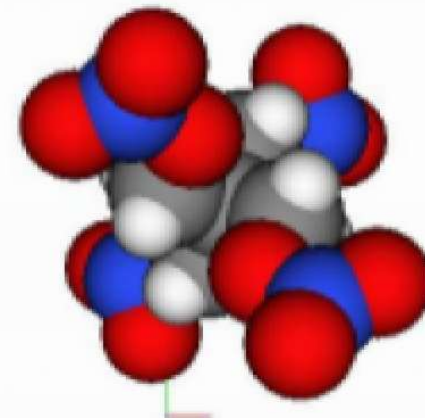


THE RIETVELD REFINEMENT METHOD

GSAS-2



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- Some history first
- Extreme examples
- The math
- Worked example

Acknowledgements: DOE/SC

HISTORY – H.M. RIETVELD



Hugo Rietveld; neutron powder diffractometer, Petten, Netherlands

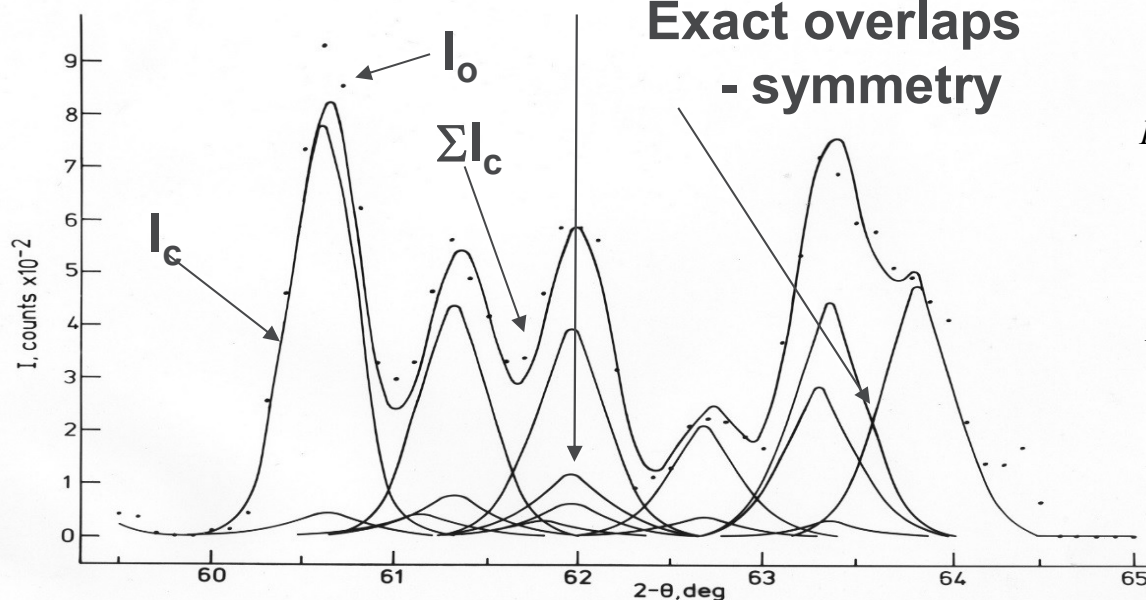
Papers: H.M. Rietveld, Acta Cryst. 22, 151-2(1967)

H.M. Rietveld, J. App. Cryst., 2, 65-71 (1969)

Multi-parameter, nonlinear LS curve fitting

Incomplete overlaps

Exact overlaps
- symmetry



Residuals:

$$R_{wp} = \sqrt{\frac{\sum w(I_o - I_c)^2}{\sum wI_o^2}}$$

Rietveld Minimize

$$M_R = \sum w(I_o - I_c)^2$$

“chi-squared” or
“goodness-of-fit”

$$\chi^2 = M_R/(n-p)$$

PLUTO REACTOR AERE HARWELL – 1970'S



PANDA Diffractometer

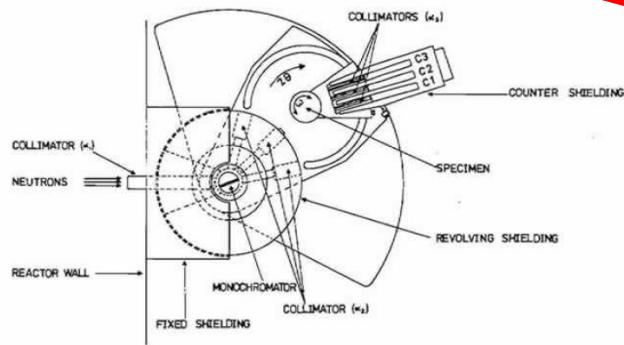
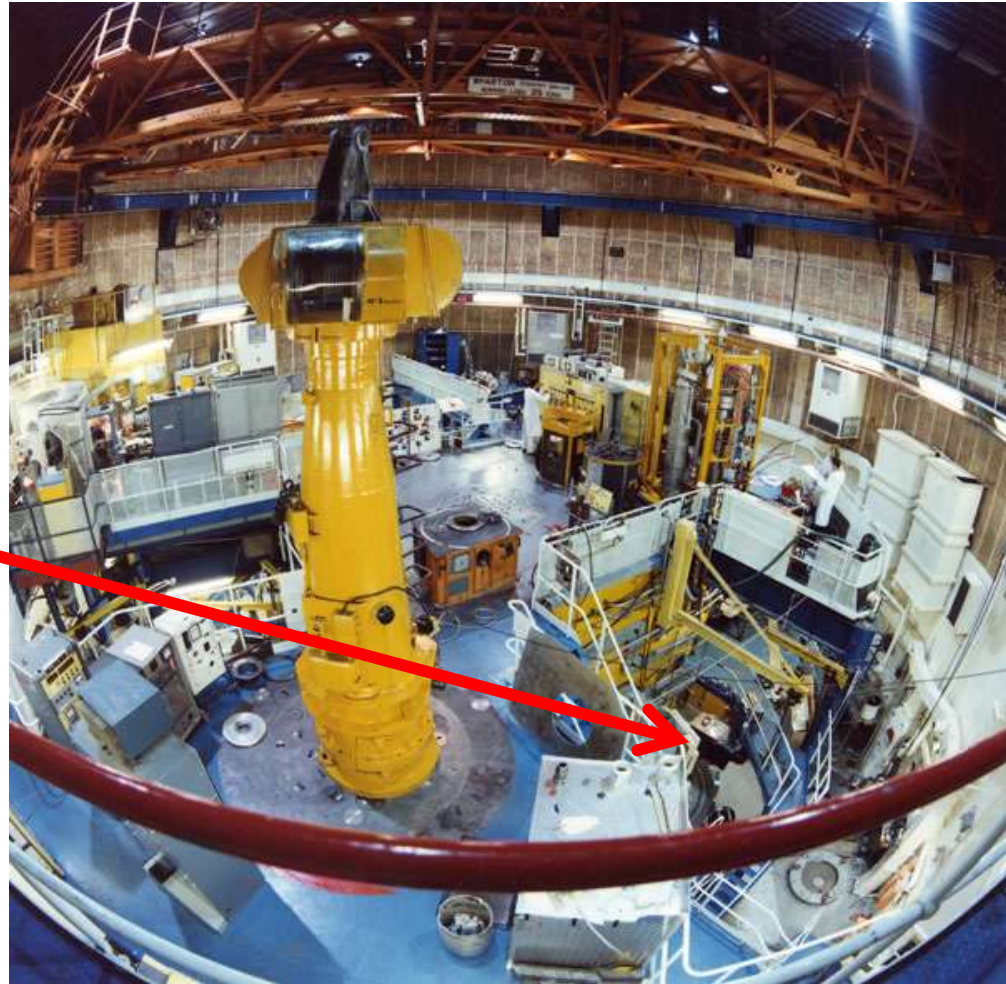
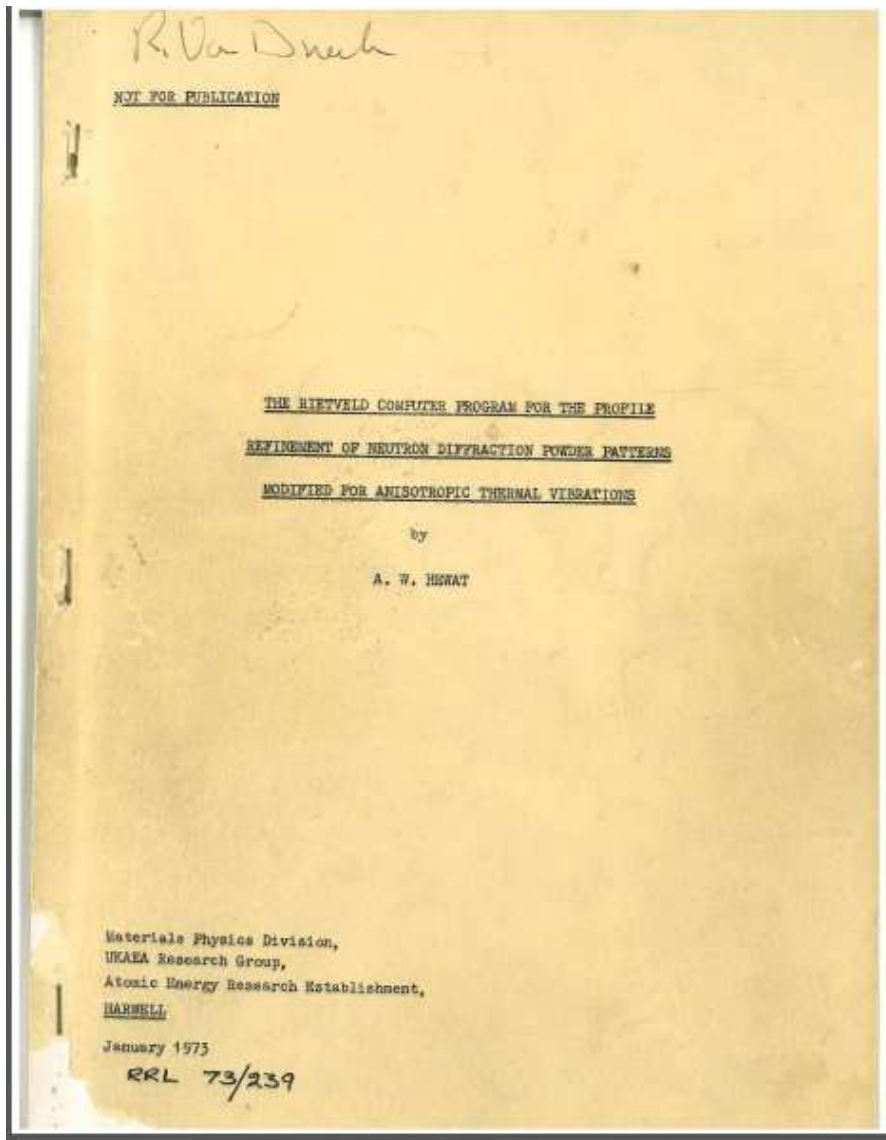


Fig. 2. A schematic diagram of a neutron powder diffractometer named PANDA which is installed at A.E.R.E. Harwell.



AKC & RBVD experiments: $2\Theta_m$ 92° ,
 $\lambda=1.57\&1.61\text{\AA}$, $2\text{-}2.5\times 10^5$ n/scm², scan @50m/deg!

This is where it starts - Alan's Manual



**Original with my
annotations of additions
to input file for my 1973
version – Gaussian peak
shapes with an
(incorrect) peak
asymmetry correction**

WHAT DID IT RUN ON?

CHILTON ICL1906A – AERE HARWELL, UK



**256k 24bit words (~
800kB)**

**OS: Georgell &
George4**

Produced ~1MW of heat

**About as much
compute power as an
old cell phone**

Banbury Rd. Oxford

ICL1906a similar

WHAT DID WE DO WITH IT? – 3 DAY SCANS! LHe TEMPS.

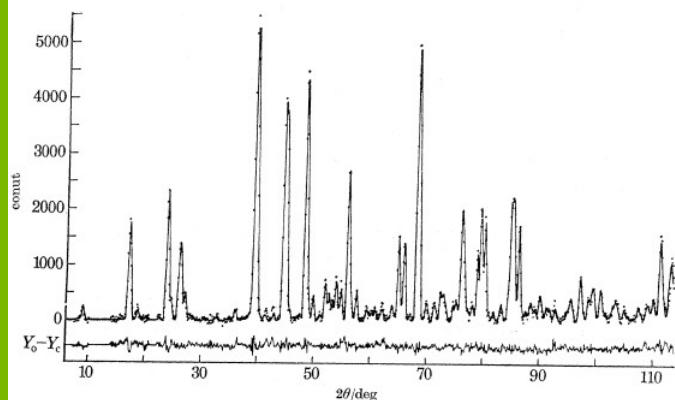
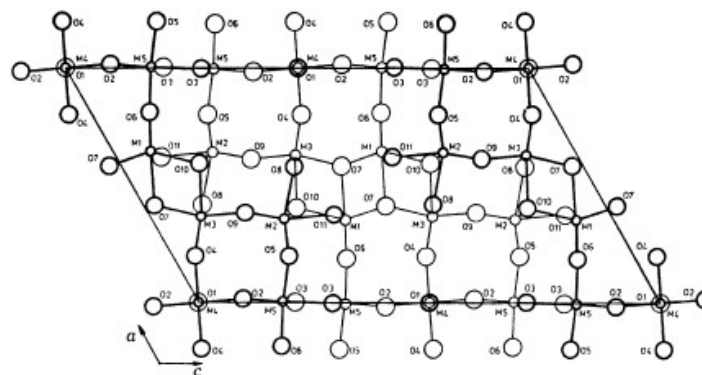


FIGURE 3. Neutron powder diffraction profile for TiNb_2O_7 . Lines and points represent calculated and observed profiles, respectively. A difference curve is shown.



TiNb_2O_7 ; $A2/m$, $a=11.89$, $b=3.80$, $c=20.37$, $\beta=120.2^\circ$
603 refl., 1077 data points

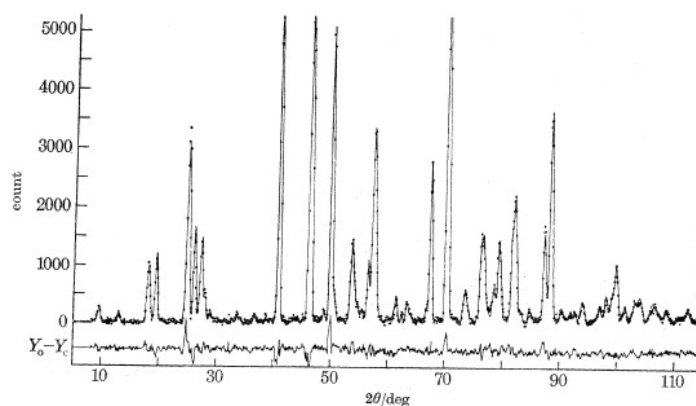
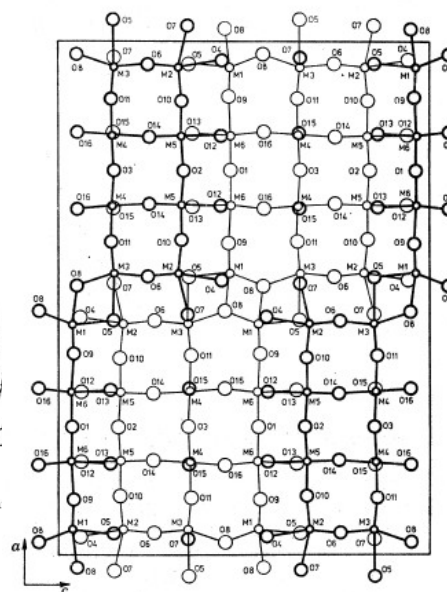


FIGURE 4. Neutron powder diffraction profile for ortho- $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. Lines and points represent calculated and observed profiles, respectively. A difference curve is also shown.

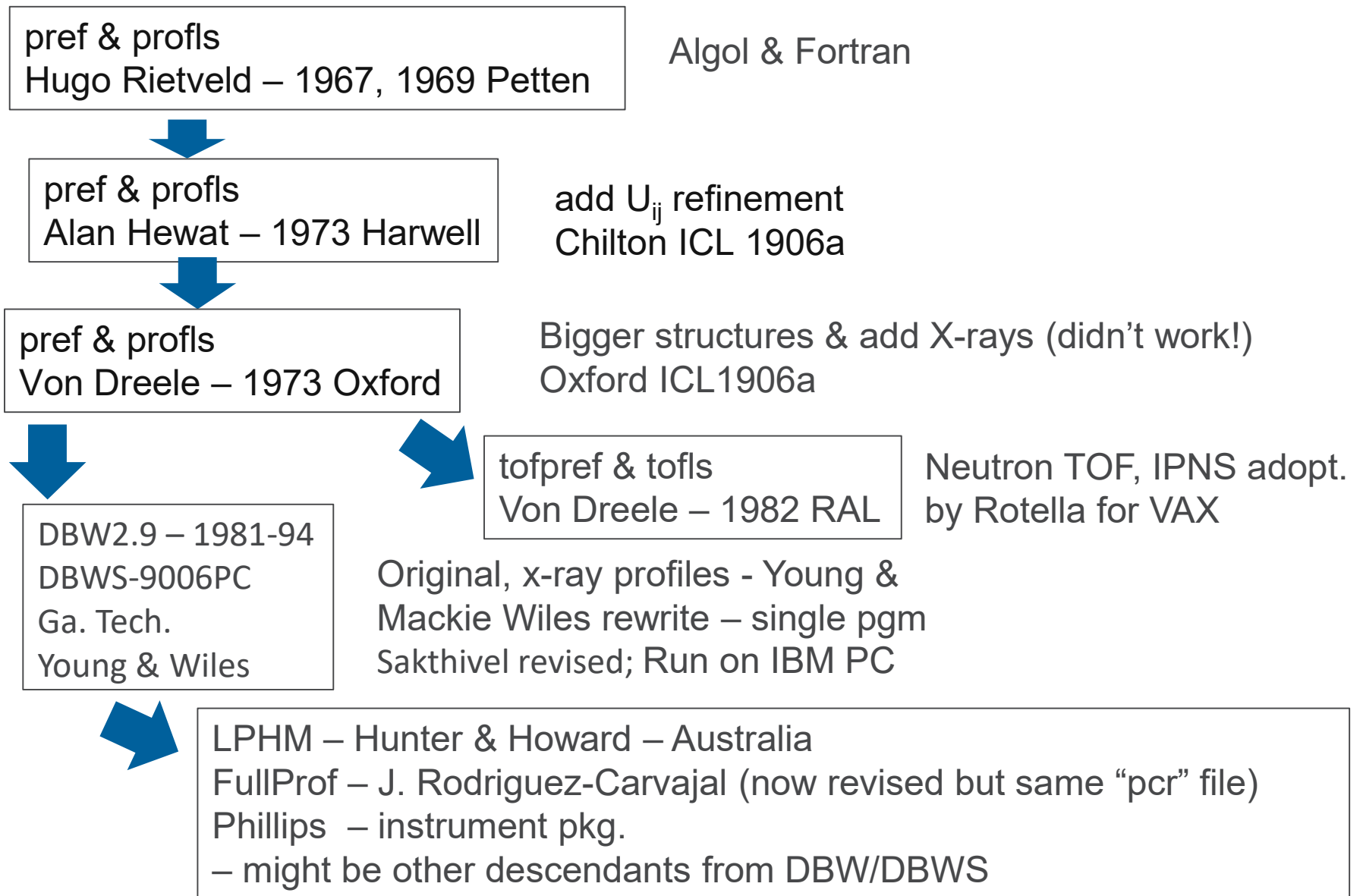


o- $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, $Amma$,
 $a=28.30$, $b=3.78$, $c=20.35$
843 ref., 1116 data points

R. B. Von Dreele and A. K. Cheetham
Proc. R. Soc. Lond. A 1974 **338**, 311-326

NB: this stuff could be the next battery material, so you just never know.

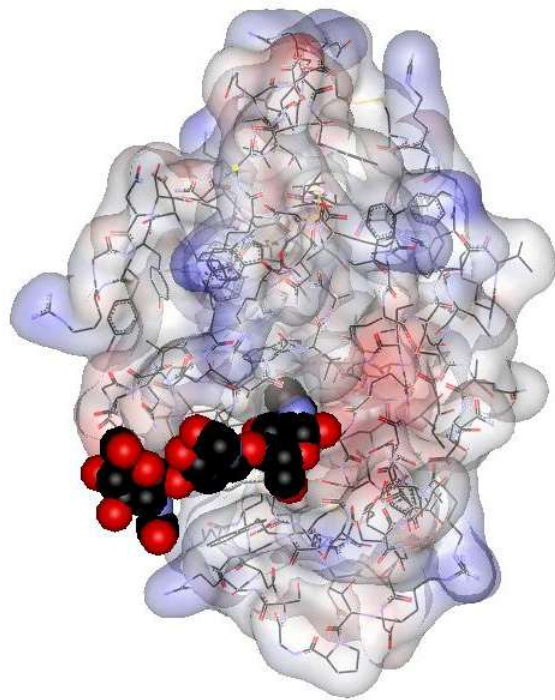
HUGO'S PROGRAM FAMILY TREE





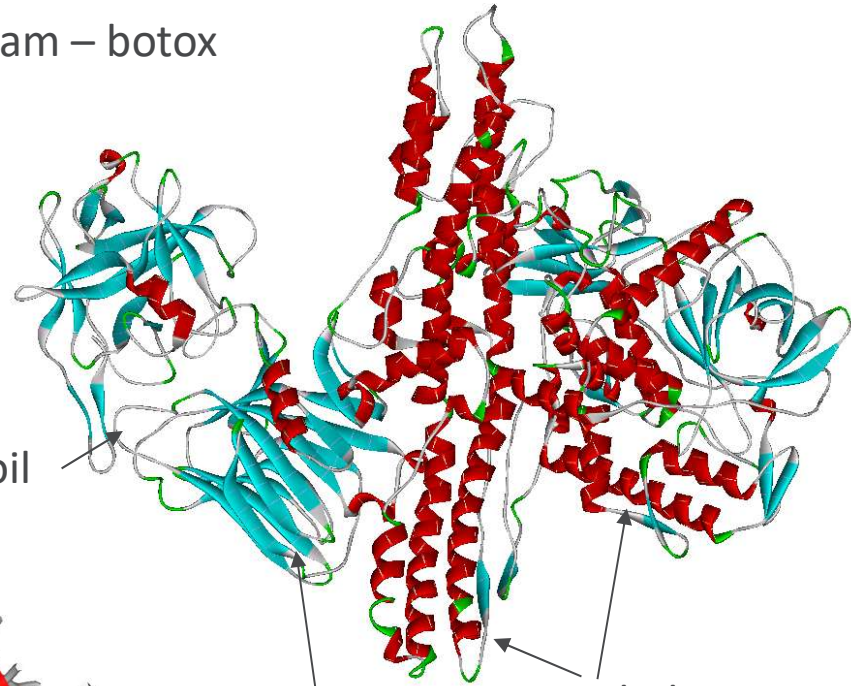
A FEW MORE RIETVELD REFINEMENT EXAMPLES – BIGGEST & FASTEST

Biggest: Proteins – polymers of amino acids - representations



Space filling (HEWL+NAG₃)
129 AA

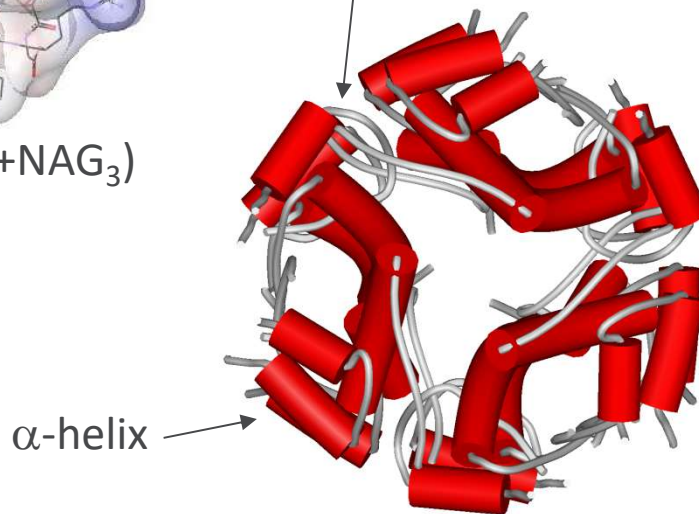
Ribbon diagram – botox
~1100AA



random coil

α -helix

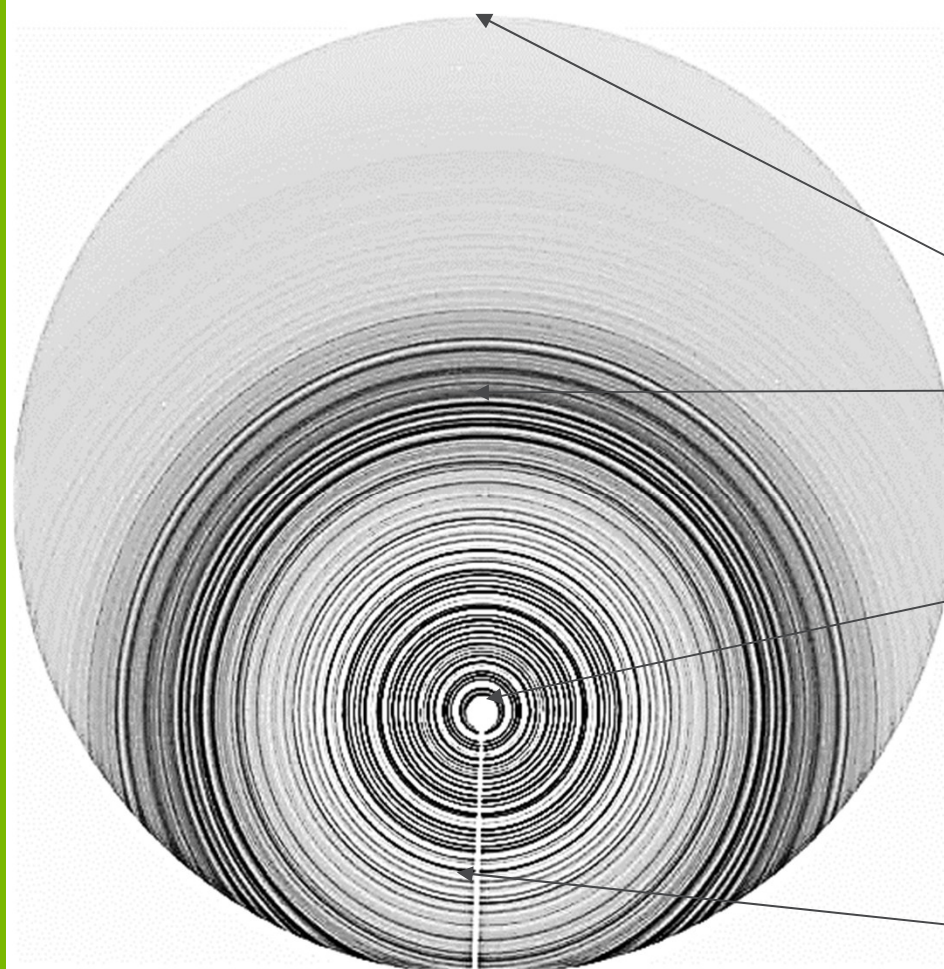
β -sheet



α -helix

Schematic – insulin
102 AA in 4 chains
1/3 of shown

Rings – protein pattern (HEWL) –
X-rays 30s @ 20kV on MAR345; <1mg HEWL

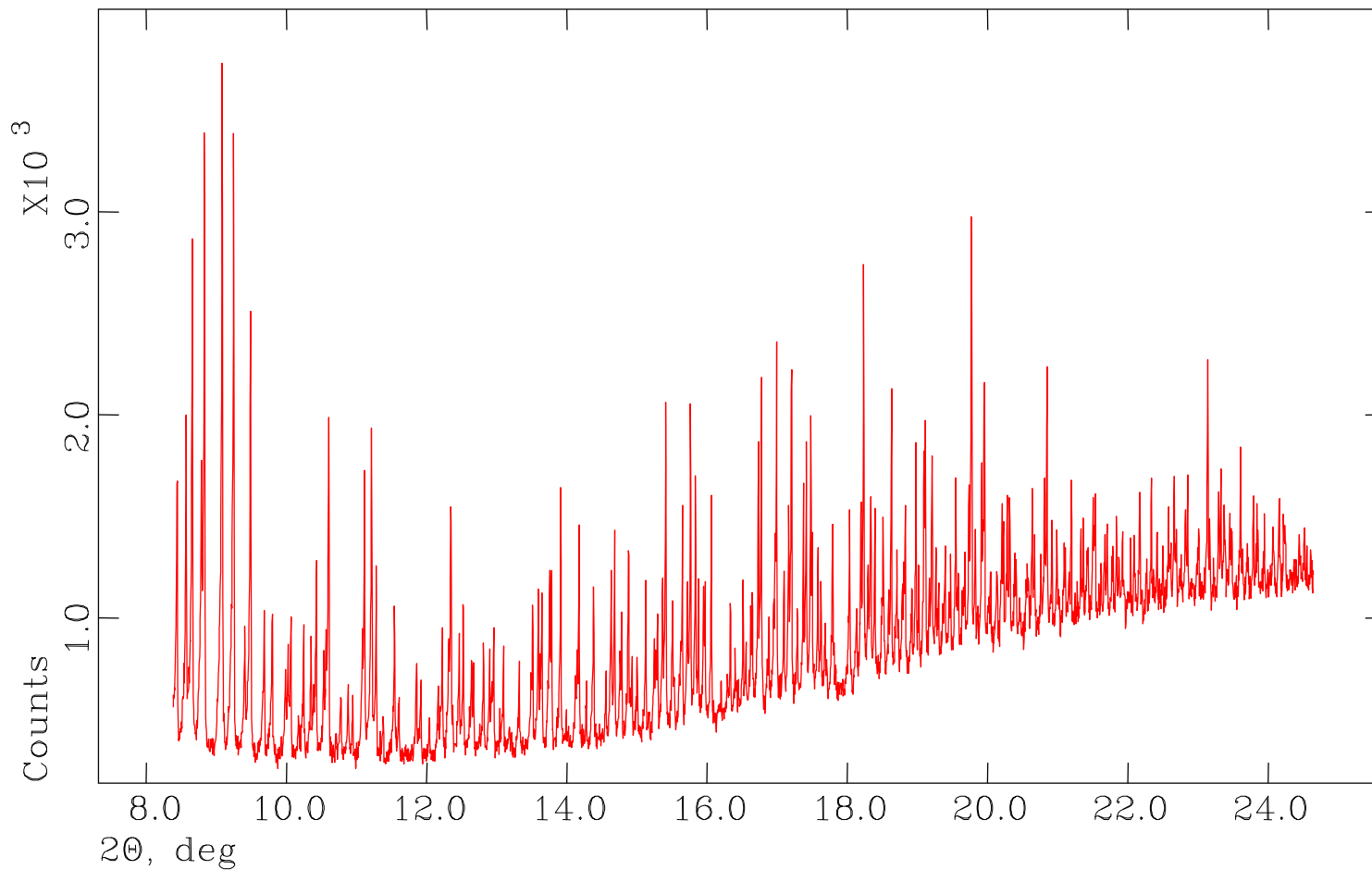


(Air, solvent & Kapton background subtracted)

- Texture free sample
& no graininess –
1 μ m “perfect” powder
- Resolution limit – 1.85Å
- Residual solvent scattering –
background
- Inner most ring – d~55Å
(110) Reflection, lowest order
for tetragonal lysozyme
2 Θ ~ 0.67deg
- Beam stop holder
- ~9000 F_{hkl} for HEWL >2Å

Protein powders – “ideal” ($1\mu\text{m}$ & no μstrain)

T₆ Zn insulin; NSLS X3b1; $\lambda=1.401\text{\AA}$

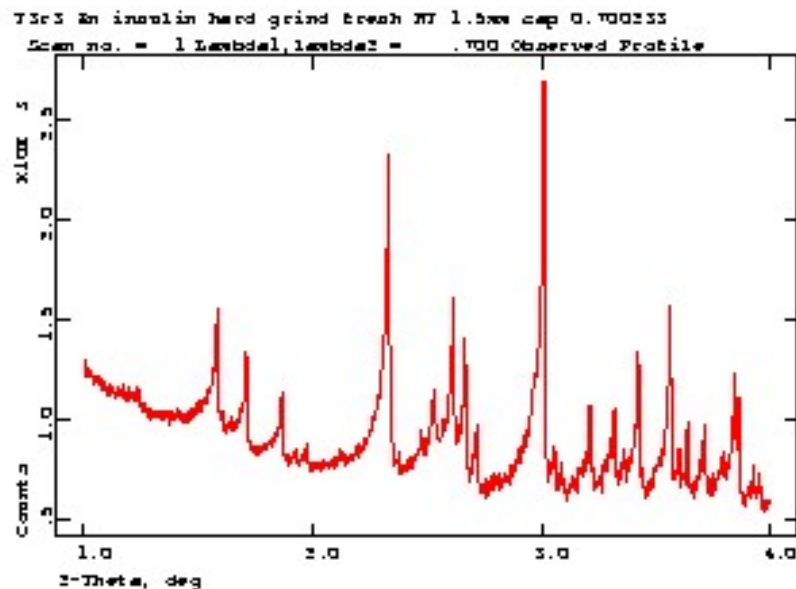


- Sharp peaks! (better than NIST SRM's!)

Initial experiments – various Zn-insulin phases T_6 , T_3R_3 , etc.

Grind T_3R_3 complex in agate mortar with mother liquor

High resolution synchrotron x-ray powder patterns (X3b1/NSLS)

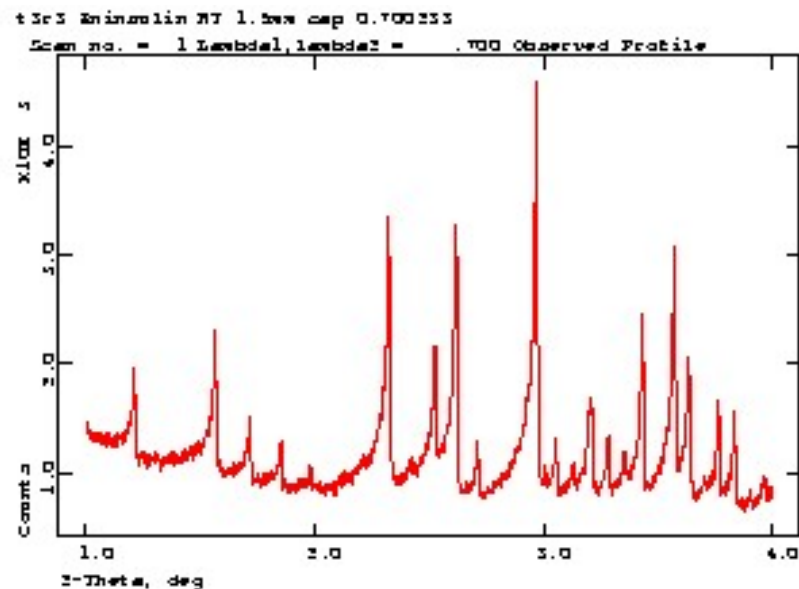


Immediately after grinding

Indexed – R3

$a=81.275\text{\AA}$, $c=73.024\text{\AA}$

New phase – T_3R_3DC



After 2 days rest

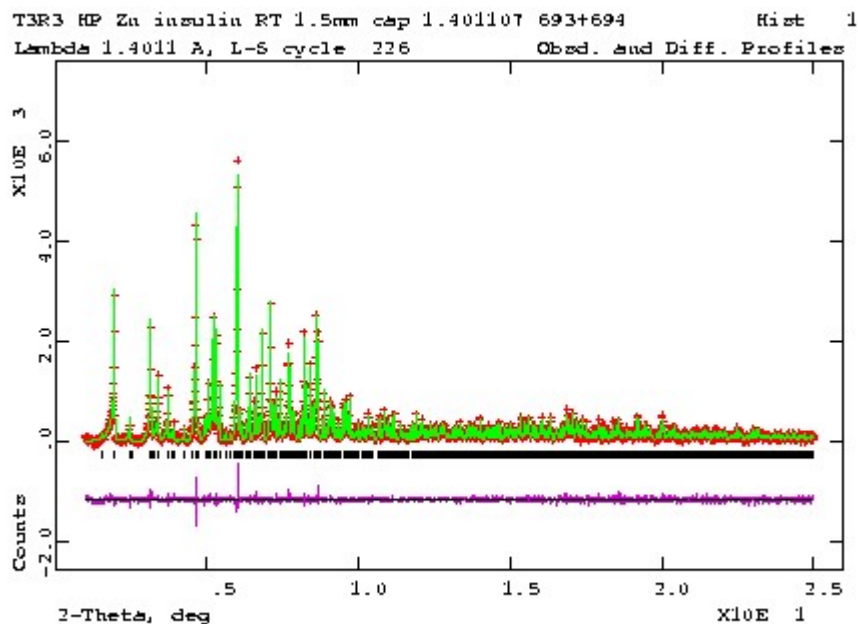
Indexed – R3

$a=81.084\text{\AA}$, $c=37.537\text{\AA}$

same as single xtal

X3b1/NSLS in Oct. 1999

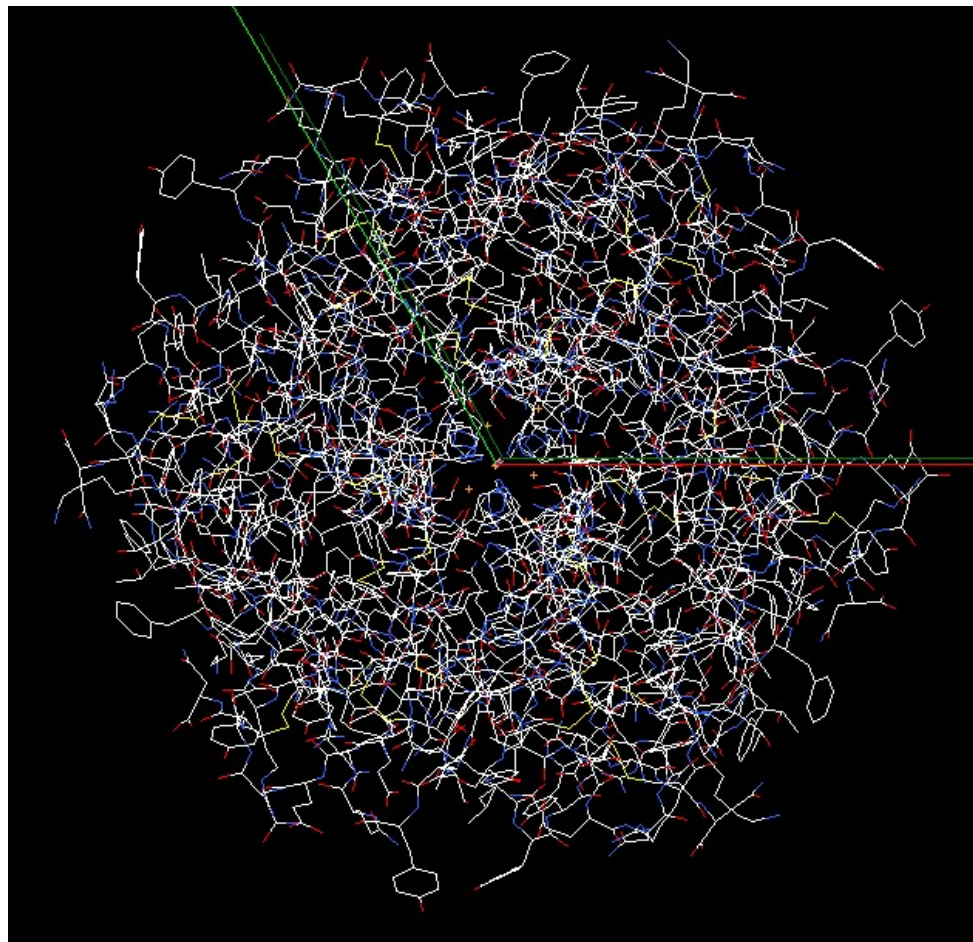
High Resolution X-ray Powder Diffraction on Proteins



Zn insulin structure determined from powder diffraction data

- R3 unit cell $a=81.276\text{\AA}$, $c=73.037\text{\AA}$
- Indexed from pattern
- $V=418,000\text{\AA}^3$!!
- >1600 atoms!!
- Rietveld refinement (GSAS)
- $R_{wp}=3.74\%$

1st Molecular replacement solution!!
3 parameter problem



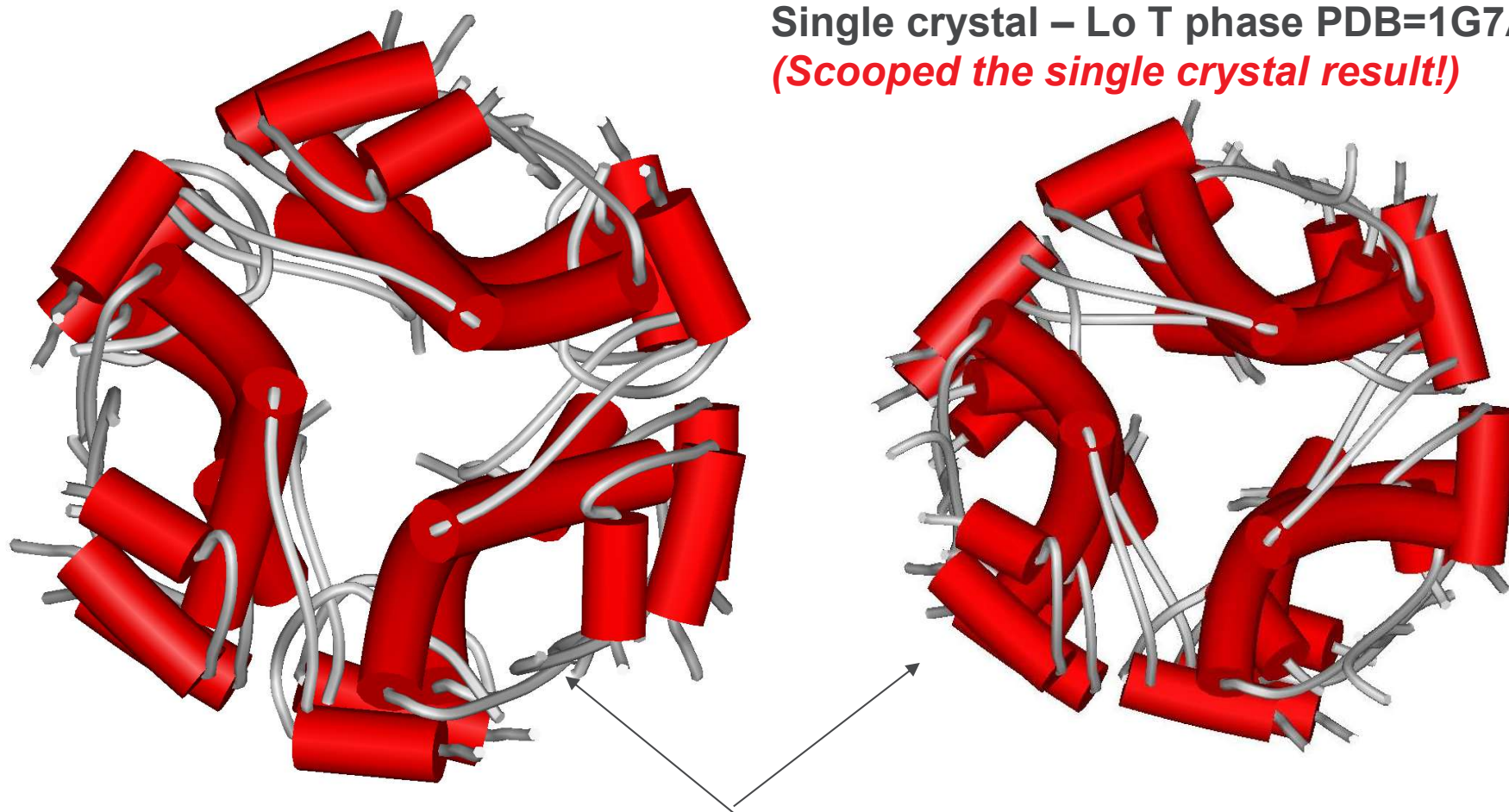
Schematic of T_3R_3 DC Zn-insulin complex.

Powder RT structure PDB=1FUB

Same structure as --

Single crystal – Lo T phase PDB=1G7A

(Scooped the single crystal result!)



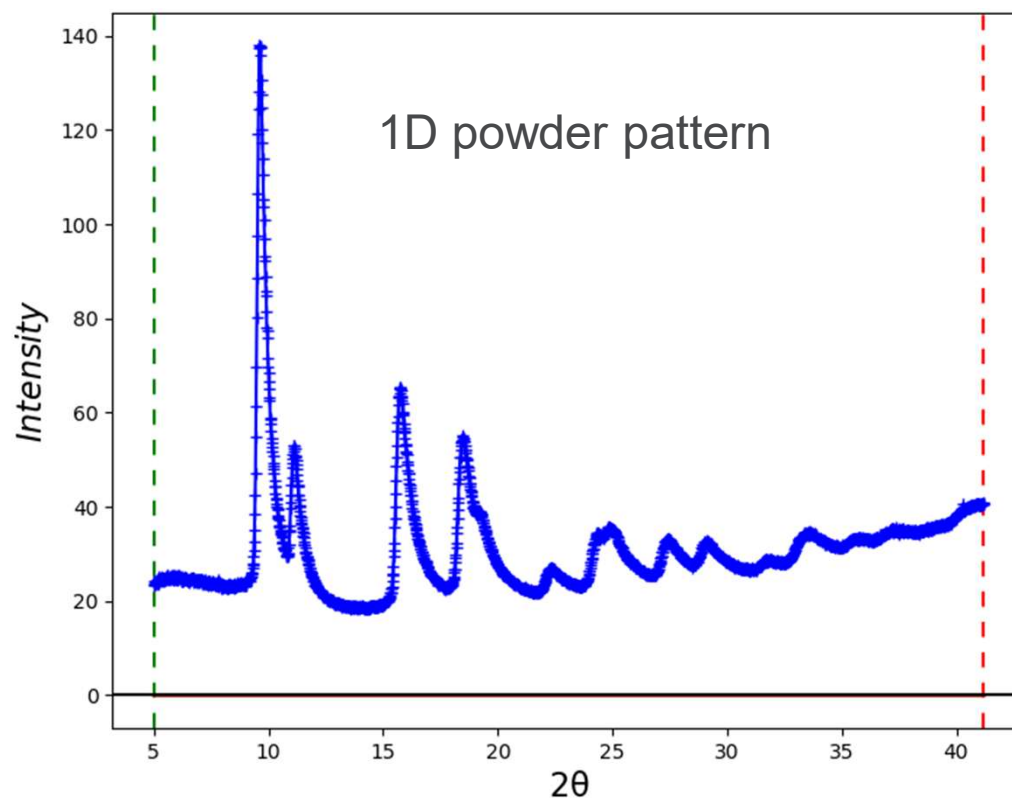
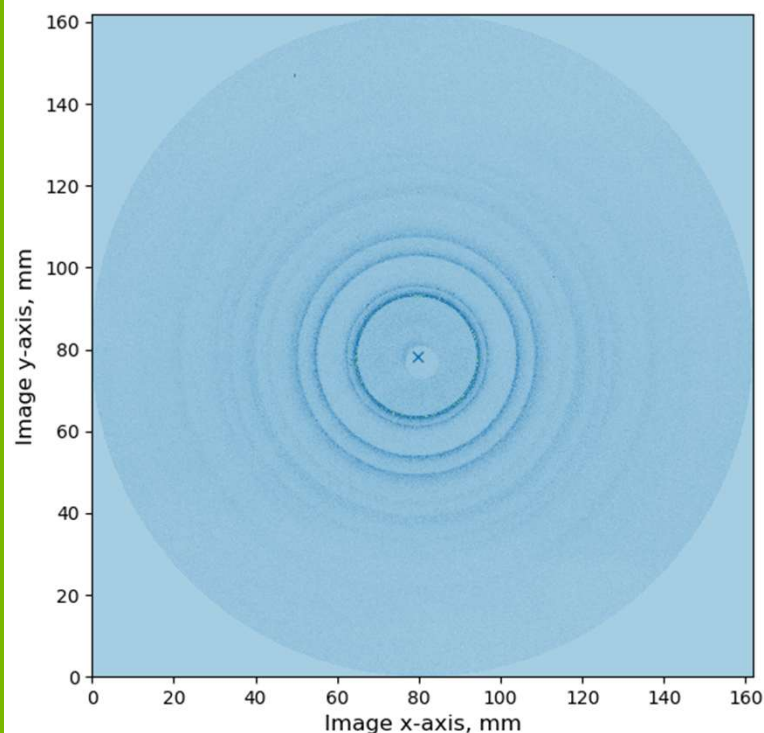
View down 3-fold axis - front T_3R_3 turned 9° wrt back T_3R_3

Von Dreele, R. B., Stephens, P. W., Blessing, R. H. & Smith, G. D. (2000). Acta Cryst. D56, 1549-1553.

Smith, G.D., Panghorn, W. & Blessing, R.H. (2001). Acta Cryst. D57, 1091-1100

FASTEST: DATA FROM LASER SHOCK STATION OF DYNAMIC COMPRESSION SECTOR AT APS

2d image from a single 100ps micropulse from APS for CeO_2



Strongly asymmetric peaks – resemble neutron TOF peaks.
NB: light travels ~3cm in 100ps!

PINK BEAM FUNCTION MATHEMATICS

Follows that of Von Dreele, Jorgenson & Windsor (1985) for TOF peaks

Back-to-back exponentials – peak position at join $\tau=0$

$$E(\tau) = \frac{\alpha\beta}{\alpha+\beta} e^{\alpha\tau} \text{ for } \tau < 0 \quad E(\tau) = \frac{\alpha\beta}{\alpha+\beta} e^{-\beta\tau} \text{ for } \tau > 0$$

Convolute with Gaussian

$$G(\Delta 2\Theta) = \frac{\alpha\beta}{2(\alpha + \beta)} e^u \operatorname{erfc}(y) + e^v \operatorname{erfc}(z)$$

where

$$u = \frac{\alpha}{2} (\alpha\sigma^2 + 2\Delta 2\Theta), v = \frac{\beta}{2} (\beta\sigma^2 - 2\Delta 2\Theta), y = \frac{\alpha\sigma^2 + \Delta 2\Theta}{\sqrt{2}\sigma^2} \text{ and } z = \frac{\beta\sigma^2 - 2\Delta 2\Theta}{\sqrt{2}\sigma^2}$$

Convolute with Lorentzian

$$L(\Delta 2\Theta) = \frac{\alpha\beta}{\pi(\alpha+\beta)} \{ \operatorname{Im}[e^p E_1(p)] + \operatorname{Im}[e^q E_1(q)] \}$$

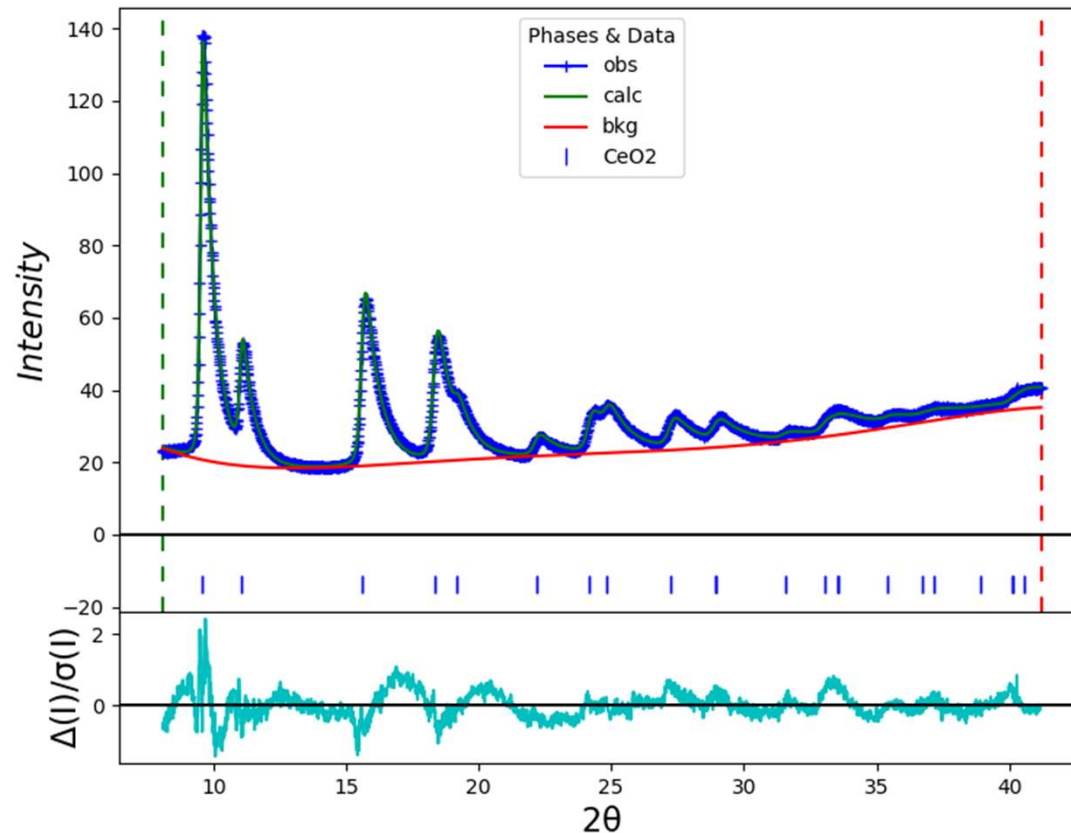
where

$$p = -\alpha\Delta 2\Theta + i\alpha\gamma/2 \text{ and } q = -\beta\Delta 2\Theta + i\beta\gamma/2$$

Combine: pseudo-Voigt $P(\Delta 2\Theta) = \eta L(\Delta 2\Theta) + (1 - \eta)G(\Delta 2\Theta)$

PINK BEAM FUNCTION & 1ST RIETVELD REFINEMENT

Assume conventional UVW Gaussian &
XY Lorentzian variation with Θ



α, β dependence with $\sin\Theta$

Good fit; $R_{wp} = 2.08\%$

∴ Crystal structures at very high pressures can be refined

RIETVELD REFINEMENT IN GSAS-II

RIETVELD MODEL: $I_C = I_i \{ \sum K_p F_p^2 M_p L_p P(\Delta_p) + I_B \}$

I_i - incident intensity - variable for fixed 2Θ (e.g. neutron TOF)

k_p - scale factor for particular phase

F_p^2 - structure factor for particular reflection

m_p - reflection multiplicity

L_p - correction factors on intensity - texture, etc.

$P(\Delta_p)$ - peak shape function - size & microstrain, etc.

Sum over all reflections under a profile point (multiple phases)

I_b – background function

More complex model than for single crystal diffraction

PROFILE FUNCTIONS $P(\Delta_p)$ – BASICS

$$\Delta_p = T_{\text{reflection}} - T_{\text{profile}} \quad (T = 2\Theta \text{ or TOF})$$

Gaussian profile - generally instrumental origin

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

Lorentzian profile - largely sample effect

$$L(\Delta T, \gamma) = \frac{2}{\pi \gamma} \frac{1}{1 + \left(\frac{2\Delta T}{\gamma} \right)^2}$$

Voigt – convolution = $G \otimes L$

Pseudo-Voigt – linear combination = $\eta L + (1-\eta)G$

η via Thompson, Cox & Hastings – pseudoVoigt = Voigt

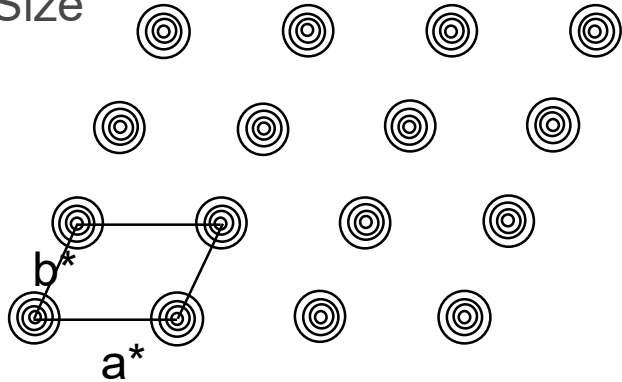
CW Asymmetry from axial divergence – Finger, Cox & Jephcoat

NB: in gsas & GSAS-II, T is 2Θ in centideg or TOF in μs

SAMPLE BROADENING

Isotropic Crystallite size & μ strain broadening

Size



Small ($<1\mu\text{m}$) crystals $\rightarrow$ not δ -functions

Size distribution $\rightarrow$

superposition of sharp to broad spots

$\rightarrow$ Shape $\sim$ Lorentzian

Width $\Delta d^* = \text{constant} = \Delta d/d^2 = \Delta \Theta \cot \Theta / d$

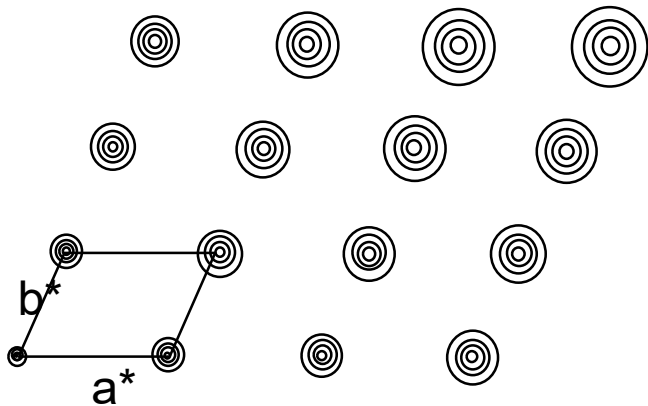
Bragg's Law: $\Delta 2\Theta = \lambda \Delta d/d^2 \cos \Theta (= X/\cos \Theta)$

$\rightarrow$ Scherrer equation

$k=1, p = \text{size}$

$$S = \frac{180k\lambda}{\pi p \cos \Theta}$$

μ strain



Unit cell variation (defects??)

Lorentzian distribution $\rightarrow$ shape

$\Delta d/d = \text{constant} = \Delta d^*/d^* = \Delta \Theta \cot \Theta$

Or: $\Delta 2\Theta = 2\Delta d \tan \Theta / d (= Y \tan \Theta)$

$$M = 180\mu \tan \Theta / \pi$$

$\mu - \mu\text{strain} (\times 10^6)$ parameter

CW PROFILE COEFFICIENTS

Lorentzian vs Gaussian sample broadening?

- Size: $S = \frac{180k\lambda}{\pi p \cos \Theta}$ μ strain: $M = 180\mu \tan \Theta / \pi$
- Need: S_Γ (Gauss) & S_γ (Lorentzian) sample broadening (2 slides back)

$$\Gamma_g^2 = 8\ln 2(U \tan^2 \Theta + V \tan \Theta + W + S_\Gamma)$$

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

- Mixing coeff for each; m_s & m_μ (NB: called 'mx' in GSAS-II; range 0-1)

$$S_\gamma = m_s S + m_\mu M$$

$$S_\Gamma = [(1 - m_s)^2 S^2 + (1 - m_\mu)^2 M^2] / 8\ln 2$$

- Normally m_s & $m_\mu = 1$ (all Lorentzian sample broadening) so:

$$S_\gamma = S + M$$

$$S_\Gamma = 0 \quad (\text{no Gaussian sample broadening})$$

- $X, Y, Z = 0$ (no Lorentzian instrument broadening)

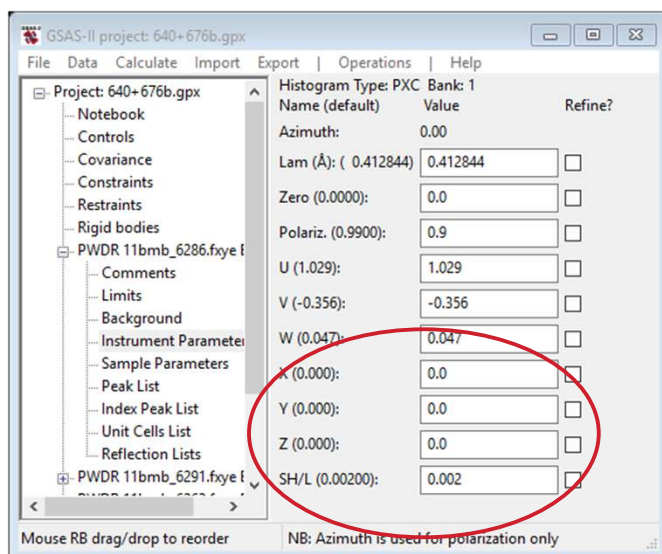
CW PROFILE PEAK BROADENING IN GSAS-II

The split of sample broadening from instrumental contribution

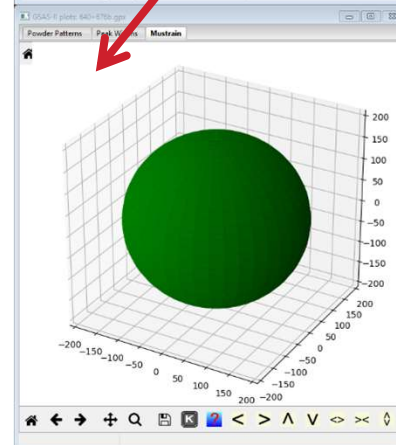
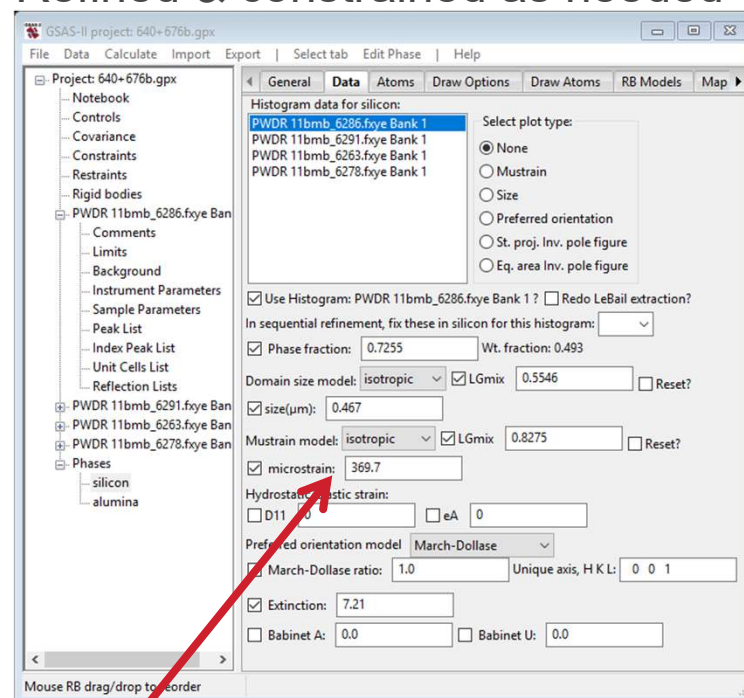
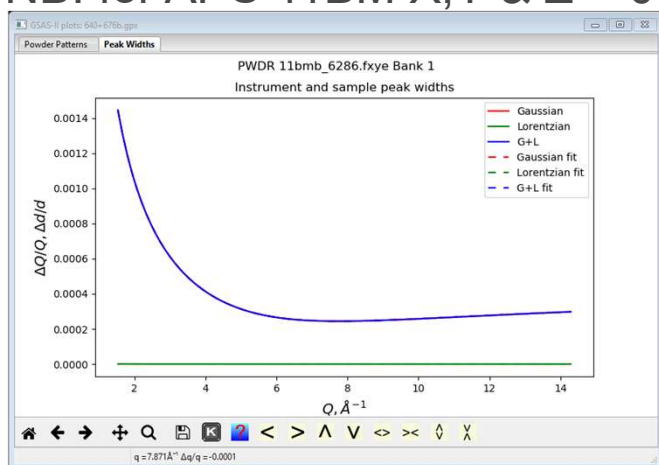
Instrument – fixed from calibration

Sample – phase & histogram dependent

Refined & constrained as needed



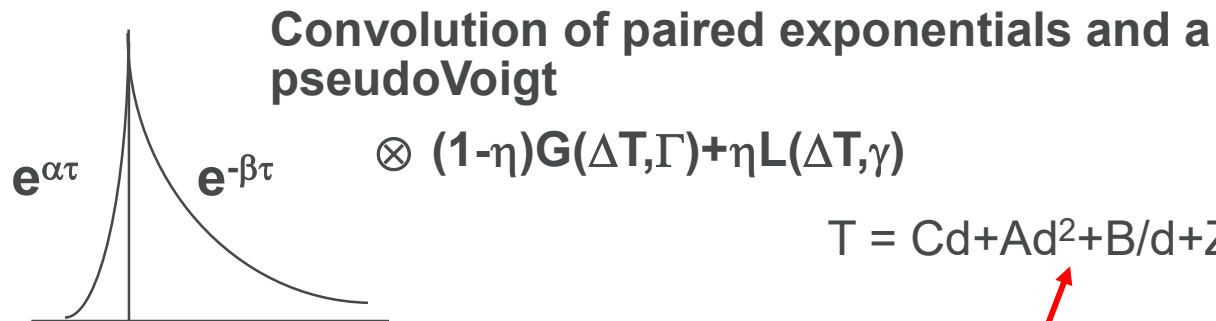
NB: for APS 11BM X, Y & Z = 0



Sample:
New NIST SRMS
640f & 676b

TOF PROFILE FUNCTION IN GSAS-II

The best of gas fxns 1, 3, 4 & 5 combined (2 is not implemented)



$$T = Cd + Ad^2 + B/d + Z$$

$$H(\Delta T) = (1 - \eta)N[e^u \operatorname{erfc} y + e^v \operatorname{erfc} z] - \frac{2N\eta}{\pi} \{ \operatorname{Im}[\exp(p)E_1(p)] + \operatorname{Im}[\exp(q)E_1(q)] \}$$

N, p, q, u, v, x & y functions of α , β , σ & γ

Empirical relationships to d-spacing

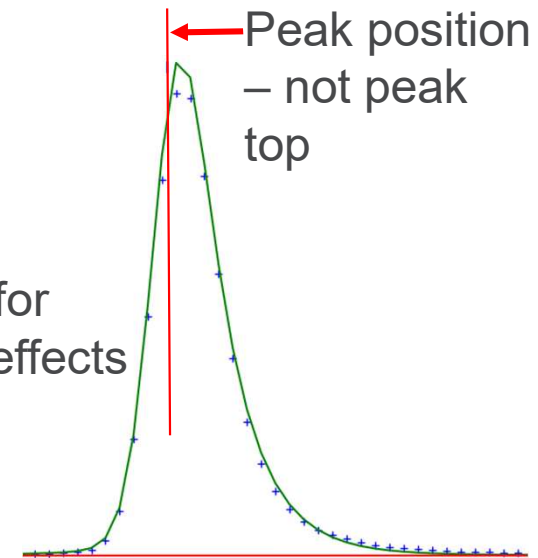
$$\alpha = \alpha_0/d; \beta = \beta_0 + \beta_1/d^4 + \beta_q/d^2$$

$$\sigma^2 = s_0 + s_1d^2 + s_2d^4 + S_qd + S_\Gamma$$

$$\gamma = Xd + Yd^2 + Z + S_\gamma$$

Sample broadening terms - earlier slide; may be hkl dependent²⁴

New terms for epithermal effects



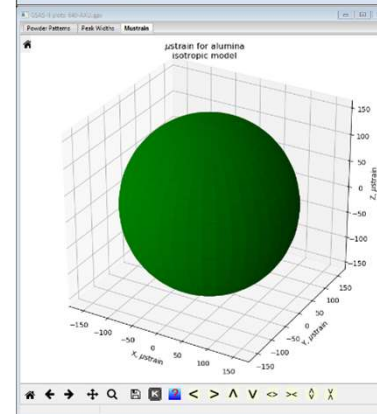
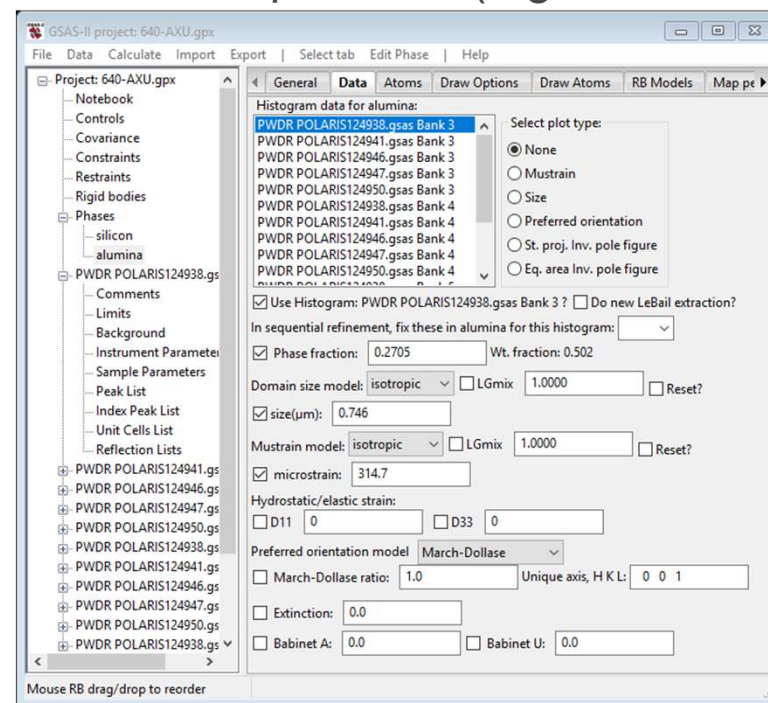
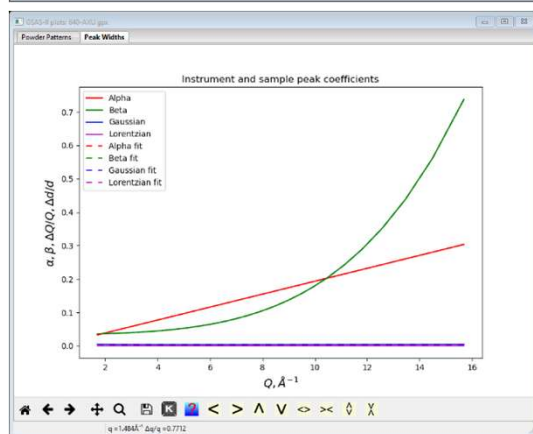
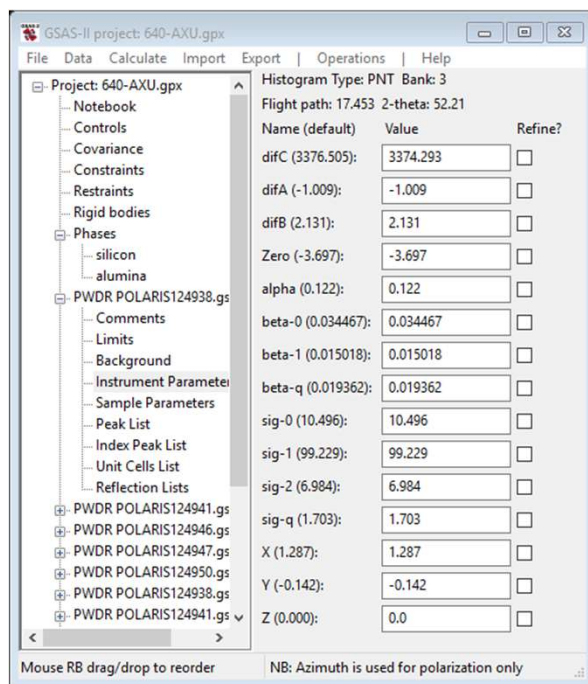
TOF PROFILE PEAK BROADENING IN GSAS-II

The split of sample broadening from instrumental contribution

Instrument – fixed from calibration

Sample – phase & histogram dependent

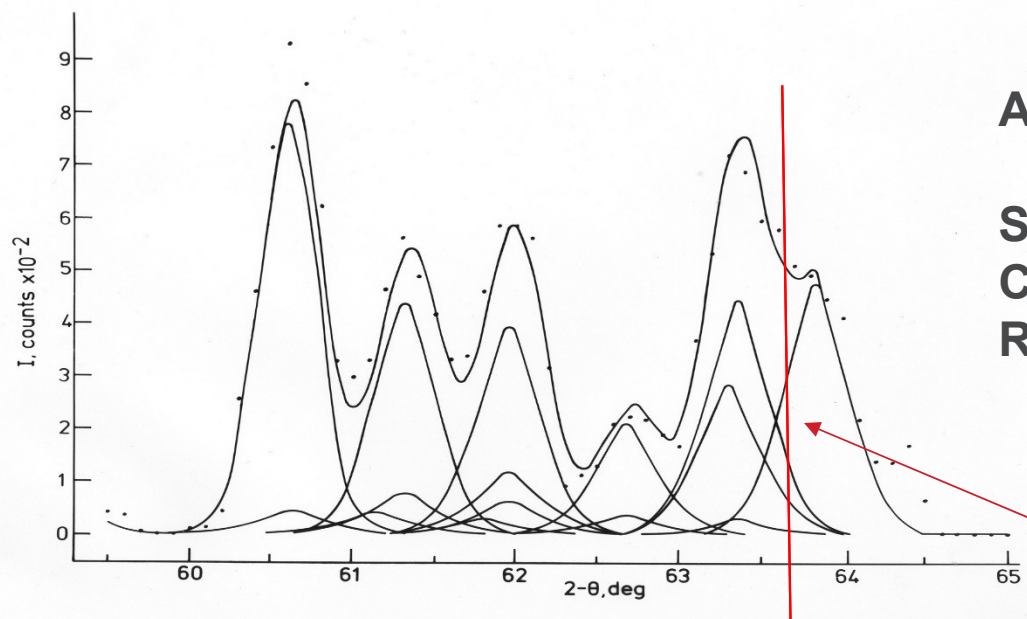
Independent of experiment (e.g. CW or TOF)



Sample:
New NIST SRMS
640f & 676b

INTENSITY EXTRACTION

Structure factors from powder patterns? → structure solution



Apportion I_o by ratios of $I_c(H)$
for contributing reflections →
Sum over all under peak profile
Correct for multiplicity & L_p , etc.
Result is $F^2(H)$

Here 4 reflections contribute

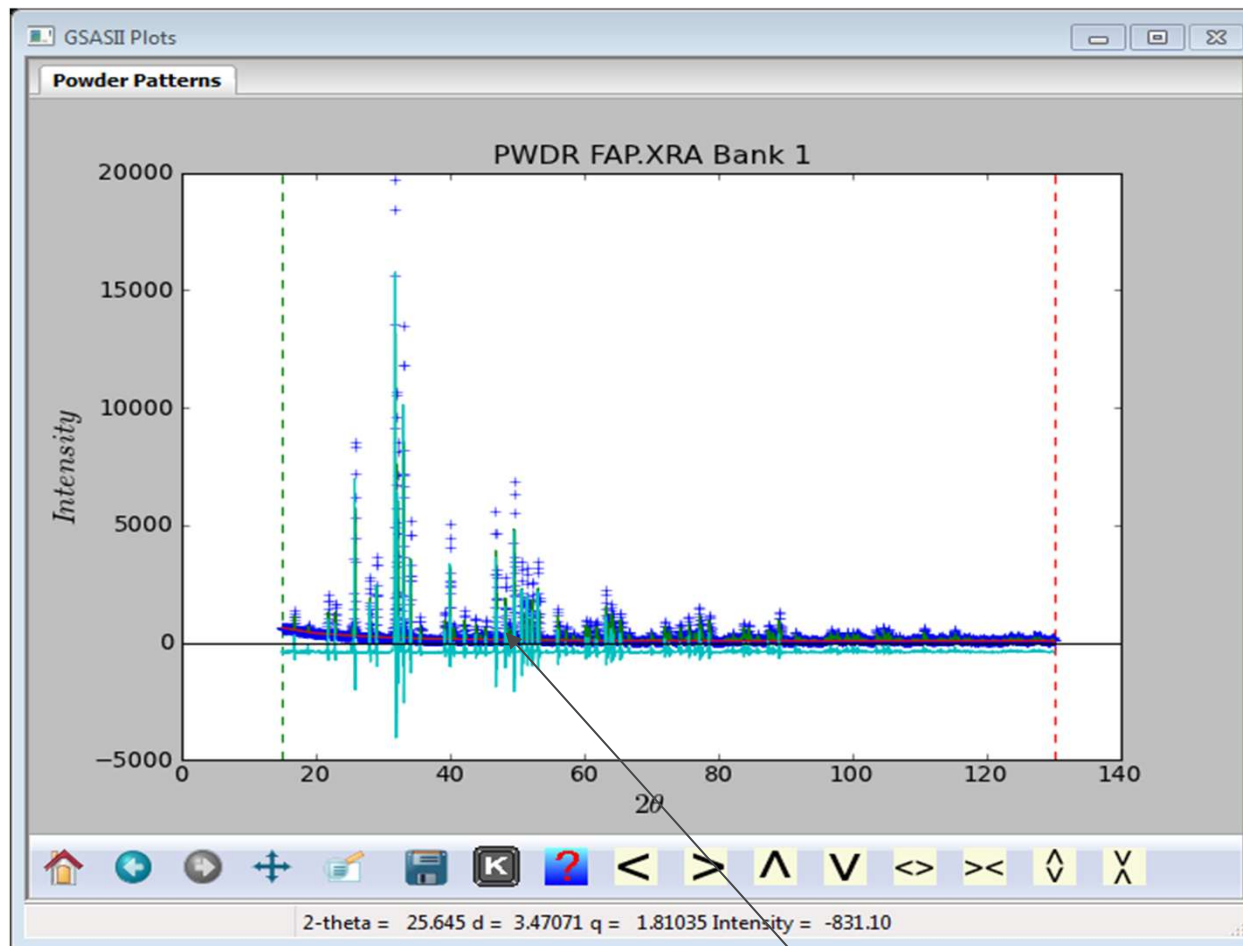
LeBail algorithm – extracted $F^2_o \rightarrow$ new F^2_c then next cycle;
refine only background, peak shapes & positions – few parameters
No constraints needed for overlaps – Simple

Pawley refinement – F^2_o are parameters
+ background, peak shapes & positions – many parameters
Constraints & restraints required for overlaps - Complex

RIETVELD REFINEMENT – A SIMPLE EXAMPLE

AN EXAMPLE: FLUROAPATITE

Add atoms & do default initial refinement
– scale & background



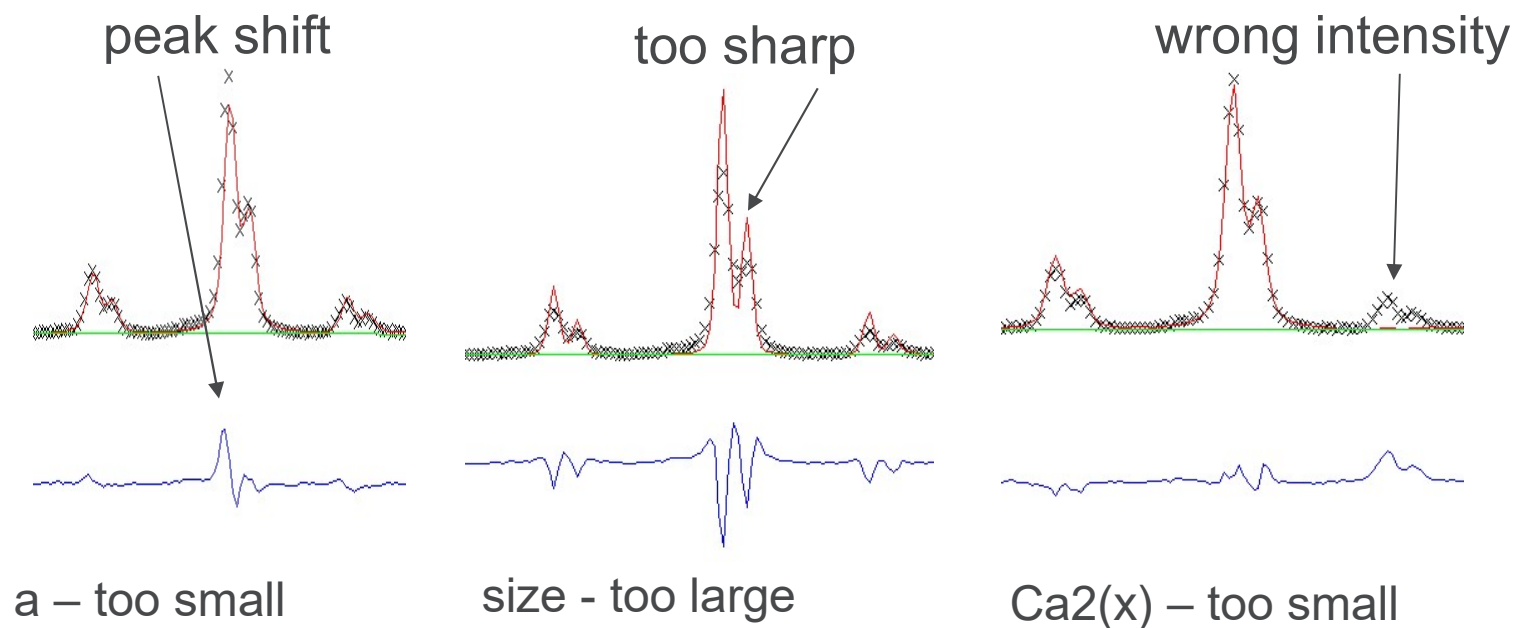
- Notice shape of difference curve – position/shape/intensity errors

ERRORS & PARAMETERS?

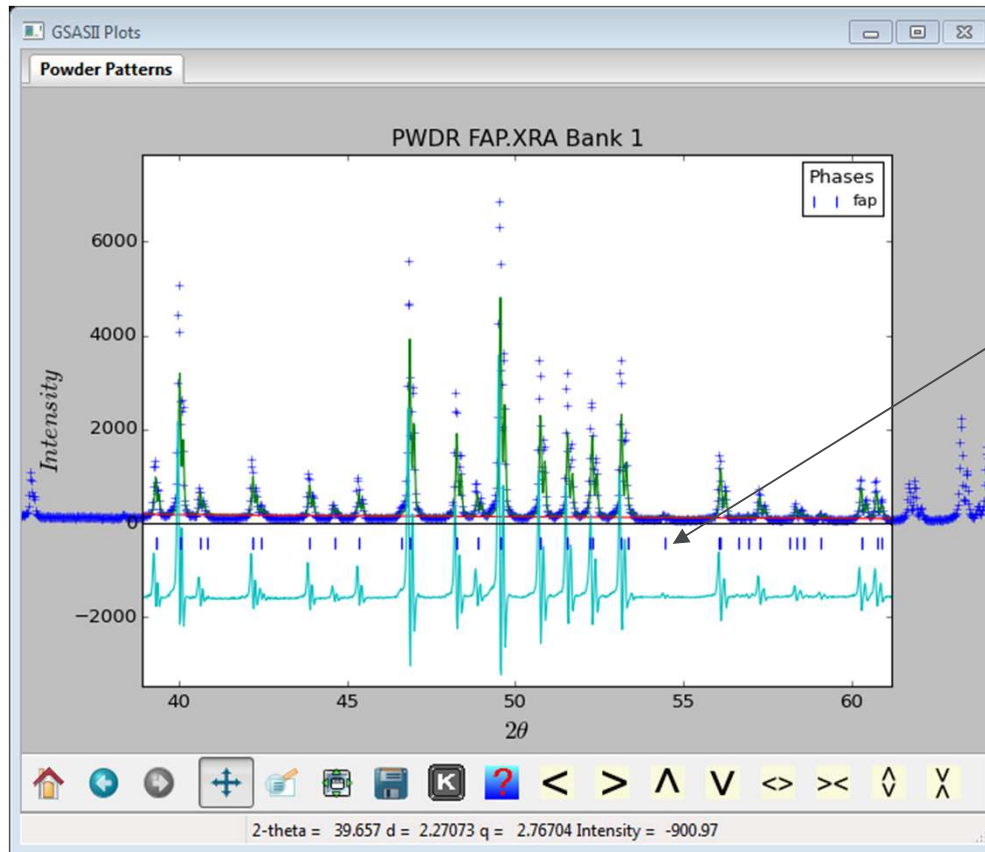
- position – lattice parameters, zero point (not common)
 - other systematic effects – sample shift/offset
- shape – profile coefficients – sample size/ μ strain
 - (U, V, W, X, Y, etc. in GSAS-II are instrument parms.)
- intensity – crystal structure (atom positions & thermal parameters)
 - other systematic effects (absorption/extinction/preferred orientation)

NB – get linear combination of all the above

NB² – trend with 2Θ (or TOF) important



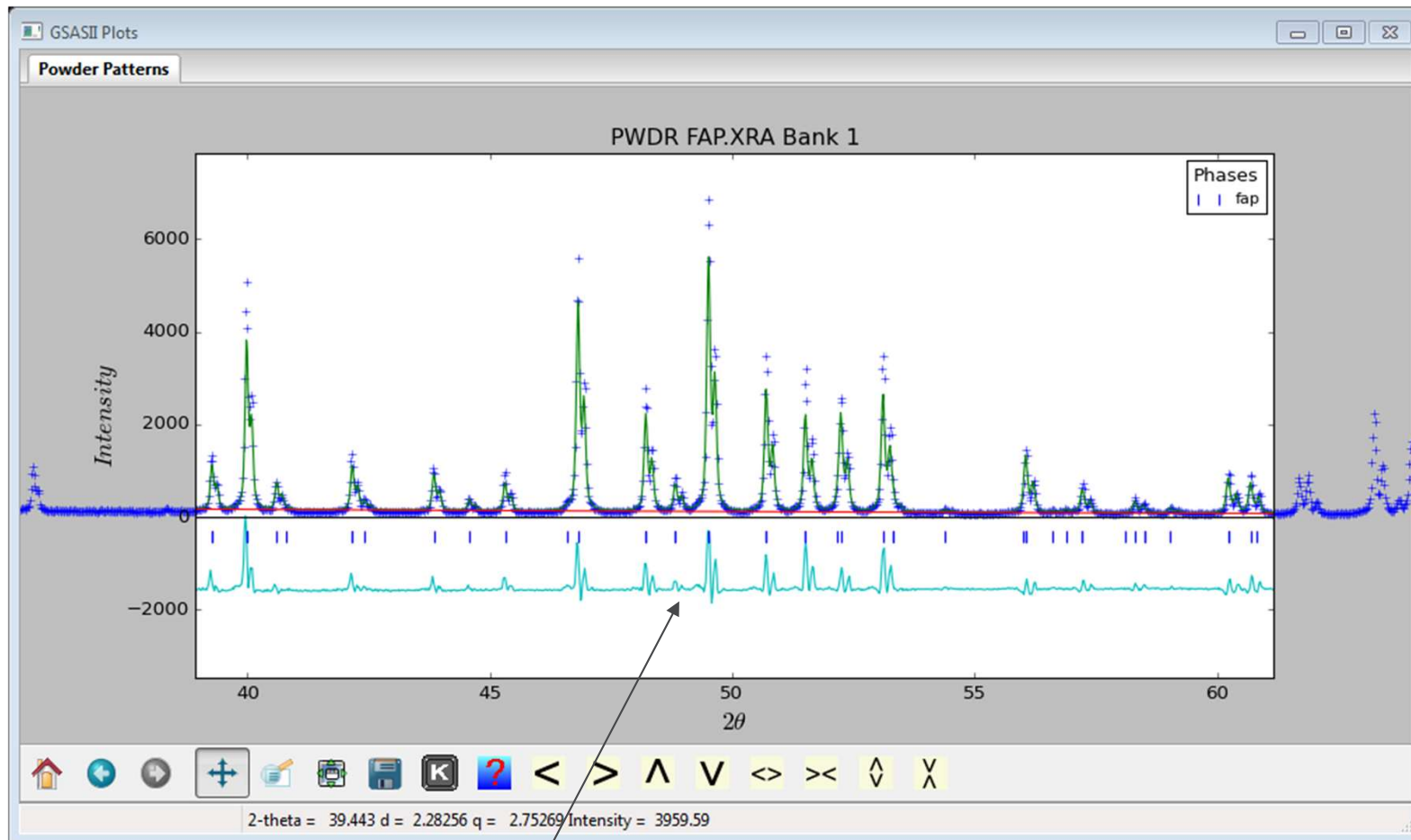
DIFFERENCE CURVE – WHAT TO DO NEXT?



Characteristic “up-down-up”
→ profile error
NB – can be “down-up-down” for too “fat” profile

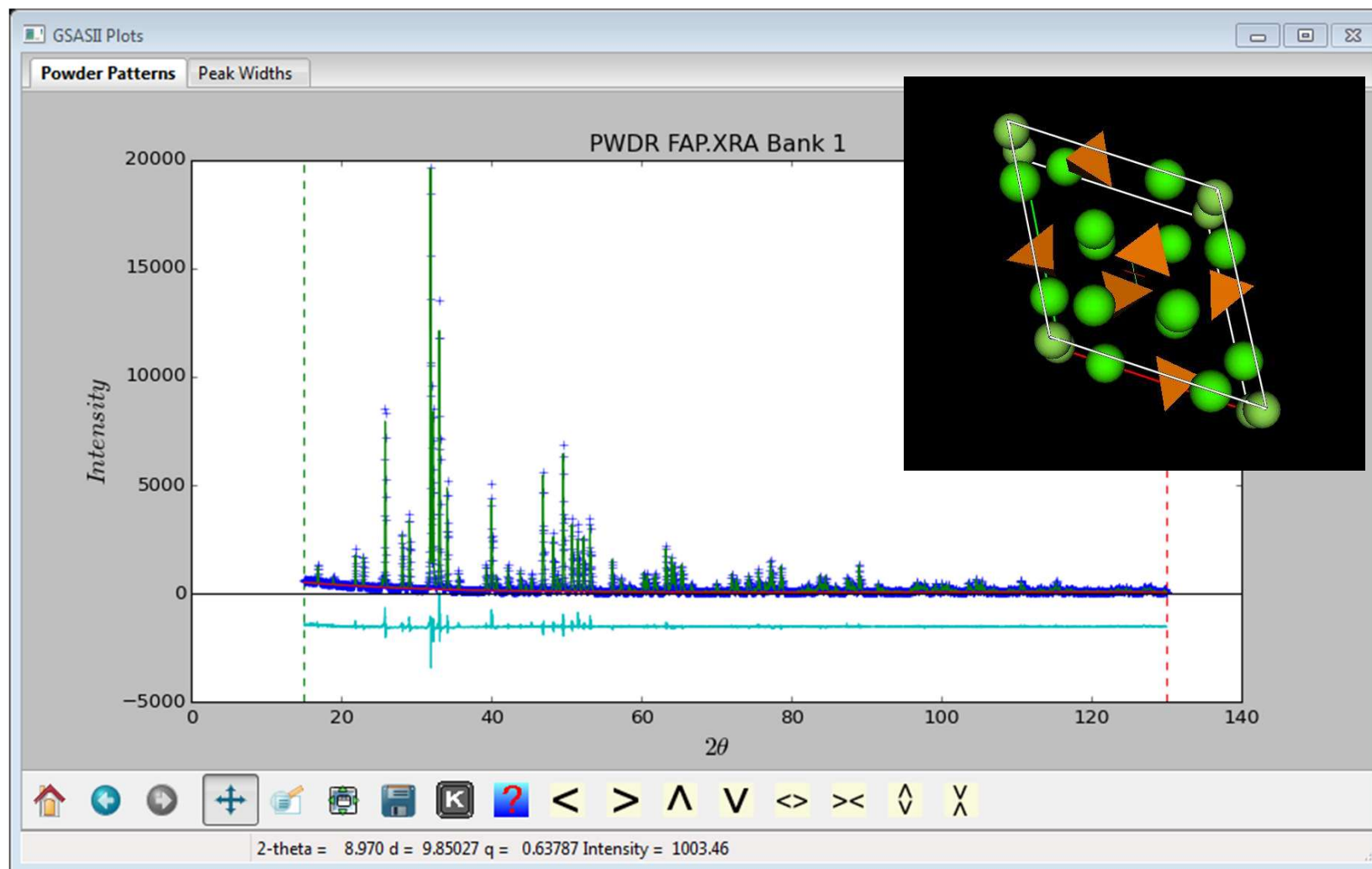
- Dominant error – peak positions? peak shapes - too sharp?
- Refine sample μ strain parameter next & include lattice parameters
- **NB - EACH CASE IS DIFFERENT – no magic recipe**

RESULT – MUCH IMPROVED!



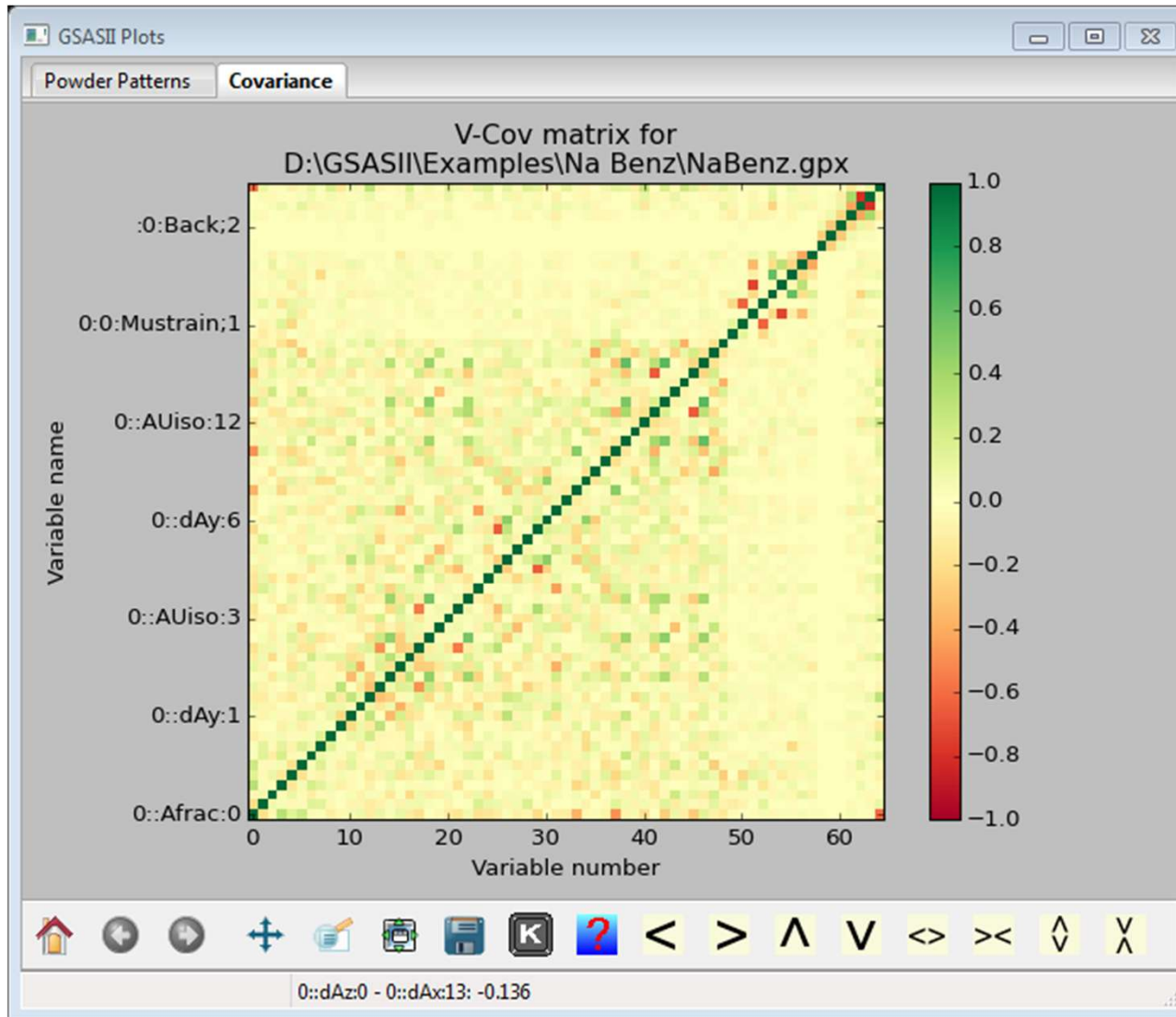
- maybe intensity differences remain
– refine coordinates & thermal parms.

RESULT – ESSENTIALLY UNCHANGED



- Thus, major error in the initial model –
peak shapes & sample displacement/lattice parameters

A USEFUL PLOT – COVARIANCE MATRIX



Green: $\text{cov} > 0$
Red: $\text{cov} < 0$
Yellow: $\text{cov} \sim 0$
Cursor
reports:
Cov or
value(esd)
on diagonal
Can be
zoomed!

**Beware white
bands & nan:
Singularities!**

THANK YOU