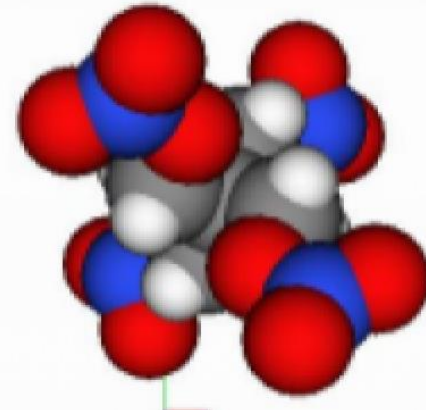


# THE RIETVELD REFINEMENT METHOD

# GSAS-2



R. B. VON DREELE  
ANL/APS (retired)  
vondreele@anl.gov

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

Acknowledgements: DOE/SC

# HISTORY – H.M. RIETVELD



Hugo Rietveld; neutron powder diffractometer, Petten, Netherlands

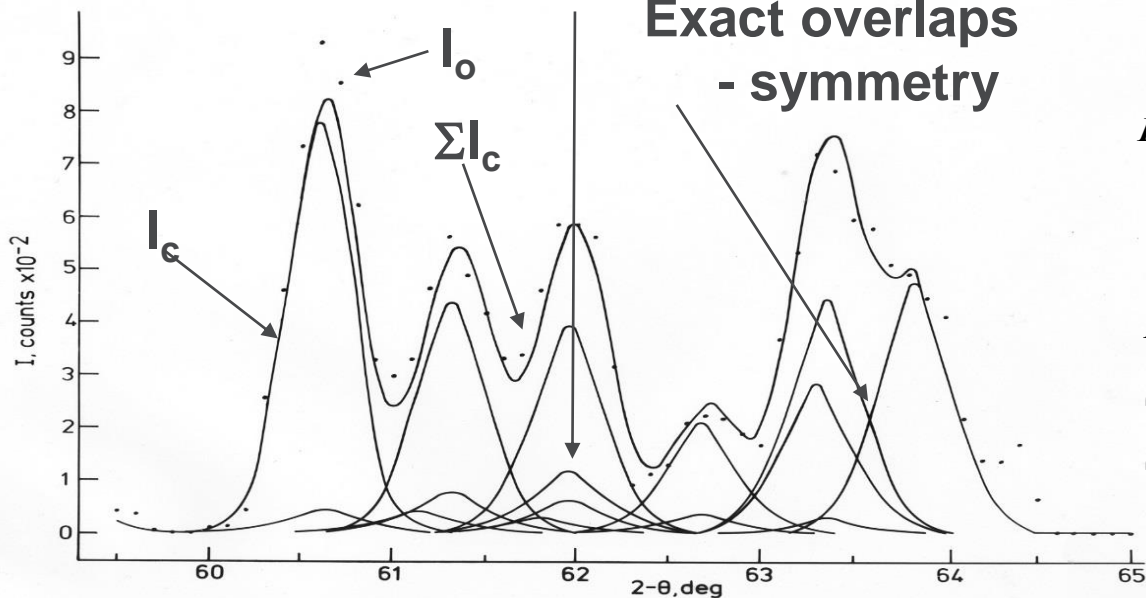
Papers: H.M. Rietveld, Acta Cryst. 22, 151-2(1967)

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

Multi-parameter, nonlinear LS curve fitting

Incomplete overlaps

Exact overlaps  
- symmetry



Residuals:

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

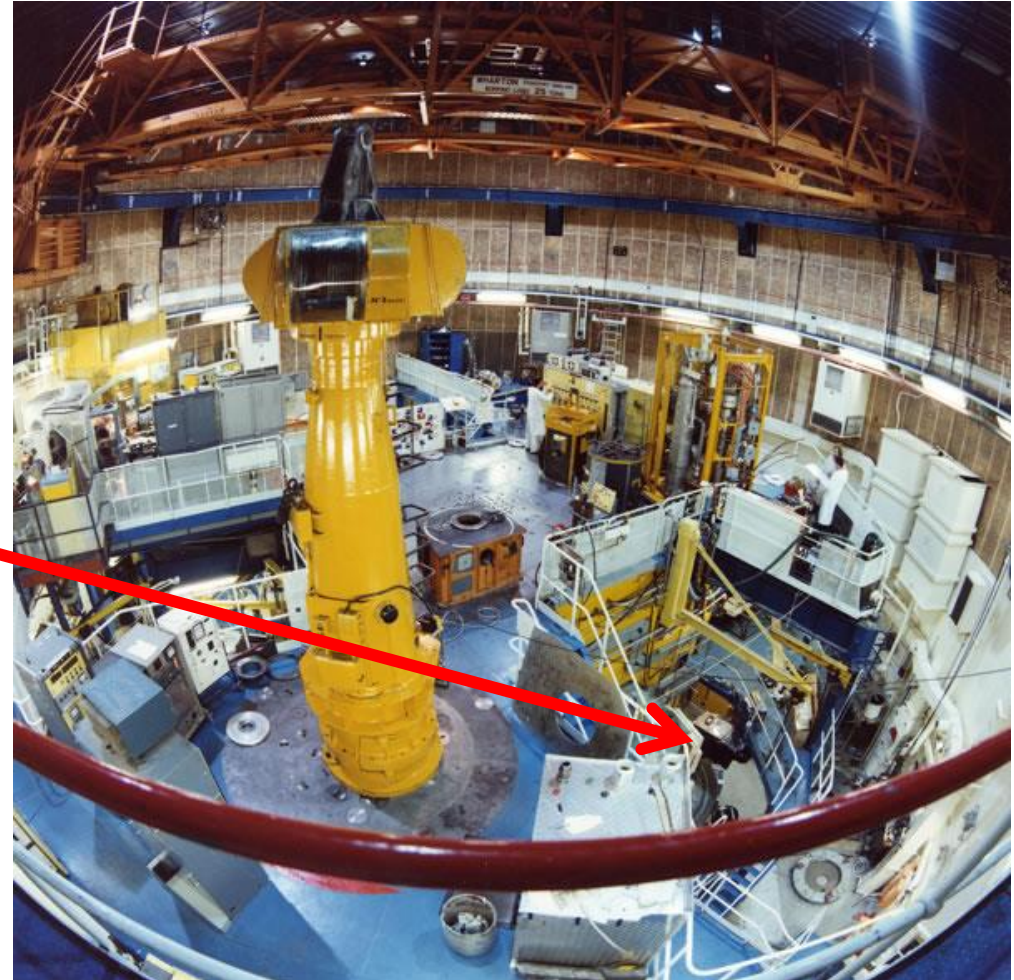
Rietveld Minimize

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

“chi-squared” or  
“goodness-of-fit”

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

# PLUTO REACTOR AERE HARWELL – 1970'S



PANDA Diffractometer ?

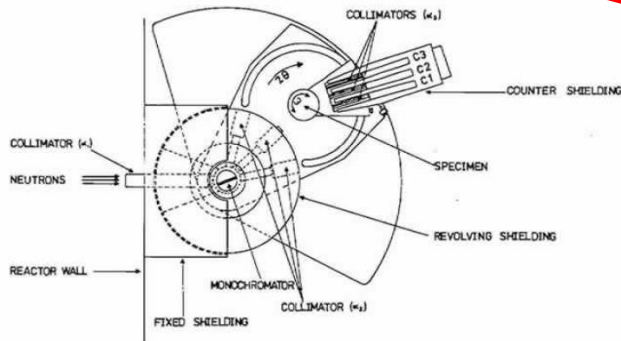
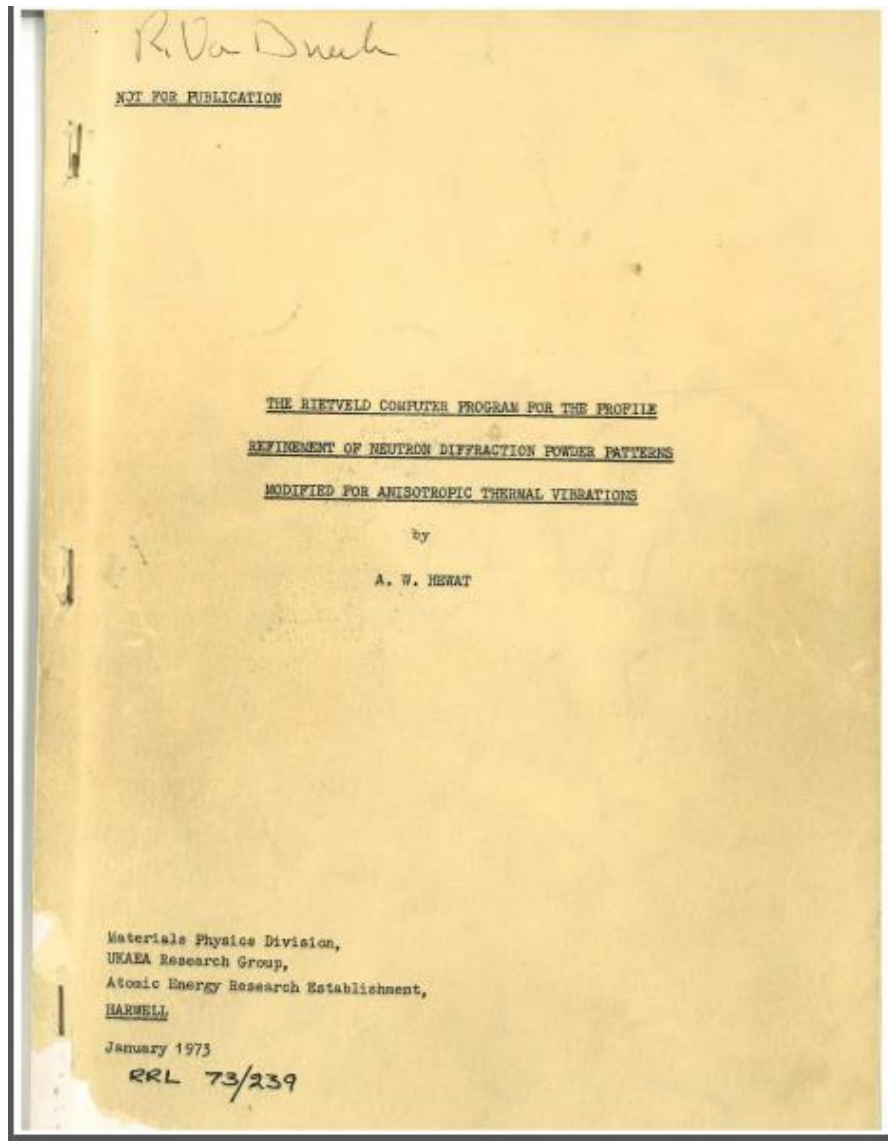


Fig. 2. A schematic diagram of a neutron powder diffractometer named PANDA which is installed at A.E.R.E. Harwell.

AKC & RBVD experiments:  $2\Theta_m$   $92^\circ$ ,  
 $\lambda=1.57\&1.61\text{\AA}$ ,  $2\text{-}2.5\times 10^5$  n/scm<sup>2</sup>, 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.

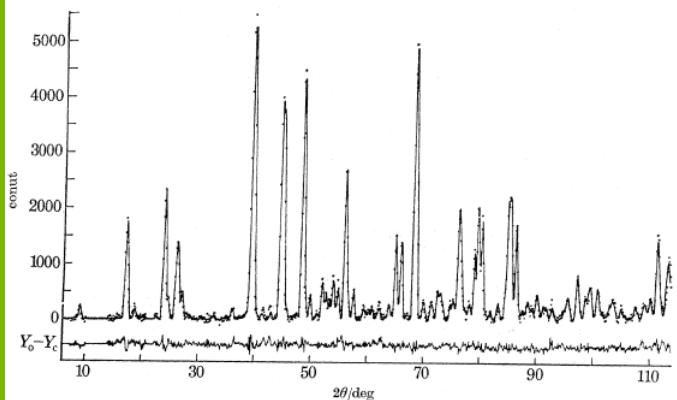
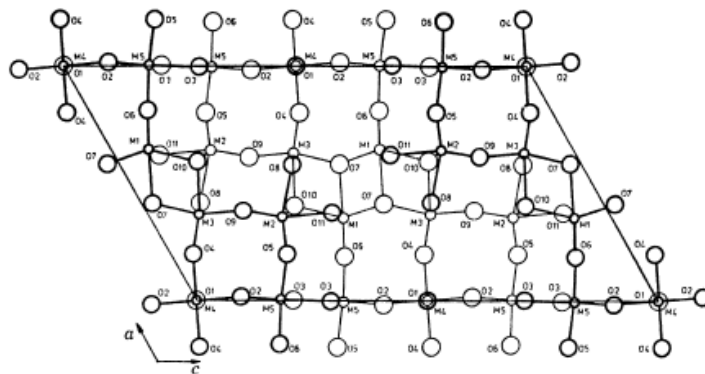


FIGURE 3. Neutron powder diffraction profile for  $\text{TiNb}_2\text{O}_7$ . Lines and points represent calculated and observed profiles, respectively. A difference curve is shown.



$\text{TiNb}_2\text{O}_7$ ;  $A2/m$ ,  $a=11.89$ ,  $b=3.80$ ,  $c=20.37$ ,  $\beta=120.2^\circ$   
603 refl., 1077 data points

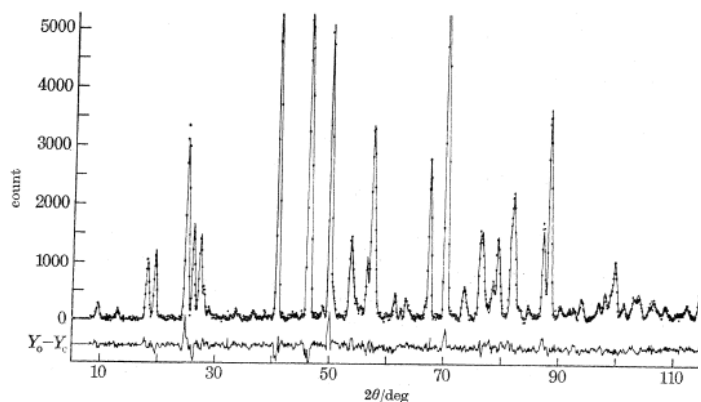
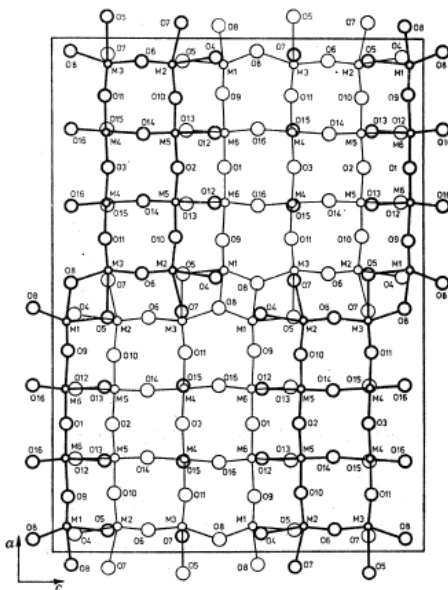


FIGURE 4. Neutron powder diffraction profile for ortho- $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ . Lines and points represent calculated and observed profiles, respectively. A difference curve is also shown.



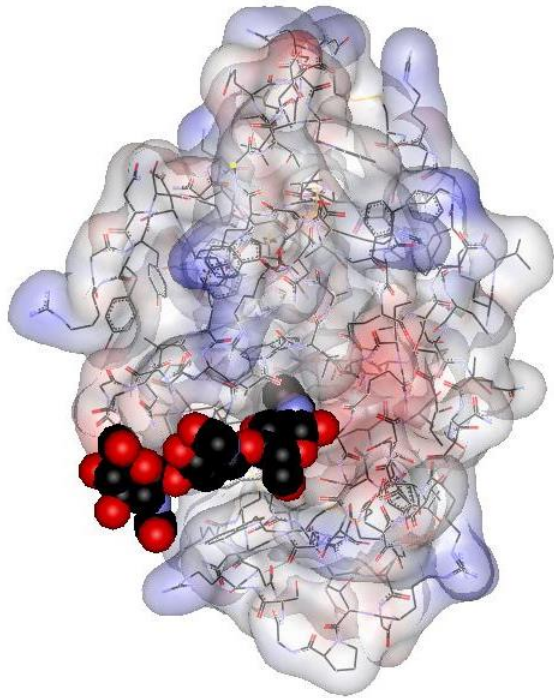
o- $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ ,  $Amma$ ,  
 $a=28.30$ ,  $b=3.78$ ,  $c=20.35$   
843 refl., 1116 data points

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.

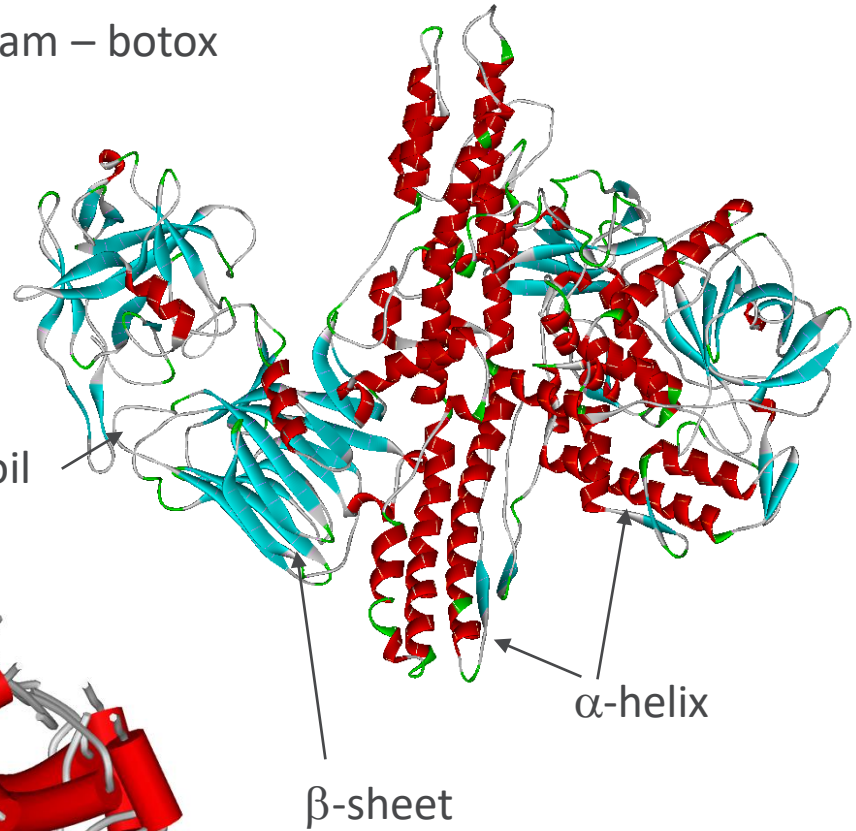
# A FEW MORE RIETVELD REFINEMENT EXAMPLES – BIGGEST & FASTEST

# Biggest: Proteins – polymers of amino acids - representations



Space filling (HEWL+NAG<sub>3</sub>)  
129 AA

Ribbon diagram – botox  
~1100AA



random coil

α-helix

β-sheet

α-helix

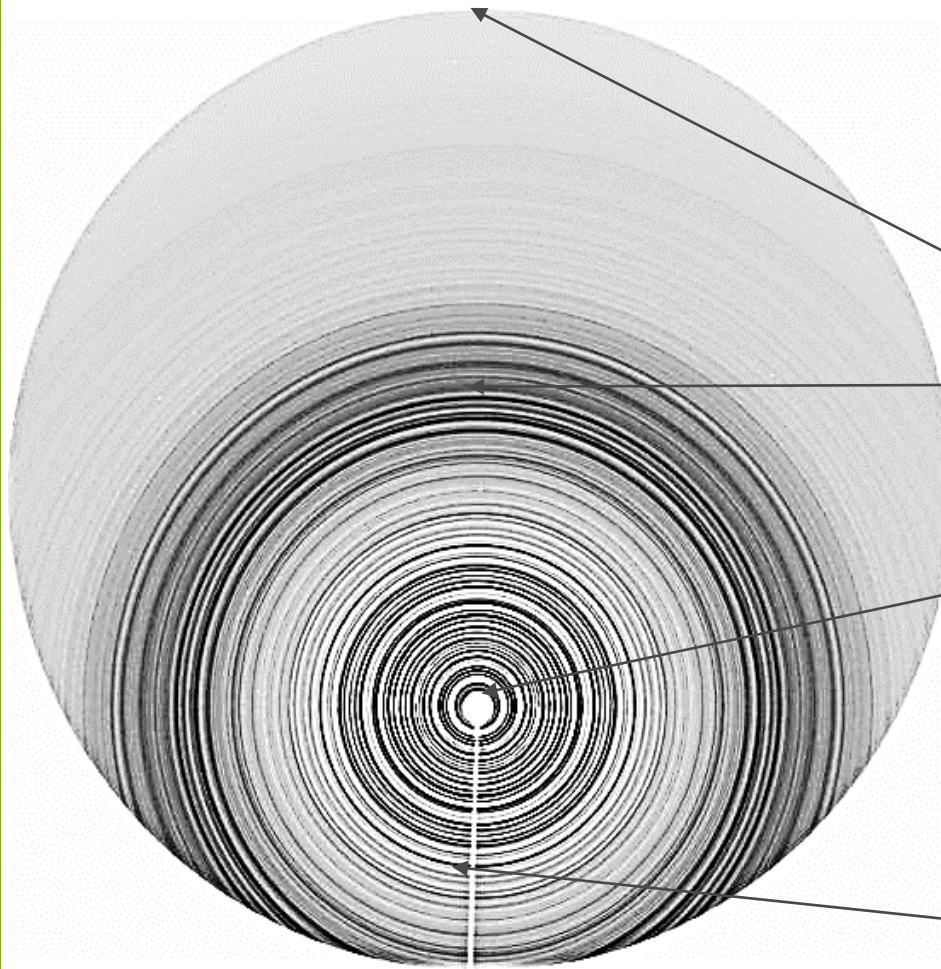


Schematic – insulin  
102 AA in 4 chains  
1/3 of shown



# Rings – protein pattern (HEWL) –

X-rays 30s @ 20kV on MAR345; <1mg HEWL



Texture free sample  
& no graininess –  
1 $\mu$ m “perfect” powder  
Resolution limit – 1.85Å  
Residual solvent scattering –  
background

Inner most ring – d~55Å  
(110) Reflection, lowest order  
for tetragonal lysozyme  
2 $\Theta$  ~ 0.67deg

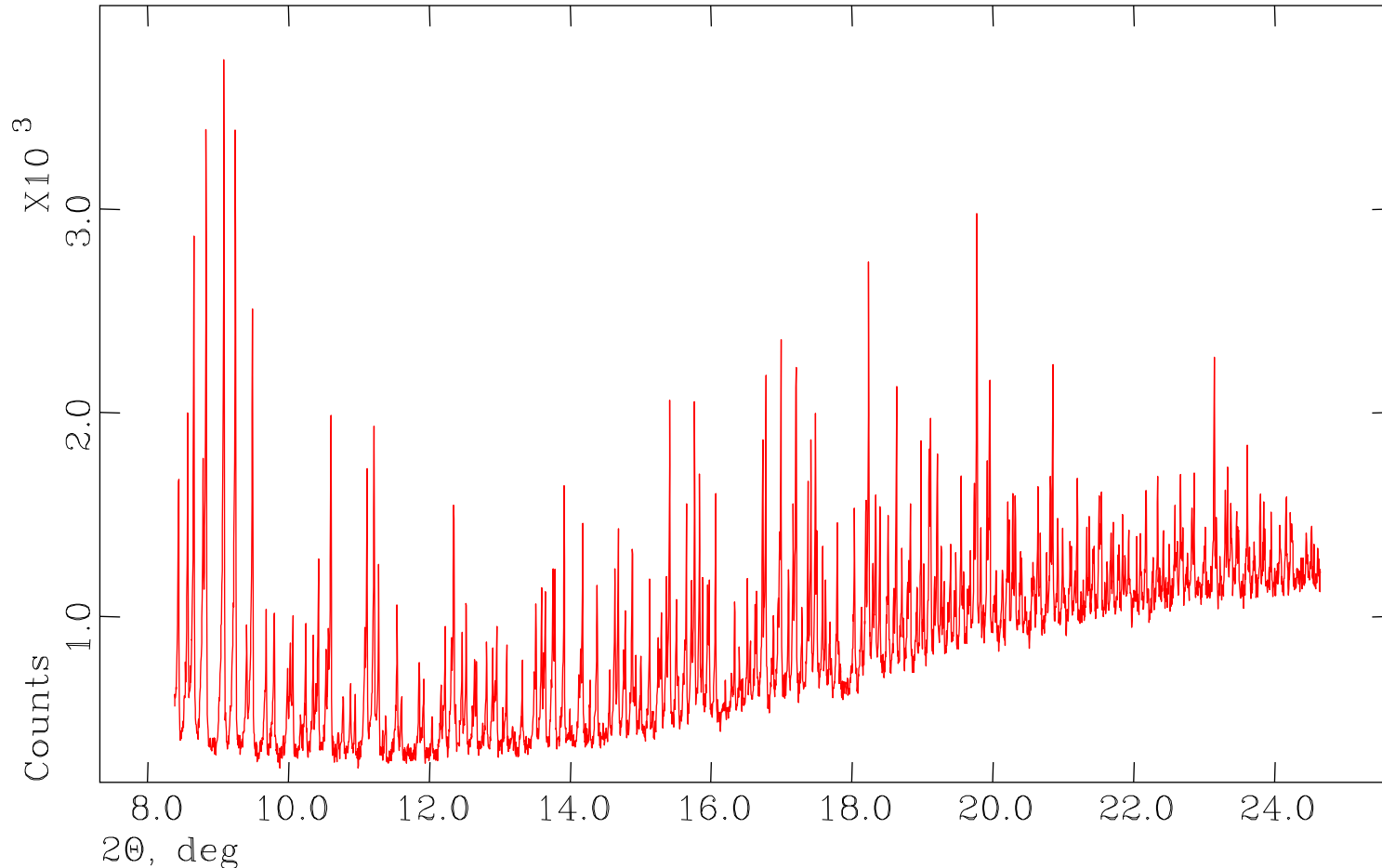
Beam stop holder

~9000  $F_{hkl}$  for HEWL >2Å

(Air, solvent & Kapton background subtracted)

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

$T_6$  Zn insulin; NSLS X3b1;  $\lambda=1.401\text{\AA}$

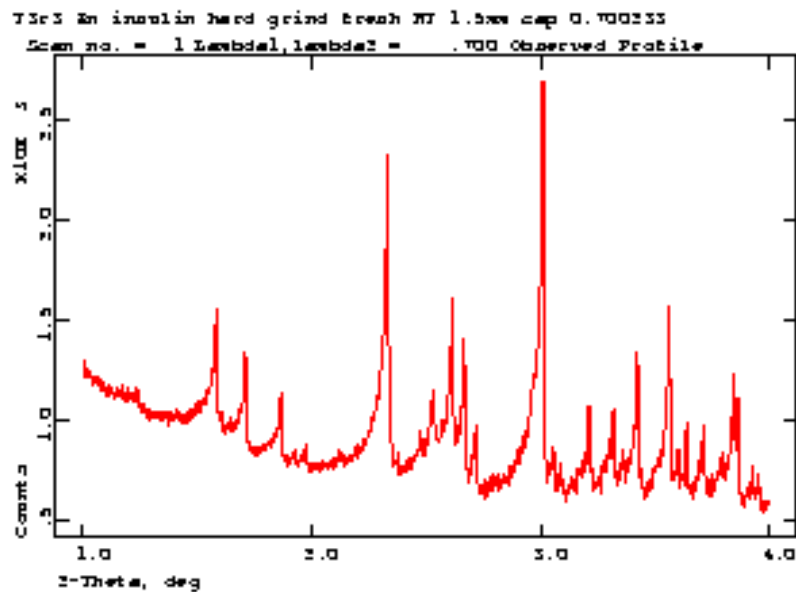


- Sharp peaks! (better than NIST SRM's!)

## 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)

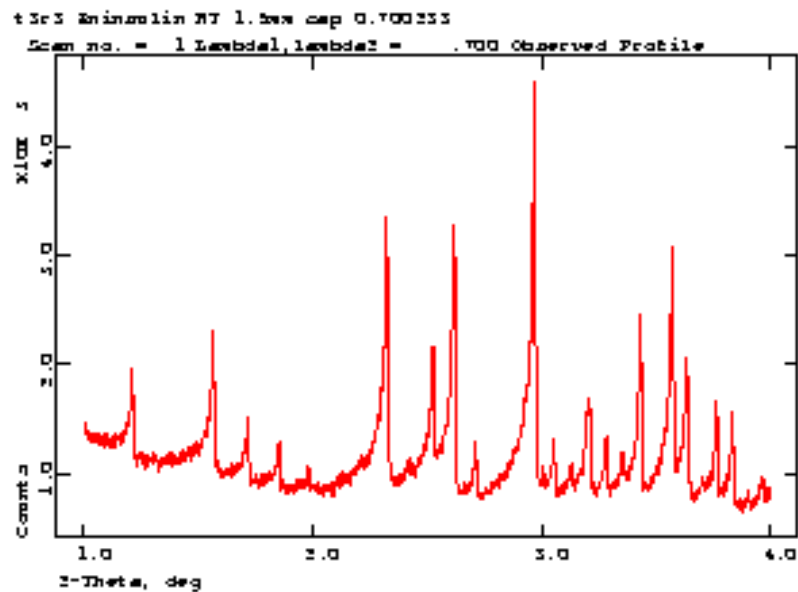


Immediately after grinding

Indexed – R3

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

New phase –  $T_3R_3DC$



After 2 days rest

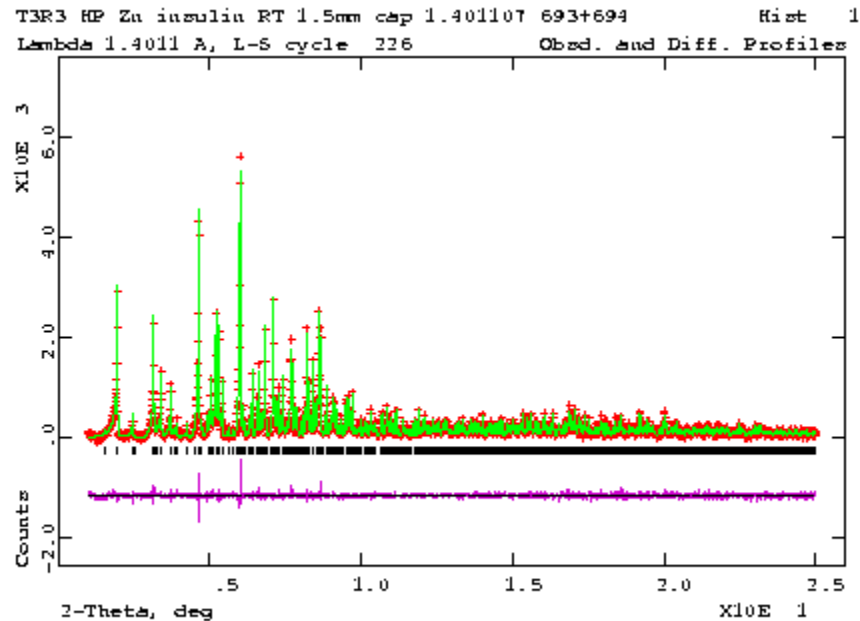
Indexed – R3

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

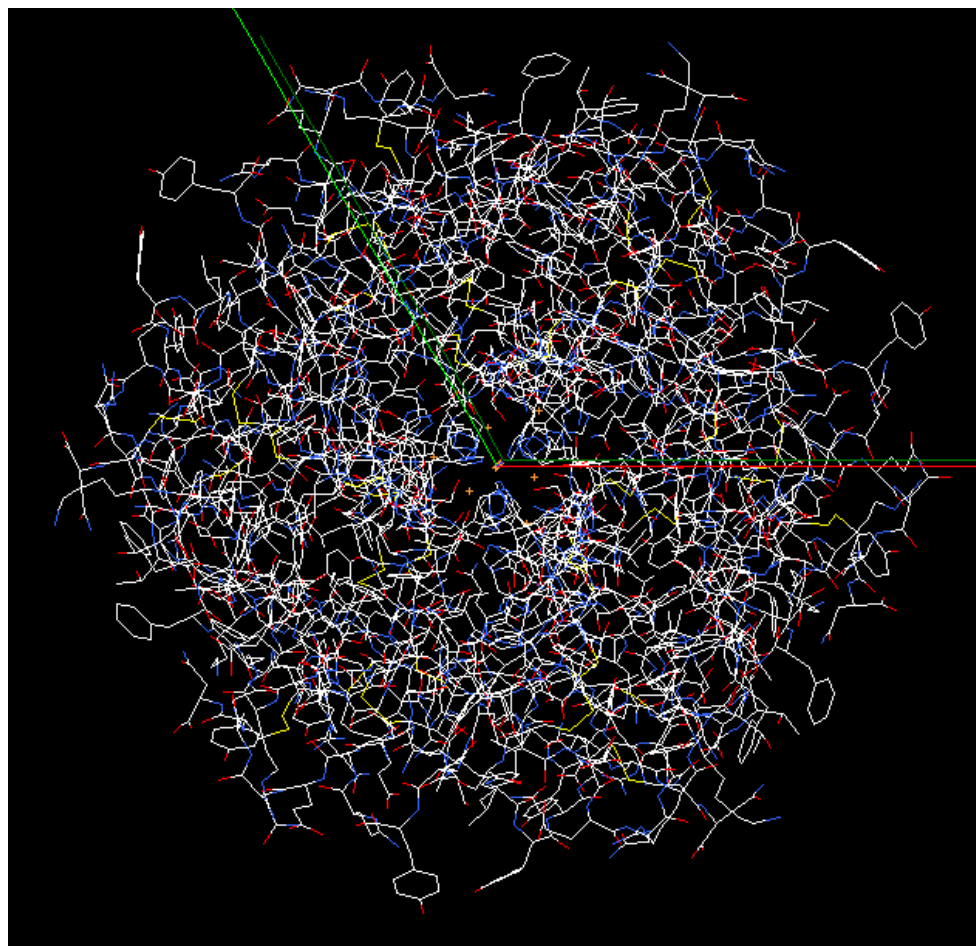
same as single xtal

*X3b1/NSLS in Oct. 1999*

# High Resolution X-ray Powder Diffraction on Proteins



**1<sup>st</sup> Molecular replacement solution!!**  
**3 parameter problem**



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)
- $R_{wp}=3.74\%$



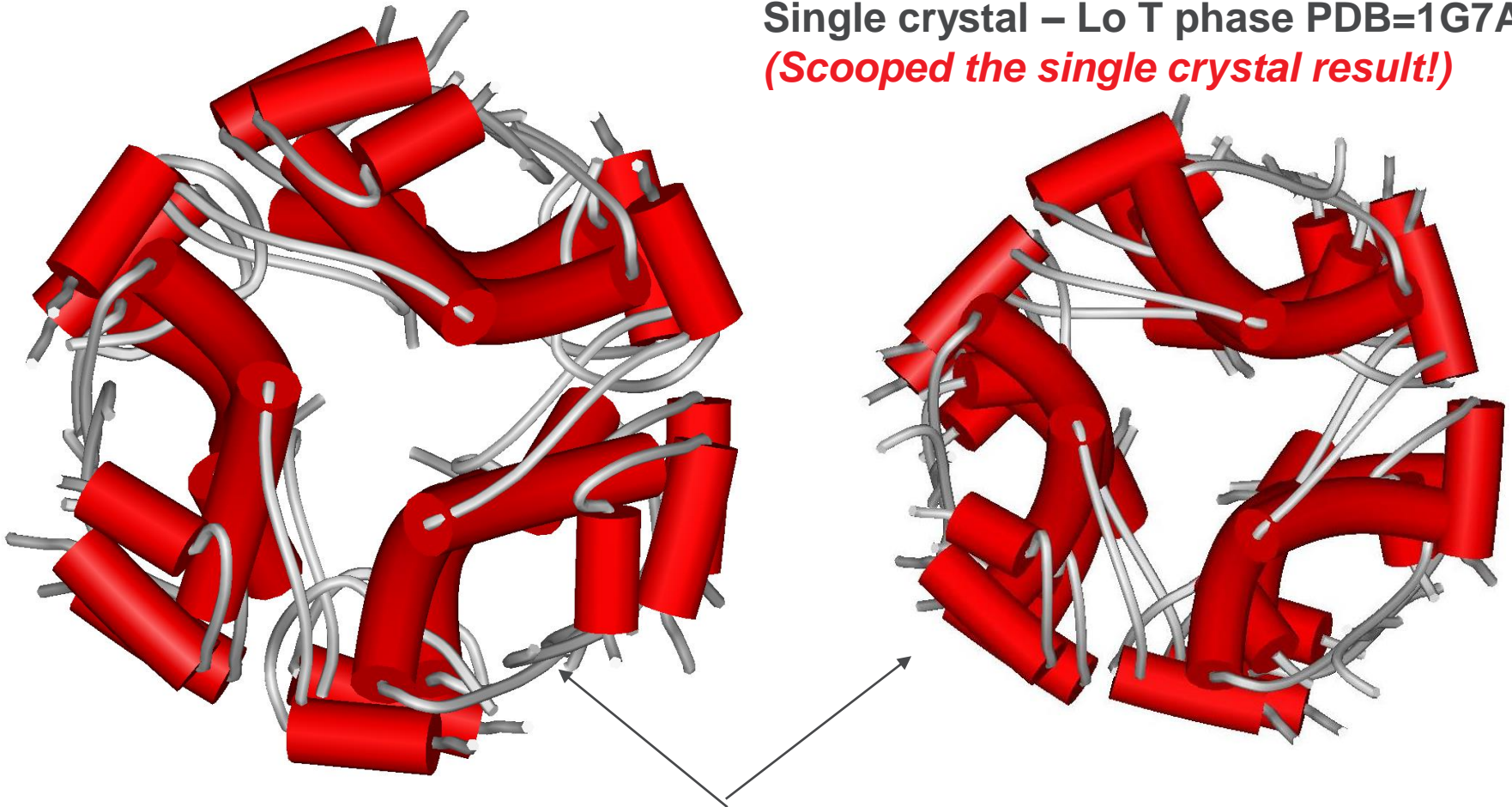
# Schematic of $T_3R_3DC$ Zn-insulin complex.

Powder RT structure PDB=1FUB

Same structure as --

Single crystal – Lo T phase PDB=1G7A

*(Scooped the single crystal result!)*



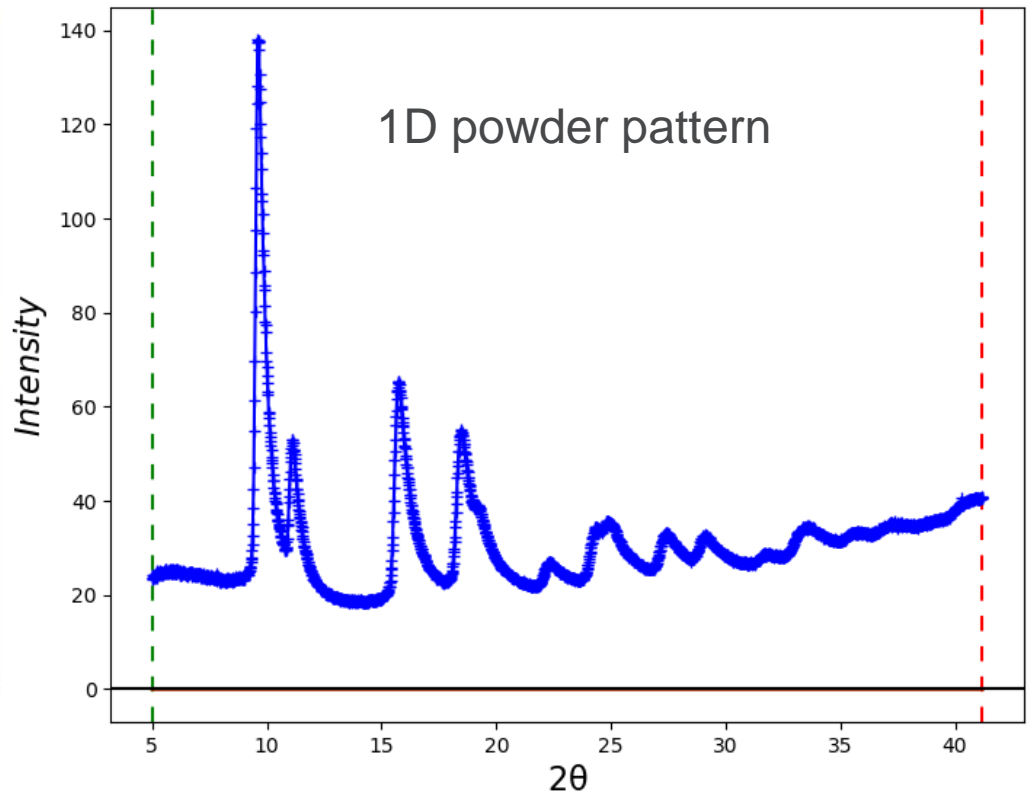
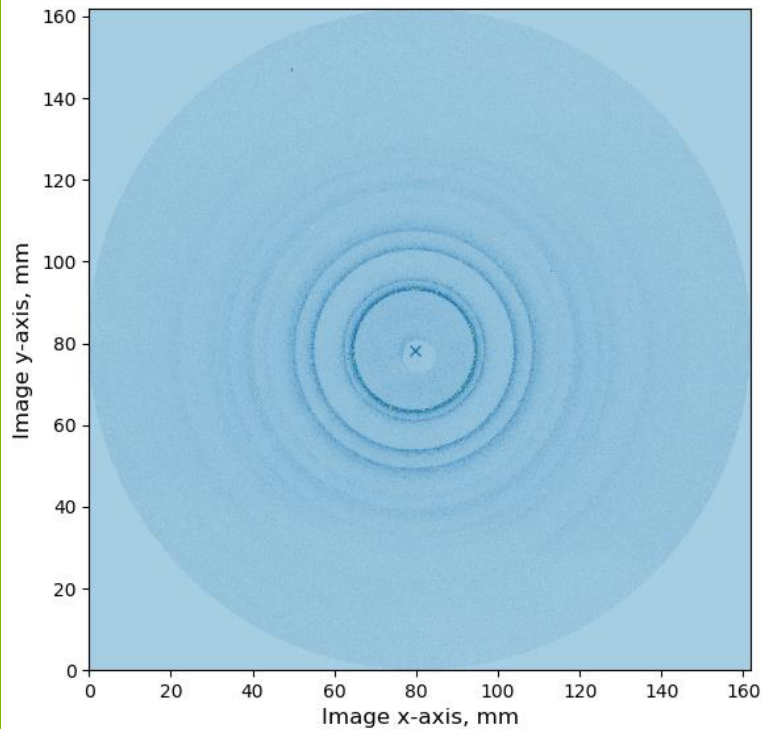
View down 3-fold axis - front  $T_3R_3$  turned  $9^\circ$  wrt back  $T_3R_3$

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  $\text{CeO}_2$



Strongly asymmetric peaks – resemble neutron TOF peaks.  
NB: light travels  $\sim 3\text{cm}$  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

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

Convolute with Lorentzian

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

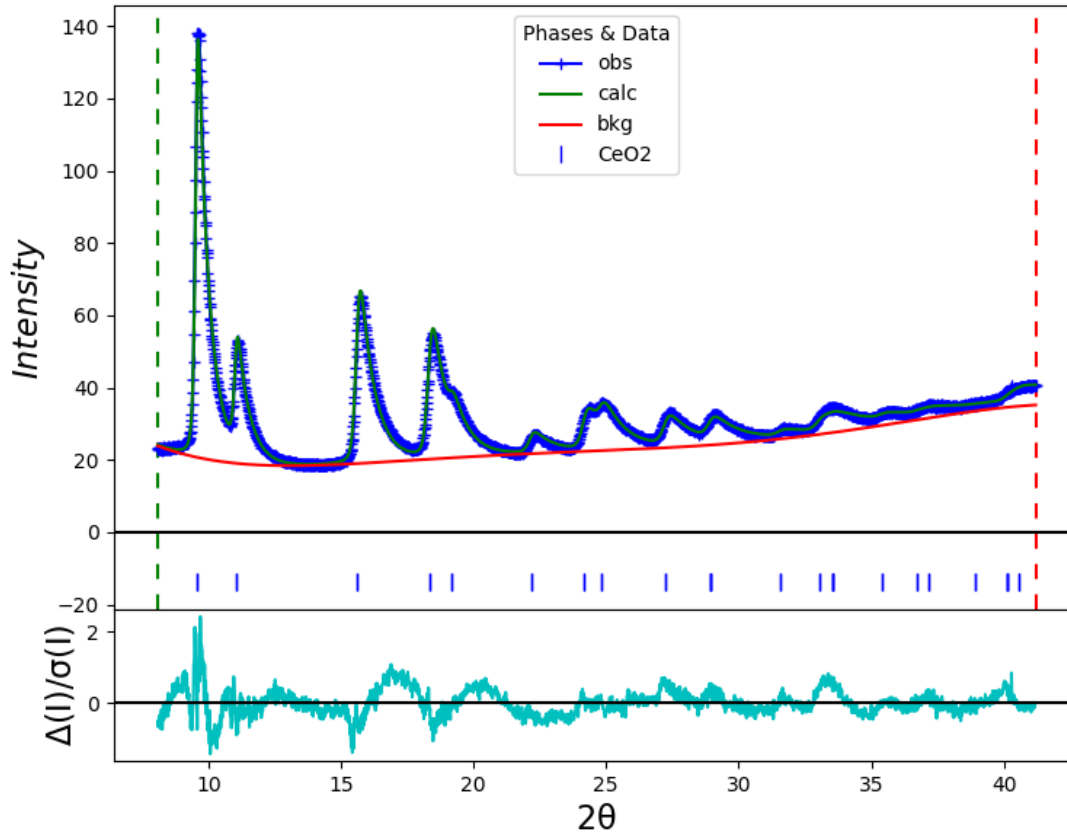
where

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

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

# PINK BEAM FUNCTION & 1<sup>ST</sup> RIETVELD REFINEMENT

Assume conventional UVW Gaussian &  
XY Lorentzian variation with  $\Theta$



$\alpha, \beta$  dependence with  $\tan\Theta$   
(should be  $\sin\Theta$ ? - TBD)

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  $2\Theta$  (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 =  $\eta L + (1-\eta)G$**

$\eta$  *via* Thompson, Cox & Hastings – pseudoVoigt = Voigt

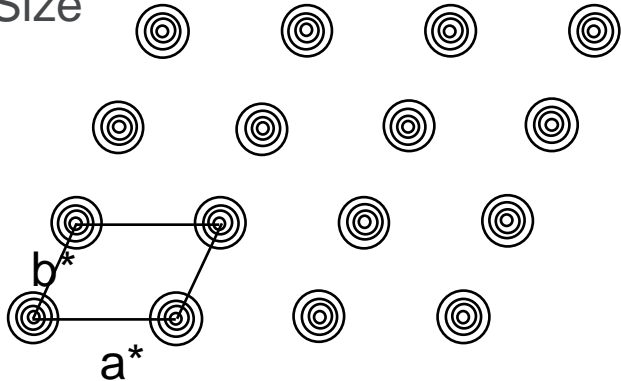
**CW Asymmetry from axial divergence – Finger, Cox & Jephcoat**

**NB: in gsas & GSAS-II, T is  $2\Theta$  in centideg or TOF in  $\mu\text{s}$**

# SAMPLE BROADENING

## Isotropic Crystallite size & $\mu$ strain broadening

Size



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

Size distribution  $\rightarrow$

superposition of sharp to broad spots

$\rightarrow$  Shape  $\sim$  Lorentzian

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

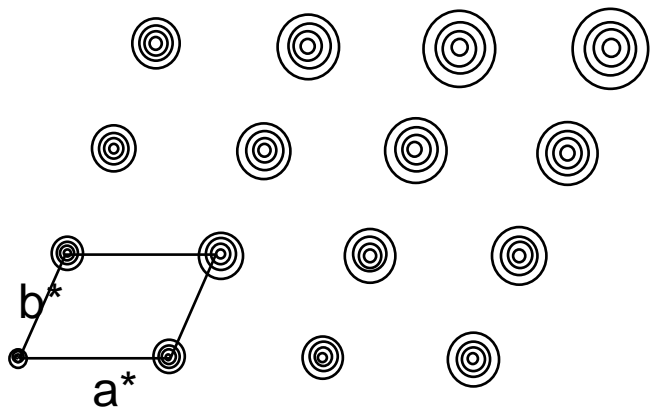
Bragg's Law:  $\Delta 2\Theta = \lambda \Delta d/d^2 \cos\Theta (= X/\cos\Theta)$

$\rightarrow$  Scherrer equation

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

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

$\mu$ strain



Unit cell variation (defects??)

Lorentzian distribution  $\rightarrow$  shape

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

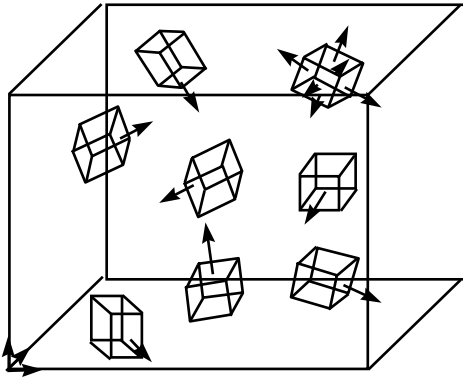
Or:  $\Delta 2\Theta = 2\Delta d \tan\Theta/d (= Y \tan\Theta)$

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

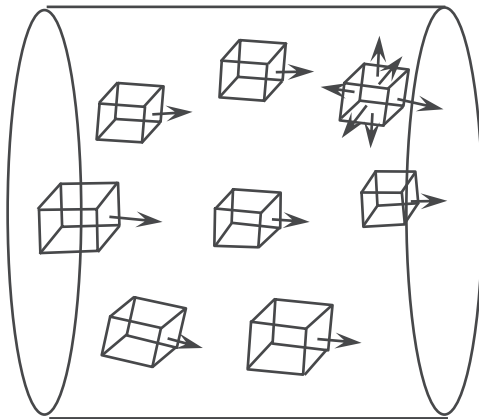
$\mu$  –  $\mu$ strain ( $\times 10^6$ ) parameter



# WHAT IS TEXTURE? “INTERESTING PREFERRED ORIENTATION”



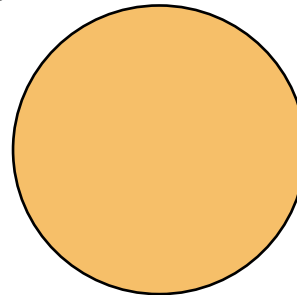
**Loose powder**



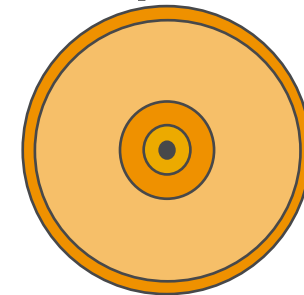
**Metal wire**

Random powder - all crystallite orientations equally probable - flat pole figure

Pole figure - stereographic projection of a crystal axis down some sample direction



(100) random texture



(100) wire texture

Crystallites oriented along wire axis - pole figure peaked in center and at the rim (100's are 90° apart)

Orientation Distribution Function - probability function for texture

# TEXTURE EFFECT ON REFLECTION INTENSITY - SPHERICAL HARMONICS

$$A(h, y) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^l \sum_{n=-l}^l C_l^{mn} K_l^m(h) K_l^n(y)$$

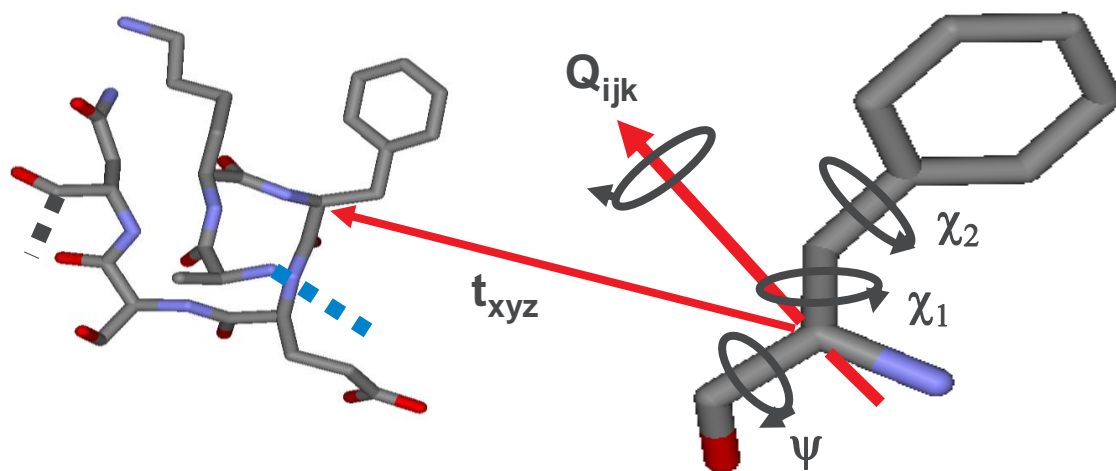
- Projection of orientation distribution function for chosen reflection (h) and sample direction (y)
- K - symmetrized spherical harmonics - account for sample & crystal symmetry
- “Pole figure” - variation of single reflection intensity as fxn. of sample orientation - fixed h
- “Inverse pole figure” - modification of all reflection intensities by sample texture - fixed y - Ideally suited for neutron TOF diffraction
- Rietveld refinement of coefficients,  $C_l^{mn}$ , and 3 orientation angles - sample alignment

# CONSTRAINTS & RESTRAINTS - “WHAT TO DO WHEN YOU HAVE TOO MANY PARAMETERS & NOT ENOUGH DATA”

Constraints – reduce no. of parameters

Derivative vector After constraints  $\frac{\partial F}{\partial v_i} = R_{il} U_{lk} S_{kj} \frac{\partial F}{\partial p_j}$  Derivative vector Before constraint

Rigid body User Symmetry Rectangular matrices



# FULL MINIMIZATION FUNCTION + RESTRAINTS: ADDITIONAL “DATA”

Least-squares – nonlinear; transcendental functions

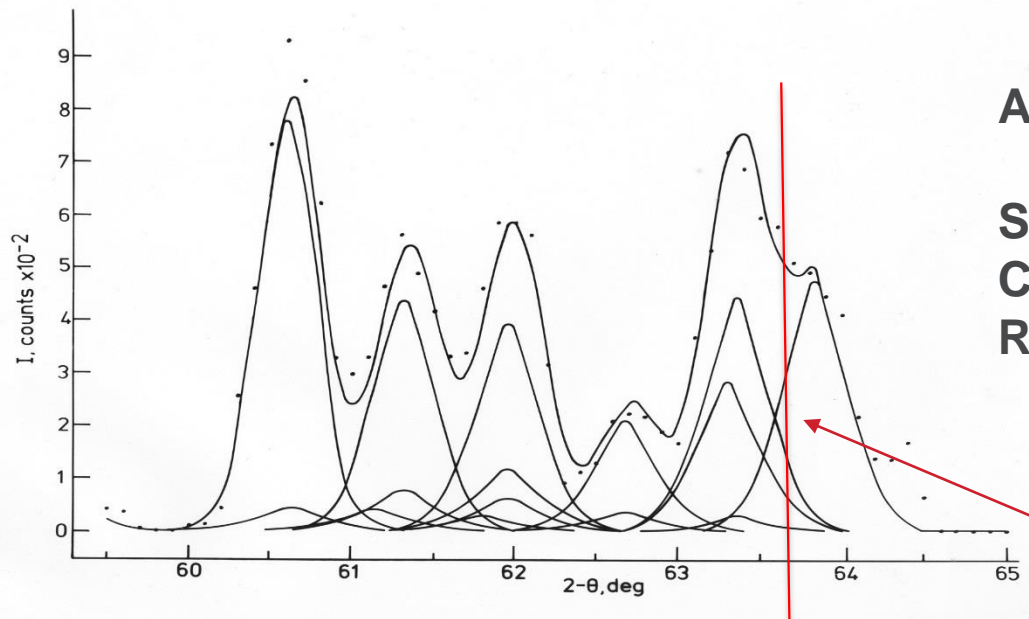
$$\begin{aligned} M = & f_Y \sum w_i (Y_{oi} - Y_{ci})^2 && \text{Powder profile (Rietveld)/Single crystal } F_{hkl} \\ & + f_a \sum w_i (a_{oi} - a_{ci})^2 && \text{Bond angles} \\ & + f_d \sum w_i (d_{oi} - d_{ci})^2 && \text{Bond distances} \\ & + f_t \sum w_i (-t_{ci})^4 && \text{Torsion angle pseudopotentials} \\ & + f_p \sum w_i (-p_{ci})^2 && \text{Plane RMS displacements} \\ & + f_v \sum w_i (v_{oi} - v_{ci})^4 && \text{van der Waals distances (if } v_{oi} < v_{ci}) \\ & + f_h \sum w_i (h_{oi} - h_{ci})^2 && \text{Hydrogen bonds} \\ & + f_x \sum w_i (x_{oi} - x_{ci})^2 && \text{Chiral volumes} \\ & + f_R \sum w_i (-R_{ci})^4 && \text{“}\phi/\psi\text{” pseudopotential} \end{aligned}$$

**NB: May be 1,000’s of these terms for e.g. proteins**



# 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

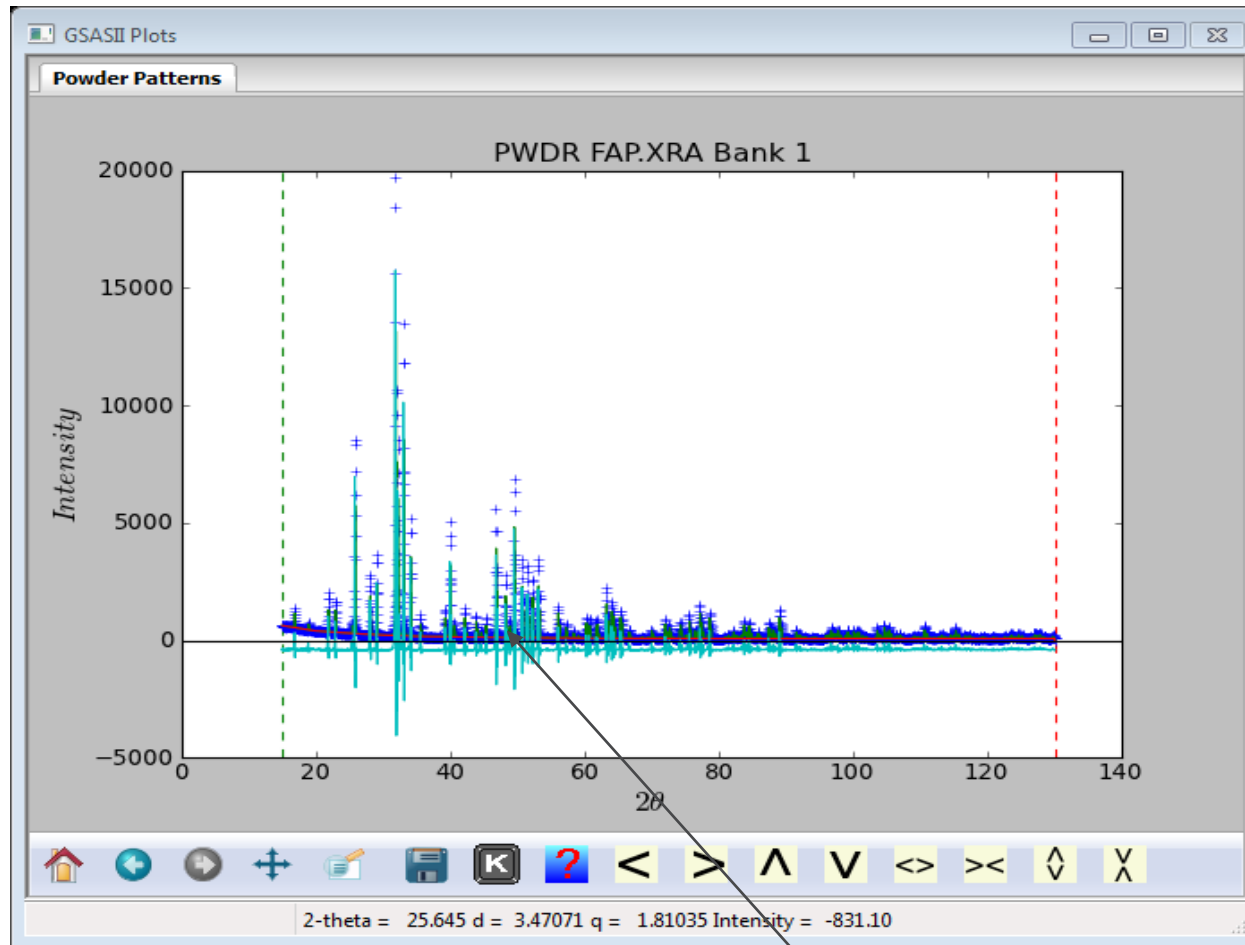
LeBail algorithm – extracted  $F^2_o$  → new  $F^2_c$  then next cycle;  
refine only background, peak shapes & positions – few parameters  
No constraints needed for overlaps – Simple

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



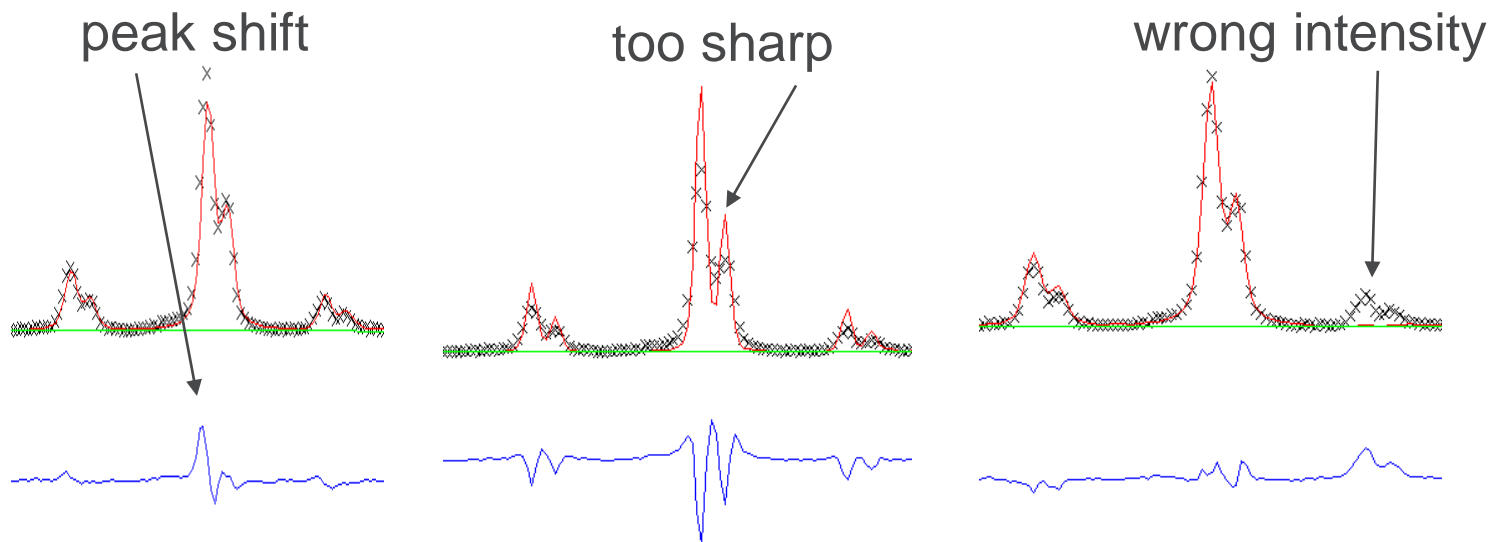
- Notice shape of difference curve – position/shape/intensity errors

# ERRORS & PARAMETERS?

- position – lattice parameters, zero point (not common)
  - other systematic effects – sample shift/offset
- shape – profile coefficients – sample size/ $\mu$ 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**

**NB<sup>2</sup> – trend with  $2\Theta$  (or TOF) important**

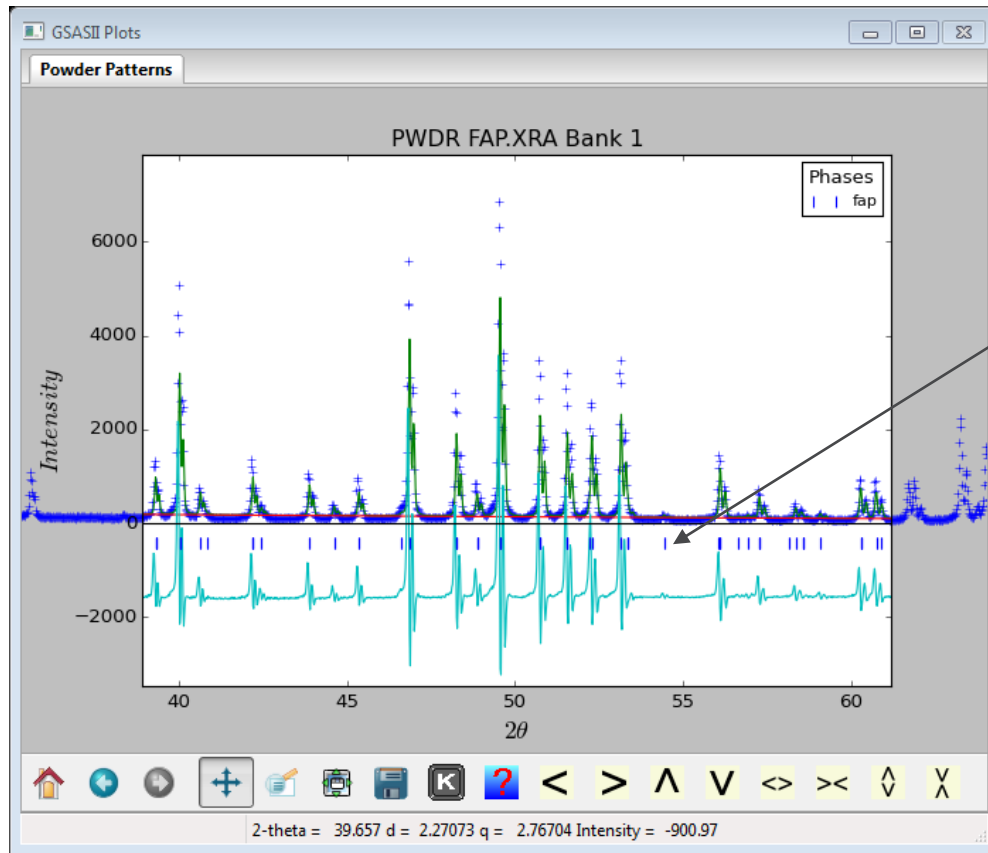


a – too small

size - too large

Ca<sub>2</sub>(x) – too small

# DIFFERENCE CURVE – WHAT TO DO NEXT?

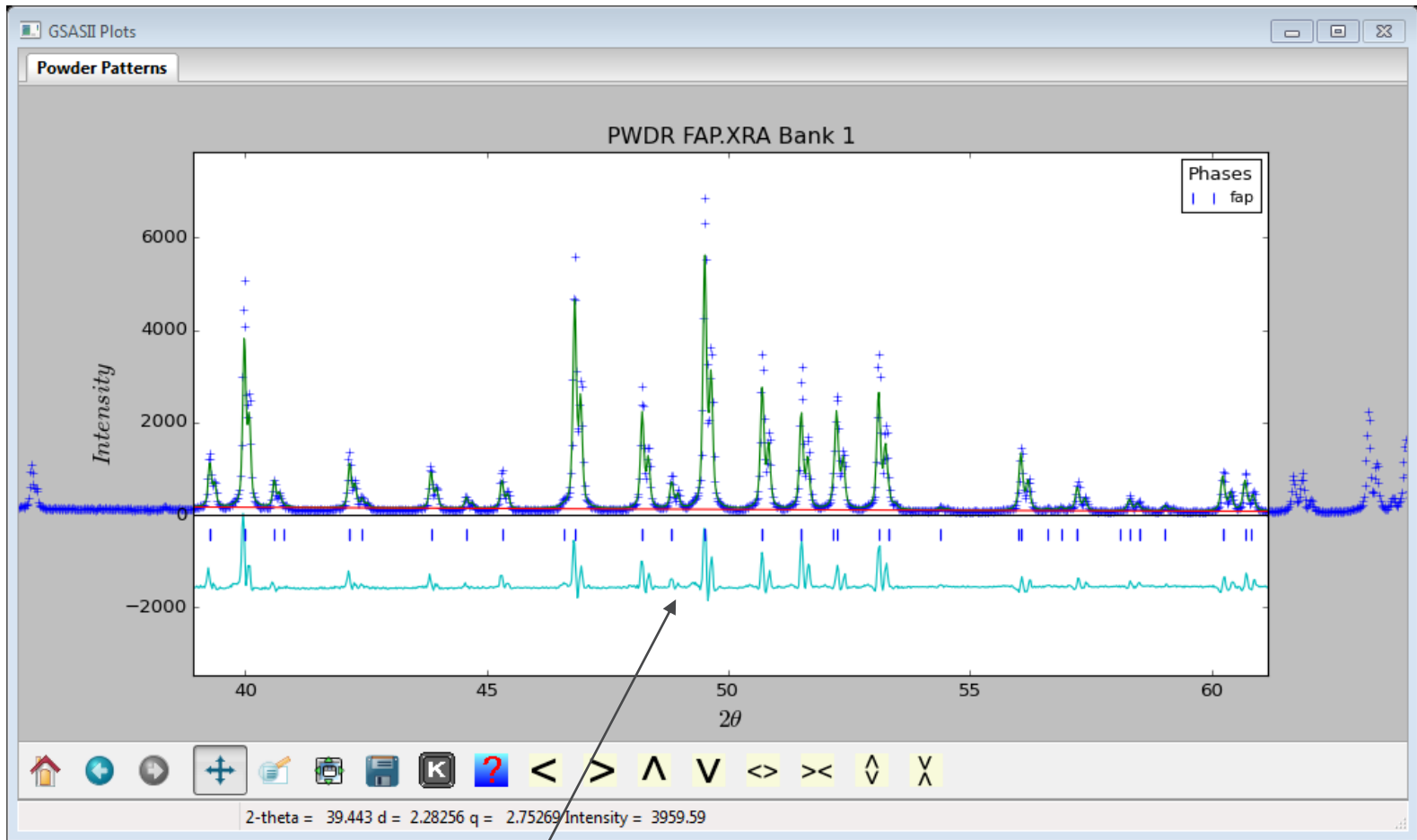


Characteristic “up-down-up”  
→ profile error  
NB – can be “down-up-down” for too “fat” profile

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

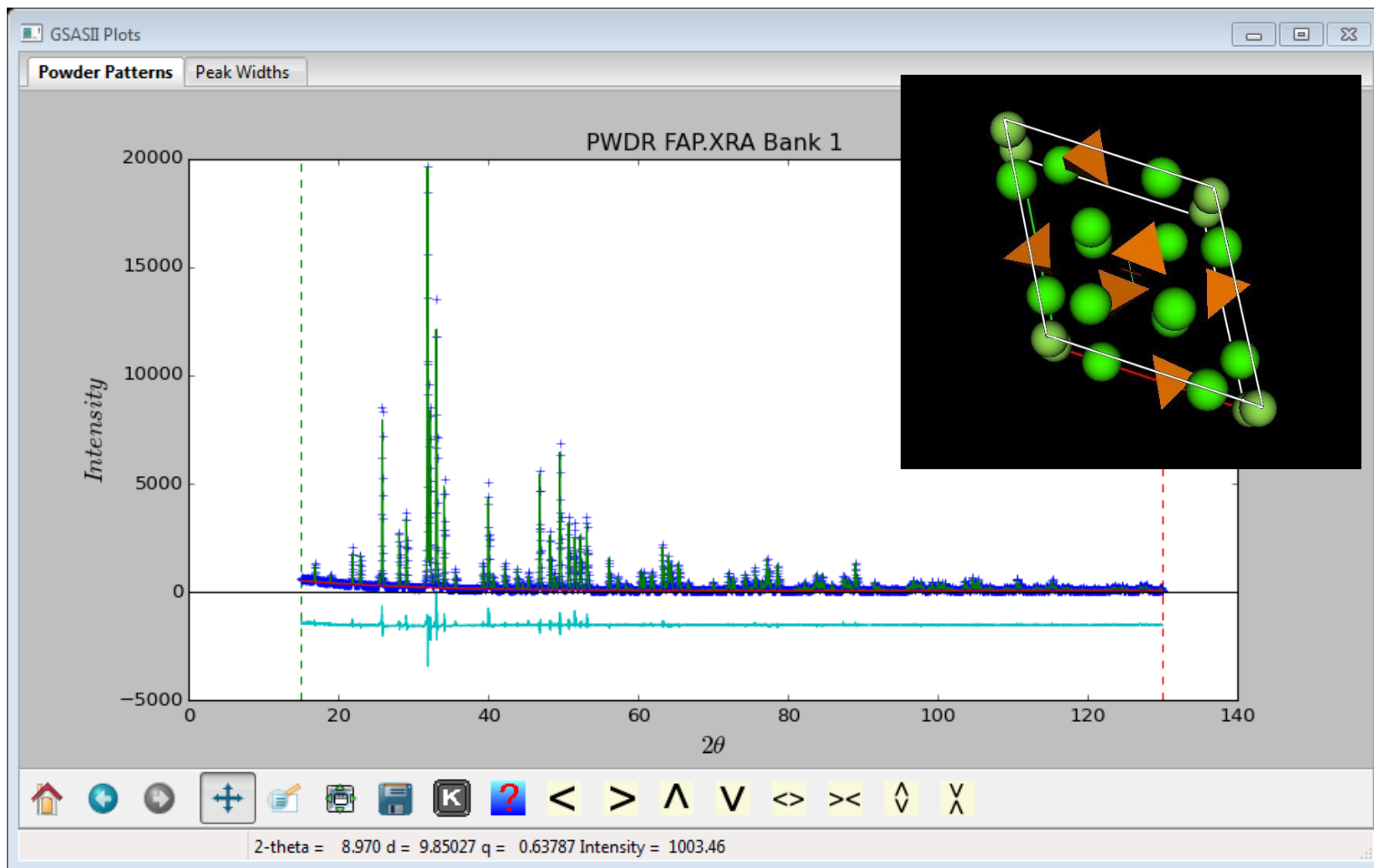


# RESULT – MUCH IMPROVED!



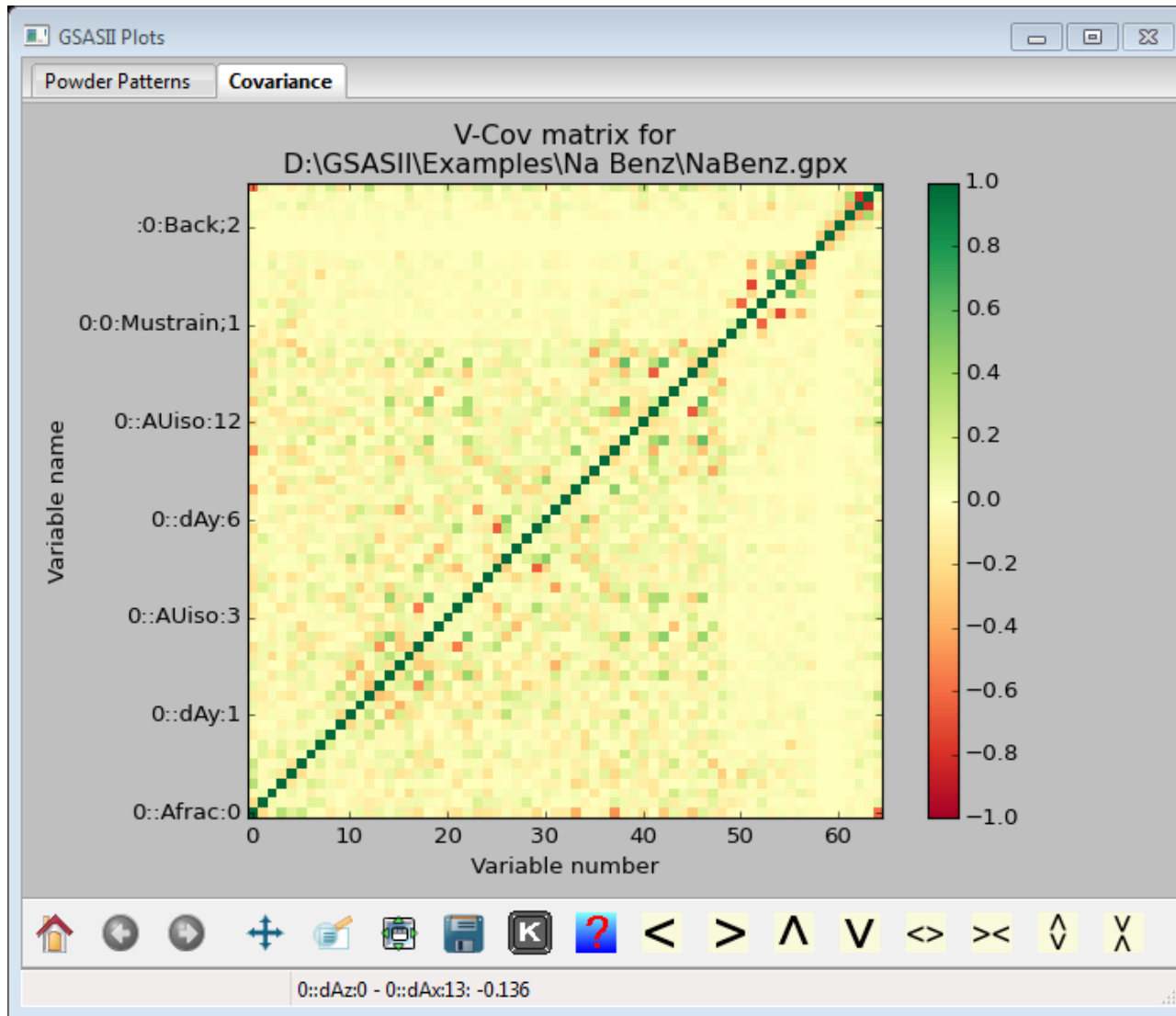
- maybe intensity differences remain  
– refine coordinates & thermal parms.

# RESULT – ESSENTIALLY UNCHANGED



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

# A USEFUL PLOT – COVARIANCE MATRIX



**Green: cov>0**  
**Red: cov<0**  
**Yellow: cov~0**  
**Cursor reports:**  
**Cov or value(esd)**  
**on diagonal**  
**Can be zoomed!**

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

**THANK YOU**