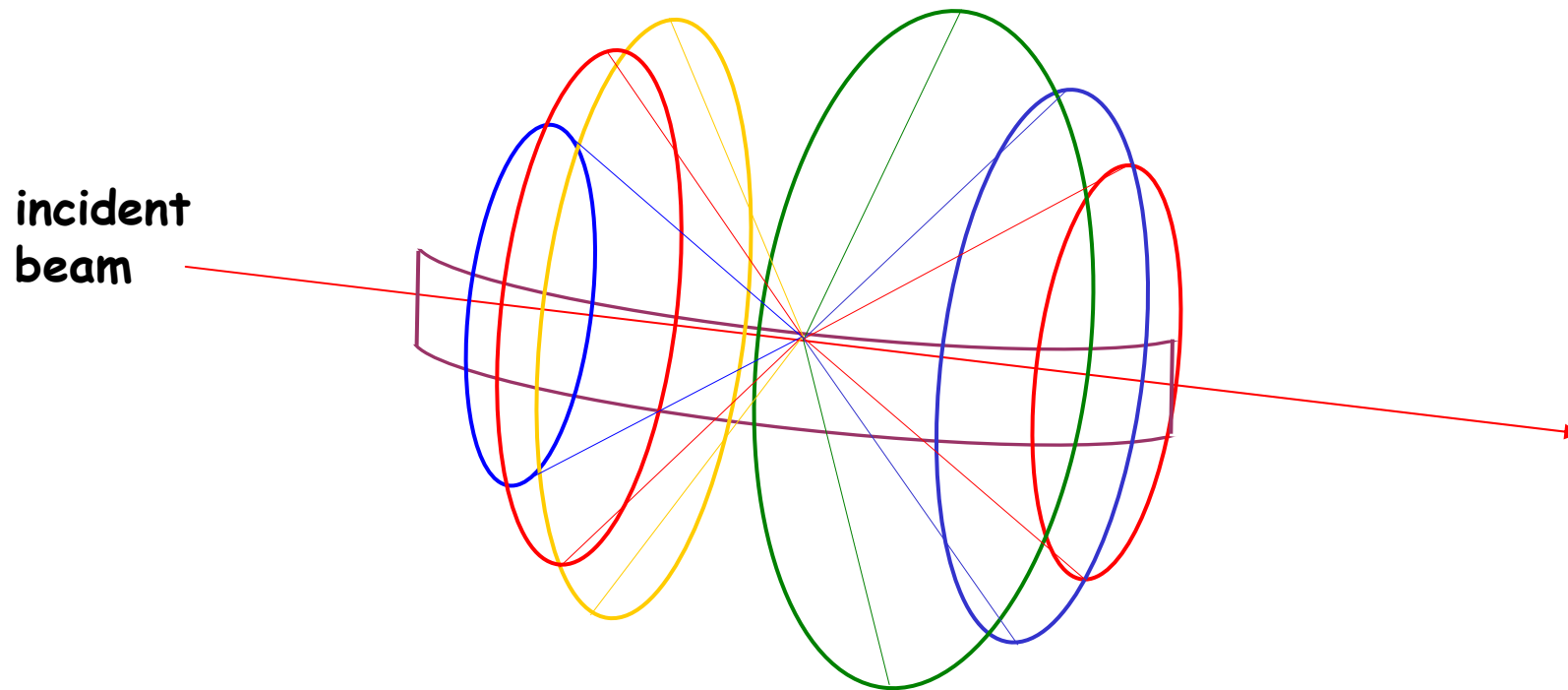


Dr. Rietveld at the neutron powder diffractometer at the High Flux Reactor of the Energy Research Foundation ECN in Petten, The Netherlands. (1987)

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}_{oi} and \mathbf{I}_{ci} are observed and calculated intensities.

From a purely mathematical point of view, R_{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

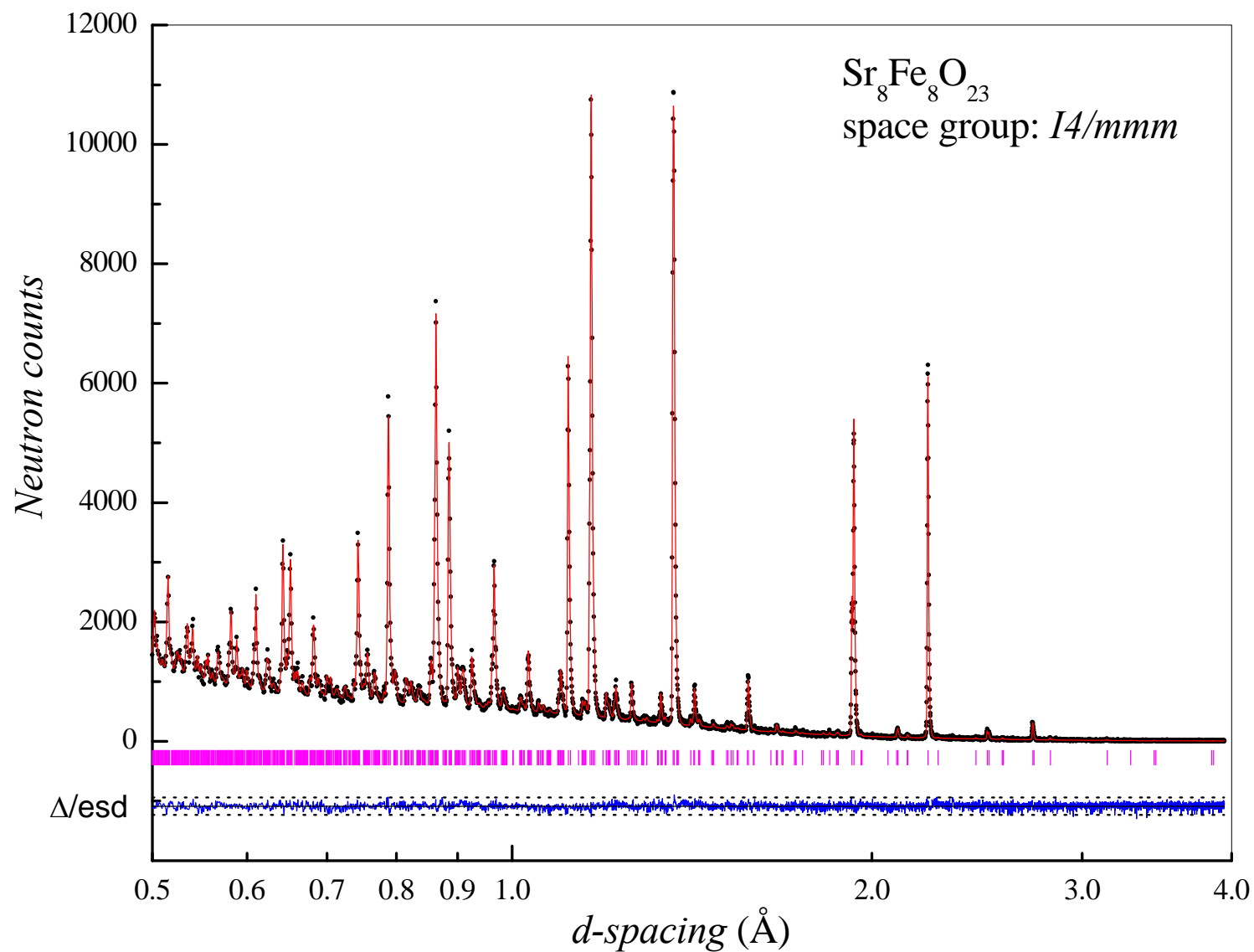


Fig. 5
2 Hodgson et al. *J. Solid State Chem.* 151, 190(2000)
for the U.S. Department of Energy

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 2Θ and a finite height slit positioned below 2Θ by τ

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

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

(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.

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:

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

(σ_{1i} = strain-free value for σ_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

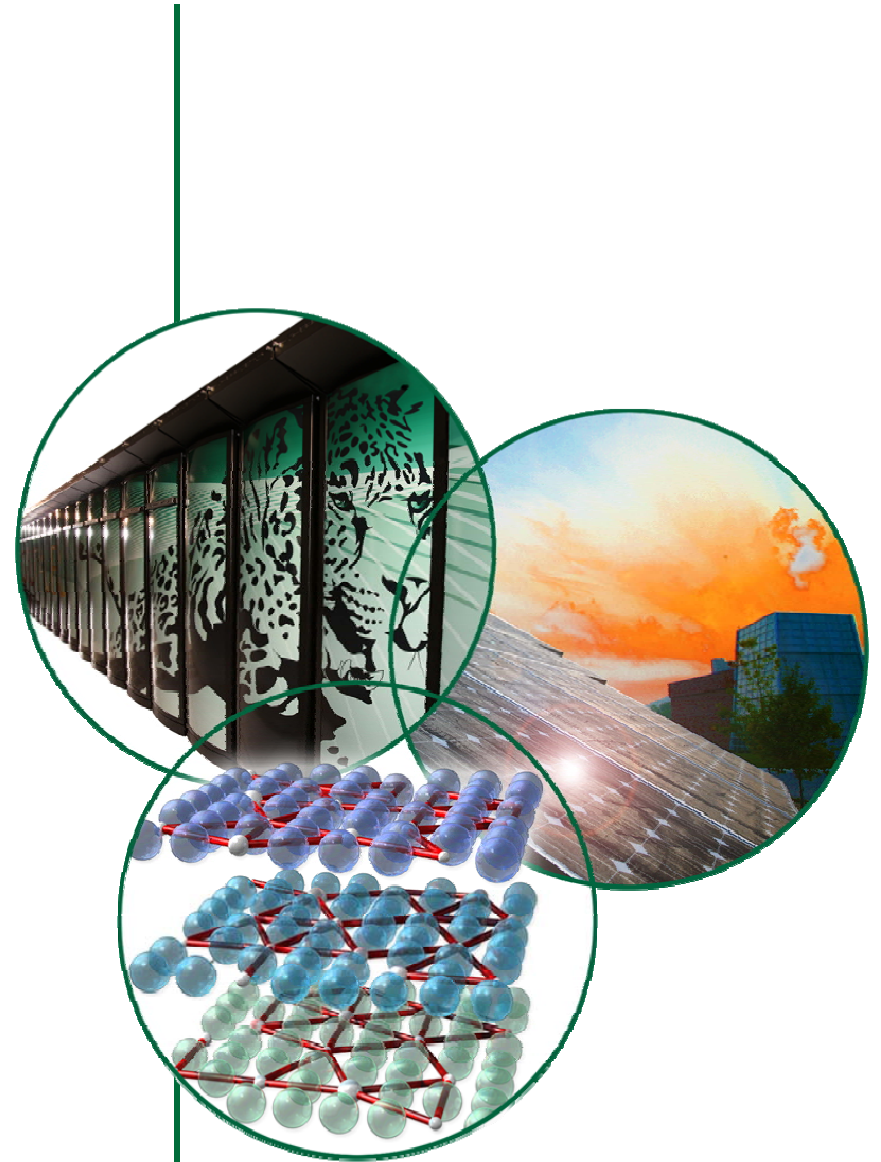
O_{ph} : Preferred orientation correction

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?



“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

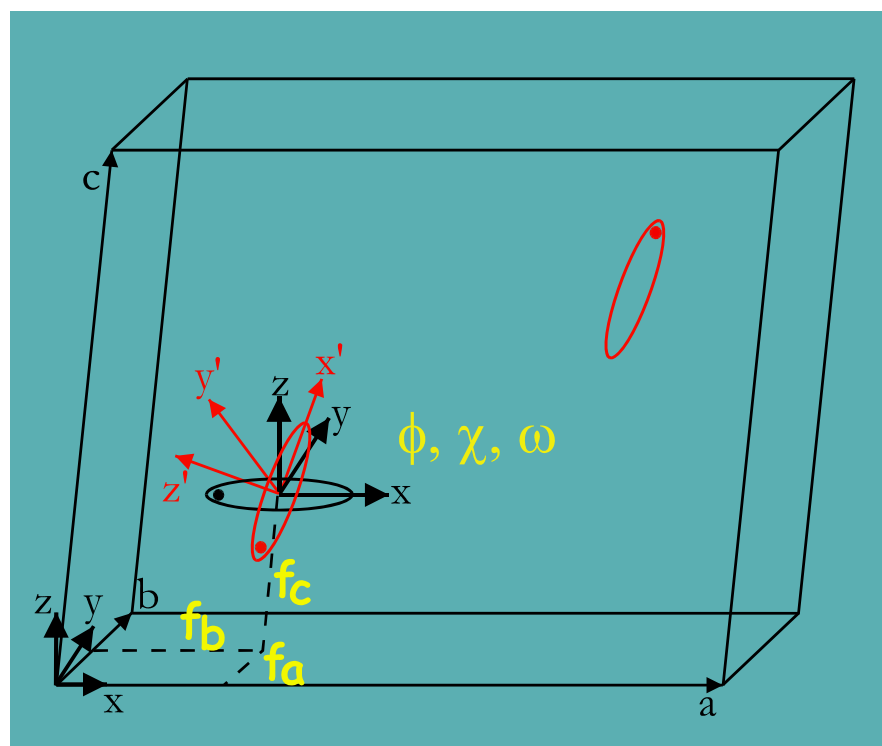
Methods of Solution:

- 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/
- FOX: <http://vincefn.net/Fox/>
- PSSP:
- Topas: 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)