Powder Data Analysis
Rietveld Method
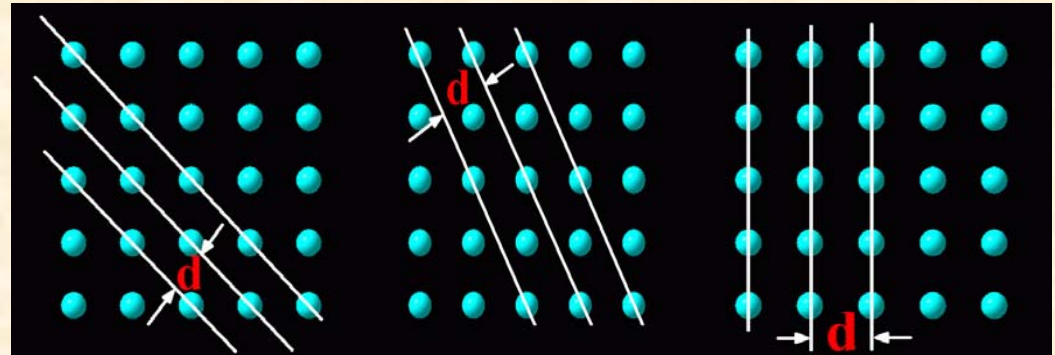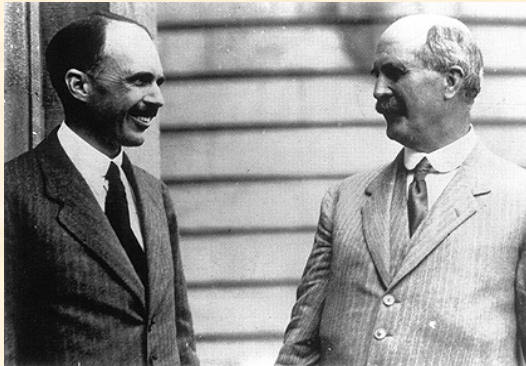
Ashfia Huq

2007 ORNL USER Meeting

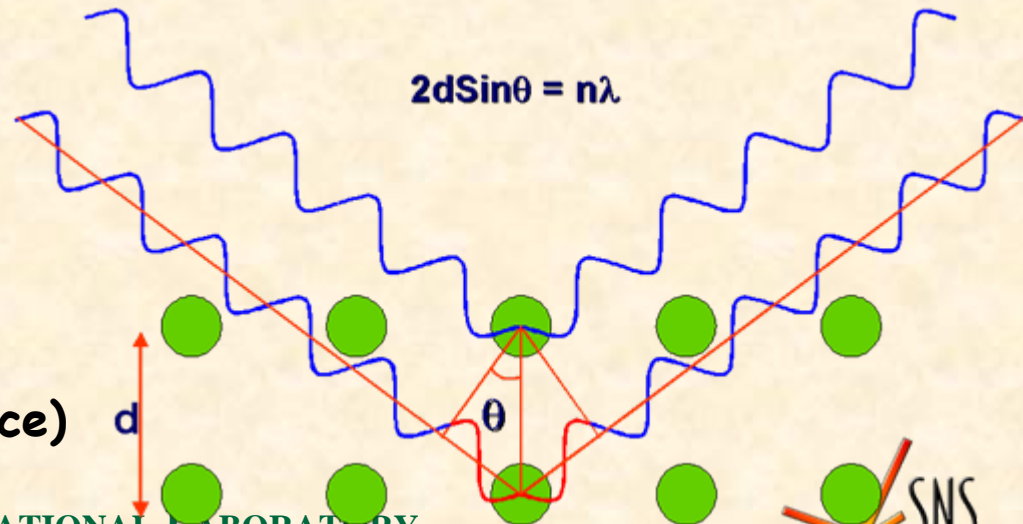# Bragg's law

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

Shared 1915 Nobel Prize

$$2dSin\theta = n\lambda$$

- Zinc Blend(fcc not sc)
- NaCl (not molecular)
- Diamond (two overlapping fcc lattice)
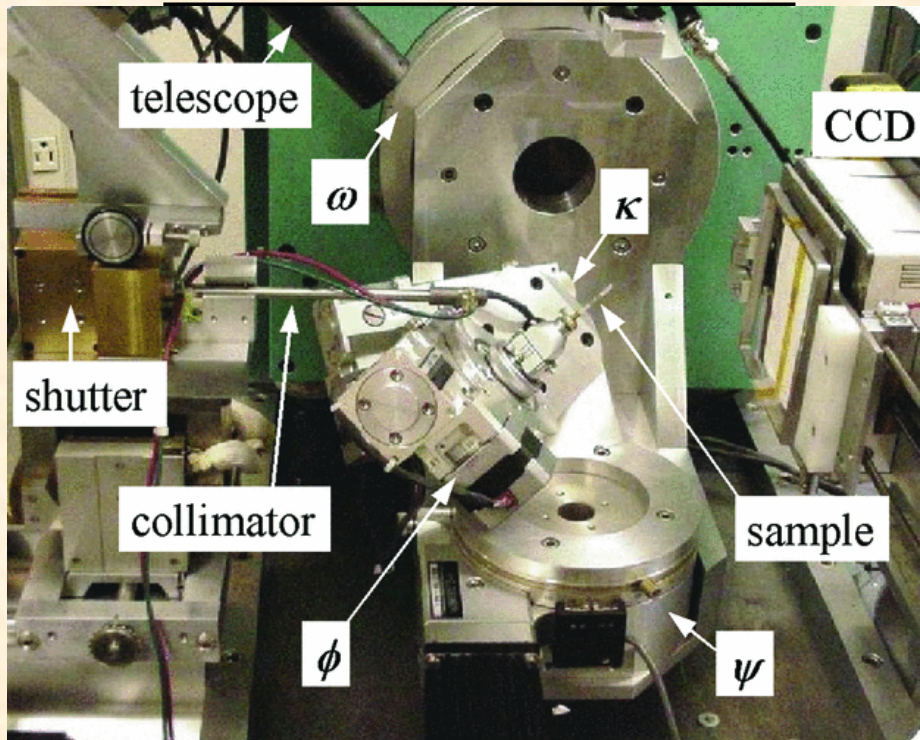
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Single Crystals *vs* Powders (2dsinΘ=λ)

Single Crystal

- **Sample must be correctly oriented in space with respect to the chosen reflection plane**
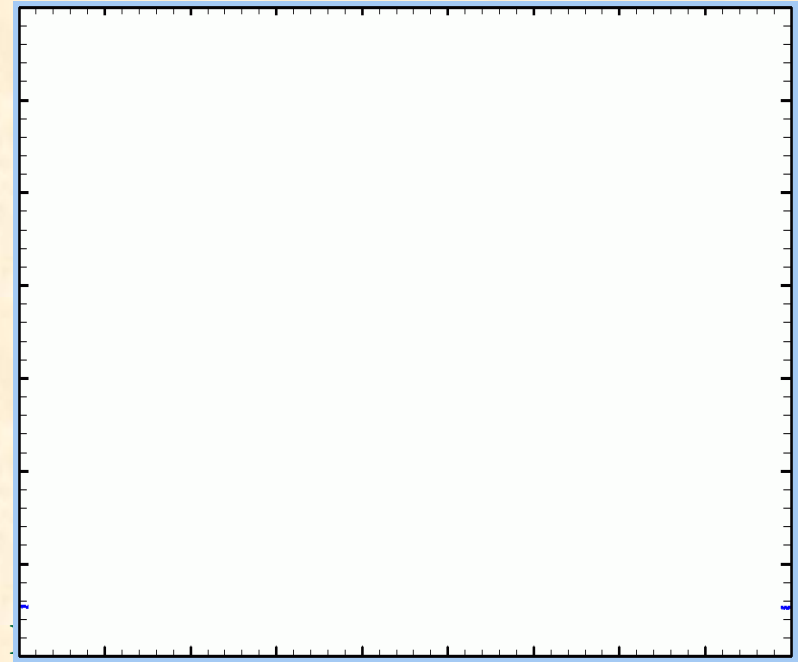
Powder

- Sizable samples have billions of crystals

- In the absence of texture, all crystal orientations are equally represented

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

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

fixed λ

sample

2Θ **varies**

detector

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Time-of-flight (2dsinΘ=λ)

sample

λ **varies**

2Θ fixed

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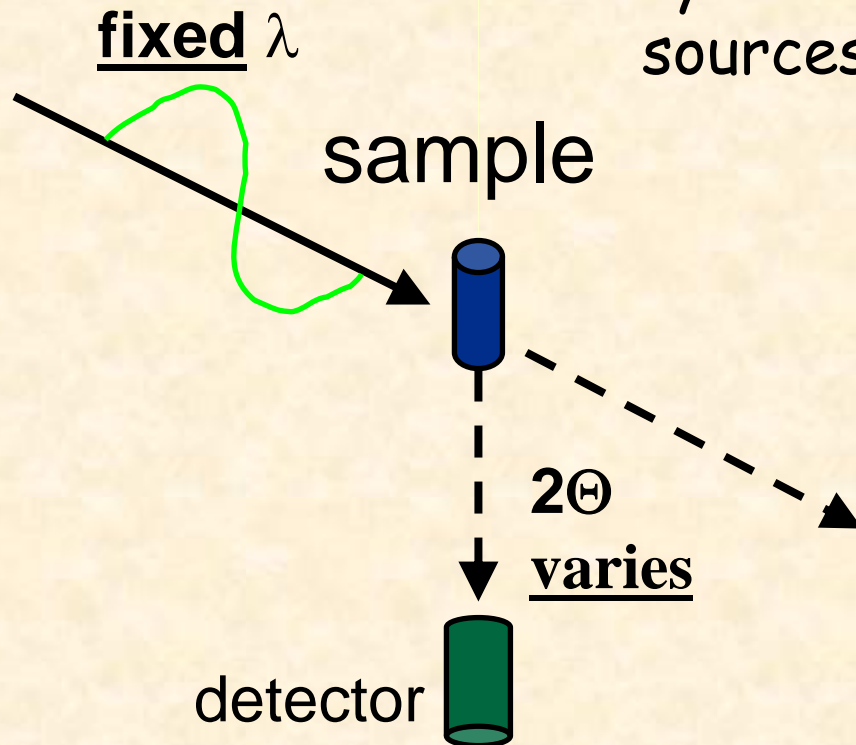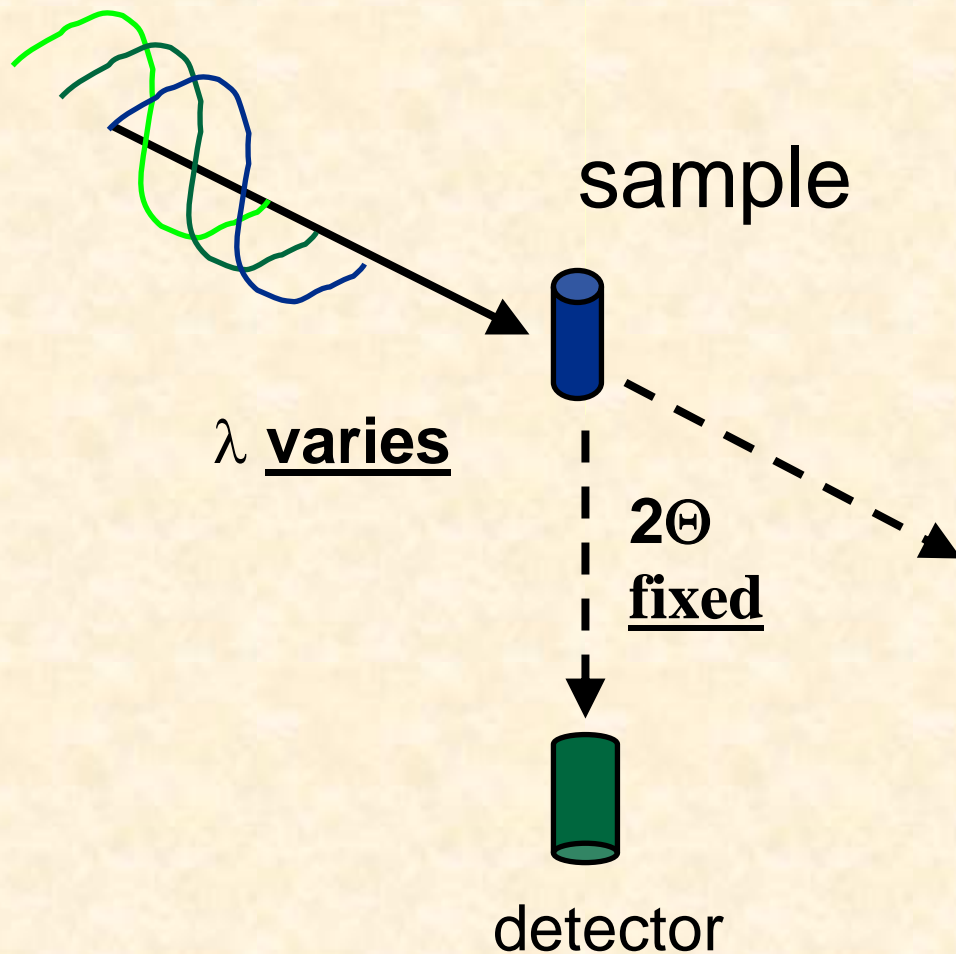
(Pulsed sources: e.g. **SNS**)

N-MAX.DAT
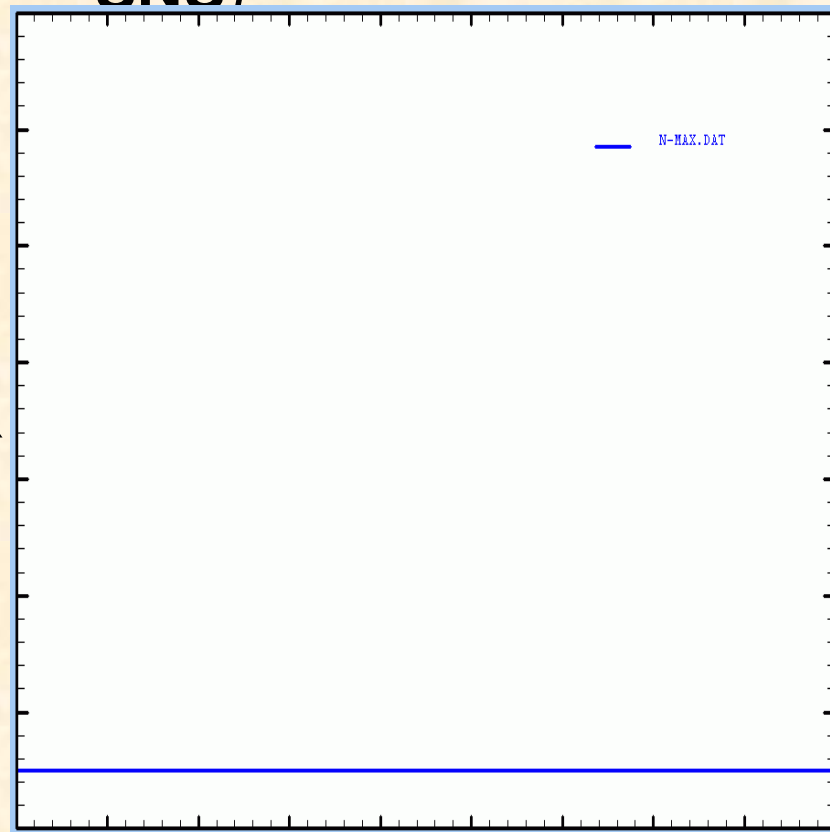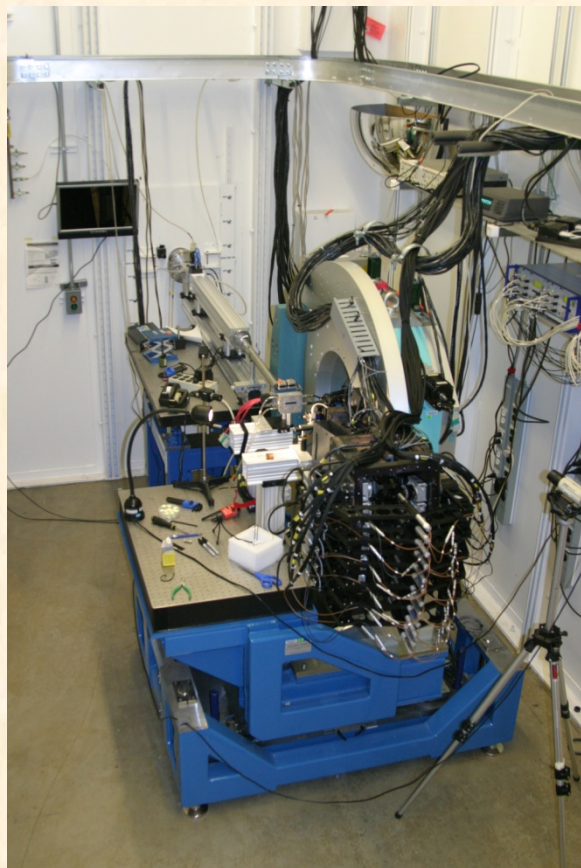
Powder Instruments
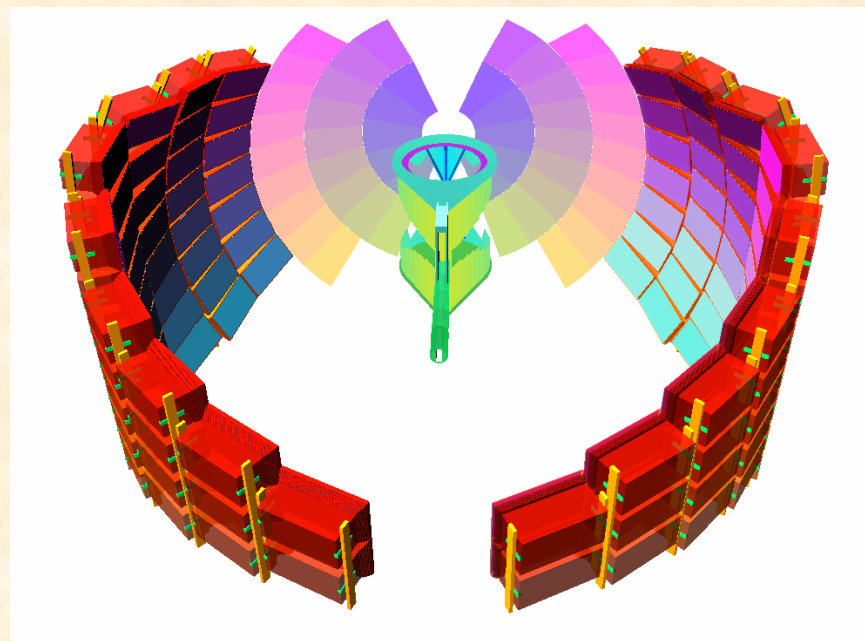
POWGEN3 at SNS

beamline HB2a at HFIR

beamline 11BM at APS

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Peak overlap problem

Form 1 -- Lab

Form 2 -- Lab

Form 1 -- Synchrotron

Form 2 -- Synchrotron

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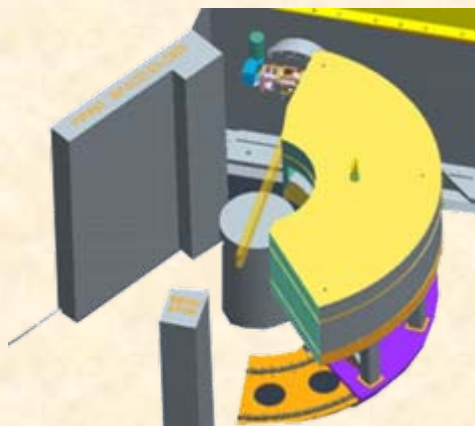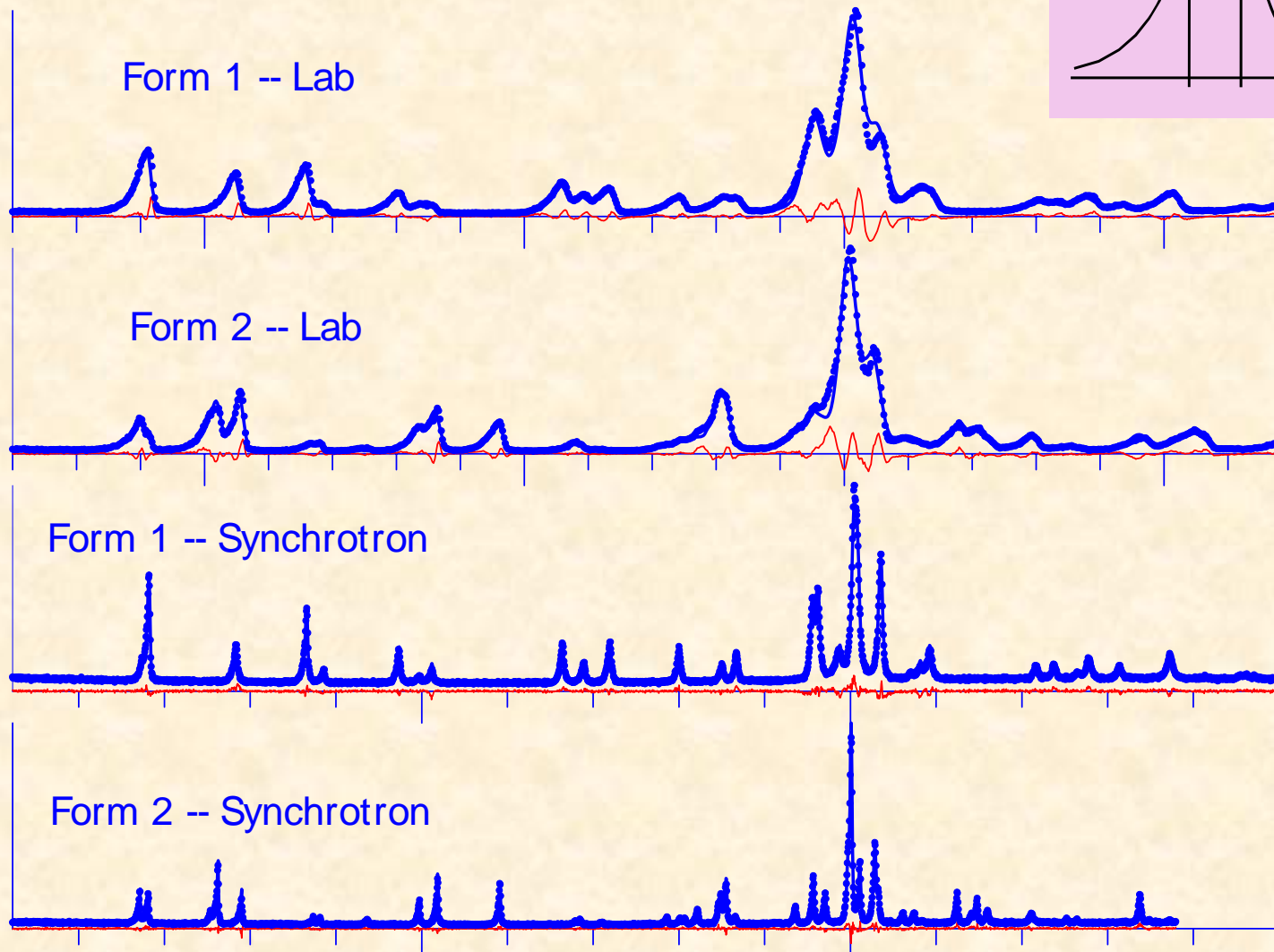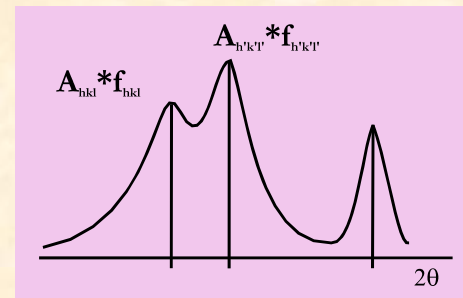
Hugo Rietveld

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."

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Rietveld Refinement
(Powder Diffraction)

In a powder diffraction experiment, there will be many grains aligned to diffract the incident beam of neutrons/x-rays.

Neutron/X-ray beam

2θ
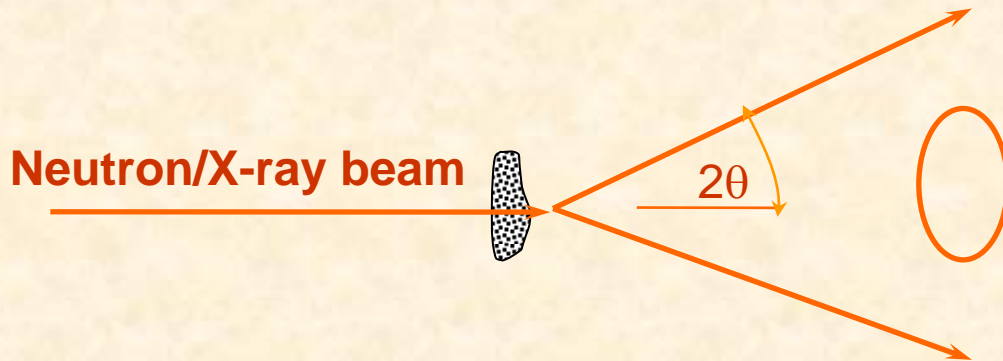
3D information is reduced to 1D, makes analysis harder than single crystal experiments.

Model that describes the structure

Profile parameters (lattice, line-shape, background etc.)

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

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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

$$F_K = \Sigma_j N_j b_j e^{2\pi i K.r_j} e^{-M_j}$$

(M_j = Debye-Waller factor, N_j = site occupancy, b_j = scattering length)

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

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

(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.

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

Here $w_i = 1/\sigma_i^2$, is the statistical weight of the ith profile observation which is the inverse of the variance of the ith observation. I_{oi} and I_{ci} are observed and calculated intensities.

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Time Of Flight Formulation

Diffraction due to Bragg's law: $\lambda = 2d\sin\theta = h/mv = ht/mL$

d interplanar distance	h Planck's constant
θ scattering angle	m neutron mass
λ wavelength	v neutron velocity
L total flight path	t neutron time-of flight

TOF (variable t)

$$d = ht/(2mL\sin\theta)$$
$$t = k*d$$

[non-linear in practice: $t = Cd + Ad^2 + Z$]

Note: in TOF, there is a t_{max} (and hence a d_{max}) at a given detector θ due to the neutron pulse frequency

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CW peak shapes

Gaussian: $\sigma = [U\tan^2\Theta + V\tan\Theta + W + P/\cos^2\Theta]^{1/2}$
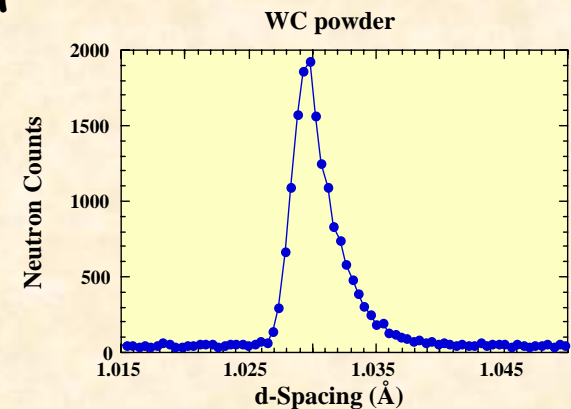
Lorentzian: $\gamma = X\tan\Theta + Y/\cos\Theta$

TOF peak shapes

Convolution of rising and falling exponentials with Gaussian

$$\alpha = \alpha_1 \ / \ d \qquad\qquad \beta = \beta_0 + \beta_1 \ / \ d^4$$
(rising exponential)   **(falling exponential)**

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

$$\gamma = [\ \gamma_0 + \gamma_1 d + \gamma_2 d^2 + (\gamma_{1e}d + \gamma_{2s}d^2)\cos\phi + \gamma_L\ ]$$
(Lorentzian)

WC powder

Neutron Counts vs d-Spacing (Å)

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Sample Broadening

CW:

$$S = (\pi/18000)[(8\ln2)(U - U_i)]^{1/2}100\%$$

$$P = 18000K \lambda/\pi X$$

TOF:

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

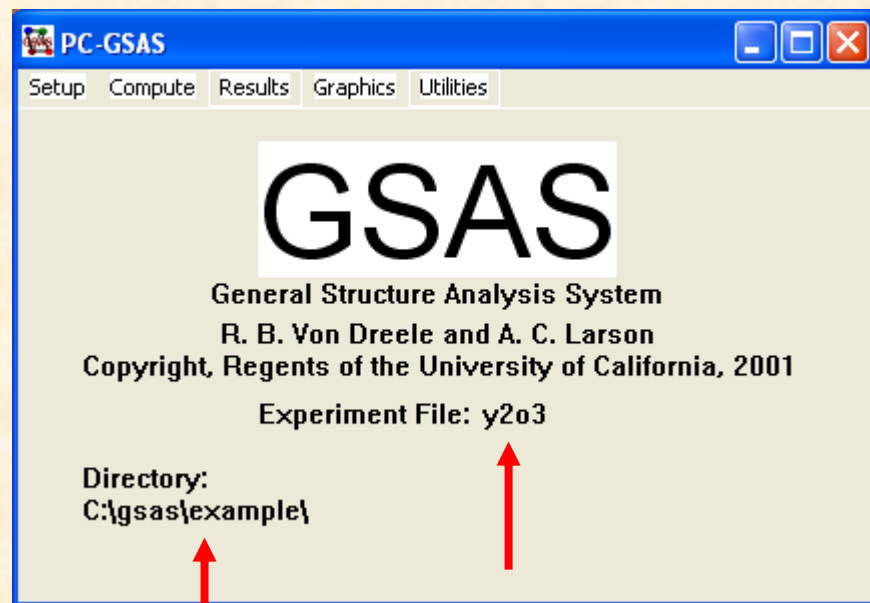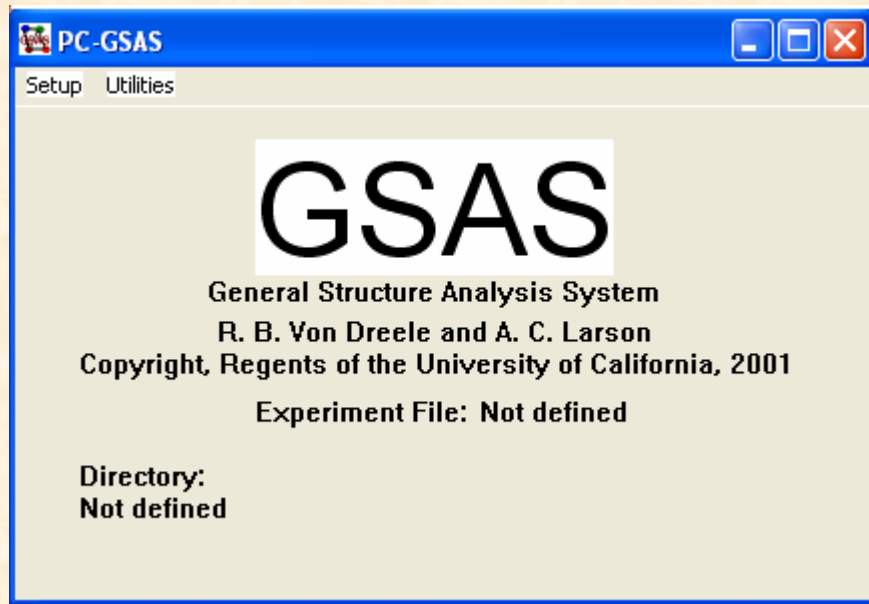$$S = 1/C [(8\ln2)(\sigma_1^2 - \sigma_{1i}^2)]^{1/2}100\%$$

(s1i = strain-free value for s1)

$$P = (CK)/[(8\ln2)\sigma_2^2]^{1/2} \text{ Å}$$

(K = Scherrer constant)

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PC GSAS

http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/

EXP-GUI
(Brian Toby)

http://rrdjazz.nist.gov/programs/crystallography/software/expgui/expgui.html
User friendly interface for Beginners to start using GSAS

Limitations :

- Constraints on profile

- Rigid body constraints

- Soft constraints

- Diffuse scattering

- Magnetic Refinement

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Files in GSAS

Experiment file
(.exp)

Parameter file
(.prm, .par etc.)

Data file
(.dat, .gda, .gsa etc.)

.lst file,.PVE file

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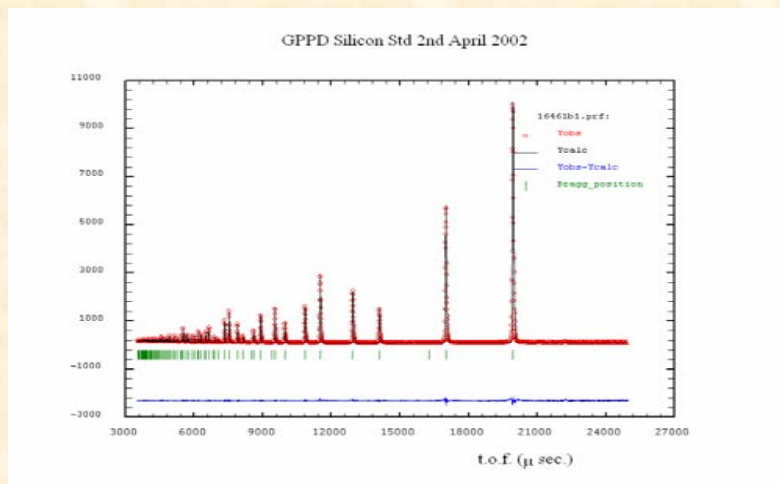
Creating an experiment file

- **Enter Space Group and Lattice Parameters**

- **Read in Histogram(s)**
  - **You will need the parameter file for this which will provide**
    - **Diffractometer Constants**
    - **Incident Spectrum (for TOF Neutron)**
    - **Initial profile parameters**
    - **Initial Background Function and parameters**

- **Then enter Fractional Coordinates, Thermal Parameters and Fractional Occupancy. (shortcuts : gsas allows the use of Macros using @r) or read from standard formats e.g. .exp,.cif etc.**

- **Finally turn on the parameters you want to refine. (It is generally a good idea to turn on a few parameters at a time if you want to avoid catastrophy!)**

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Running Refinements

- **Run Powpref to Prepare data for Least Square Analysis**

    - **Associate the position, channel or step width, incident intensity, refinement weight and a list of contributing reflections with each observation in a powder pattern.**
    - **Set Flags for excluded regions, reflection markers etc.**

- **Run Genles : To Do the least square refinement**

- **Powplot: View the results of the refinement.**

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Some Useful Resources:

- **Fullprof (packaged with Winplotr)**
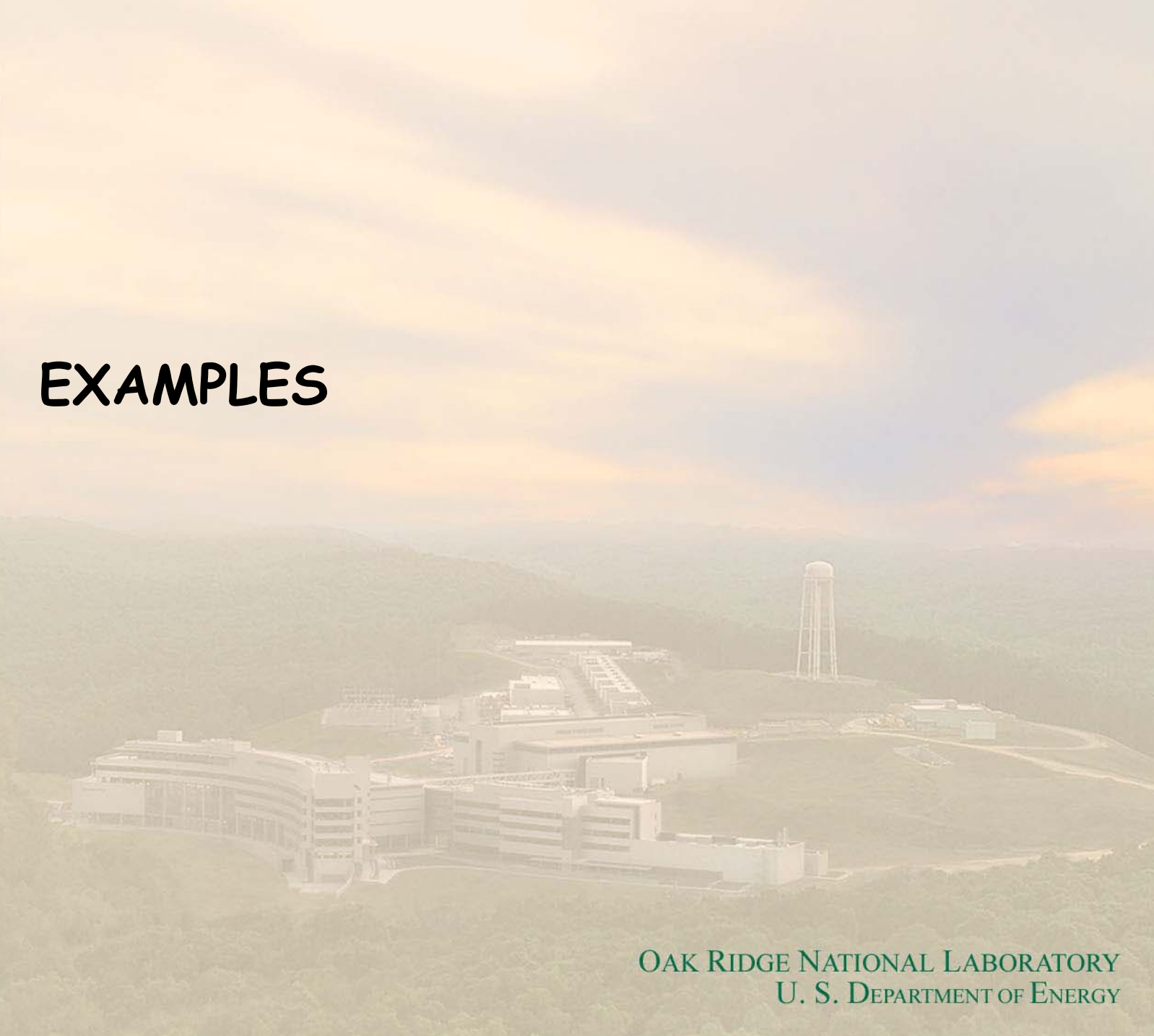 - **http://www-llb.cea.fr/fullweb/winplotr/winplotr.htm**

- **For a more exhaustive list check out**
  - **http://www.ccp14.ac.uk/solution/rietveld_software /**

- **Rietveld Mailing List**
  - **http://ccp14.sims.nrc.ca/ccp/ccp14/ftp-mirror/howardflack/pub/soft/crystal/stxnews/riet/welcome.htm**

Total Scattering Methods
http://nirt.pa.msu.edu/software.php

- Powder diffraction data contain a great deal of information in the form of diffuse scattering about defects and disorder which is often of interest.

- When the properly normalized powder diffraction data are Fourier transformed (reliable only when quality high Q data are available) into real-space coordinates we obtain the atomic pair distribution function (PDF).

- The PDF has peaks at characteristic distances separating pairs of atom and by calculating the PDF from model structures and comparing them to the measured PDF we can extract information about the local structure.

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EXAMPLES

Phase ID: "Finger Printing"

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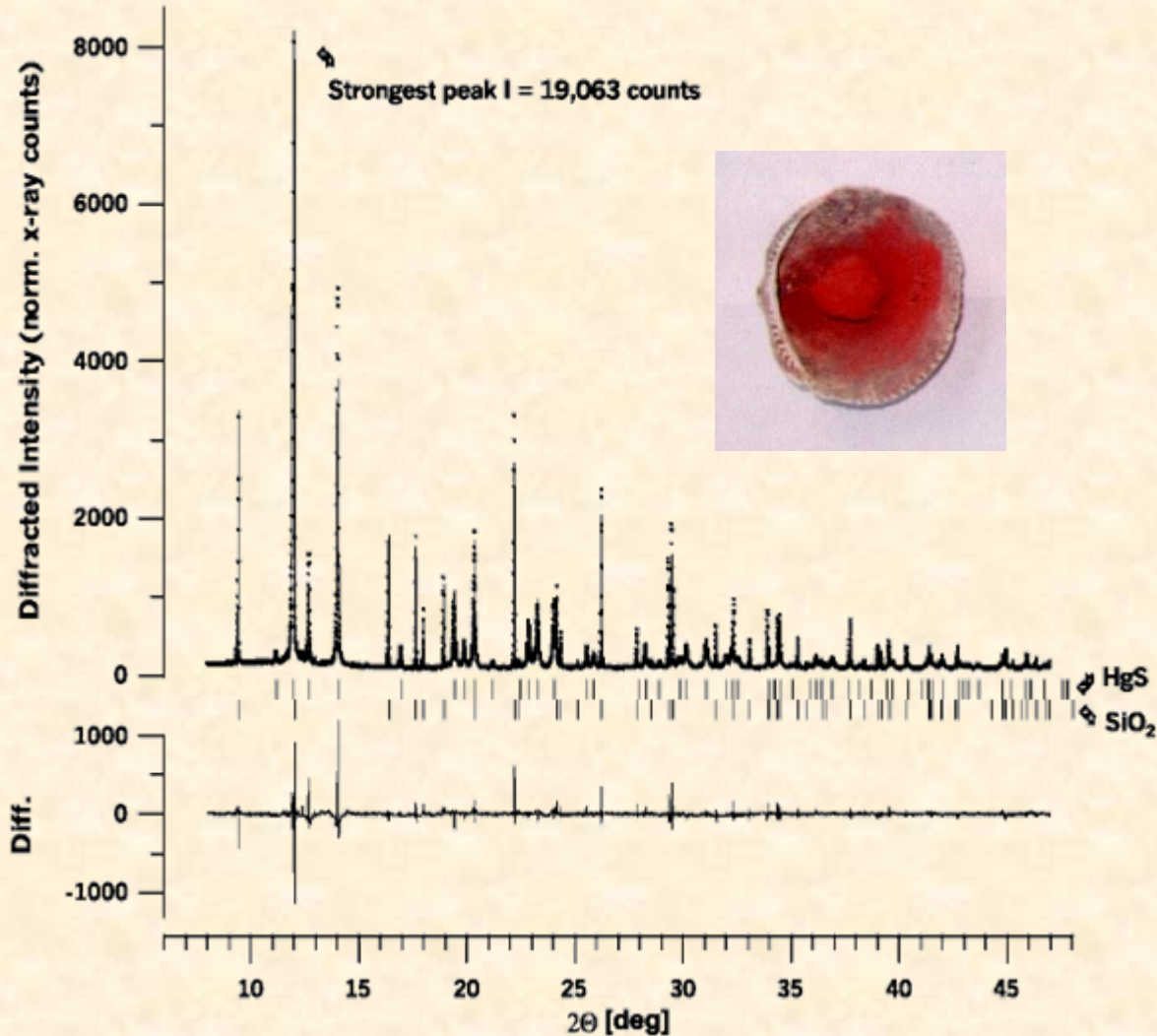
The pigments were discovered during different excavations in archaeological sites of Tunisia (Carthage, Kerkouane, Bekalta, Bouaarada and elsewhere).

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KERKOUANE ♥

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Sample : FCC5
Cinnabar and Quartz

Strongest peak I = 19,063 counts

❖**fit peak: search database for matches.**

❖**Look up structure.**

❖**Rietveld refinement.**

❖**For mixture quantitative phase analysis.**

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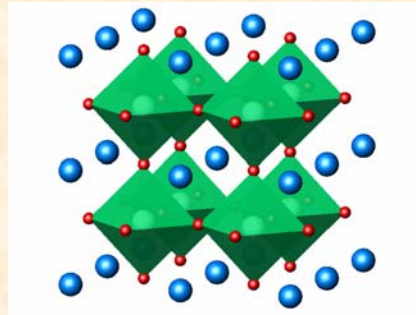
Sample : C41C
Goyazite, Quartz and Purpurin
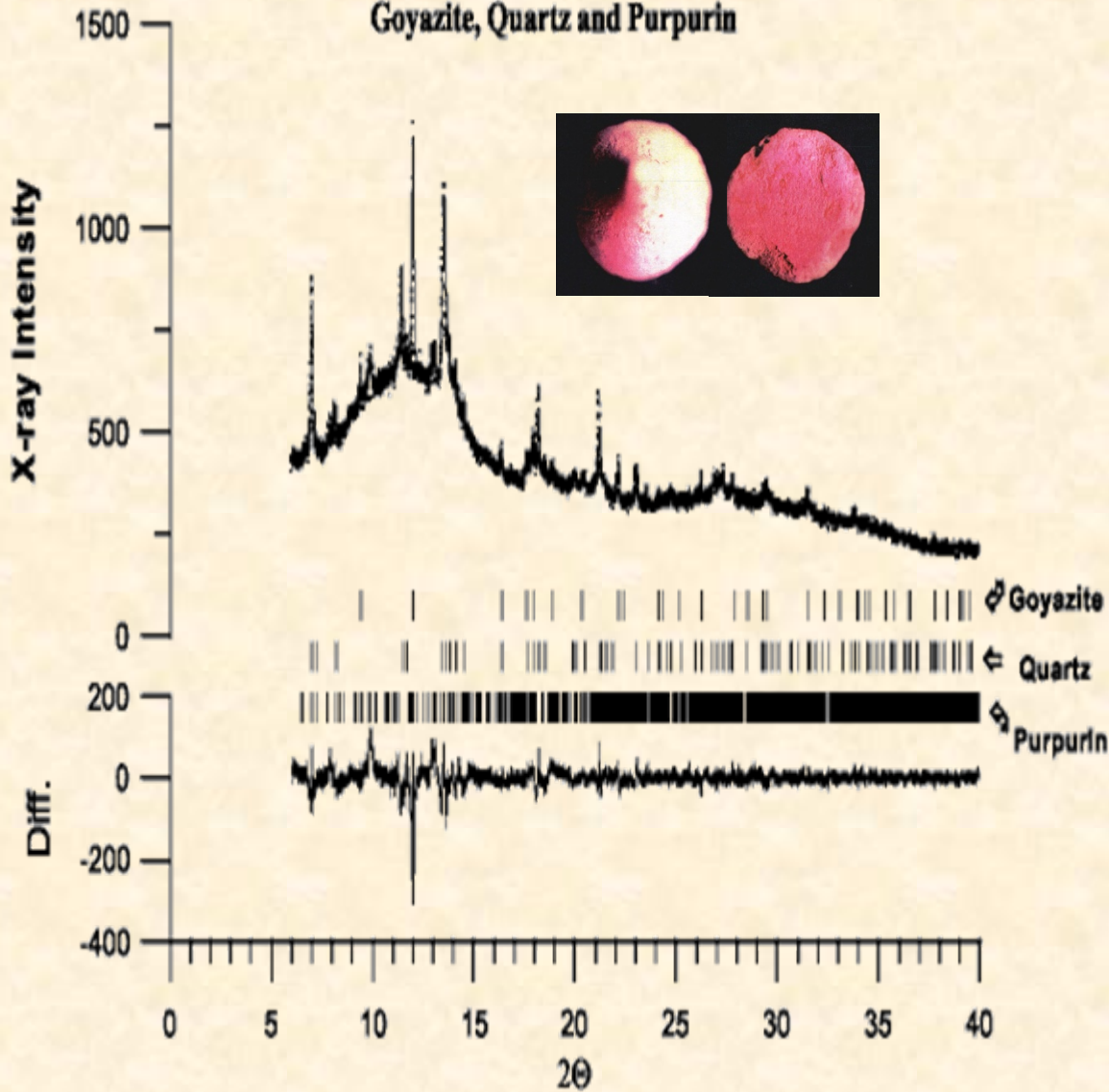
Conclusions

   Ten punic make-up samples were studied with SR-XRD using a 2D CDD 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.

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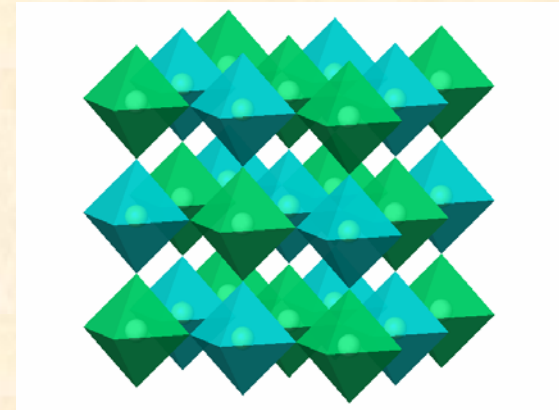# Ba$_2$CuWO$_6$: An Ordered Tetragonal Perovskite

Simple cubic AMX$_3$ perovskite: a = 3.8045.

Double Perovskites A$_2$MM'O$_6$: Out of 3 possible ordering only 2 observed
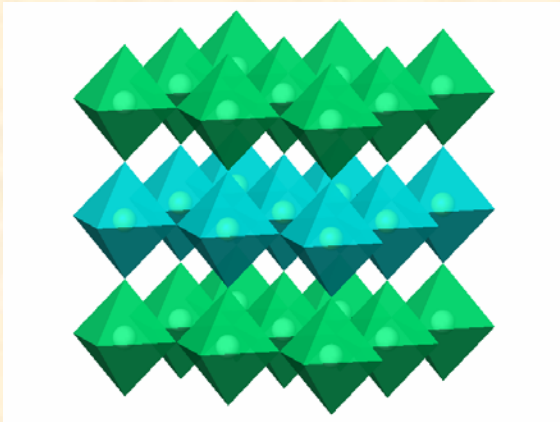
Model #1: Ordered alternation of MO$_6$ and M'O$_6$ octahedra in one direction, leading to formation of layered perovskite.

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

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Model #1 – Layered Ordering: **Model #2 – Rock Salt Type 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

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

<u>Jahn Teller Distortion?</u> Iwanaga et. al. J. Solid State. Chem. 147, 291(1999)

Recall Cu^{2+} electronic configuration $(t_{2g})^6(e_g)^3$: So in fact CuO_6 octahedra are elongated along the c axis. The e_g orbital is split into
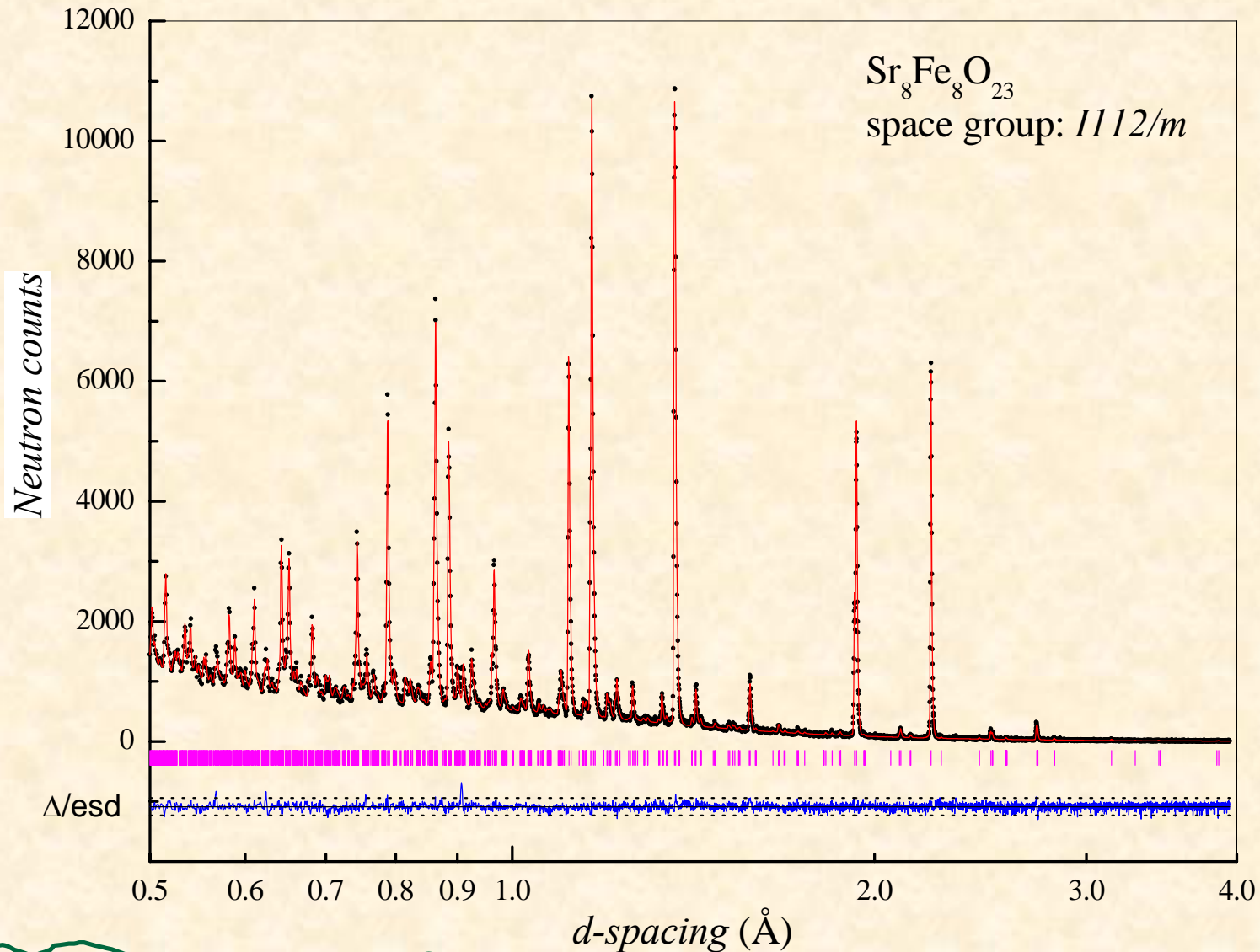
$$(d_{x^2-y^2} \text{ and } d_{z^2})$$

Incorrect Crystal Structure

$Sr_8Fe_8O_{23}$
space group: $I112/m$

Neutron counts

Δ/esd

d-spacing (Å)

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Correct Crystal Structure

$Sr_8Fe_8O_{23}$
space group: *I4/mmm*

Neutron counts (vertical axis)

Δ/esd

d-spacing (Å)
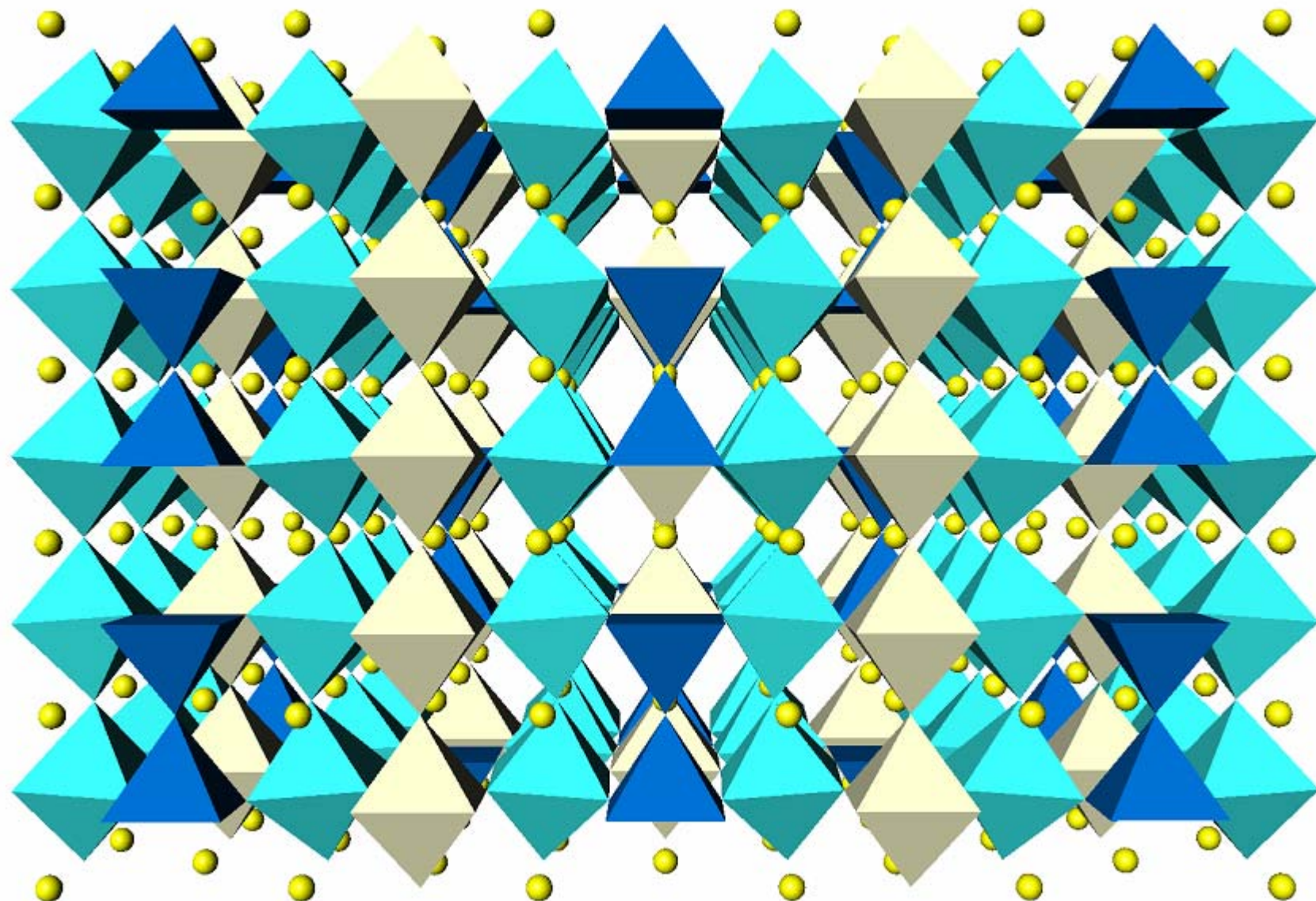
UT-BATTELLE
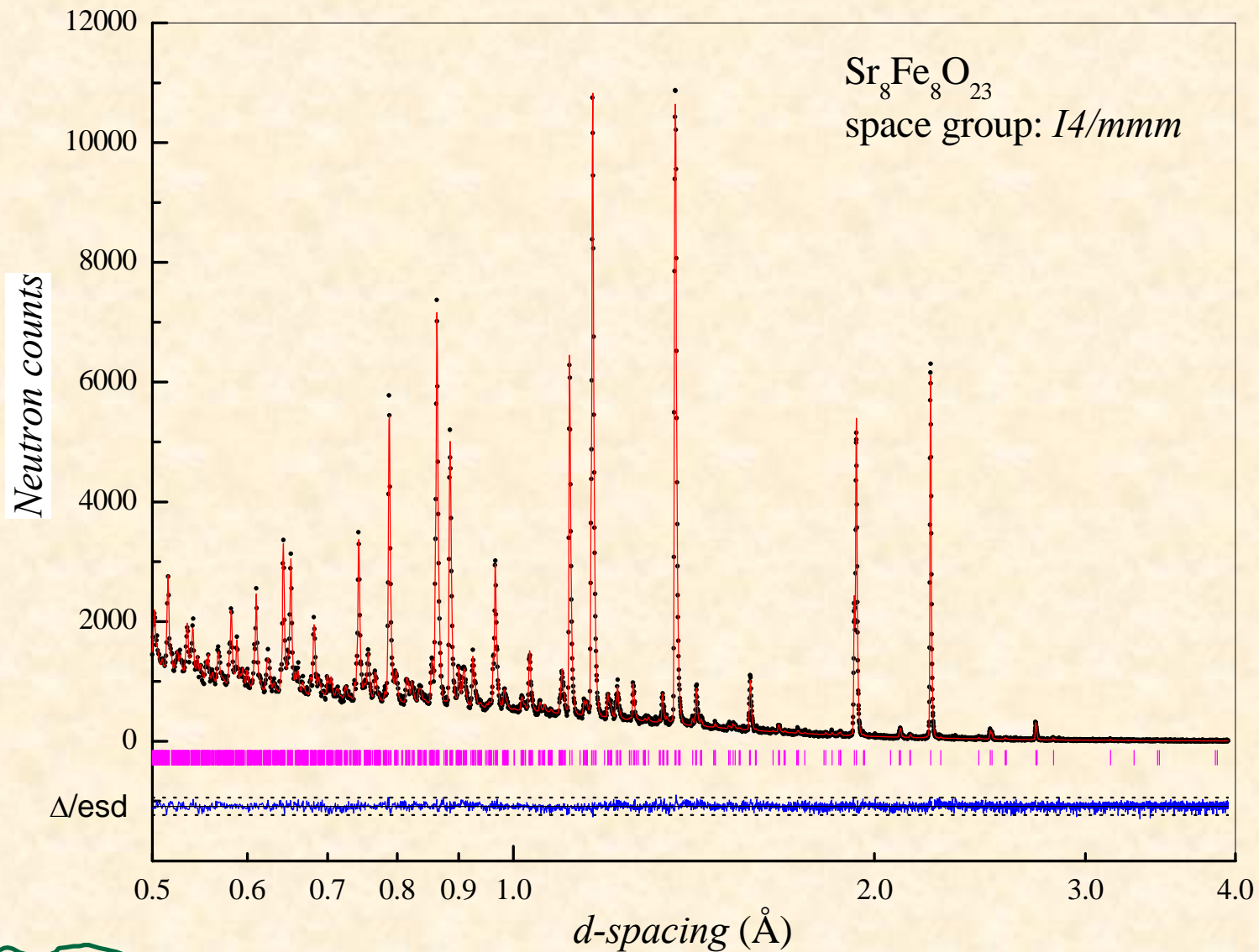
FERRIMAGNETIC AB$_2$O$_4$ SPINEL STRUCTURE

(Mn$_{0.81}$Fe$_{0.19}$)(Fe$_{0.80}$Mn$_{0.20}$)$_2$O$_4$

2-phase refinement nuclear + magnetic structure

Results give
- lattice parameter
- oxygen position
- distribution of Mn/Fe on T and O sites
- atomic displacement parameters
- magnetic moments on the T and O sites (e.g., -2.9 and 2.0 μ_B)

Zhang ZJ et. al. JACS, 120 1800 (1998)

nuclear phase

name	type	ref/damp	fractional coordinates			Mlt*	Occupancy	Uiso
5 O	O	X0 U0 0	0.261035	0.261035	0.261035	32	1.0000	0.01250
3 B	MN	0 U0 F0	0.500000	0.500000	0.500000	16	0.1978	0.00788
4 B	FE	0 U0 F0	0.500000	0.500000	0.500000	16	0.8022	0.00788
1 A	MN	0 U0 F0	0.125000	0.125000	0.125000	8	0.8101	0.01850
2 A	FE	0 U0 F0	0.125000	0.125000	0.125000	8	0.1899	0.01850
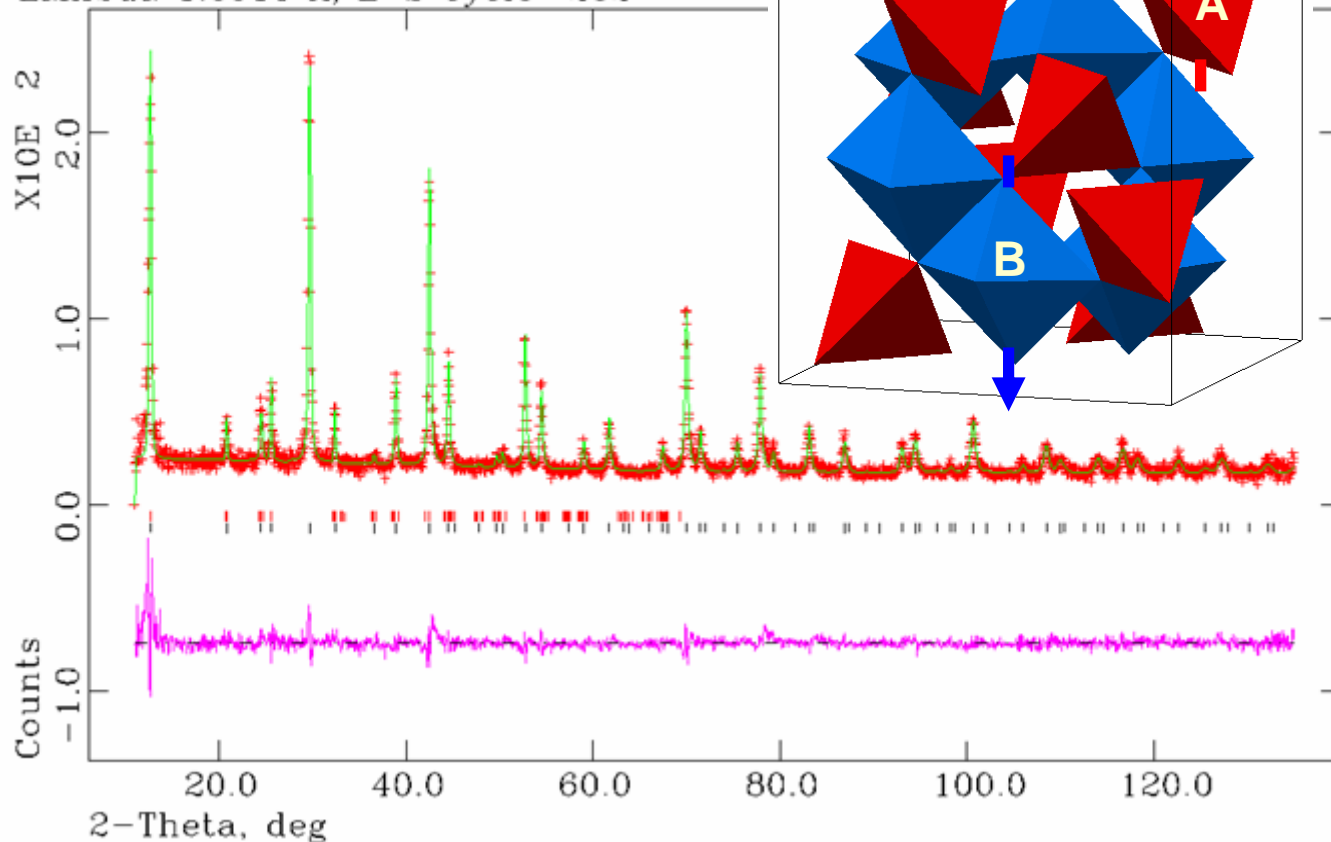
magnetic phase

name	type	ref/damp	fractional coordinates			Mlt*	Occupancy	Uiso
2 B	FE	0 0 0	0.500000	0.500000	0.500000	16	1.0000	0.00700
1 A	MN	0 0 0	0.125000	0.125000	0.125000	8	1.0000	0.01800

06-G00576almm

Magnetic Ordering: Oxygen-deficient A-site Layered Perovskite $NdBaCo_2O_{5+\delta}$

Burley et. al. J. Solid State. Chem. 170, 339 (2003)
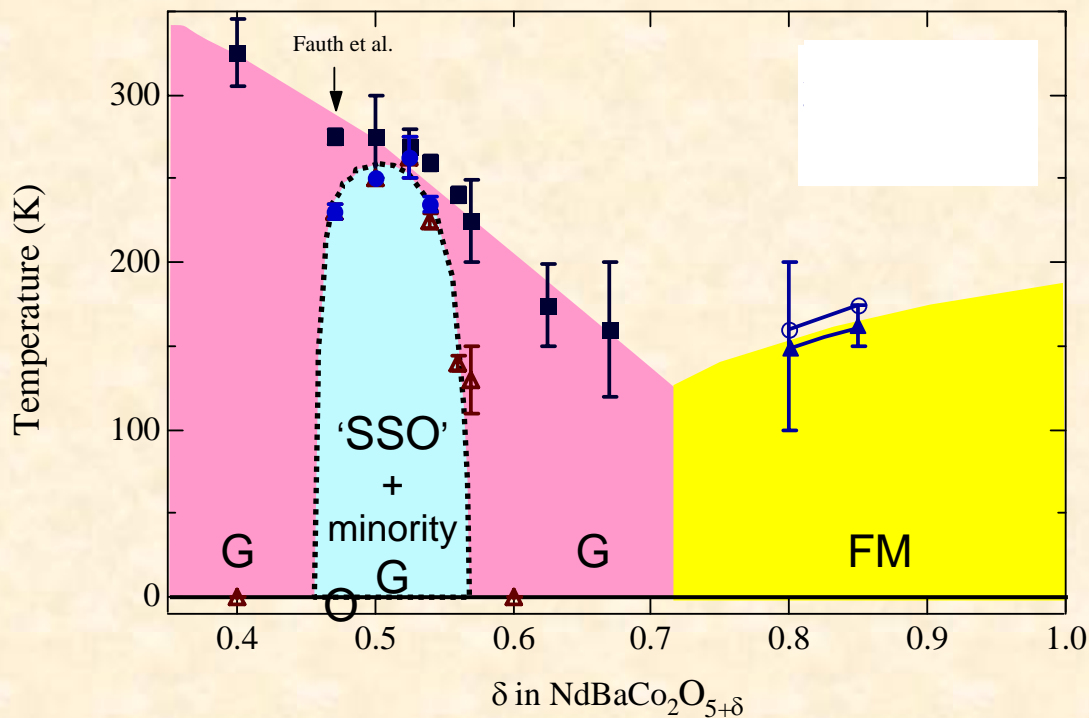
Magnetic phase diagram
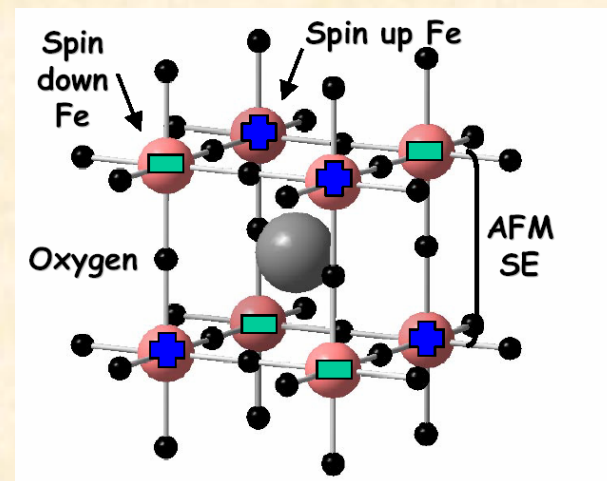
G type AF ordering in a simple perovskite

300K: Pmmm	12K: Pmma' (Pmmm)
a=3.8979	7.7938
b=7.8074	7.8033
c=7.5871	7.5844

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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
   a. Momentum space - Direct methods
   b. Real space
6. Refine

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Solution of structures of organic molecules from powder data:

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

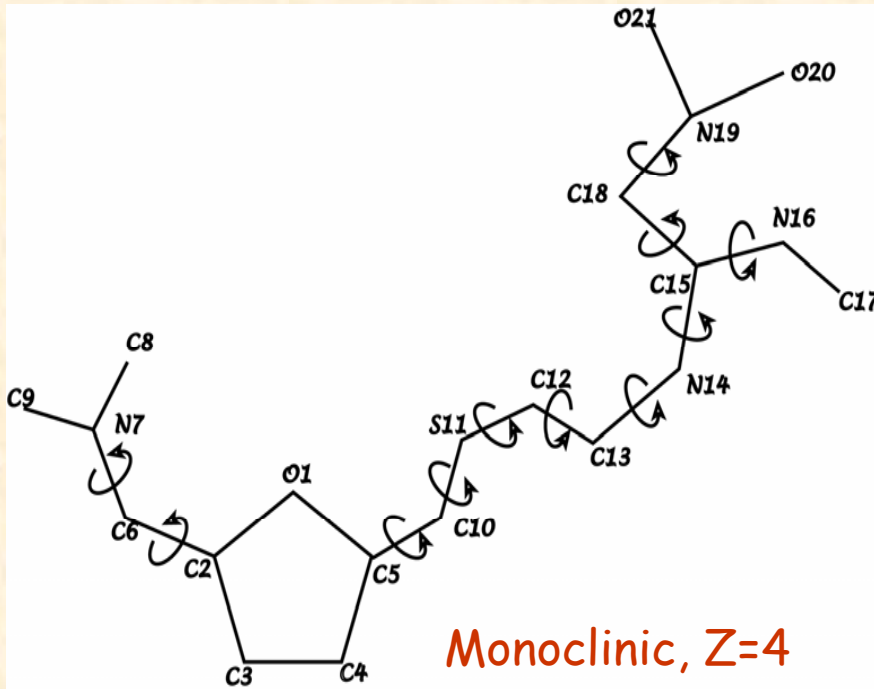Use of known molecular geometry is helpful -- make a model, put it into the lattice, and test it against the data.
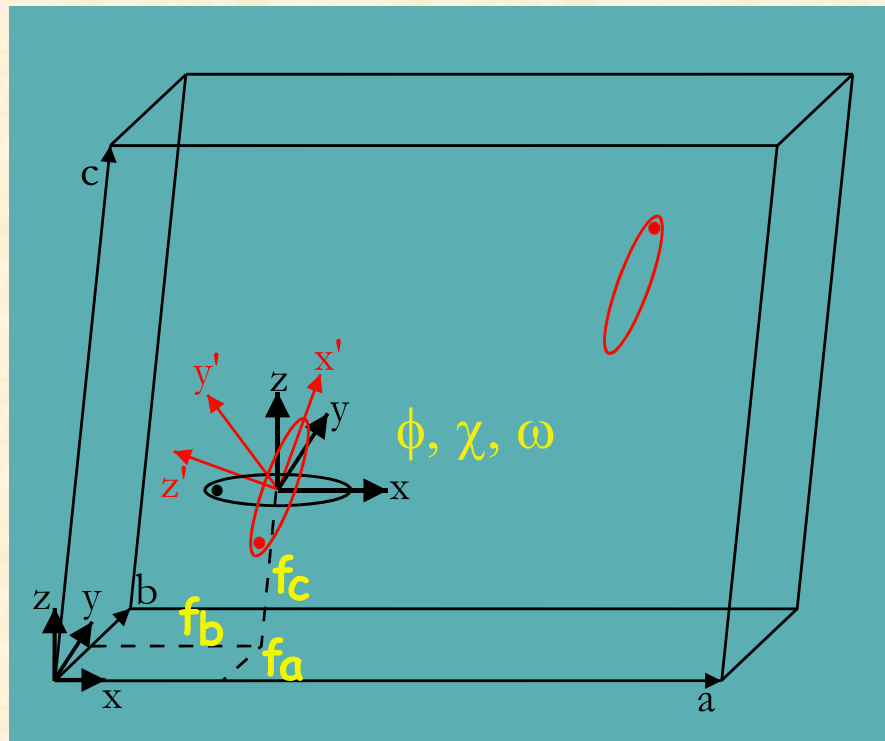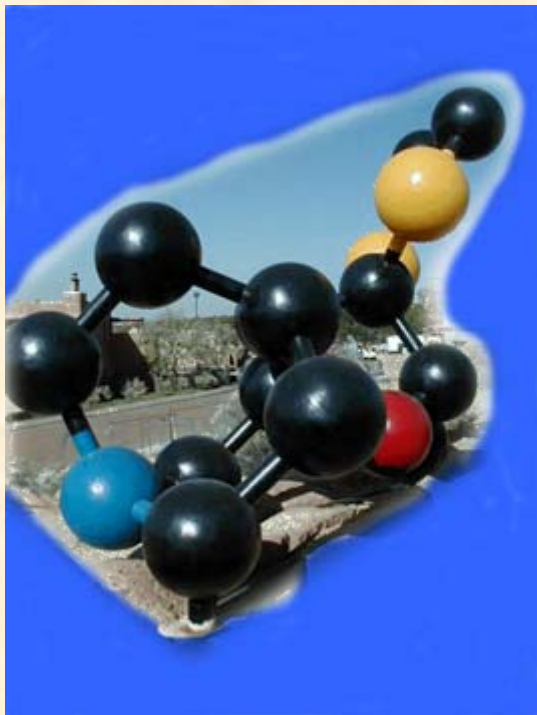
(How do you know if you are done? If the best solution is right?)

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Undertake a project like this with very good data

Ranitidine HCL form II
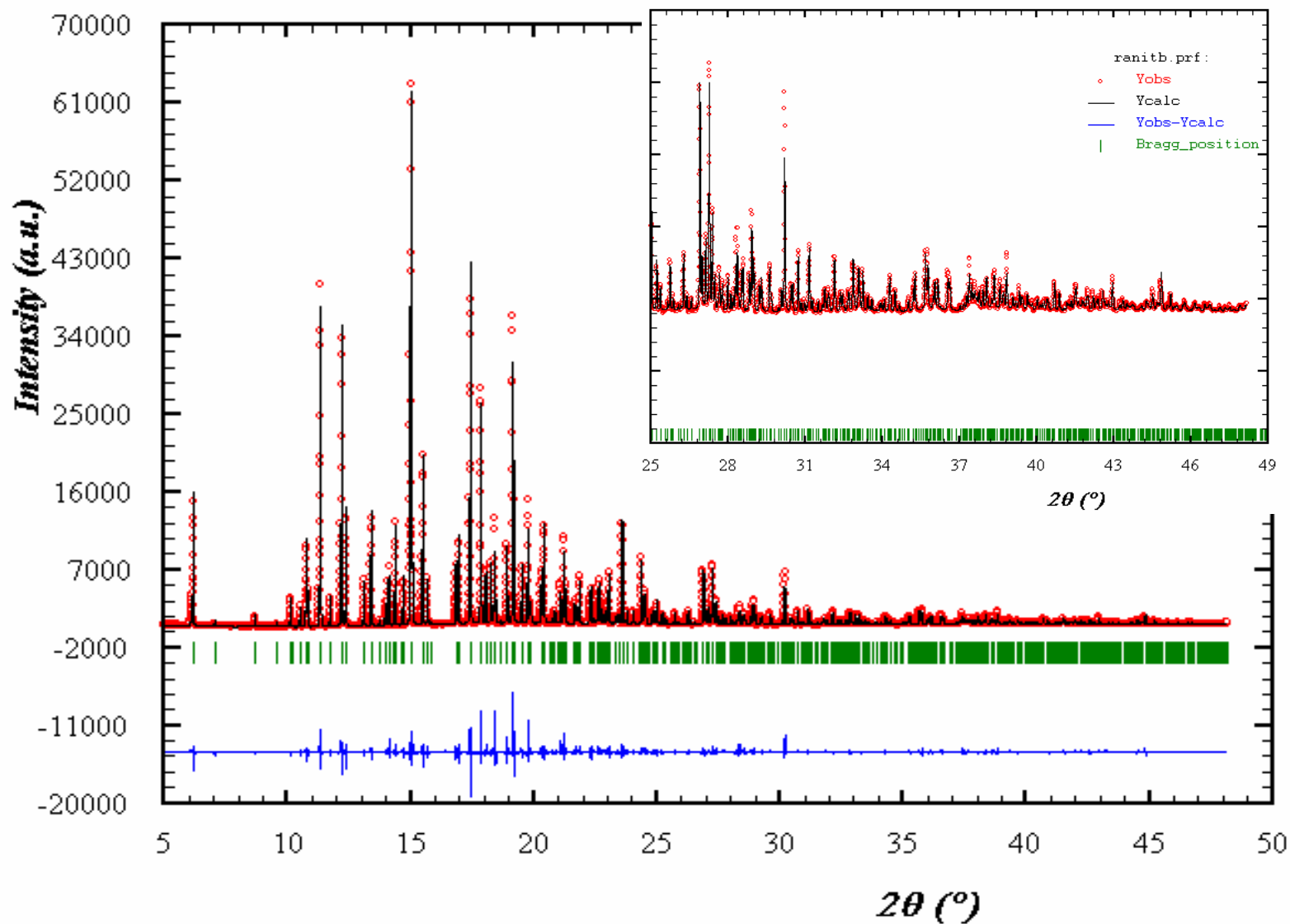
Ranitidine HCl (Zantac®) is a very widely used drug for ulcers, excess production of stomach acid. There is an interesting subtlety in its crystal structure. Huq et. al. J. Pharm. Sci. 92, 244 (2003)

Space Group : P $2_1/n$

6 spatial coordinates : position
3 Eulerian angles : orientation
11   torsions.

Monoclinic, Z=4

a=18.808Å,

b=12.981Å,

c=7.211Å

β=95.057°,

Ranitidine HCl, 10^6 cycles/temp.
100 reflections, to d = 2.66 Å

Best S

Temperature Parameter

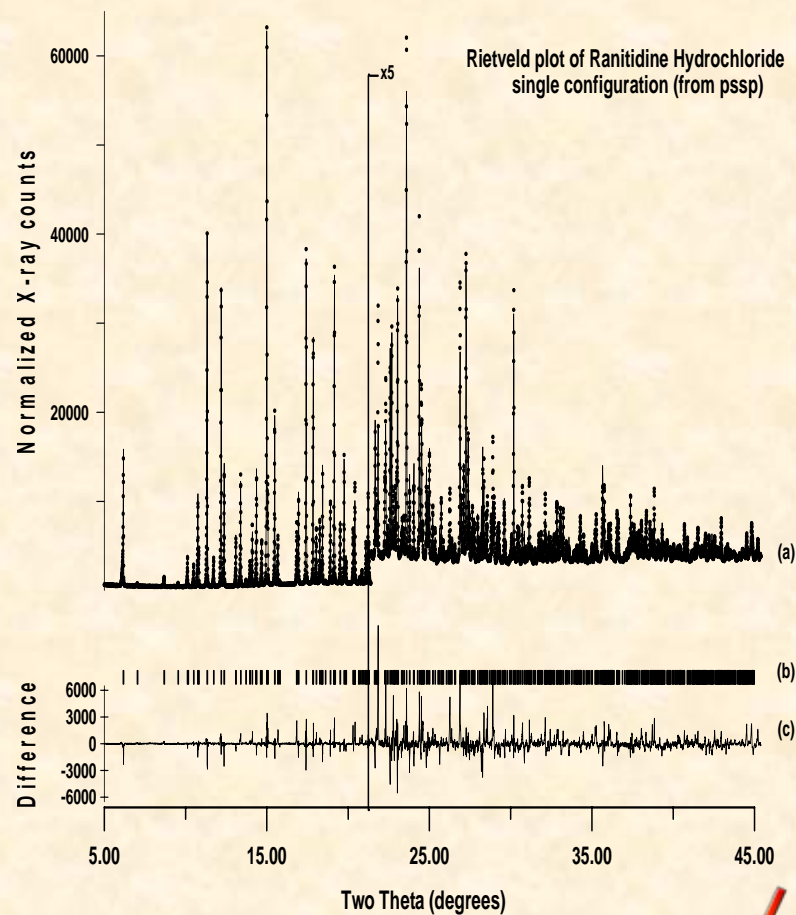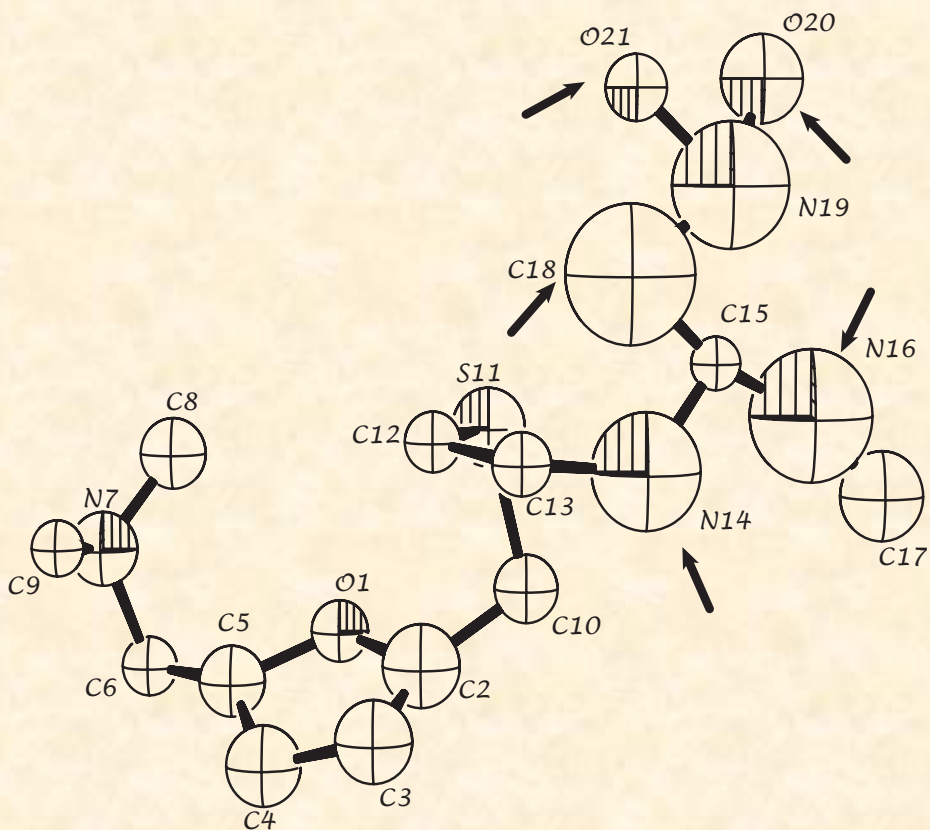Two others
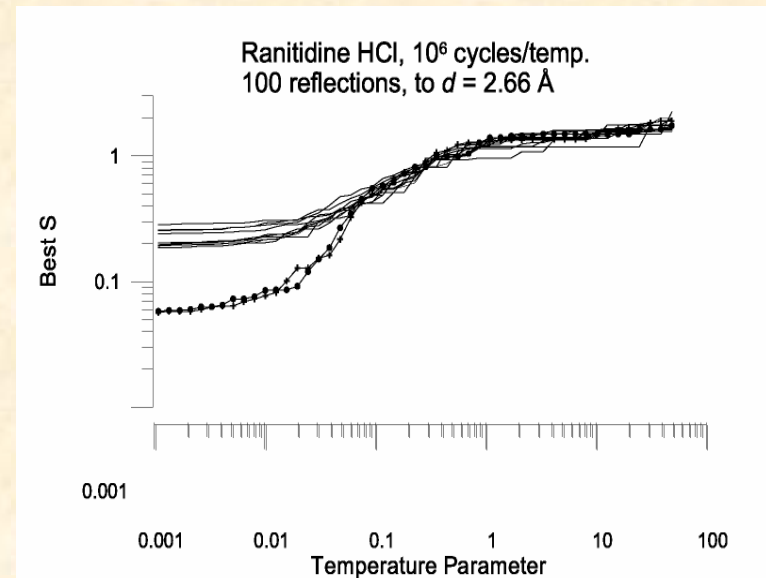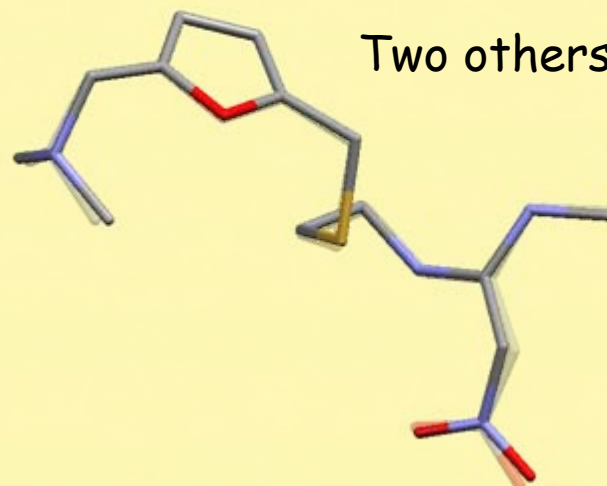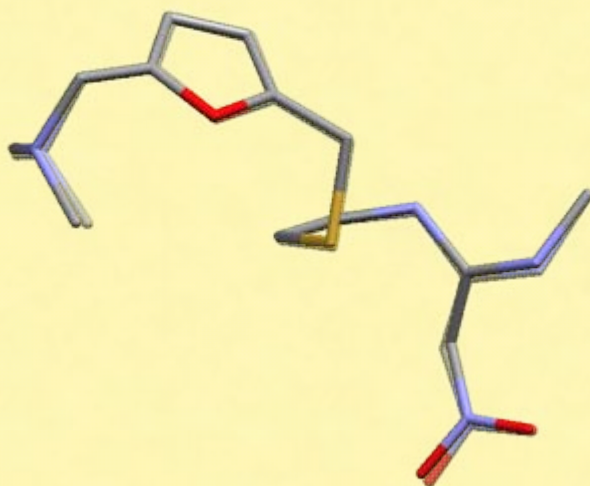
Two candidate solutions from PSSP
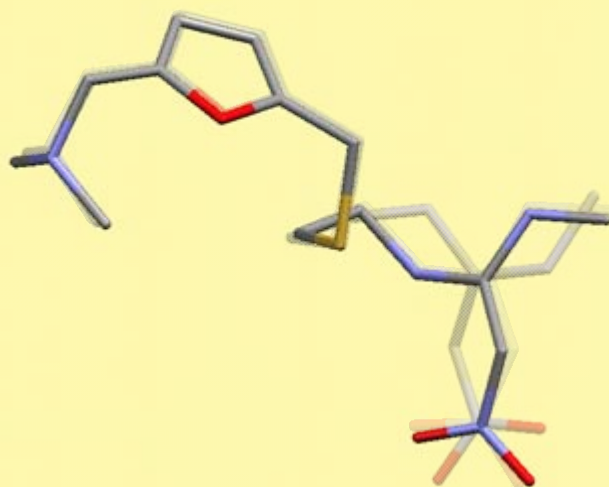
All four,
superimposed.

Disorder,

or inability of powder

data to distinguish

a few of the atoms?

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Atomic structure of our best Rietveld refinement of a single molecule. Essentially independent of which solution we start from.

R_{wp} = 11.12%, χ^2 = 10.56

Rietveld plot of Ranitidine Hydrochloride single configuration (from pssp)
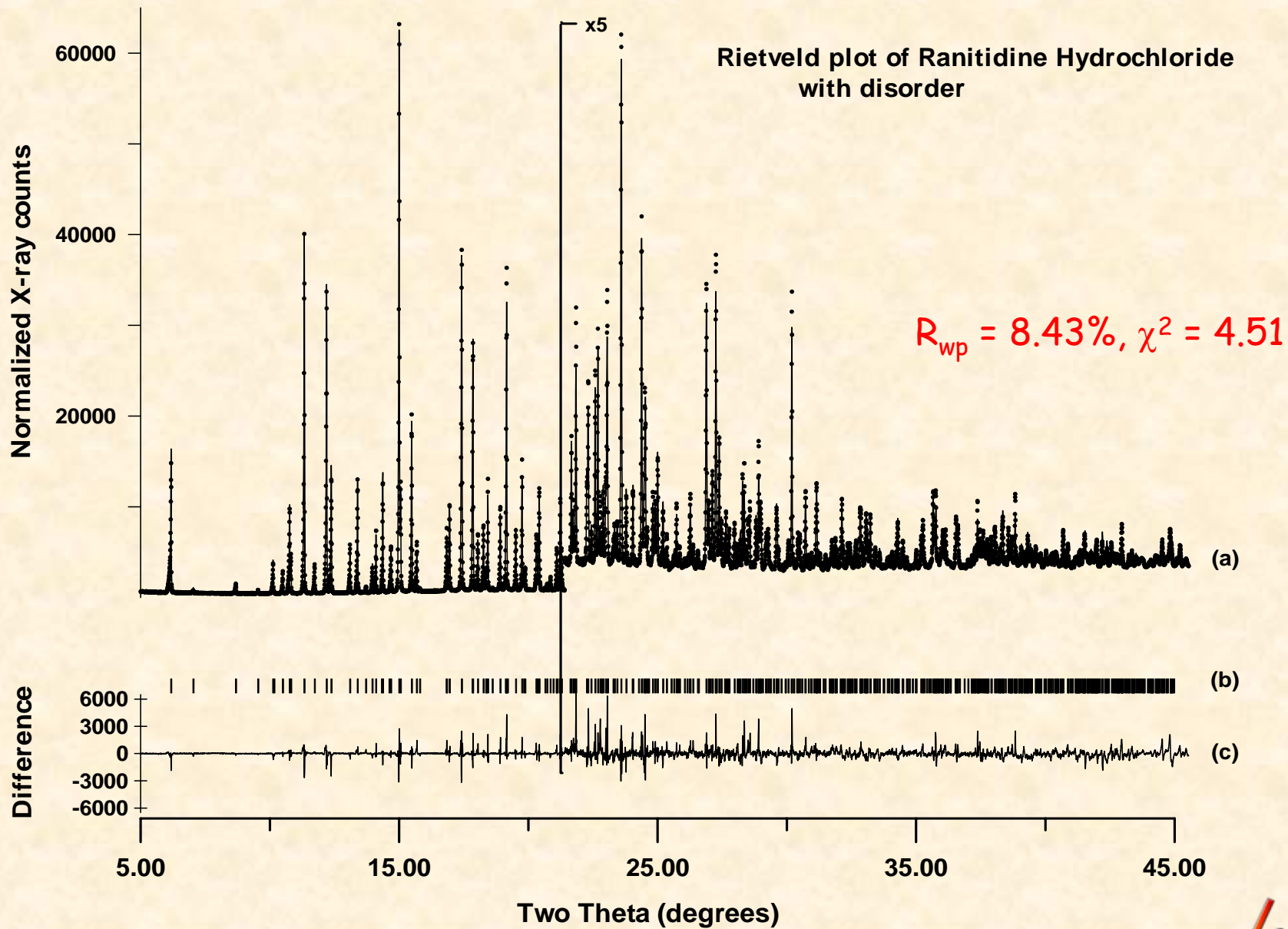
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Refinement incorporating disorder. 50% occupancy of each of two sites for N14, C16, C18, O20, and O21.

R_{wp} =8.39%, χ^2 = 4.51
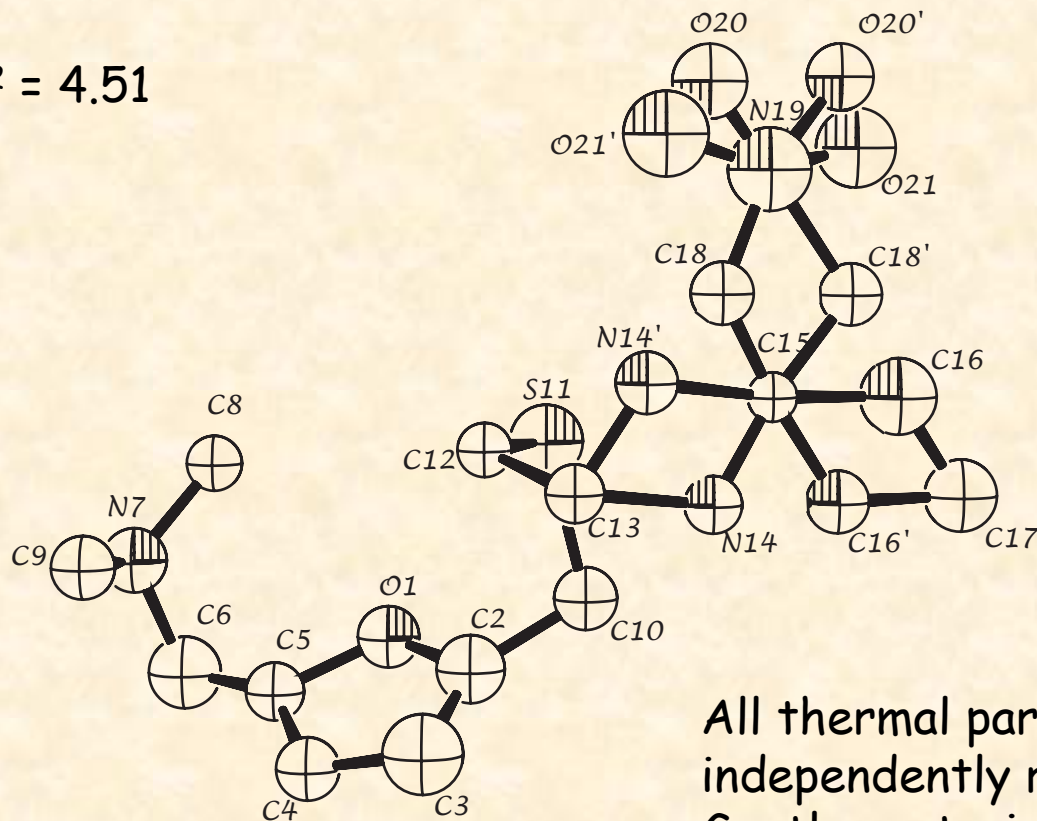
This is clearly the correct solution, which includes molecular disorder.

All thermal parameters independently refined! Gentle restraints on bond lengths.

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Rietveld plot of Ranitidine Hydrochloride with disorder

$R_{wp} = 8.43\%$, $\chi^2 = 4.51$

x5

Normalized X-ray counts

60000

40000

20000

Difference

6000
3000
0
-3000
-6000

(a)
(b)
(c)

5.00   15.00   25.00   35.00   45.00

Two Theta (degrees)

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The answer, including disorder,
was already known from single
crystal experiment.
T. Ishida, Y. In, M. Inoue (1990)
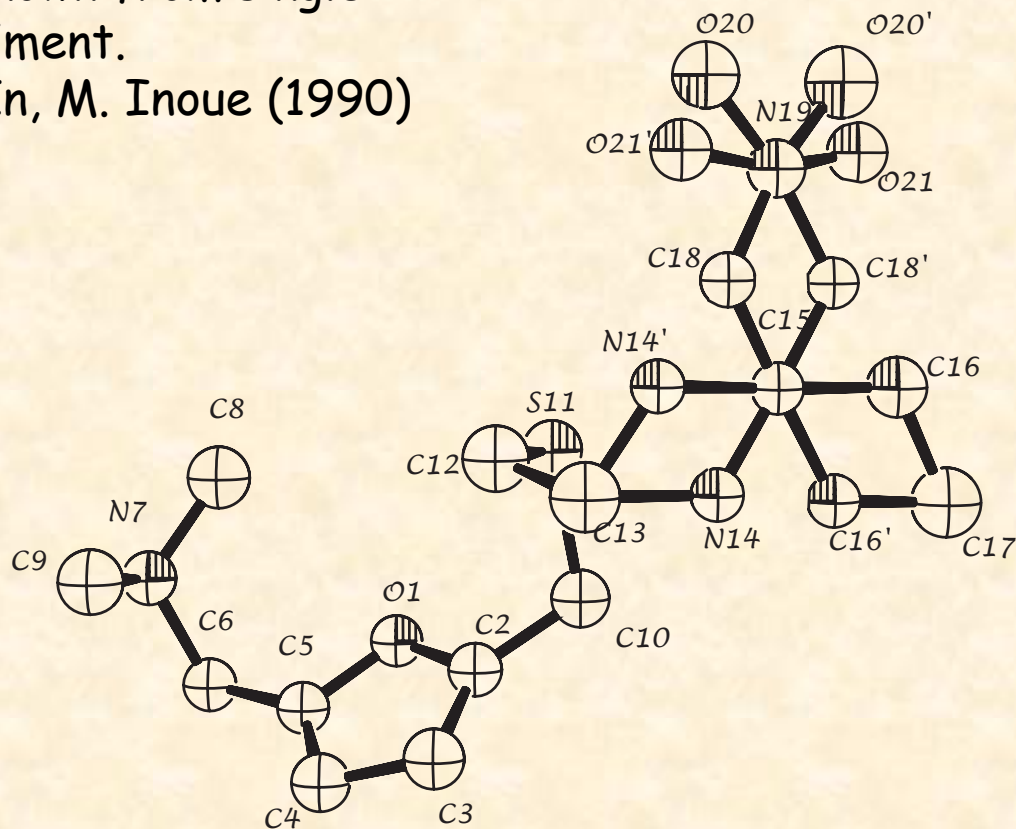
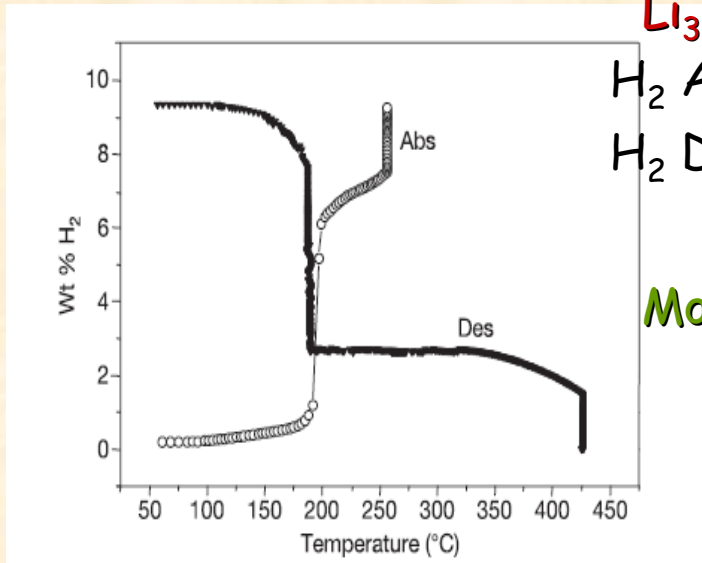# Li$_3$N : Hydrogen Storage Candidate

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

More recently (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.

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

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In situ Deuteration & De-deuteration

Time (2 days)

34h: deuteration
10h: pumping
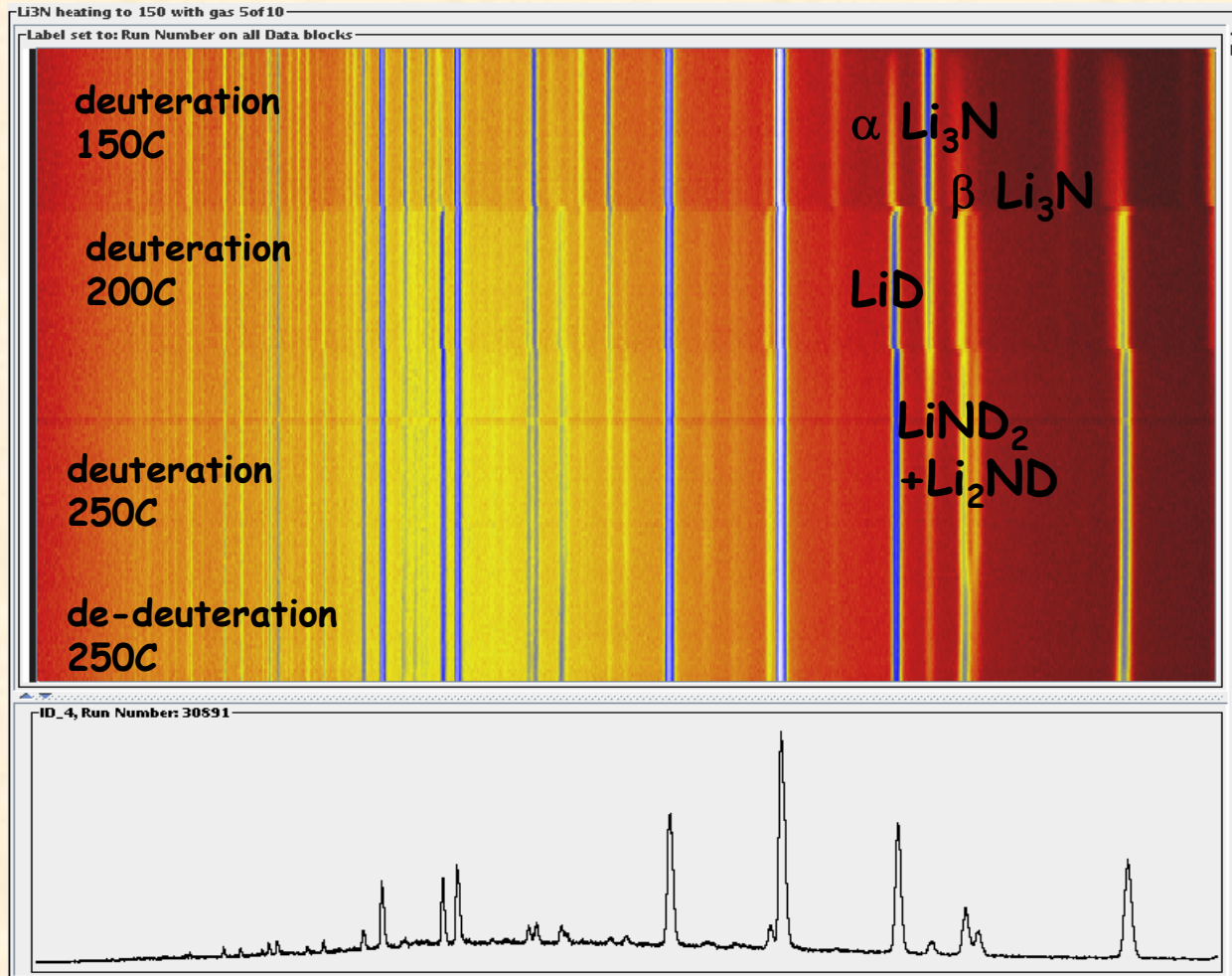
d spacing

Normalize Volume (V/V$_0$)

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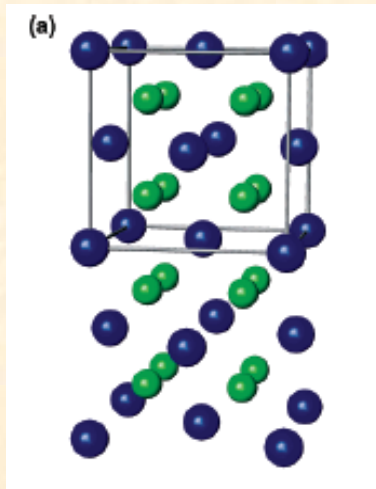
SNS
SPALLATION NEUTRON SOURCE
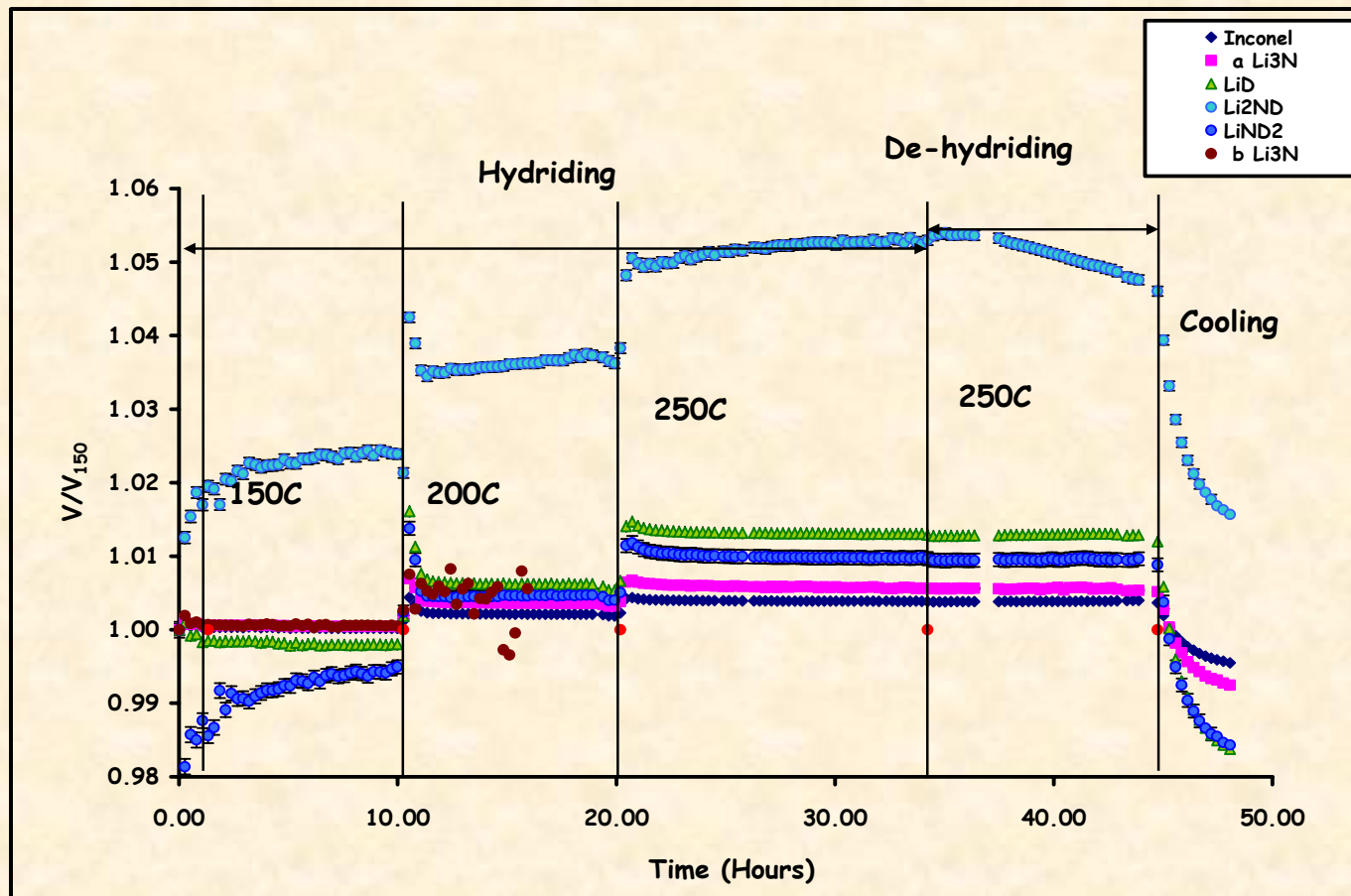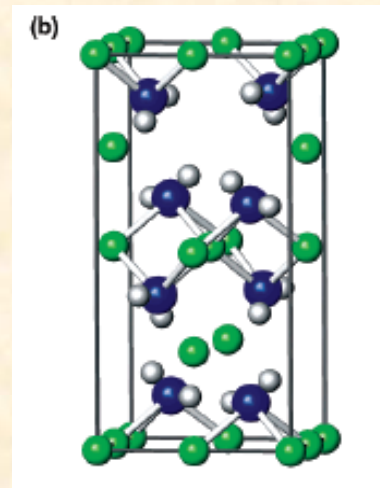
Moles of Phases Present
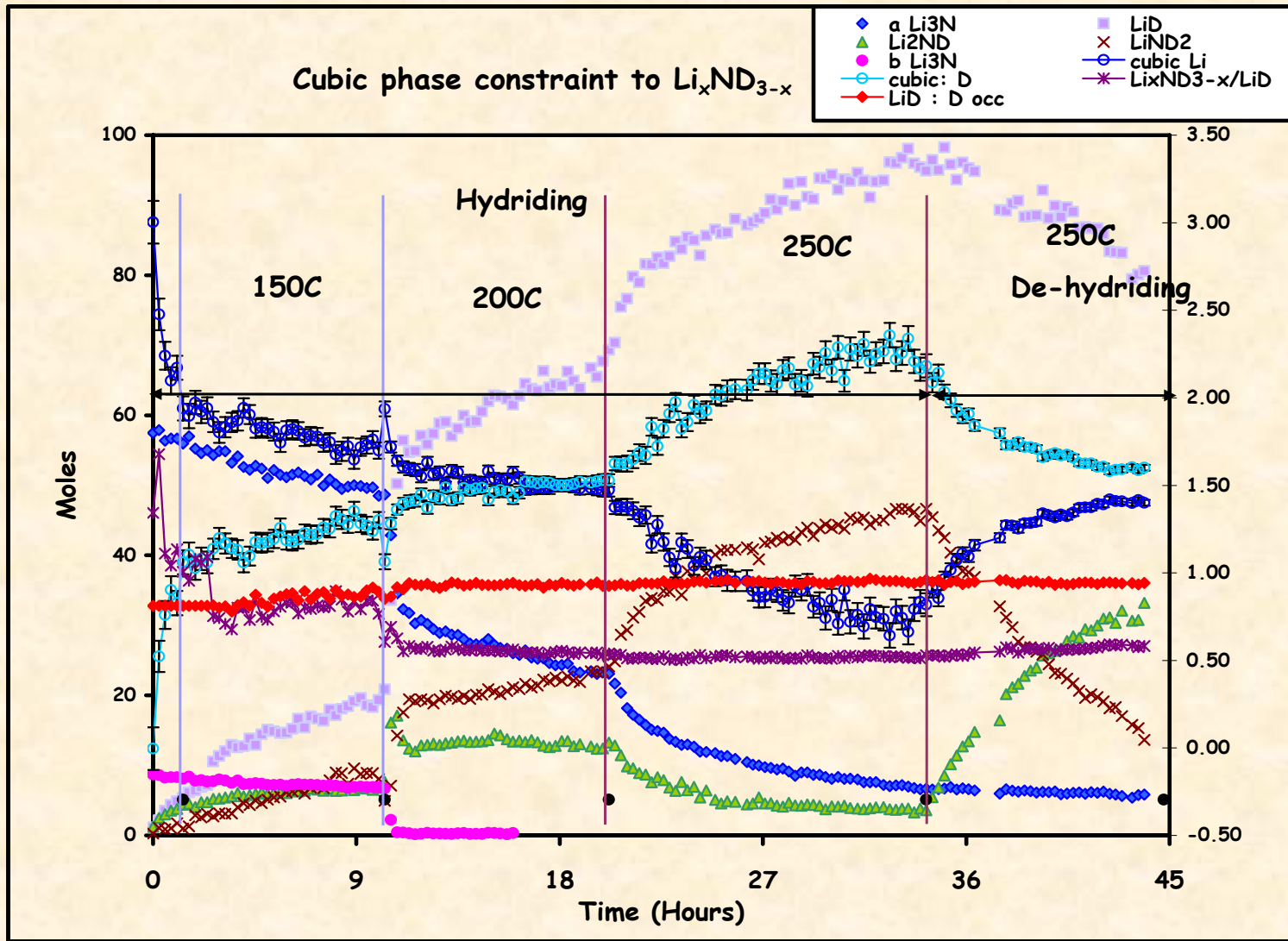
Imide – Amide : Structural relationship

David et. al., JACS 129,1594

Anti fluoride cubic imide

blue: N
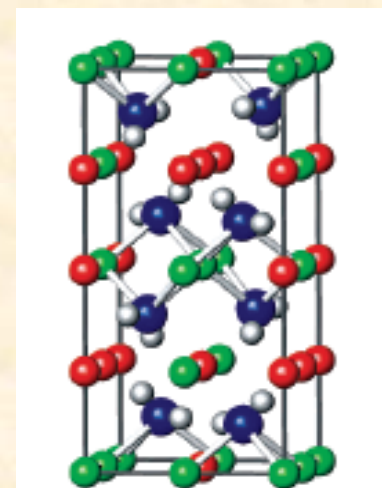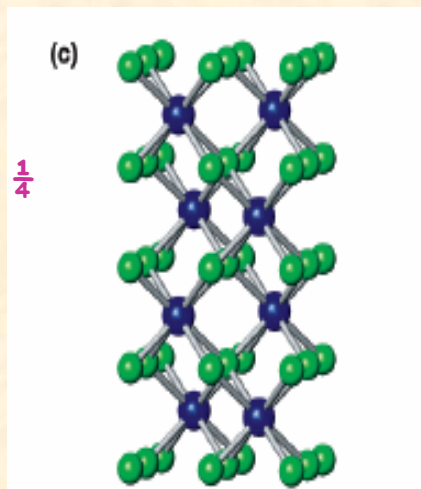green: Li
grey: H

Tetragonal amide

shift origin ¼ ¼ ¼

a × a × 2a,

show unoccupied Li sites by red

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Concluding Remarks

- **Rietveld refinement is a very powerful technique for analyzing powder diffraction data.**

- **However, do not use 'GSAS' as a black box! Keep in mind what you are trying to achieve, if the answers make physical sense, if the quality of your data is really sufficient for your conclusions.**