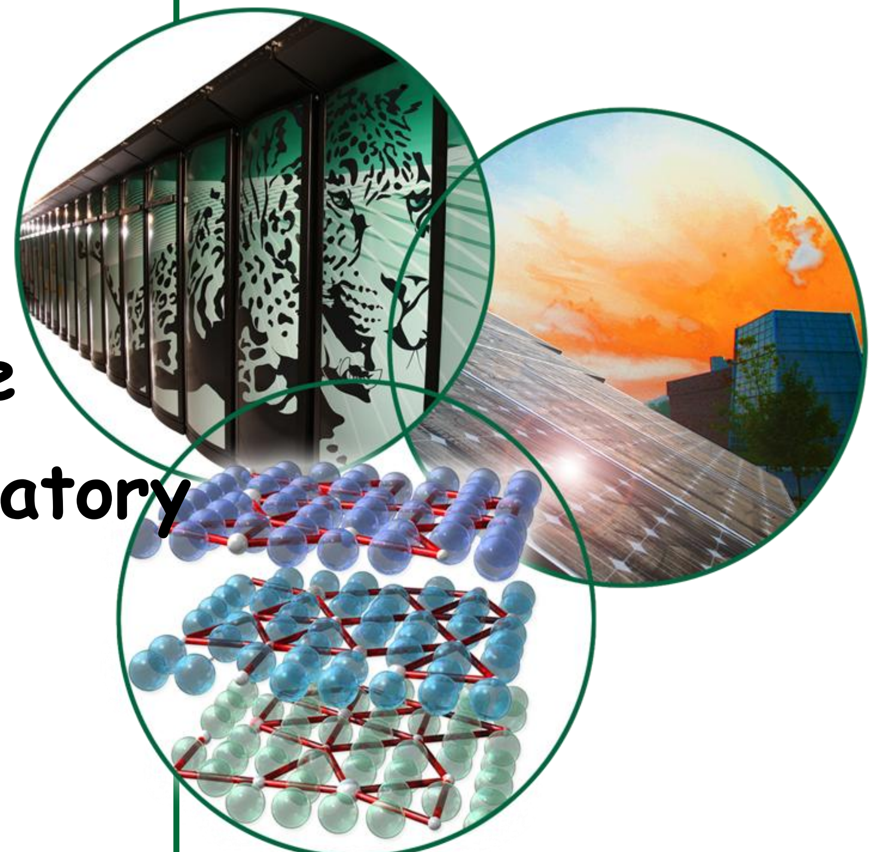
Powder Diffraction

Ashfia Huq

Spallation Neutron Source

Oak Ridge National Laboratory



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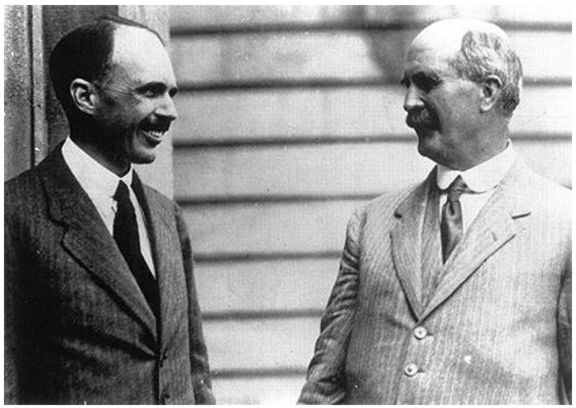
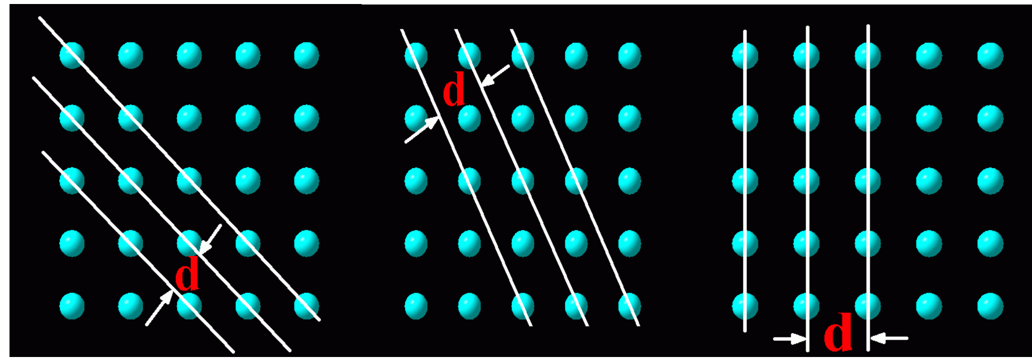
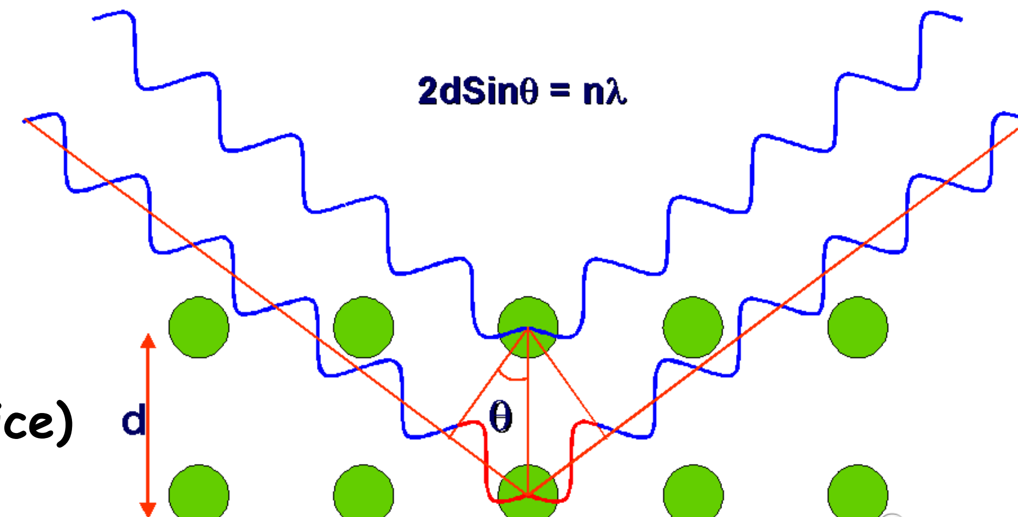
Bragg's law

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



Shared 1915 Nobel Prize



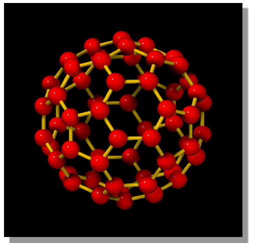


- Zinc Blend (fcc not sc)
- NaCl (not molecular)
- Diamond (two overlapping fcc lattice)

Where are the atoms?

We need wavelength (λ) ~ Object size (for condensed matter that is Å)





X-ray:

(λ : 10^{-9}m - 10^{-11}m)

$\lambda[Å] = 12.398/E_{ph}[keV]$

Source:

- Lab diffractometers
- Synchrotron Sources

Neutron:

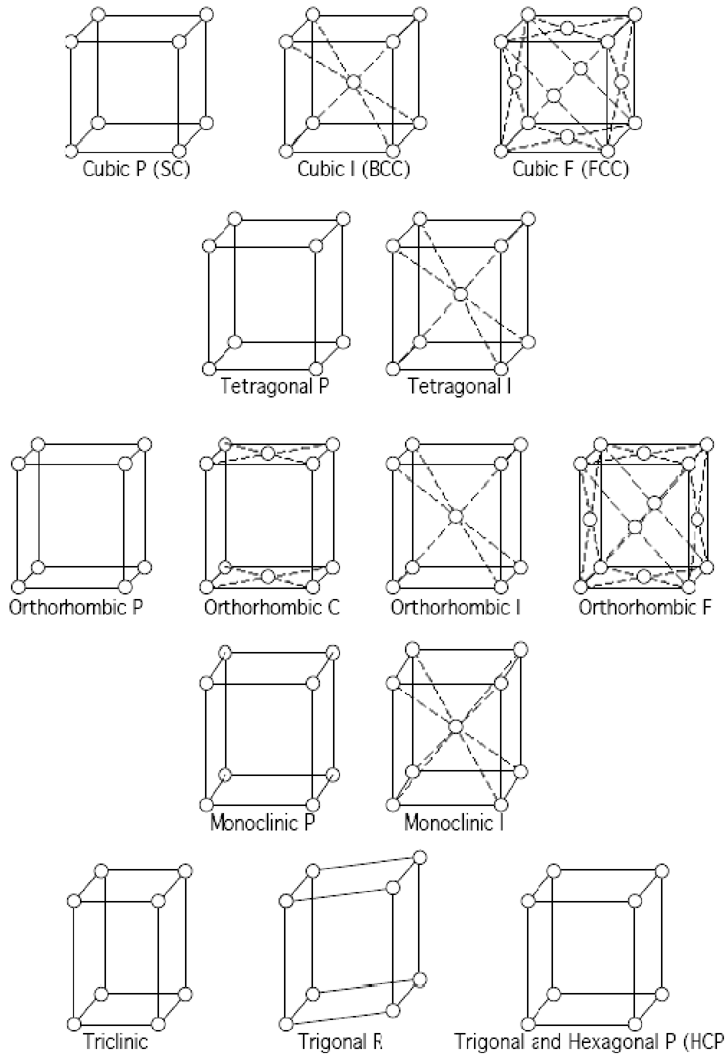
(thermal λ : 1-4Å)

$E_n[meV] = 81.89/\lambda^2[Å]$

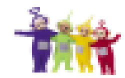
Source:

- Reactors (fission)
- Spallation Source

Crystal Structure = Basis + Lattice



Basis



$\otimes$

Lattice

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

3d Bravais Lattices:
14 types in 7 classes

Des McMorrow, Xray Neutron summer school 2008

Bragg Scattering from a crystal

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

Simple Example:

Simple cubic cell with one atom basis at (000)

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

For bcc lattice : SC with (000, ½ ½ ½) basis

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

Simple Example:

Rewrite Bragg's Law for cubic system:

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

$(h^2+k^2+l^2)$	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 θ using Cu K_α radiation. The Bragg angles are 19.48°,22.64°, 33.00°,39.68°, 41.83°, 50.35°, 57.05°, 59.42°. Determine the type of lattice and the lattice parameter.

θ	$\sin^2\theta$	$\sin^2\theta/\sin^2\theta_i$	$3*\sin^2\theta/\sin^2\theta_i$
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. λ = 1.5417. Plug in any of these values to eqn (1) to find a = 4.004Å.

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

General Formula:

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

recall (reciprocal lattice vector)

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

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

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

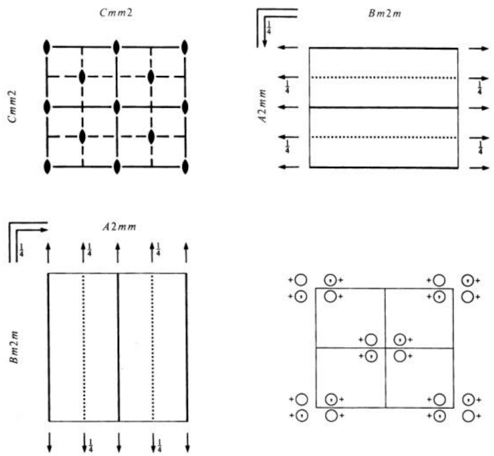
http://en.wikipedia.org/wiki/Crystal_system

Space Groups

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

$Cmm2$ $\quad C_{2v}^{11}$ $\quad mm2$ $\quad$ Orthorhombic

No. 35 $\quad Cmm2$ $\quad$ Patterson symmetry $Cmmm$



Origin on $mm2$

Asymmetric unit $\quad 0 \le x \le \frac{1}{4};\quad 0 \le y \le \frac{1}{2};\quad 0 \le z \le 1$

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 $\;\frac{1}{4},\frac{1}{4},z$	(3) $a\;\; x,\frac{1}{4},z$	(4) $b\;\; \frac{1}{4},y,z$

Generators selected $\quad$ (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 $(0,0,0)+\quad(\frac{1}{2},\frac{1}{2},0)+$				Reflection conditions
							General:
8	f	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $x,\bar{y},z$	(4) $\bar{x},y,z$	$hkl: h+k=2n$ $0kl: k=2n$ $h0l: h=2n$ $hk0: h+k=2n$ $h00: h=2n$ $0k0: k=2n$
							Special: as above, plus
4	e	$m\,.\,.$	$0,y,z$	$0,\bar{y},z$			no extra conditions
4	d	$.\,m\,.$	$x,0,z$	$\bar{x},0,z$			no extra conditions
4	c	$.\,.\,2$	$\frac{1}{4},\frac{1}{4},z$	$\frac{1}{4},\frac{3}{4},z$			$hkl: h=2n$
2	b	$m\,m\,2$	$0,\frac{1}{2},z$				no extra conditions
2	a	$m\,m\,2$	$0,0,z$				no extra conditions

Symmetry of special projections

Along [001] $c2mm$	Along [100] $p1m1$	Along [010] $p11m$
$\mathbf{a}'=\mathbf{a}\quad \mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\frac{1}{2}\mathbf{b}\quad \mathbf{b}'=\mathbf{c}$	$\mathbf{a}'=\mathbf{c}\quad \mathbf{b}'=\frac{1}{2}\mathbf{a}$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $0,y,0$

Maximal non-isomorphic subgroups

I	[2] $C1m1$ (Cm, 8)	(1; 3)+
	[2] $Cm11$ (Cm, 8)	(1; 4)+
	[2] $C112$ ($P2$, 3)	(1; 2)+
IIa	[2] $Pba2$ (32)	1; 2; (3; 4) + $(\frac{1}{2},\frac{1}{2},0)$
	[2] $Pbm2$ ($Pma2$, 28)	1; 3; (2; 4) + $(\frac{1}{2},\frac{1}{2},0)$
	[2] $Pma2$ (28)	1; 4; (2; 3) + $(\frac{1}{2},\frac{1}{2},0)$
	[2] $Pmm2$ (25)	1; 2; 3; 4

IIb $\quad$ [2] $Ima2$ ($\mathbf{c}'=2\mathbf{c}$) (46); [2] $Ibm2$ ($\mathbf{c}'=2\mathbf{c}$) ($Ima2$, 46); [2] $Iba2$ ($\mathbf{c}'=2\mathbf{c}$) (45); [2] $Imm2$ ($\mathbf{c}'=2\mathbf{c}$) (44); [2] $Ccc2$ ($\mathbf{c}'=2\mathbf{c}$) (37); [2] $Cmc2_1$ ($\mathbf{c}'=2\mathbf{c}$) (36); [2] $Ccm2_1$ ($\mathbf{c}'=2\mathbf{c}$) ($Cmc2_1$, 36)

Maximal isomorphic subgroups of lowest index

IIc $\quad$ [2] $Cmm2$ ($\mathbf{c}'=2\mathbf{c}$) (35); [3] $Cmm2$ ($\mathbf{a}'=3\mathbf{a}$ or $\mathbf{b}'=3\mathbf{b}$) (35)

Minimal non-isomorphic supergroups

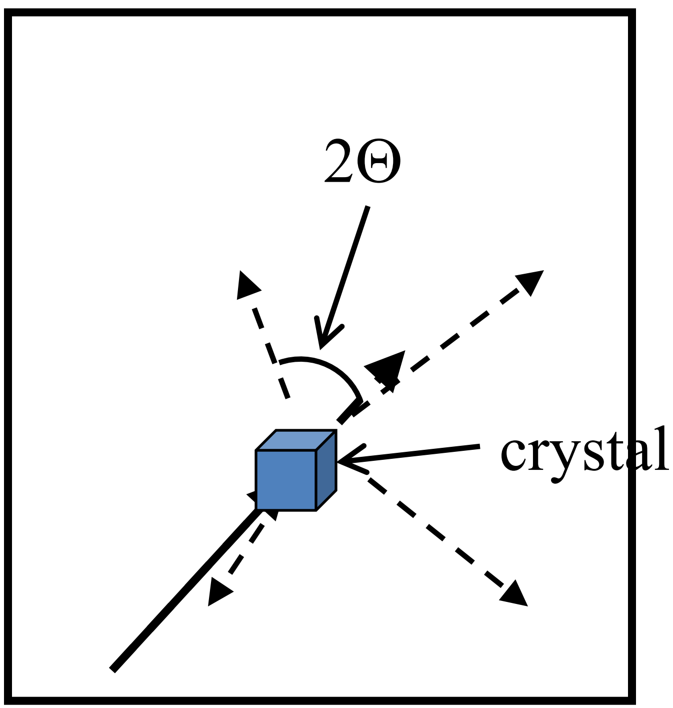
I $\quad$ [2] $Cmmm$ (65); [2] $Cmme$ (67); [2] $P4mm$ (99); [2] $P4bm$ (100); [2] $P4_2cm$ (101); [2] $P4_2nm$ (102); [2] $P\bar{4}2m$ (111); [2] $P\bar{4}2_1m$ (113); [3] $P6mm$ (183)

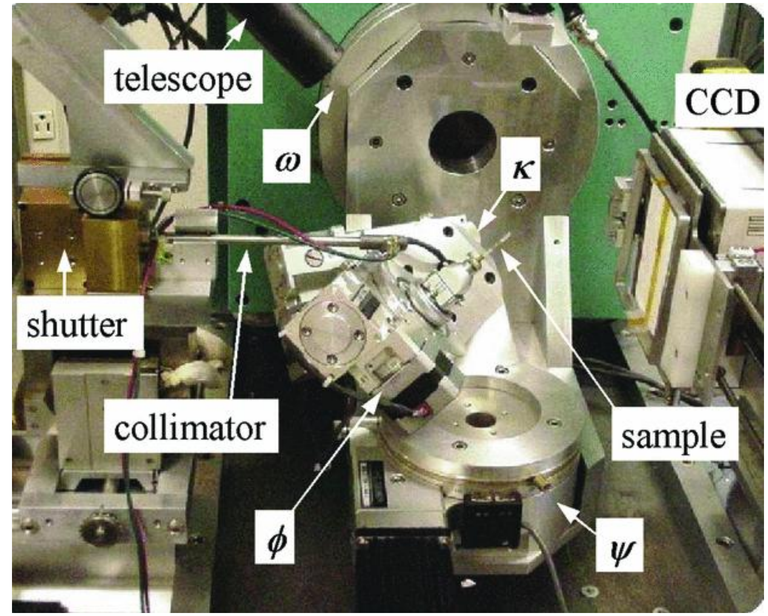
II $\quad$ [2] $Fmm2$ (42); [2] $Pmm2$ ($\mathbf{a}'=\frac{1}{2}\mathbf{a}, \mathbf{b}'=\frac{1}{2}\mathbf{b}$) (25)

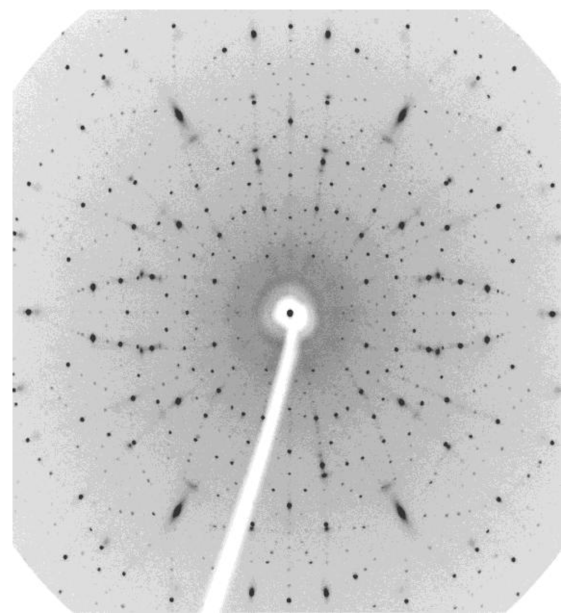
International Tables for Crystallography

Single Crystals:

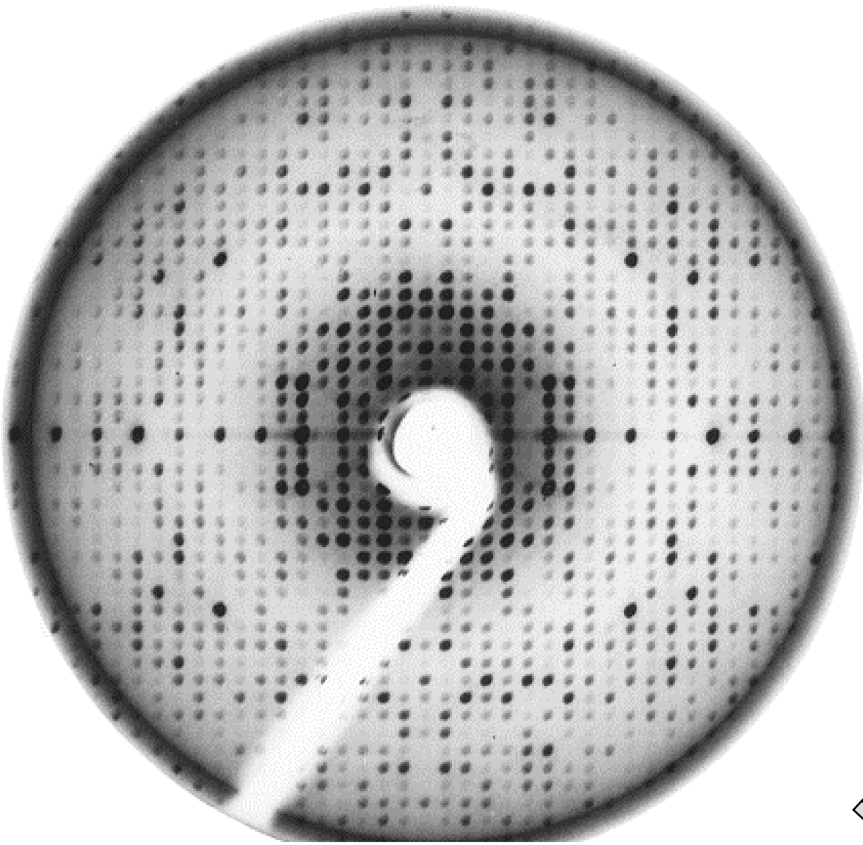
Sample must be correctly oriented in space with respect to the chosen reflection plane.

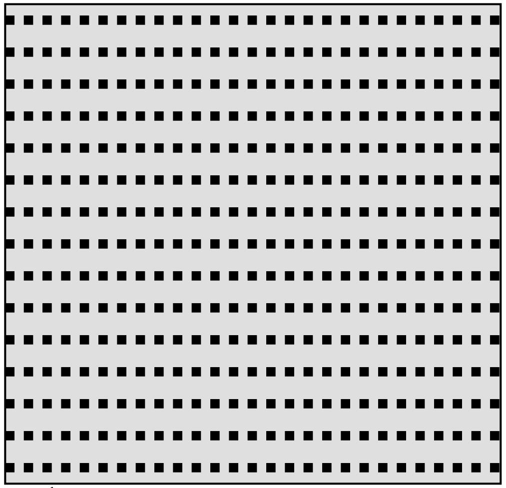


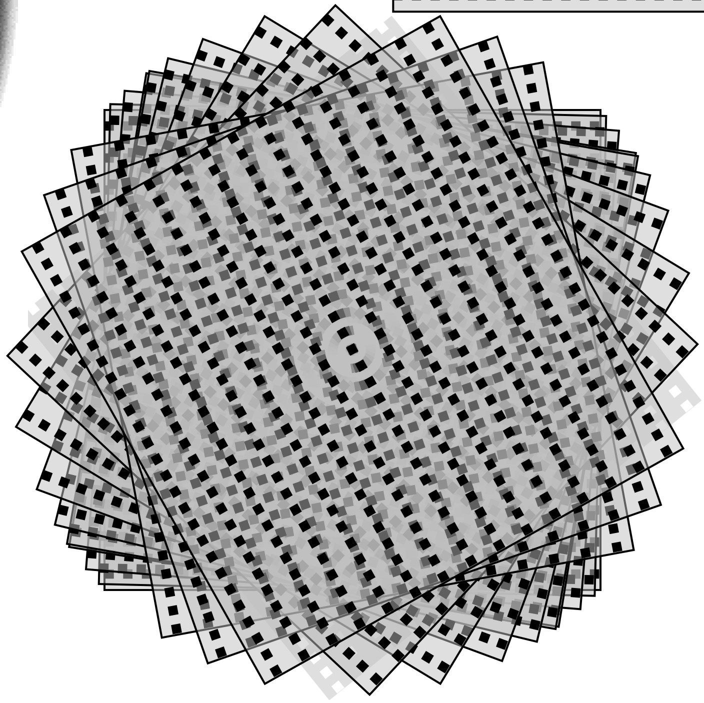




What if you don't have a single crystal?



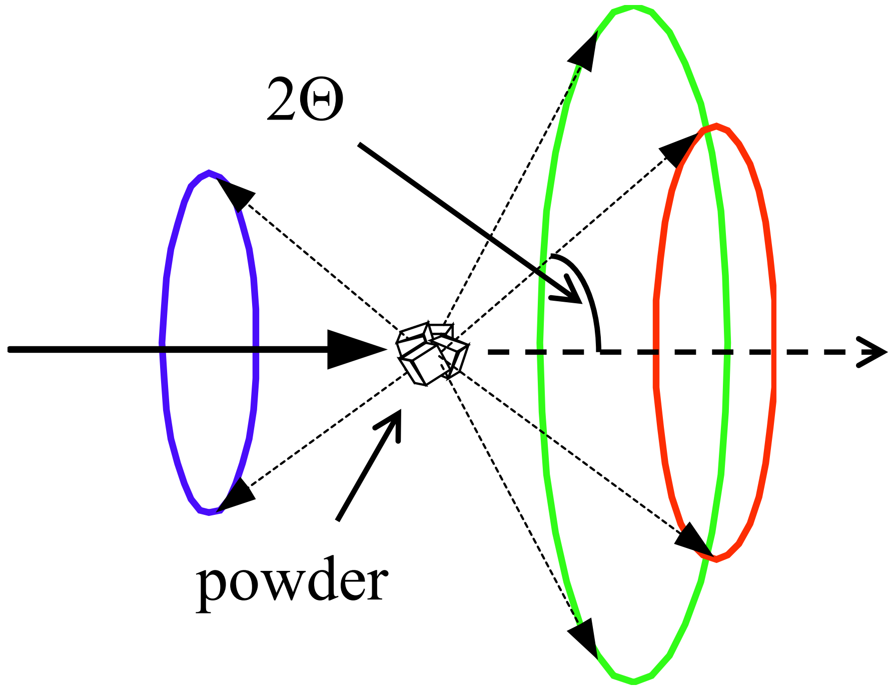


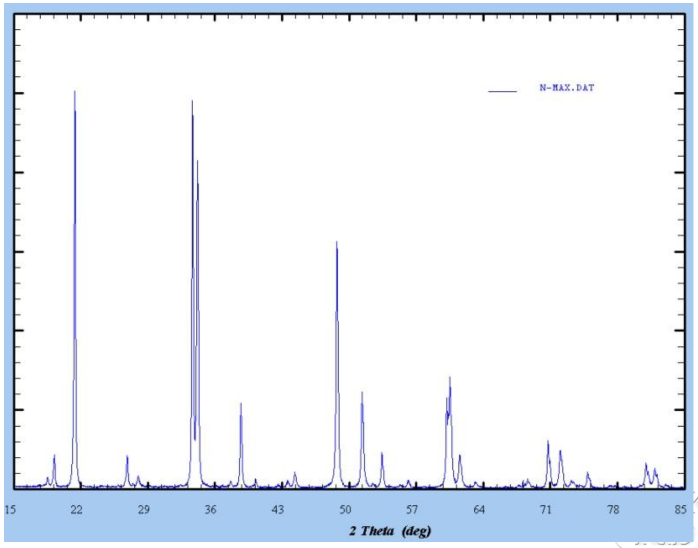


R.J. Cernik, summer school, Chester 2004

Powder Diffraction

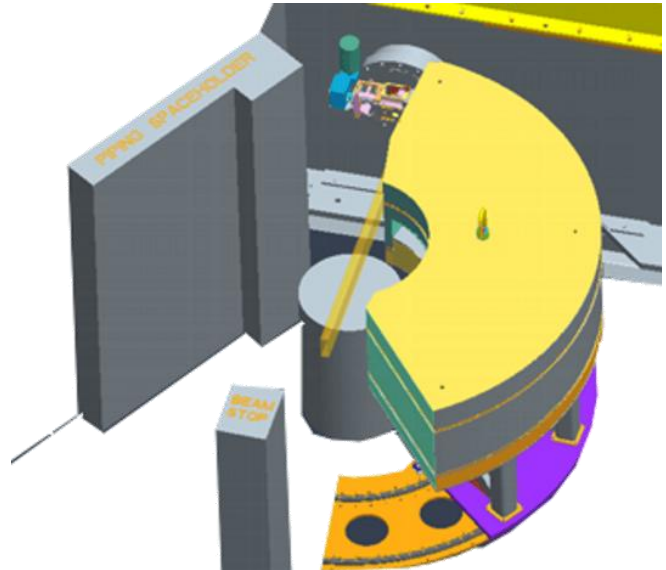
- Powder
  - Sizable samples have billions of crystals
  - In the absence of texture, all crystal orientations are equally represented

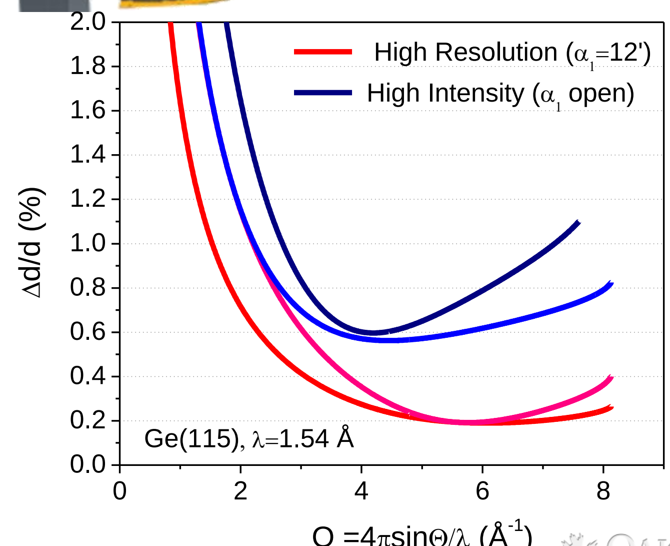




Powder Instruments at user facilities

beamline 11BM at APS

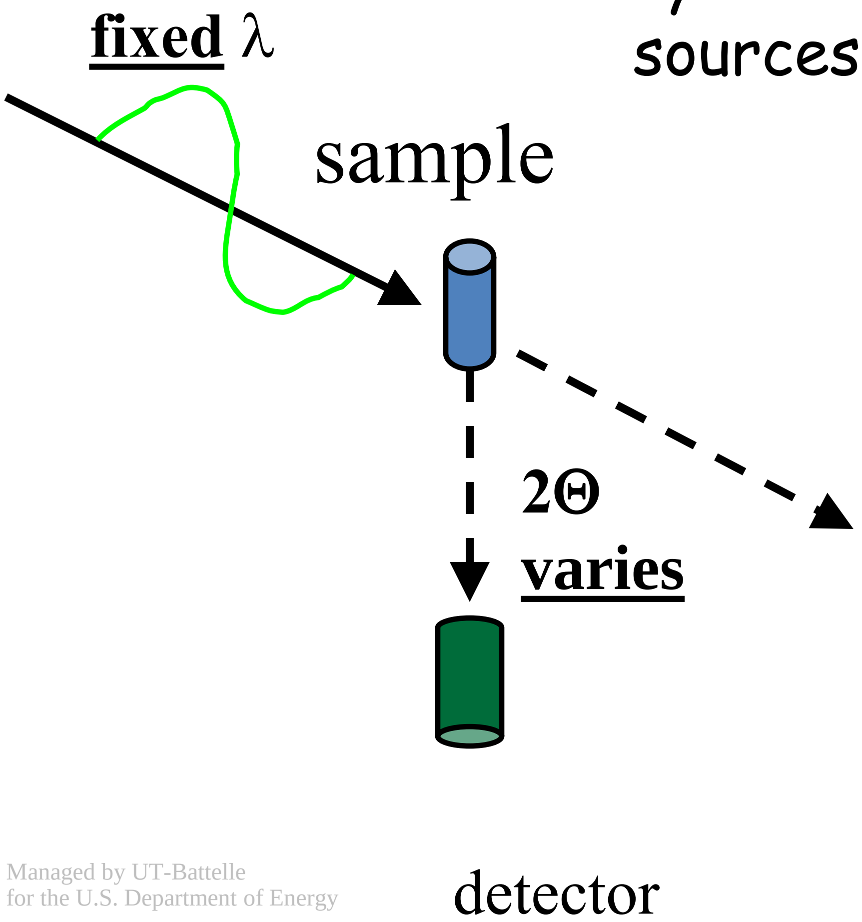


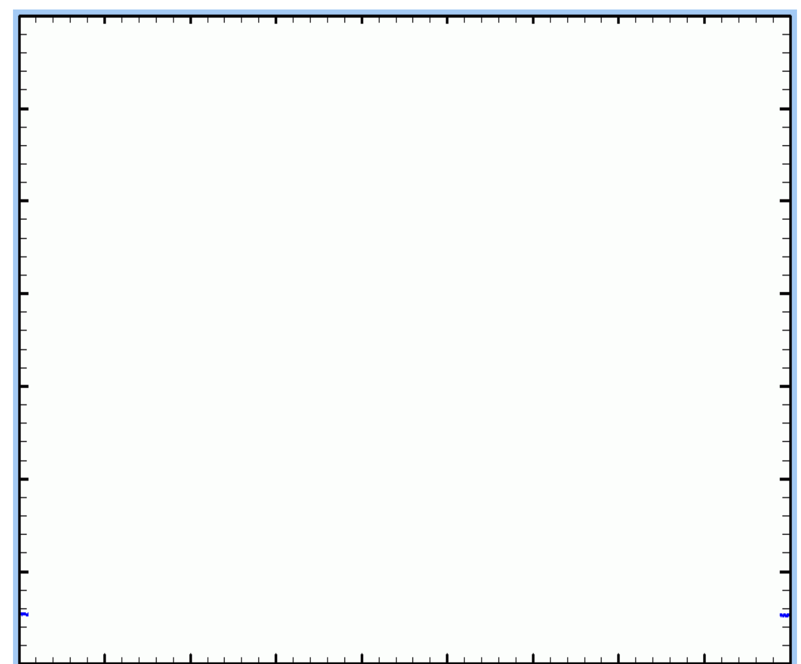


beamline HB2a at HFIR

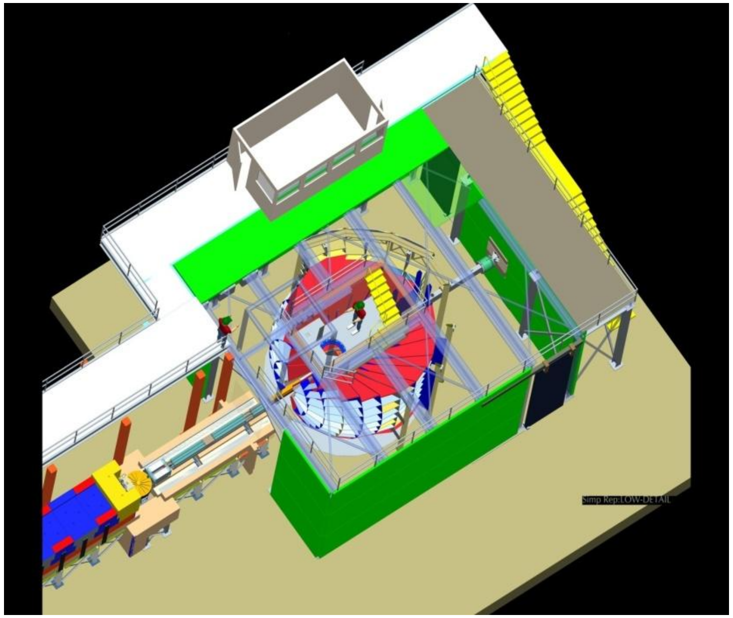
Constant wavelength ($2d\sin\Theta=\lambda$)

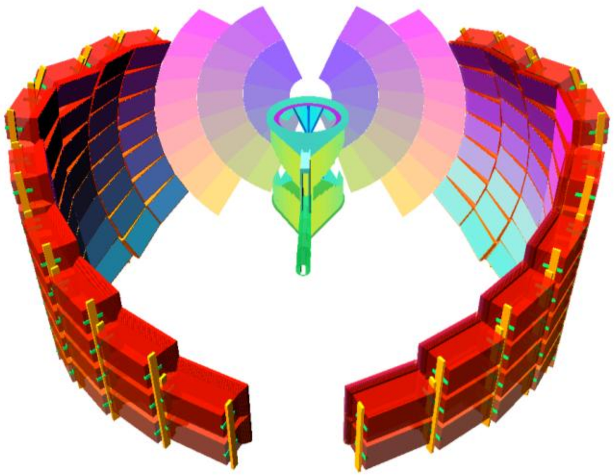
(X-ray tubes and monochromated synchrotron or steady neutron sources)

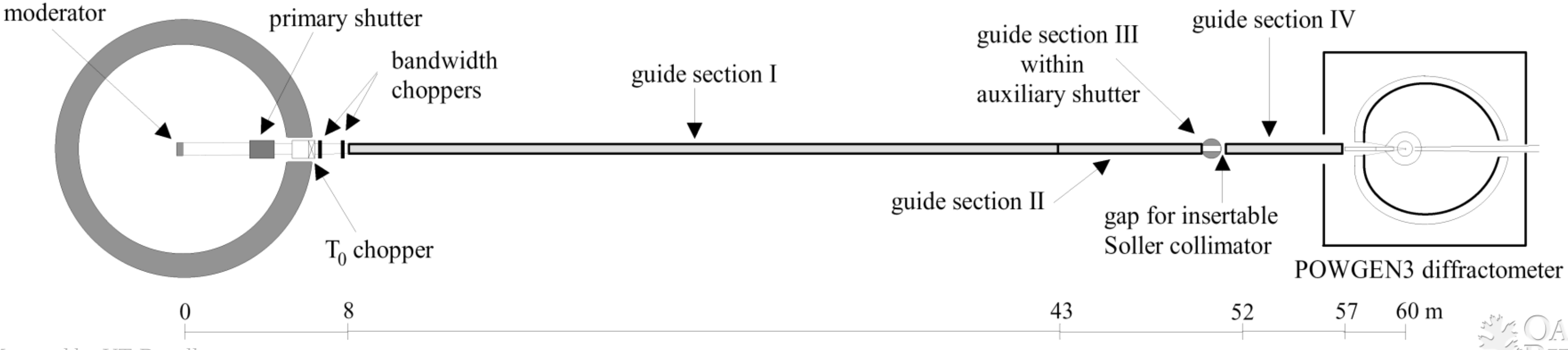




Time of flight instrument (POWGEN)

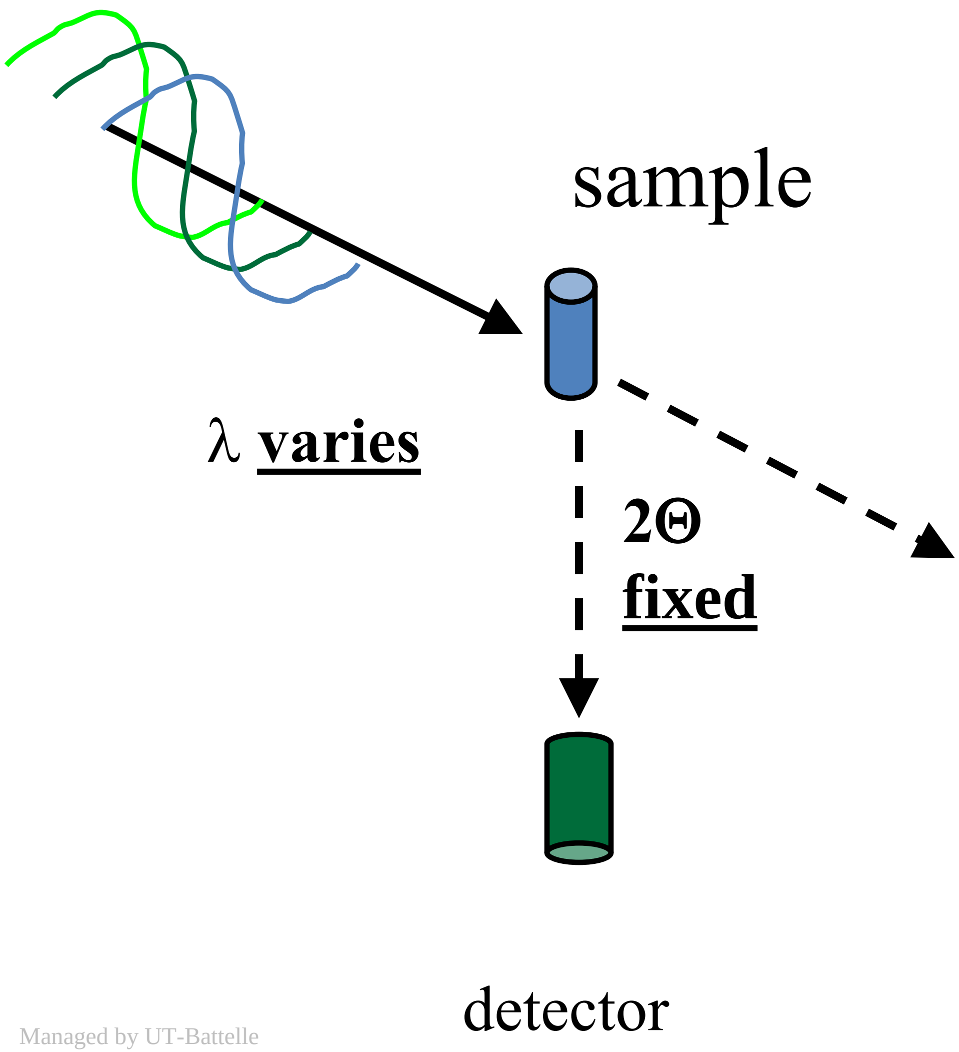




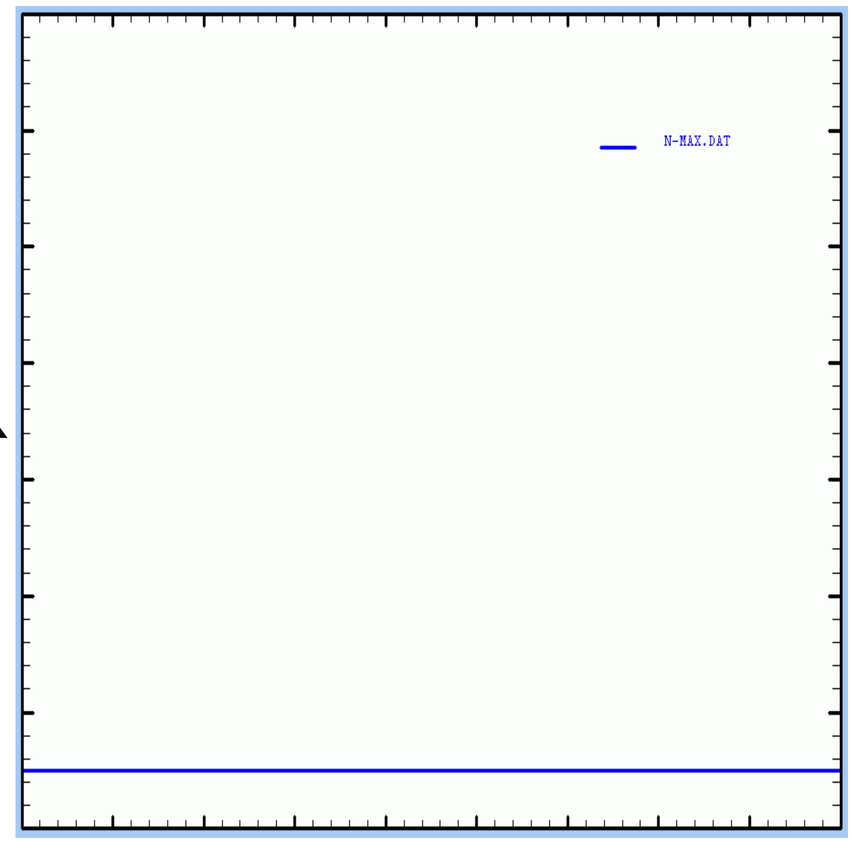


Installation:

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

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

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

However there is correction to this due to the moderator

$$t_{hkl} = DIFC*d_{hkl} + DIFA*d_{hkl}^2 + Zero \text{ (GSAS notation)}$$

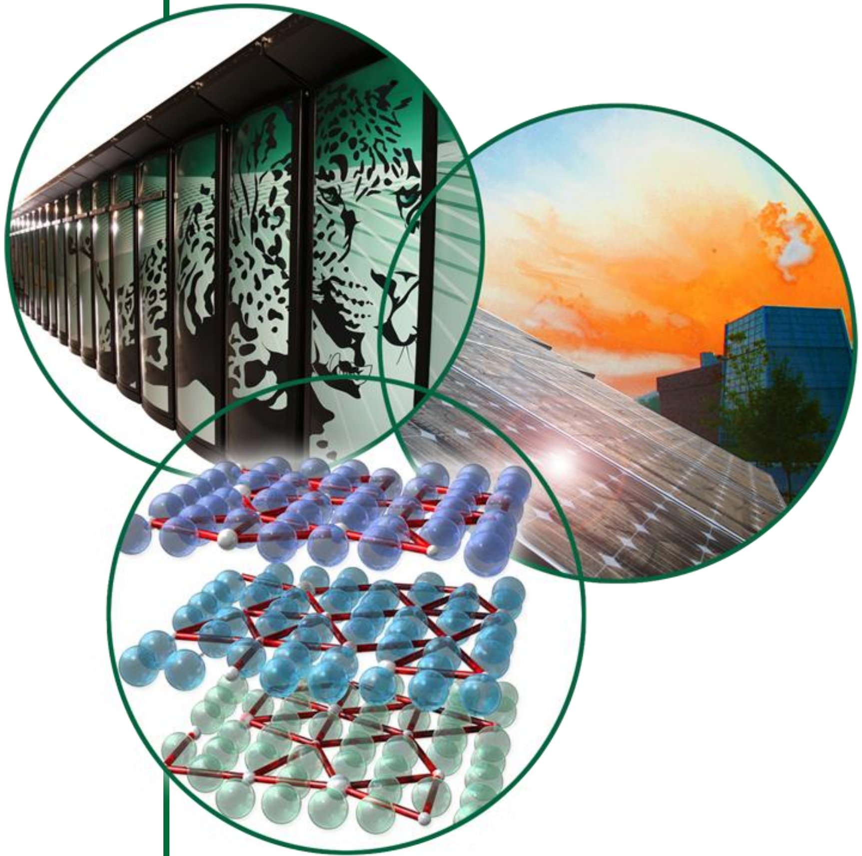
Resolution:

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

Bragg Intensity:

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

Rietveld Refinement



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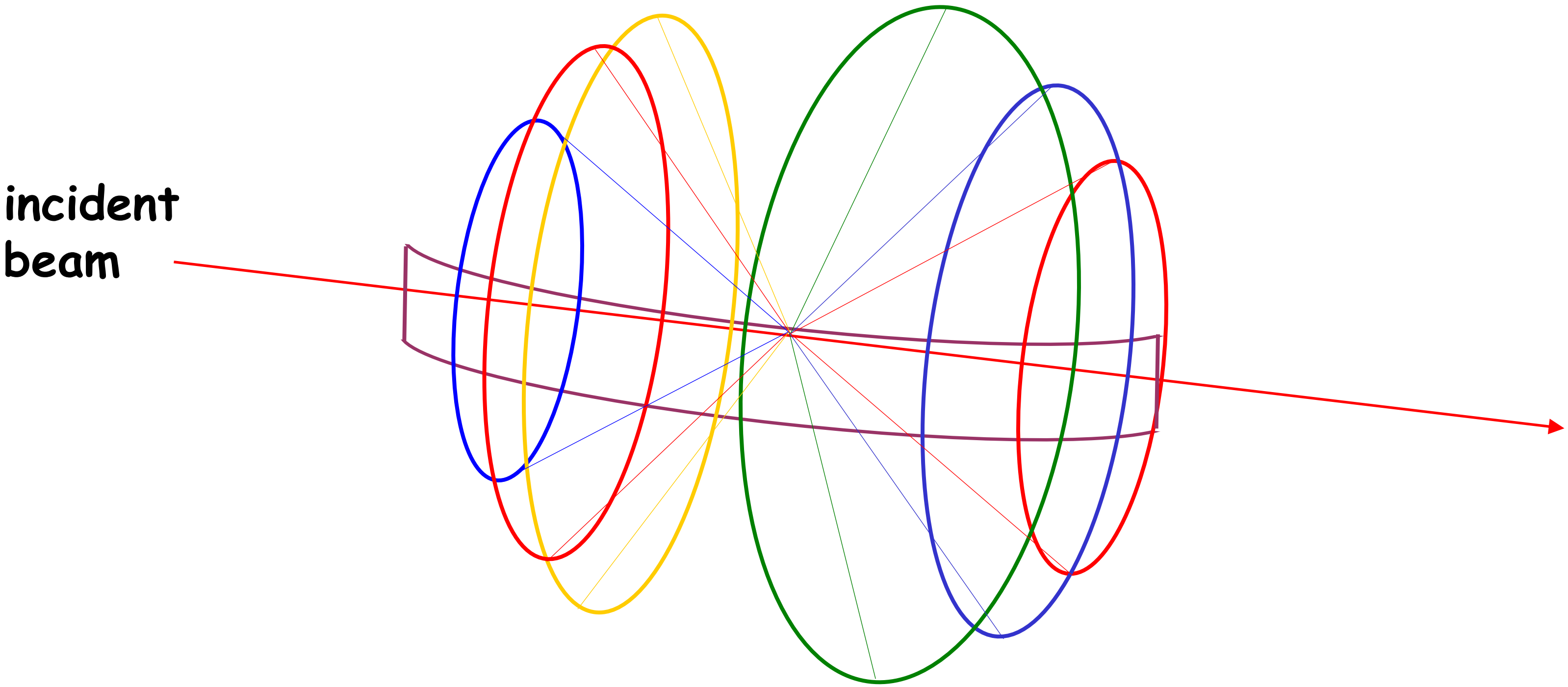
Hugo Rietveld

Dr. Rietveld at the neutron powder diffractometer at the High Flux Reactor of the Energy Reseach 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

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

(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:

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

(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.

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

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. I_{oi} and 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.

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

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

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.

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 (α, β)

$\alpha = \alpha_1 / d$ (rising exponential)

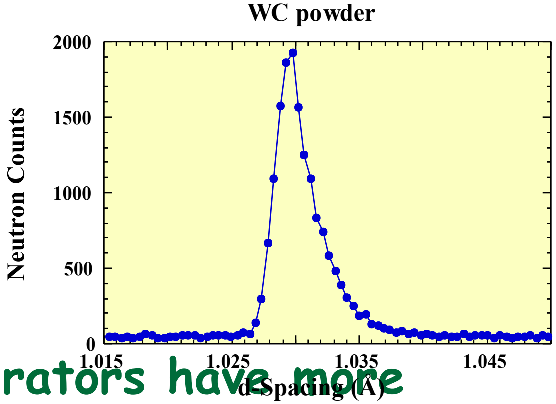
$\beta = \beta_0 + \beta_1 / d^4$ (falling exponential)

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

(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 α, β and peak position.

Ref: R.B. Von Dreele et. al., J. Appl. Cryst. **15**, 581 (1982)

TOF Peak Profiles (powgen):

T=DIFC*d+DIFA*d^2+ZERO

However the new formulation gives you how to calculate the relationship between time and d spacing which include epithermal and thermal parameters.

$$T_h = nT_h^e + (1-n)T_h^t$$
$$T_h^e = Z_0^e + D_1^e d_h$$
$$T_h^t = Z_0^t + D_1^t d_h - \frac{A^t}{d_h}$$
$$n = \frac{1}{2} erfc\{w_{cross}(T_{cross} - \frac{1}{d_h})\}$$

The exponentials also includes the epithermal and thermal component.

$$\frac{1}{\alpha} = n\alpha^e + (1-n)\alpha^t \qquad \frac{1}{\beta} = n\beta^e + (1-n)\beta^t$$
$$\alpha^e = \alpha_0^e + \alpha_1^e d_h \qquad \beta^e = \beta_0^e + \beta_1^e d_h$$
$$\alpha^t = \alpha_0^t - \frac{\alpha_1^t}{d_h} \qquad \beta^t = \beta_0^t - \frac{\beta_1^t}{d_h}$$

The rest is the standard back to back exponential that one uses for TOF function
We saw before peak shape is a convolution of a pseudo-Voigt function with a pair of back-to-back exponentials.
So if t is the origin of time at the Bragg position the peak shape is given by

$$\Omega(x) = pV(x) \otimes E(x) = \int_{-\infty}^{+\infty} pV(x-t)E(t)dt$$

where

$$E(t) = 2Ne^{\alpha t} \qquad t \le 0$$
$$E(t) = 2Ne^{-\beta t} \qquad t > 0$$
$$N = \frac{\alpha\beta}{2(\alpha+\beta)}$$

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)

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

(K = Scherrer constant)

Other things to be keep in mind

Recall $K_{ph}=E_{ph}A_hO_{ph}M_pL/V_p$

E_{ph}: Extinction correction

A_h: Absorption correction

O_{ph}: Preferred orientation correction

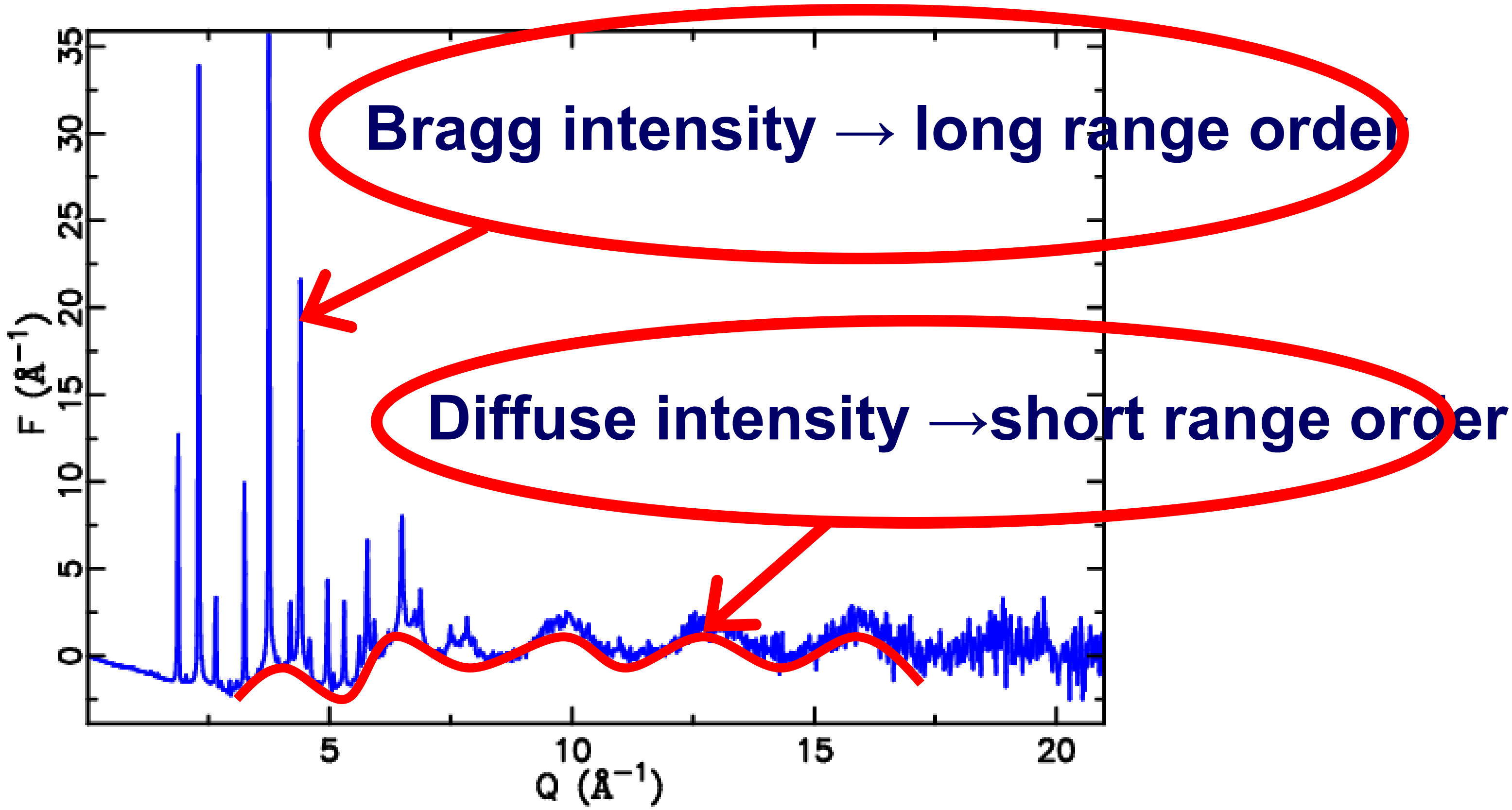
M_p: Reflection multiplicity

L: Angle dependent correction (Lorentz-polarization)

V_p: Unit cell volume for the phase

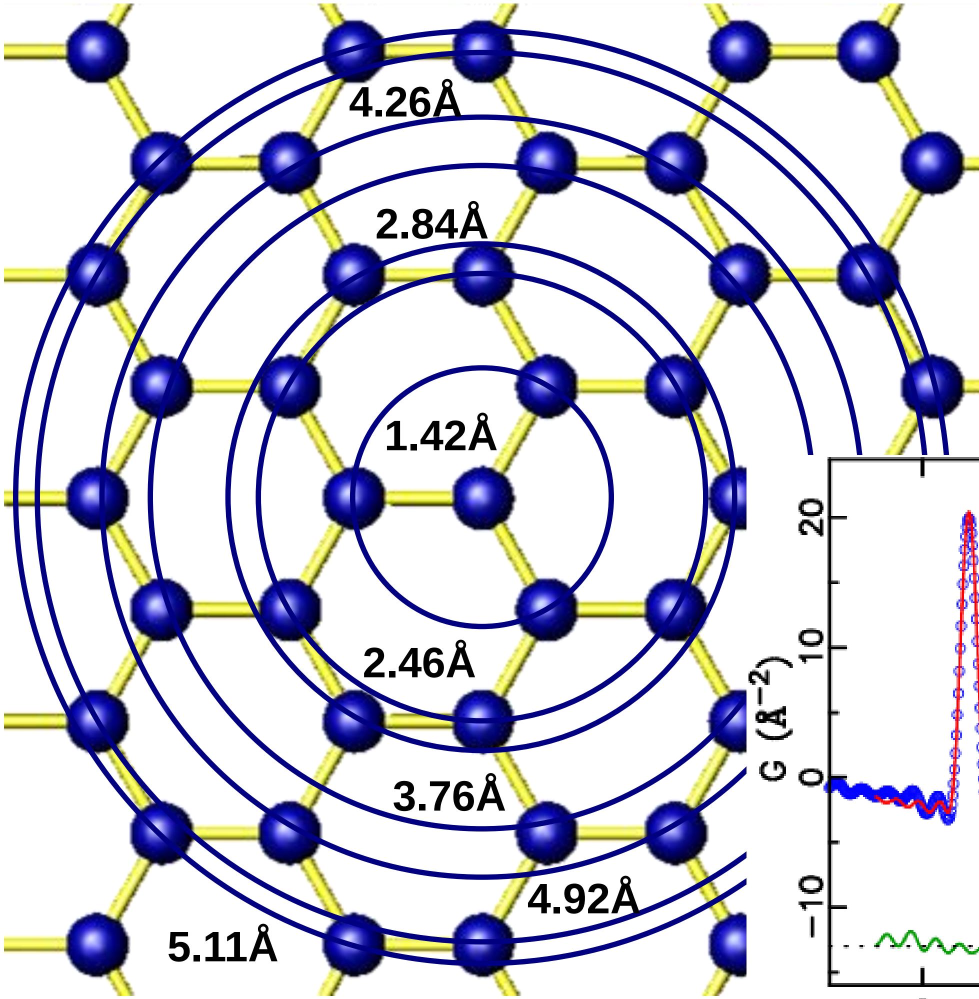
Pair Distribution Function from total scattering experiments

How can we get short range structural information?

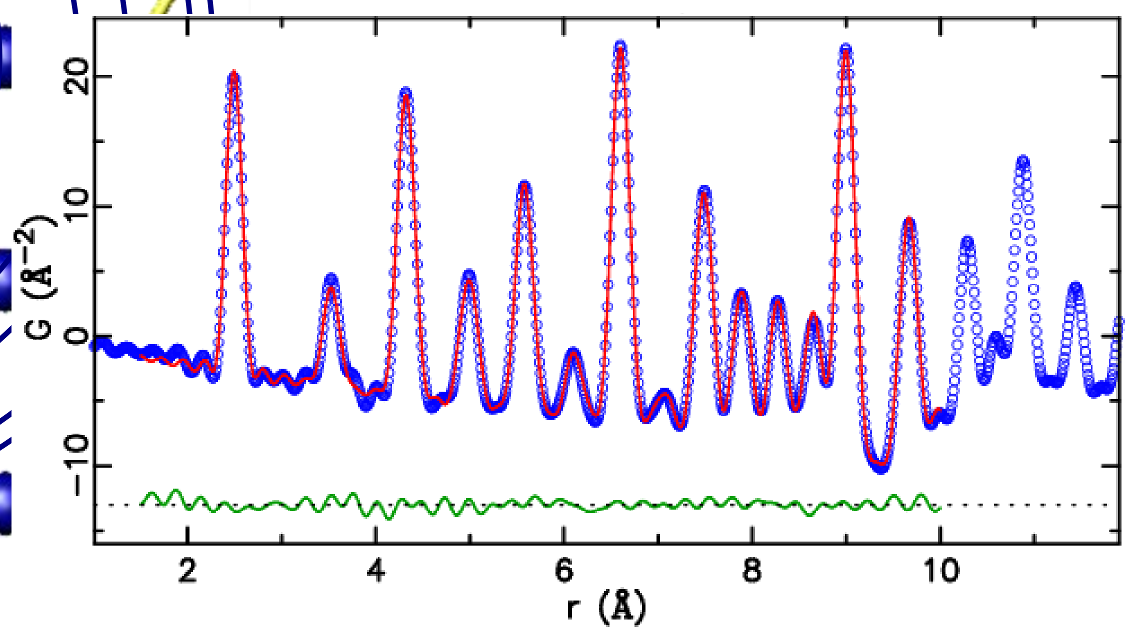


$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$

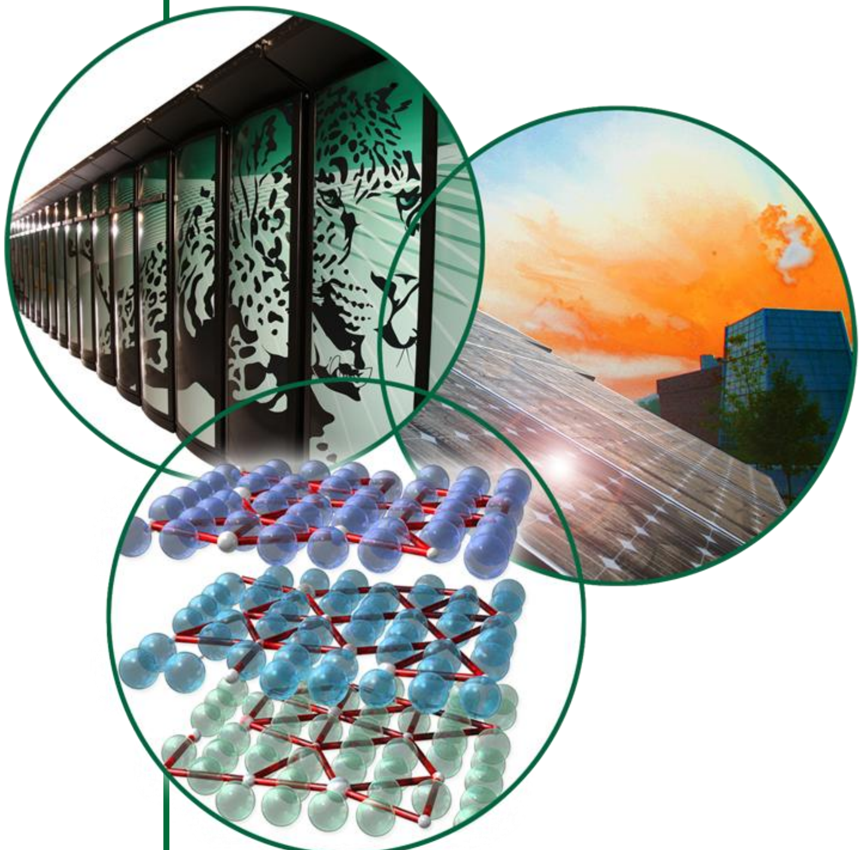
Total Scattering Based Atomic Pair Distribution Function (PDF)



Pair distribution function (PDF) gives the probability of finding an atom at a distance "r" from a given atom.



Applications of Powder Diffraction



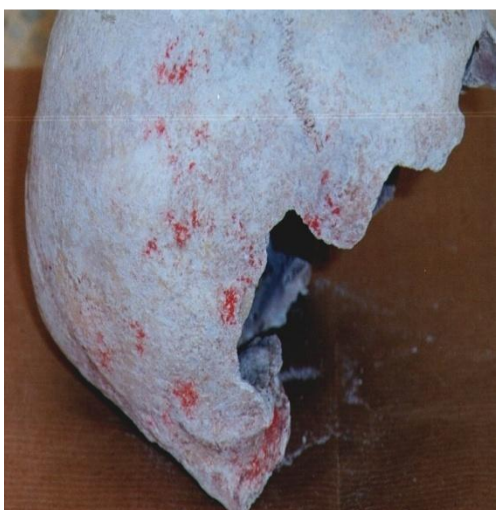
- Phase ID and Quantitative analysis
- Structure and transport
- Neutron Powder Diffraction
- Time resolved in-situ studies
- Ab-initio structure solution
- Proteins Crystallography and Powder Diffraction

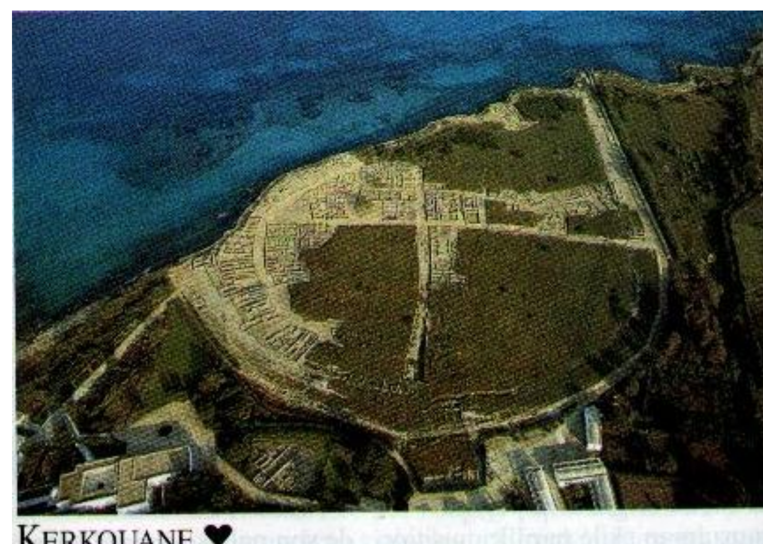
Phase ID: "Finger Printing"

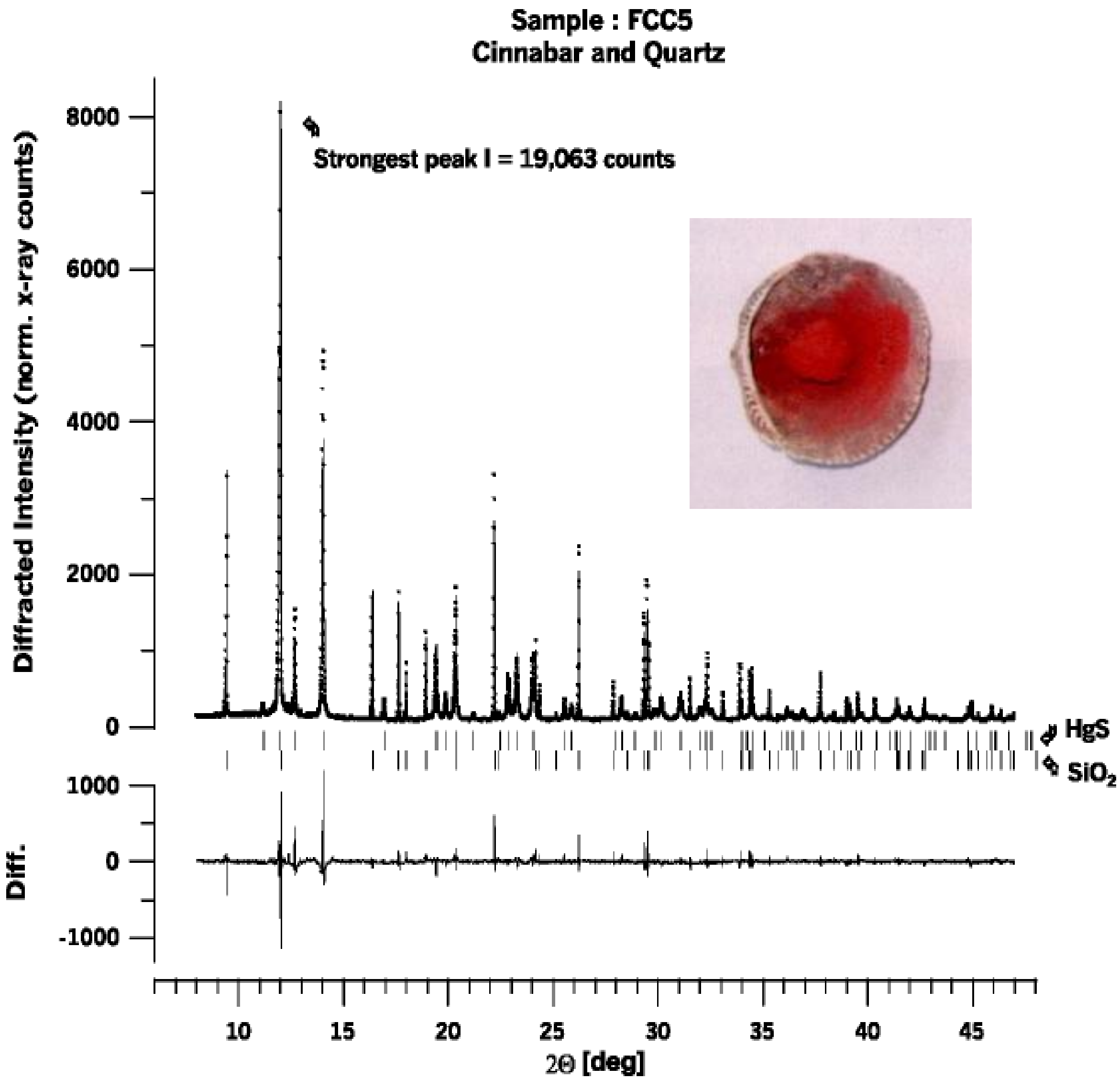
Huq et.al. Appl. Phys. A 83, 253 (2006)

Natural antique colorants include red pigments such as cinnabar and ochre and pink pigments such as madder. These archaeological pigments have been used as ritual and cosmetic make-up and they are a material proof of handcraft activities and trade in the Mediterranean.

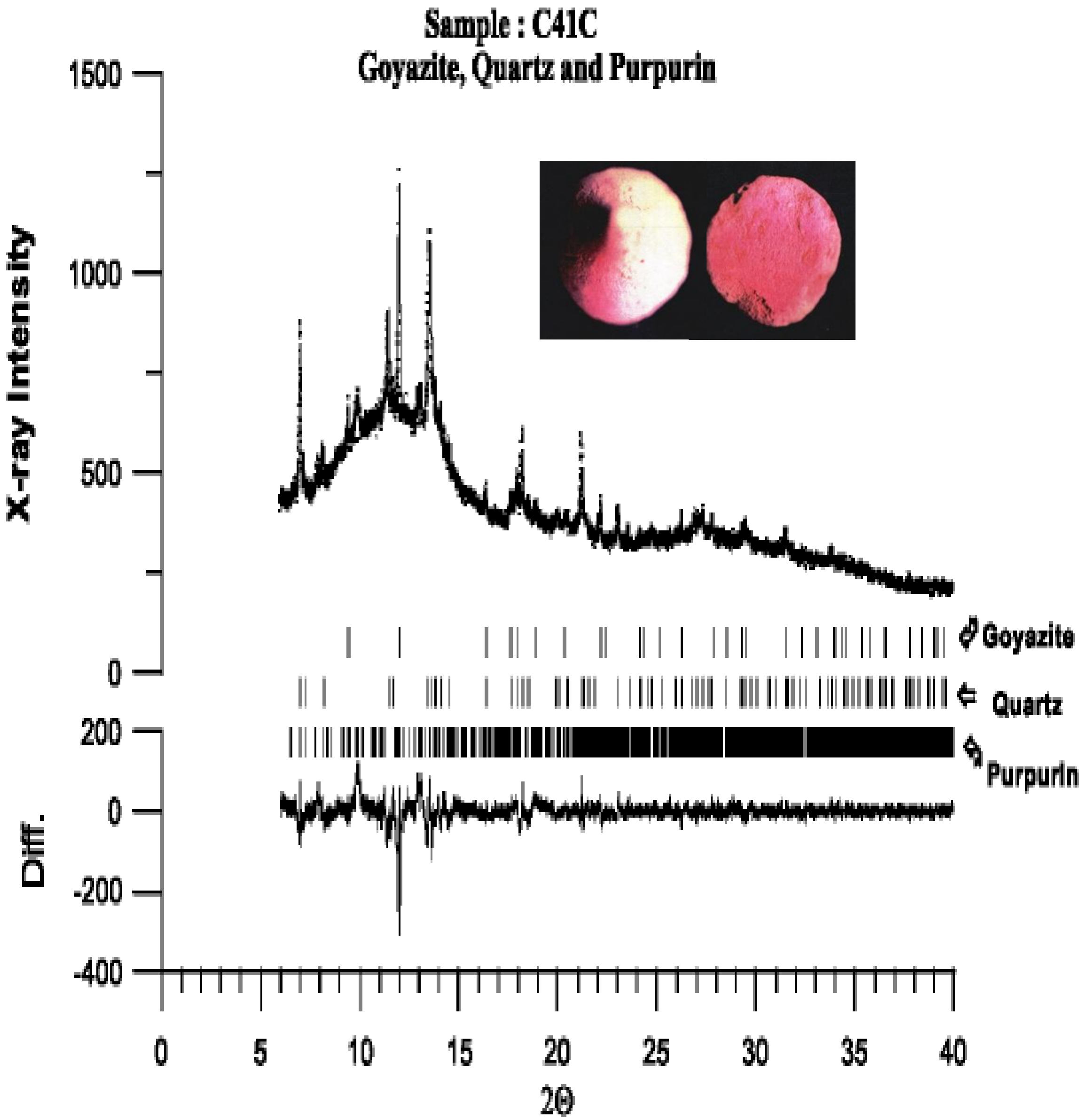
The pigments were discovered during different excavations in archaeological sites of Tunisia (Carthage, Kerkouane, Bekalta, Bouaarada and elsewhere).







- fit peak: search database for matches.
- Look up structure.
- Rietveld refinement.
- For mixture quantitative phase analysis.



Conclusions

Ten punic make-up samples were studied with SR-XRD using a 2D CCD detector and high angular resolution powder diffraction. Four samples (B1, B2, B3 and FCC5) contain quartz and cinnabar while four other samples (B10, FCC4, FCC6 and OCRB) contain quartz and hematite. The presence of quartz is probably due to sand/clay from the excavation area.

These results are similar to what would be obtained from raw materials indicating that these eight samples were not subject to any preparation by the Carthaginians. These eight samples were used as ritual make-up. However, the last two samples (FCC2 and C41C) showed an amorphous background, their preparation required sophisticated techniques corresponding to cosmetic make-up; they contain purpurin as major pigment which is formulated in a similar fashion as a lacquer.

Resources (databases)

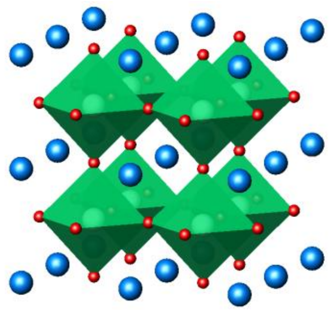
- Powder diffraction file, maintained by ICDD: Release 2008 of the Powder Diffraction File contains 622,117 unique material data sets. Each data set contains diffraction, crystallographic and bibliographic data, as well as experimental, instrument and sampling conditions and select physical properties in a common standardized format. http://www.icdd.com/products/overview.htm

  * CCDC (Chembridge Crystallographic database): organic structures
  * ICSD (Inorganic crystal structure database): FIZ
  * NIST & MPDS

Why Neutrons ?

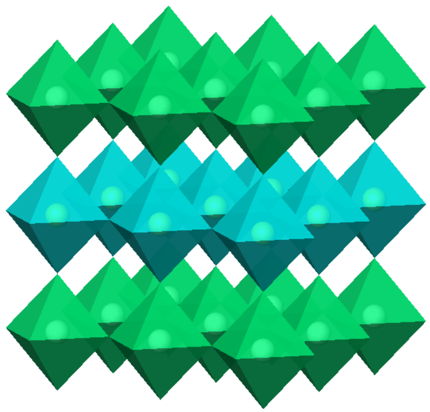
- Electrically neutral; penetrates centimeters of bulk material (allows non-destructive bulk analysis)
- Detects light atoms even in the presence of heavy atoms (organic crystallography) – H is special!
- Distinguishes atoms adjacent in Periodic table and even isotopes of the same element (changing scattering picture without changing chemistry)
- Magnetic moment (magnetic structure)
- Ease of *in-situ* experiments, e.g. variable temperature, pressure, magnetic field, chemical reaction etc.

Ba_2CuWO_6: An Ordered Tetragonal Perovskite

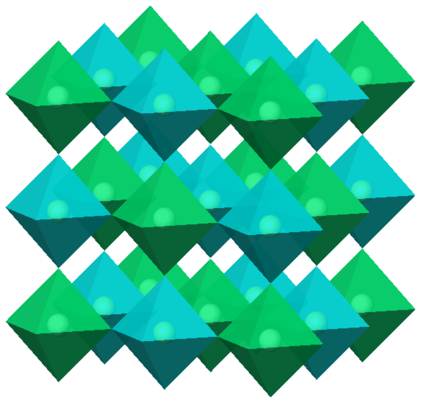


Simple cubic AMX_3 perovskite: a = 3.8045.

Double Perovskites $A_2MM'O_6$: Out of 3 possible ordering only 2 observe



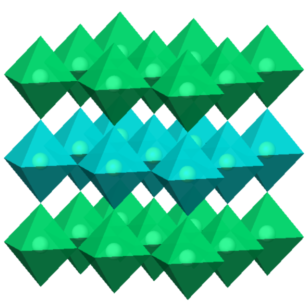
Model #1: Ordered alternation of MO_6 and $M'O_6$octahedra in one direction, leading to formation of layered perovskite.



Model #2: Ordered alternation in the three directions of space, resulting in rock-salt ordered superstructure.

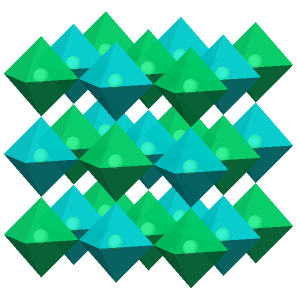
Model #1 – Layered Ordering:

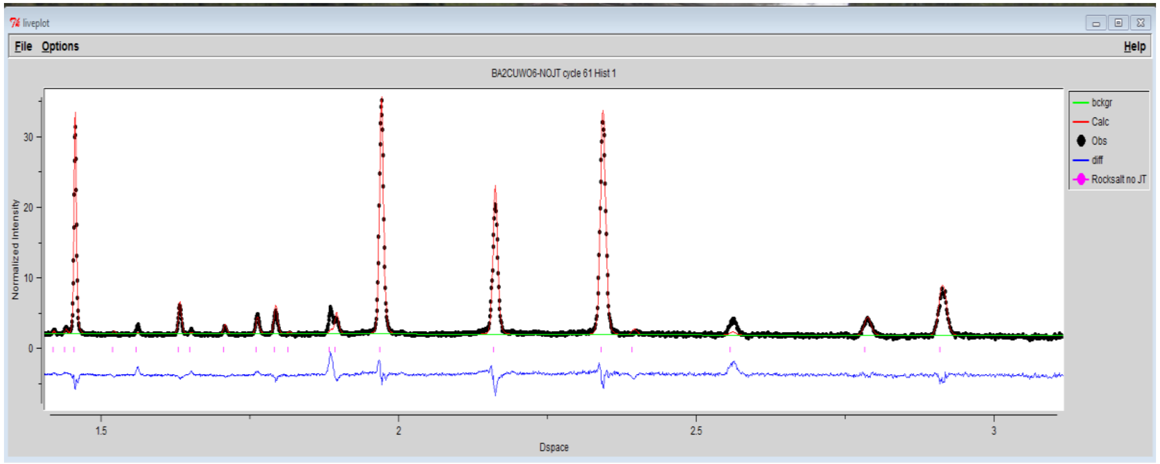
Space Group	*P4/mmm*			
Lattice	*a* = 3.94 Å; *c* = 8.64 Å			
Atom	***x***	***y***	***z***	**Occupancy**
Ba	¼	¼	½	1
Cu	0	0	0	1
W	0	0	0	1
O(1)	0	0	¼	1
O(2)	½	0	0	1
O(3)	½	0	½	1



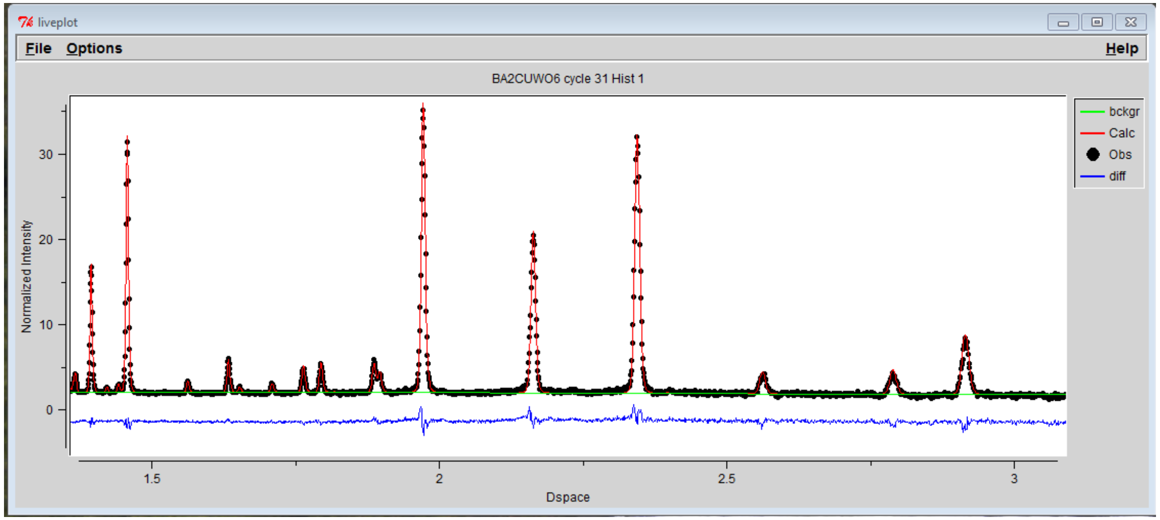
Model #2 – Rock Salt Type Ordering:

Space Group	*I4/m*			
Lattice	*a* = 5.57 Å; *c* = 8.64 Å			
Atom	***x***	***y***	***z***	**Occupancy**
Ba	0	½	¼	1
Cu	0	0	0	1
W	0	0	0	1
O(1)	0	0	0.25	1
O(2)	0.25	0.25	0	1





Recall Cu^{2+} electronic configuration $(t_{2g})^6(e_g)^3$: Jahn Teller Distortion?

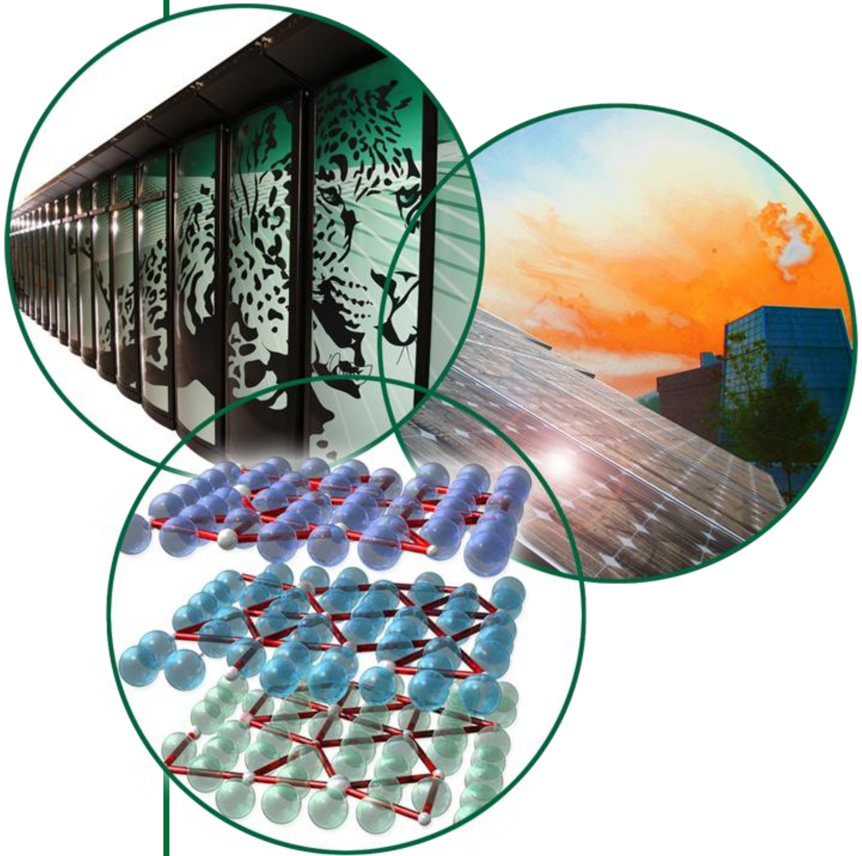


So in fact CuO_6 octahedra are elongated along the c axis. The e_g orbital is split into

$(d_{x^2-y^2}$ and $d_{z^2})$

Iwanaga et. al. J. Solid State. Chem. 147, 291(1999)

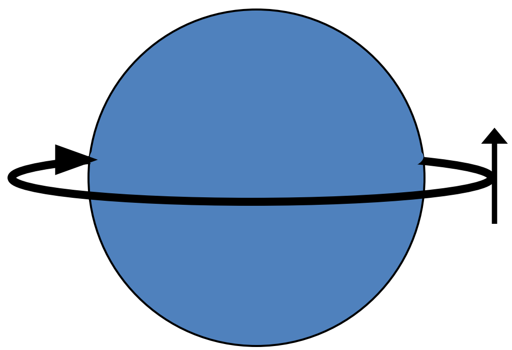
Magnetism & powder diffraction



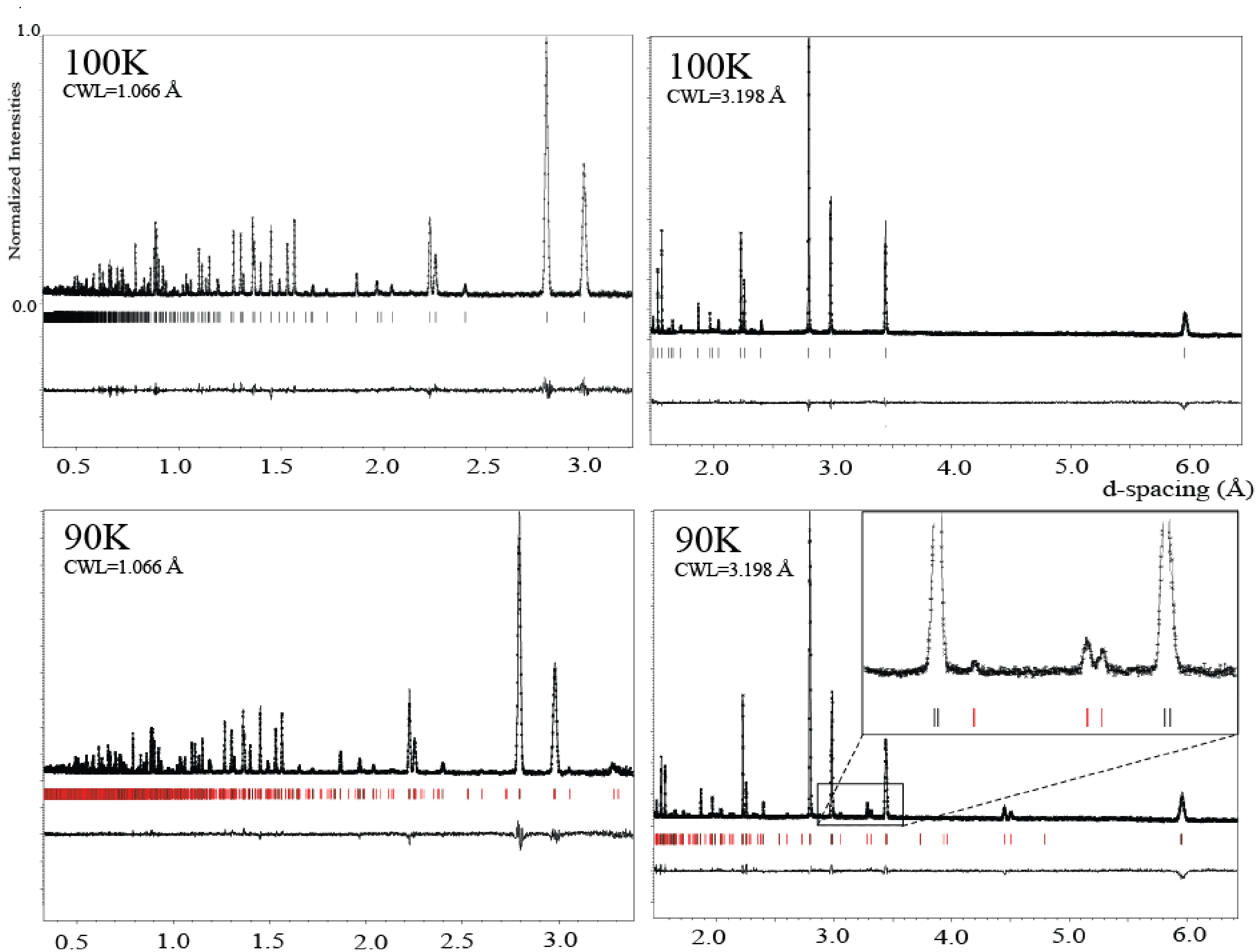
Introduction to Magnetism

- Origin of magnetism – electrons.
  - Electrons have a magnetic moment (dipole; μ_S). Magnetic moments arise from two properties of an electron:

1. Motion around the nucleus (gyromagnetic ratio)
2. Total spin quantum number ($S = \Sigma\, s$; $s = \pm\frac{1}{2}$)

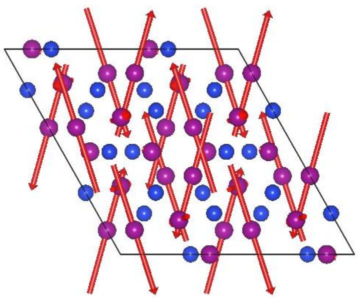


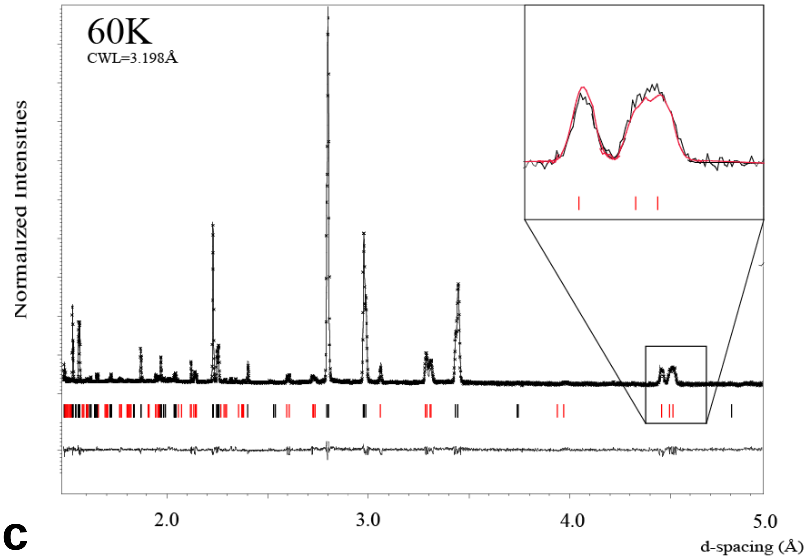
- Dipole unit – Bohr magnetons (μ_B). 1 $\mu_B = 9.2742\times10^{-24}$ J/T


1.0
0.0
Normalized Intensities
100K
CWL=1.066 Å
0.5
1.0
1.5
2.0
2.5
3.0
100K
CWL=3.198 Å
2.0
3.0
4.0
5.0
6.0
d-spacing (Å)
90K
CWL=1.066 Å
0.5
1.0
1.5
2.0
2.5
3.0
90K
CWL=3.198 Å
2.0
3.0
4.0
5.0
6.0

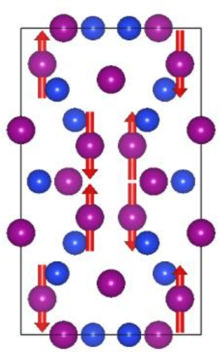
Reinvestigation of the Magnetocaloric effect (MCE) in Mn_5Si_3

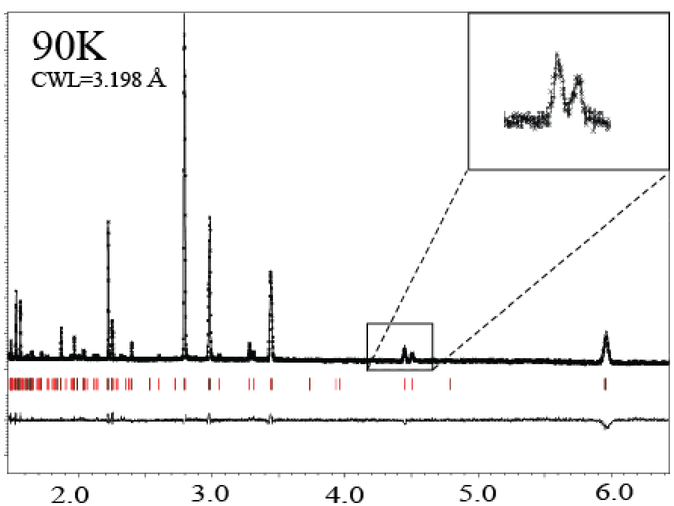
Monoclinic

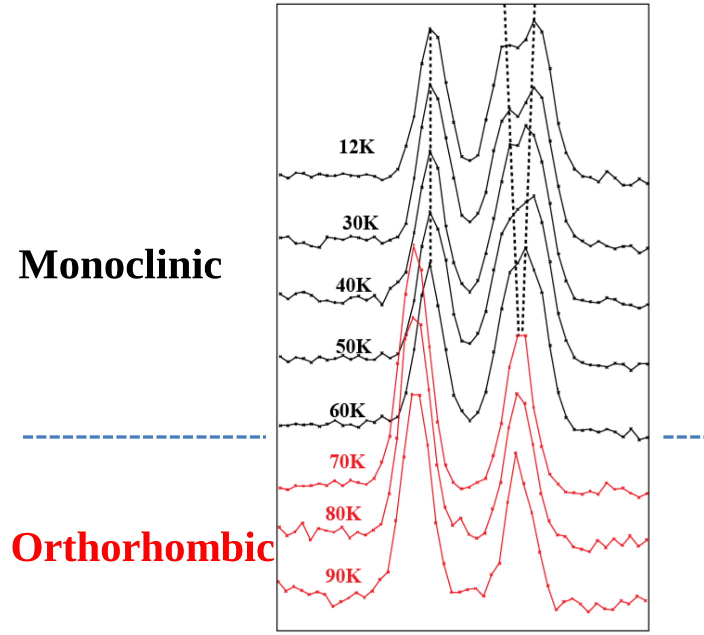




Orthorhombic



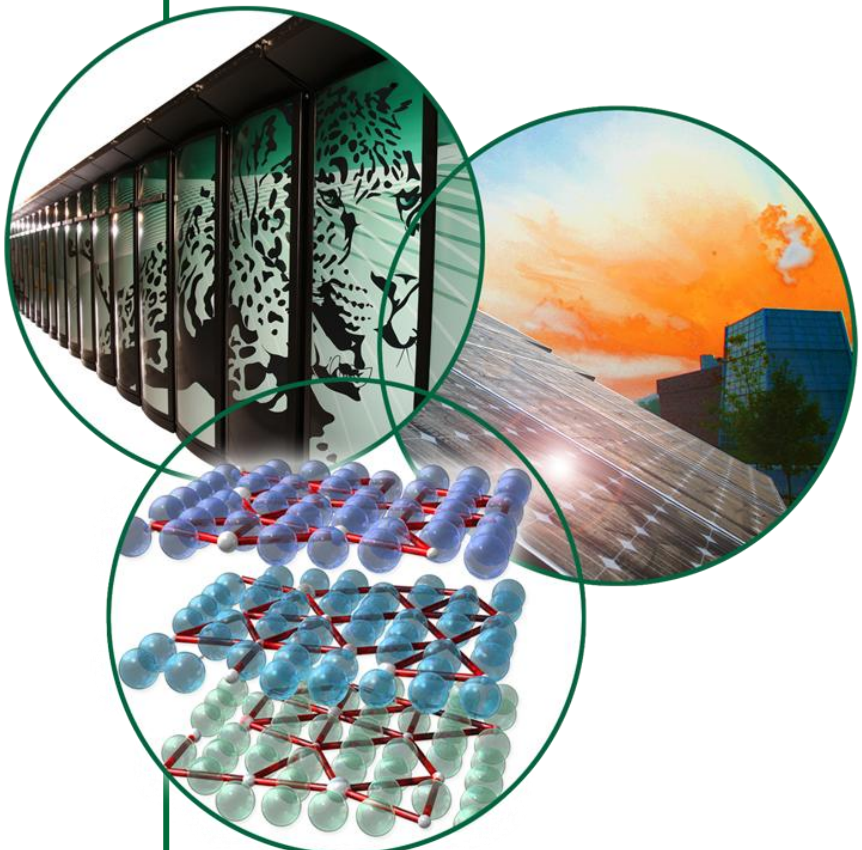




High resolution up to high *d*-spacing allow to have perfect information on the variation of the magnetic ordering and symmetry.

Crucial information to understand and to interpret the Magneto Caloric effect in some magnetic intermetallic phases such as Mn_5Si_3.

Time resolved Powder Diffraction: Hydrogen Storage Materials for mobile application

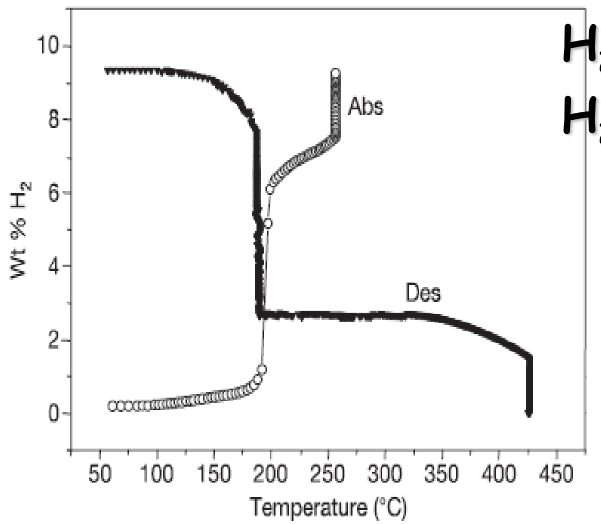


Li_3N : Hydrogen Storage Candidate.

Chen et. al: (Nature Nov 2002)

Li Imide / Li Amide

$$Li_3N + 2H_2 \longleftrightarrow Li_2NH + LiH + H_2 \longleftrightarrow LiNH_2 + 2LiH$$



H_2 Absorption 9.3 wt% gain at 255°C

H_2 Desorption 6.3 wt% at 200°C + 3wt % above 320°C

Later (2004-2005) Meisner et. al. & others:

1. $Li_3N + 2H_2 \longrightarrow Li_2NH + LiH + H_2$
2. $Li_2NH + LiH + H_2 \longleftrightarrow LiNH_2 + 2LiH$

(~5.2% cyclable H_2)

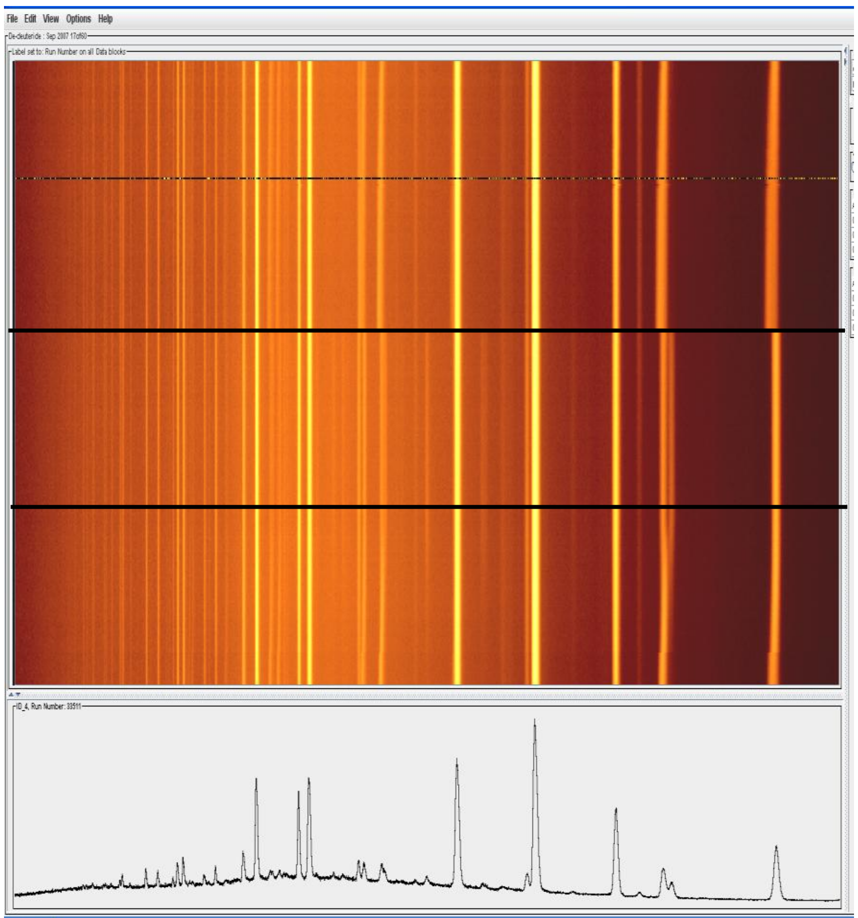
Our Goal: To study this reaction in-situ in bulk material.

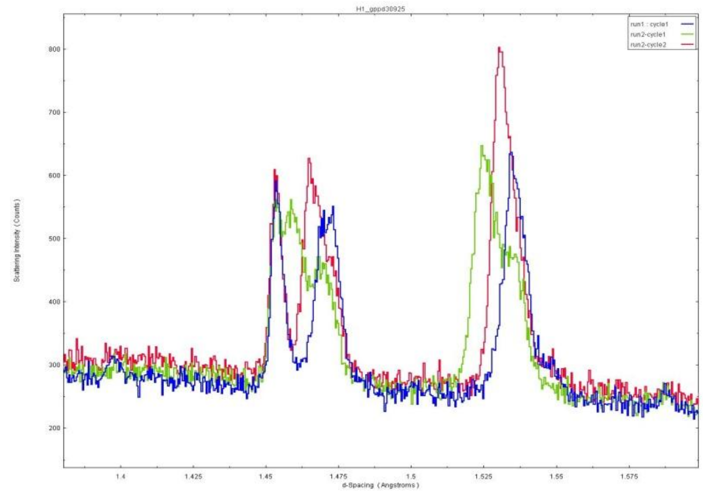
OAK RIDGE National Laboratory

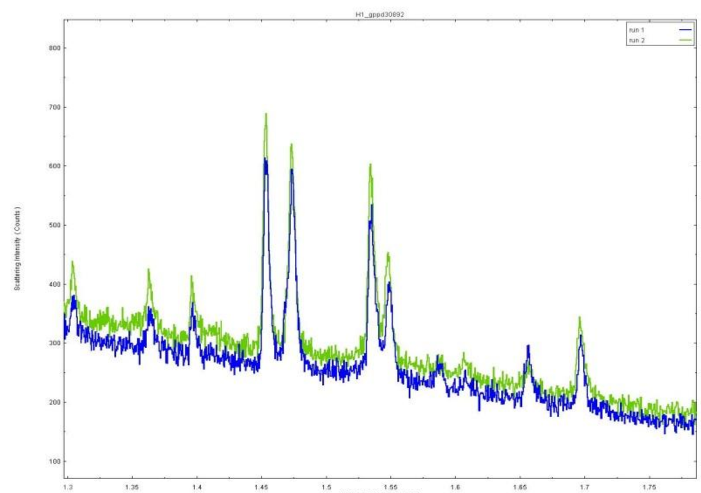
Neutron in-situ measurement (IPNS)

30.5h dedeuteride, 22.5h deuteride, 19h dedeuteride : cubic phase has changing lattice parameter (implying varying stoichiometry) while tetragonal phase has same (line phase)

Huq et. al., J Phys Chem C,111,10712,2007





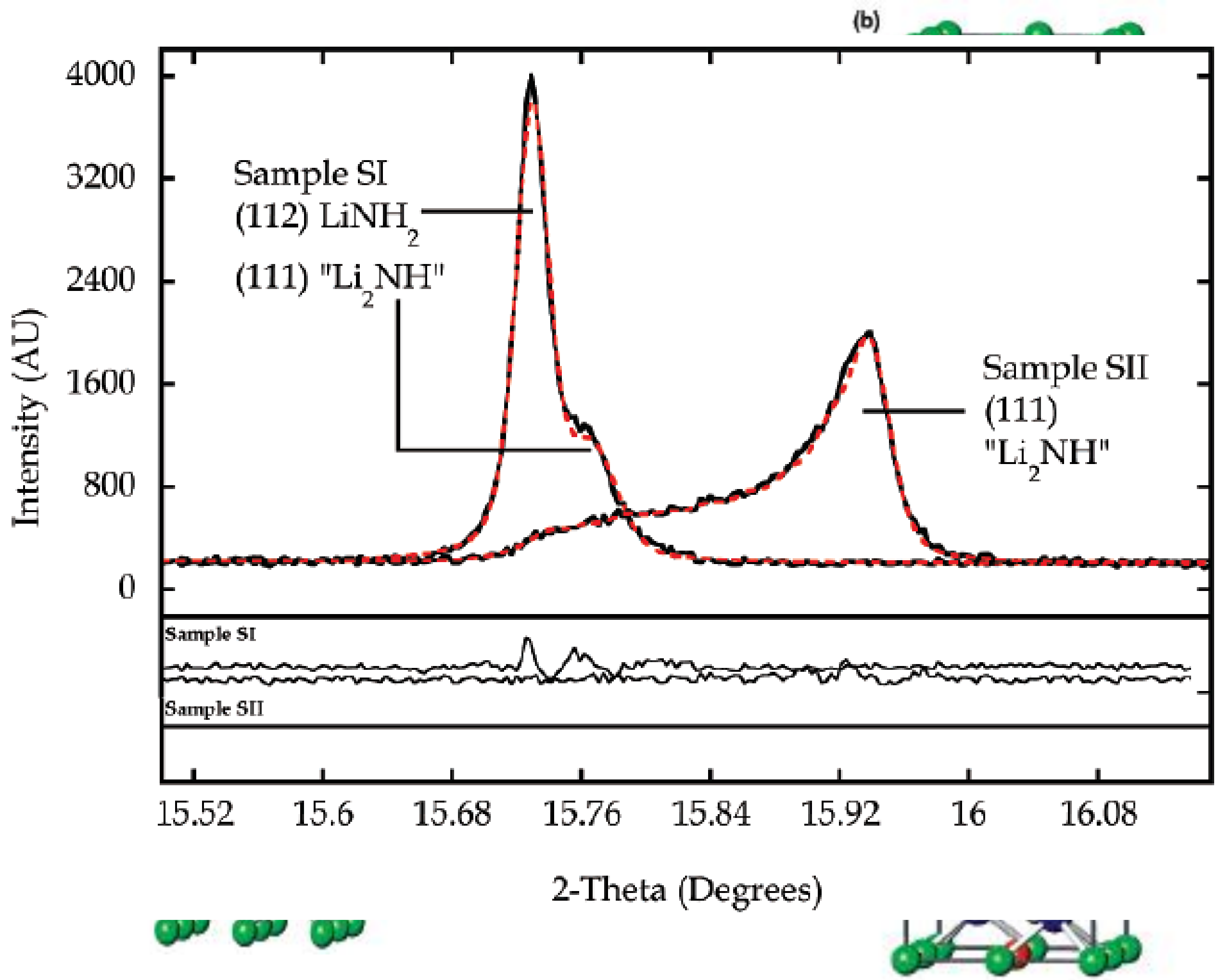


Imide – Amide : Structural relationship (Ex-situ synchrotron experiment)

David et. al., JACS 129,1594,2006

Anti flu
cubic im

nal

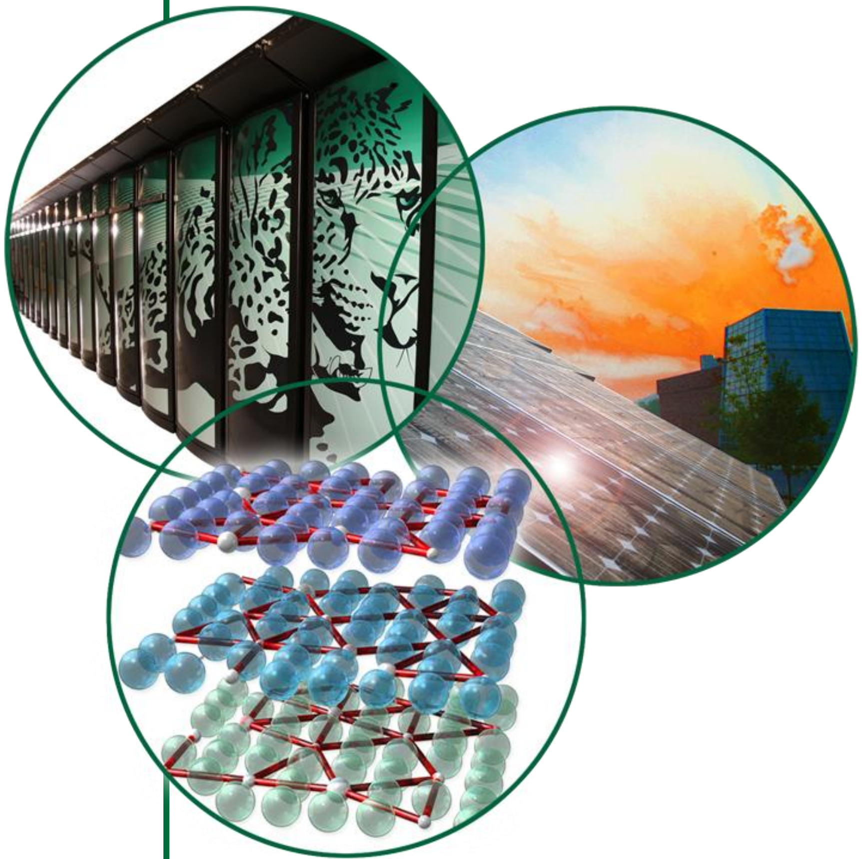


shift or

:upied
red

a x a x

Ab-initio Structure Solution from Powder Diffraction



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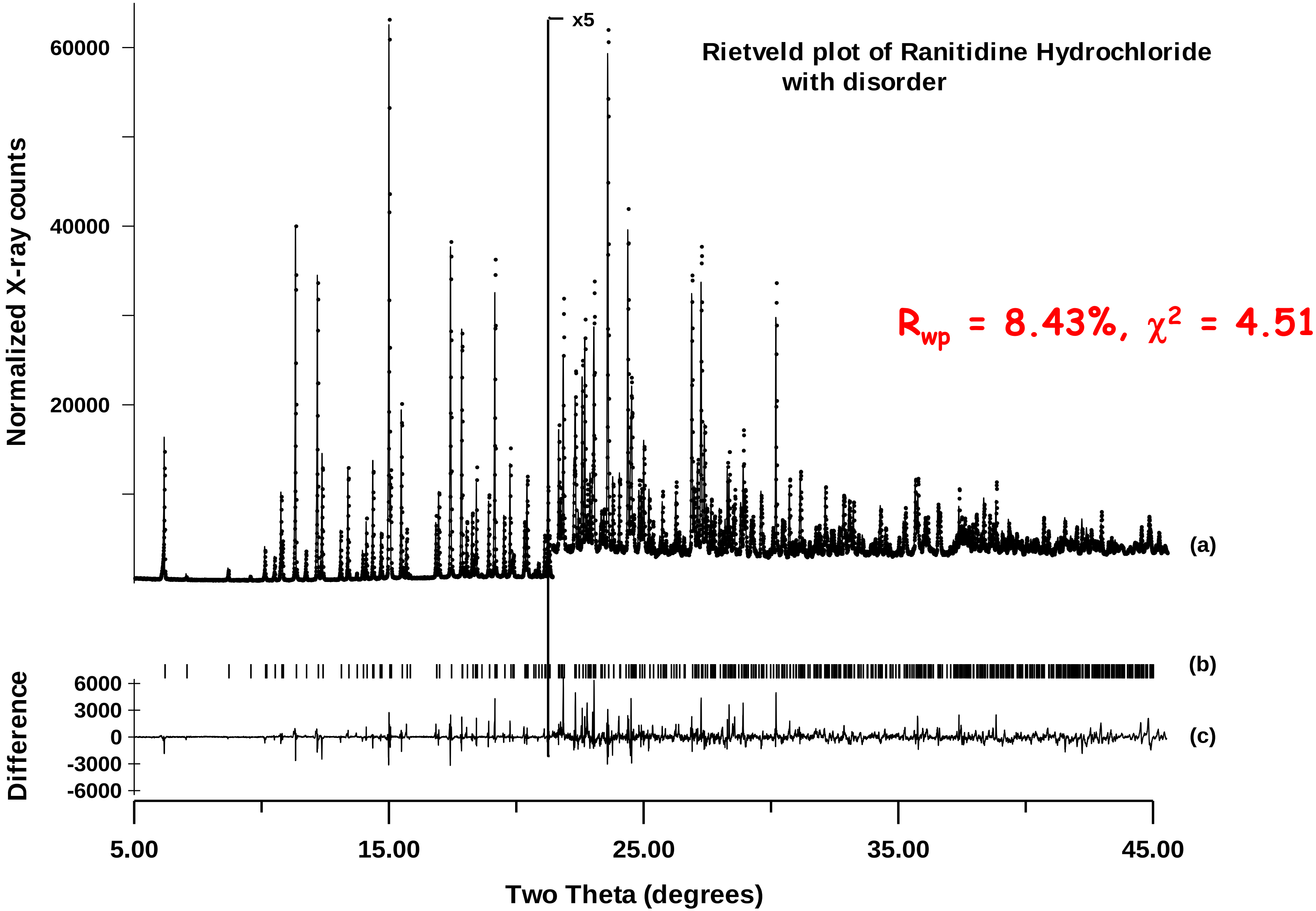
Structure solution from powder data:

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

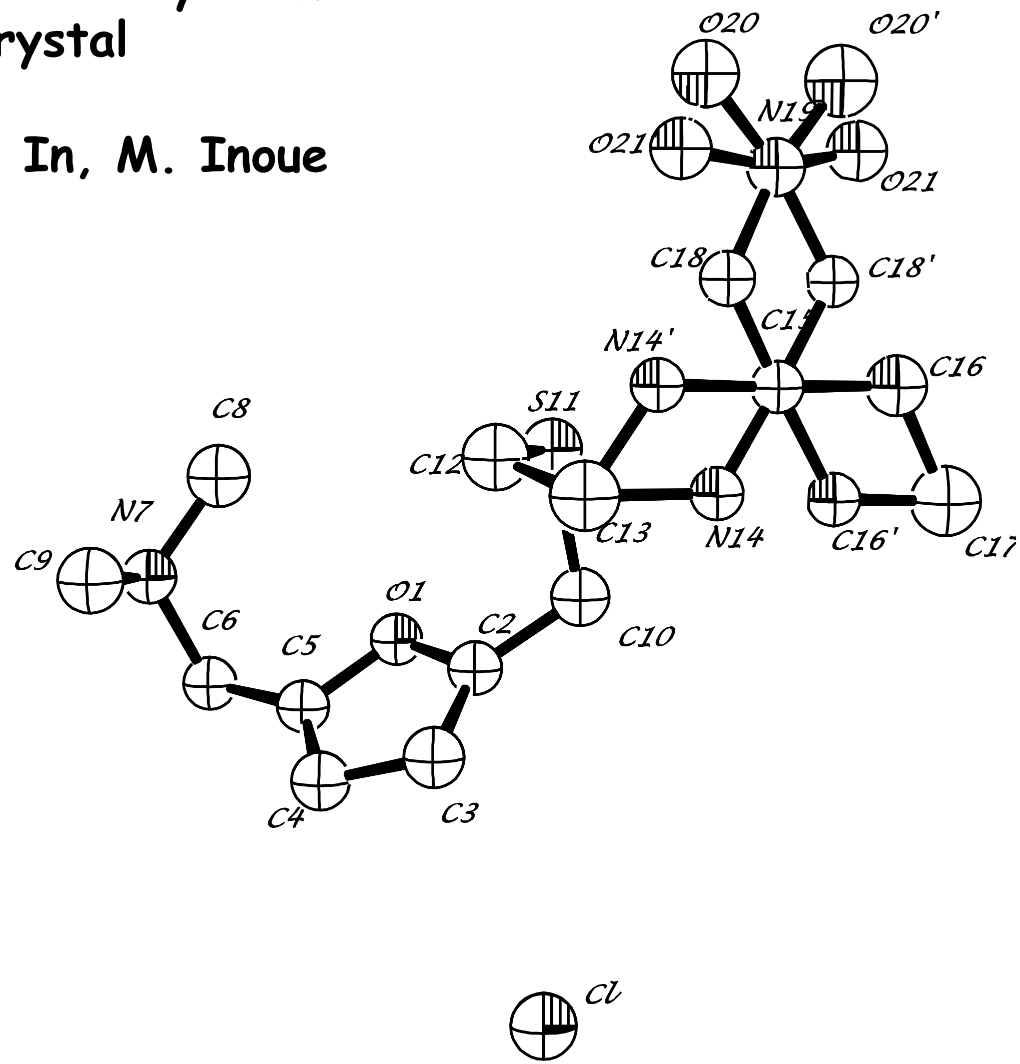
$$\boxed{I_{hkl} = \left| \sum_{\text{atoms } j} f_j \exp(i\vec{Q}_{hkl} \cdot \vec{R}_j) \right|^2}$$

Solve a new structure from powder data

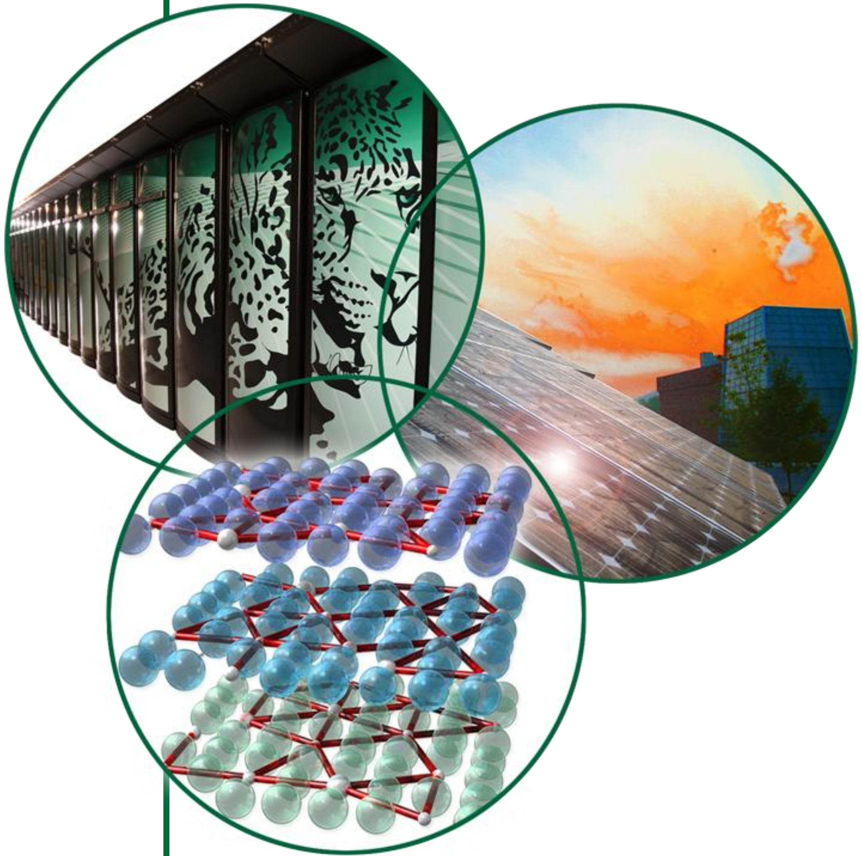
1. Get data
2. Find the lattice
3. Space group (internal symmetries) systematic absences, density, guess, luck
4. Extract intensities of each individual (*hkl*) peak
5. Solve structure
6. Refine


Rietveld plot of Ranitidine Hydrochloride
with disorder
R_{wp} = 8.43%, χ^2 = 4.51
x5
Normalized X-ray counts
60000
40000
20000
(a)
(b)
(c)
Difference
6000
3000
0
-3000
-6000
5.00
15.00
25.00
35.00
45.00
Two Theta (degrees)

The answer, including disorder, was already known from single crystal experiment.
T. Ishida, Y. In, M. Inoue (1990)



Proteins and Powder Diffraction



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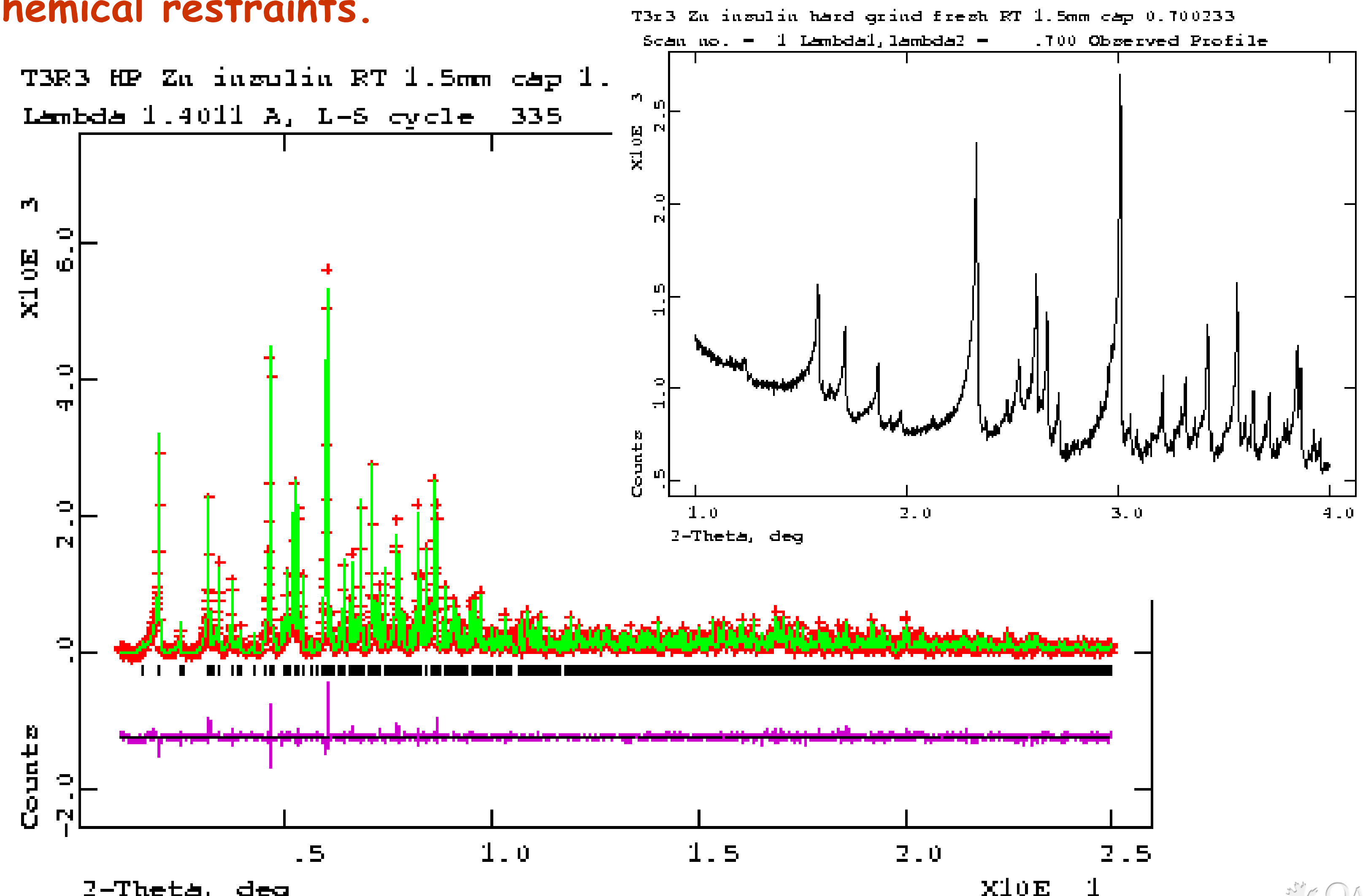
Extreme limit: Proteins
Work done by R. Von Dreele (Los Alamos) & P.W. Stephens
It is possible to get usable data, and to refine it with sufficient chemical restraints.



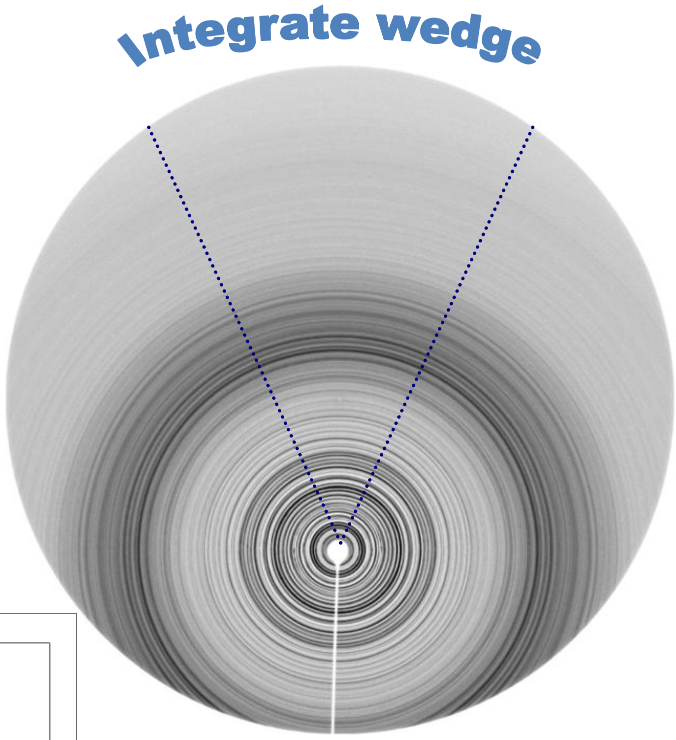
Structure solved from powder data & Rietveld refinement

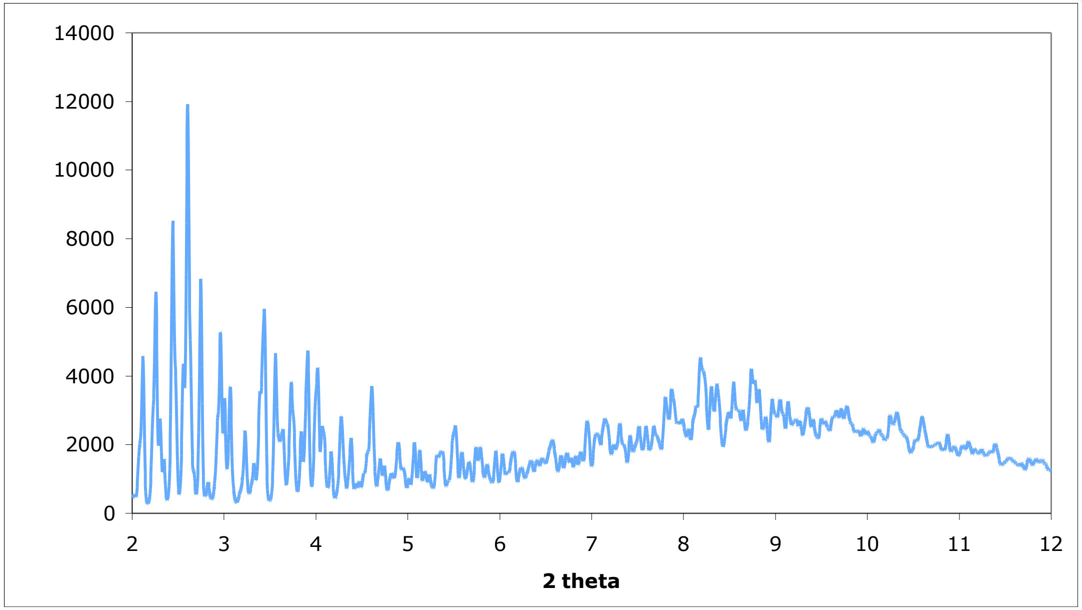
Human Insulin Zn complex

Native	Ground
a=80.96Å	81.28Å
c=37.59Å	73.04Å
Nrefined = 1754	2925
Nrestraints=3871	7934
Nreflections=9871	12734
Resolution 3.06Å	3.22Å
Rwp=3.34%	3.77%

R.B. Von Dreele, P.W. Stephens, G.D. Smith, and R.H. Blessing, "The First Protein Crystal Structure Determined from X-ray Powder Diffraction Data: a Variant of T_3R_3 Human Insulin Zinc Complex Produced by Grinding," ***Acta Crystallographica D*** **56, 1549-53 (2000).**

Current work at APS: Structure solution via molecular replacement





Take home message

Powder diffraction is an extremely powerful technique to study structural properties of a very wide variety of materials. To understand physical and chemical properties of materials it is crucial that we know how the "atoms are put together" and if you cannot grow those big single crystals….you can still learn quite a lot about your system using powder diffraction.

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)

Software and other resources:
http://www.ccp14.ac.uk/

Indexing:

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

Rietveld:

- **GSAS: https://subversion.xor.aps.anl.gov/trac/EXPGUI/wiki**
- **Fullprof: http://www.ill.eu/sites/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/**
- **Topas: http://www.dur.ac.uk/john.evans/topas_academic/topas_main.htm**