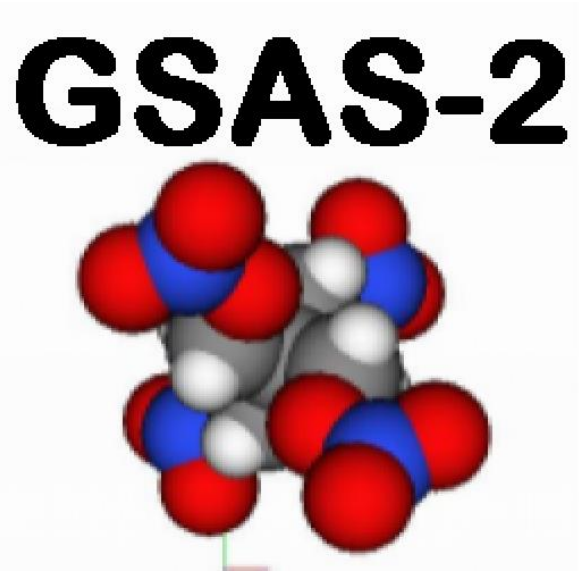
THE RIETVELD REFINEMENT METHOD



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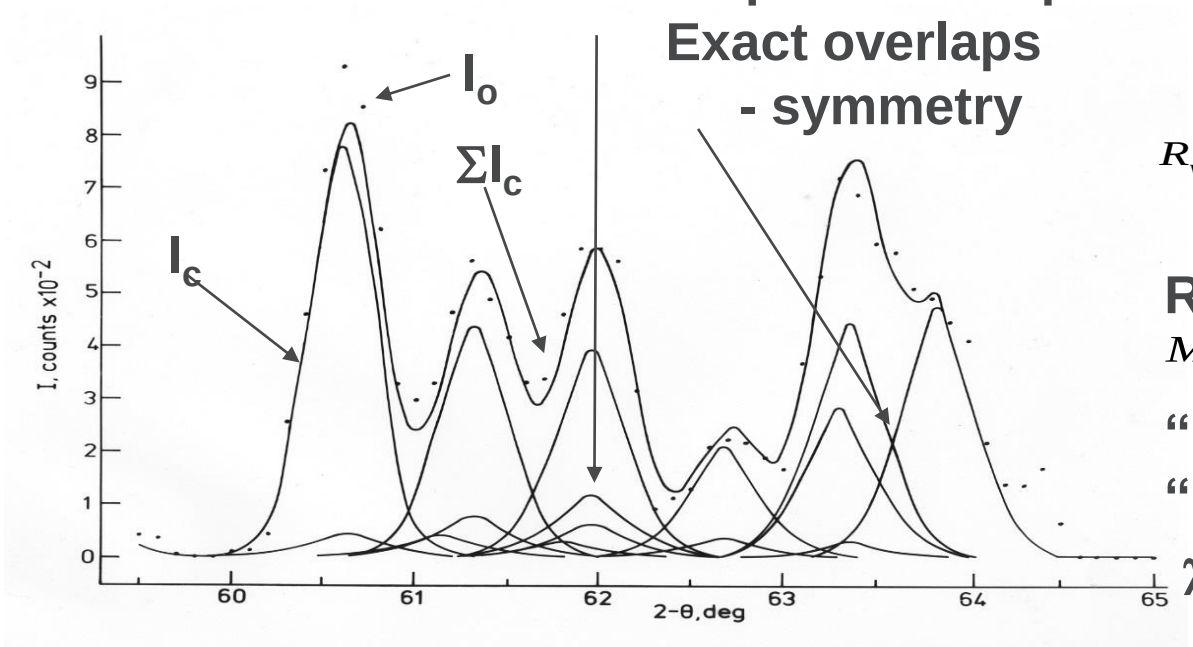
- Some history first
- Extreme examples
- The math
- Worked example

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:

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

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

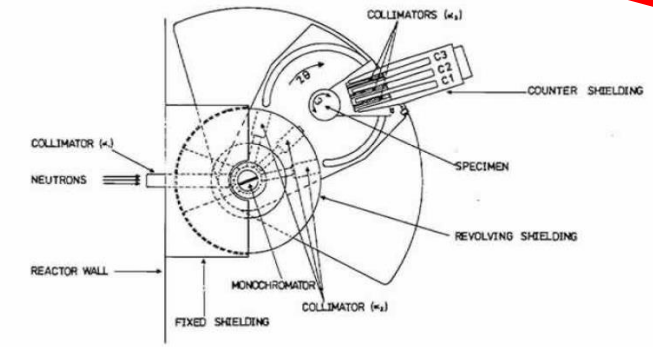
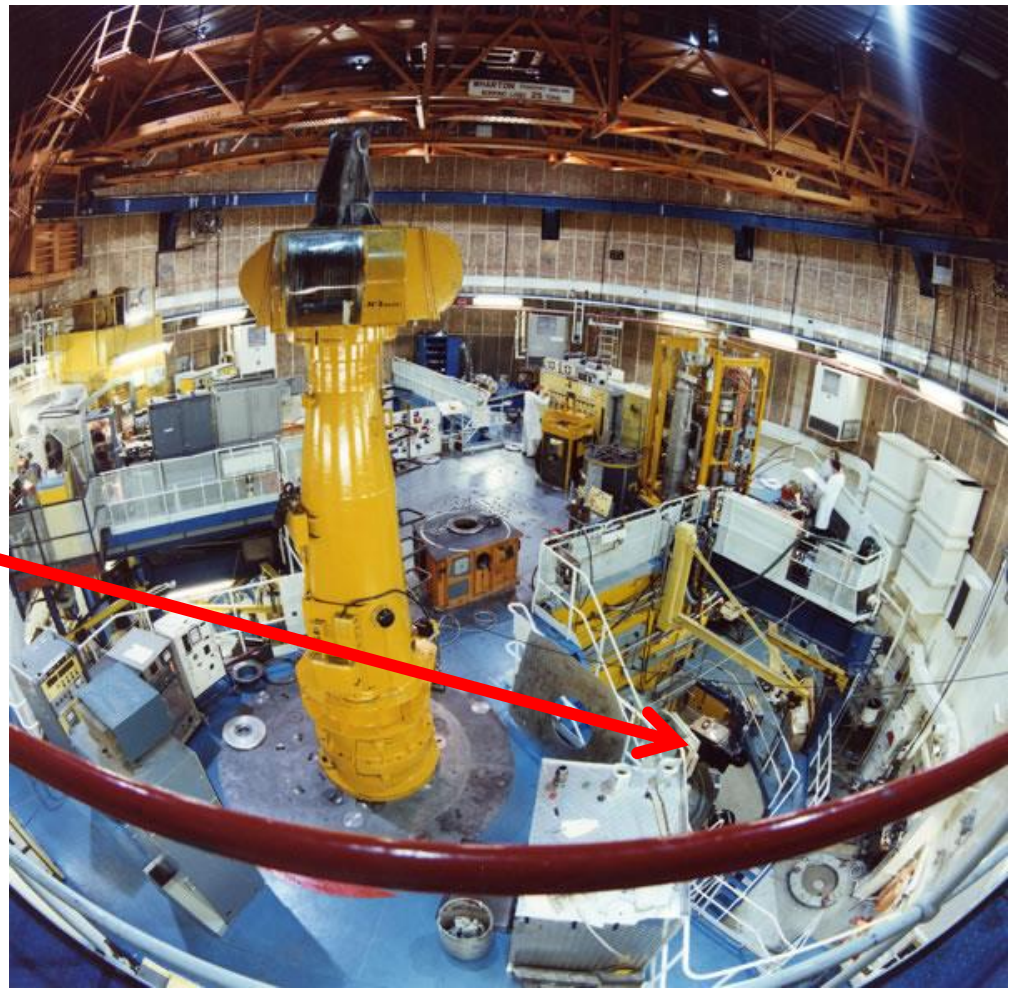


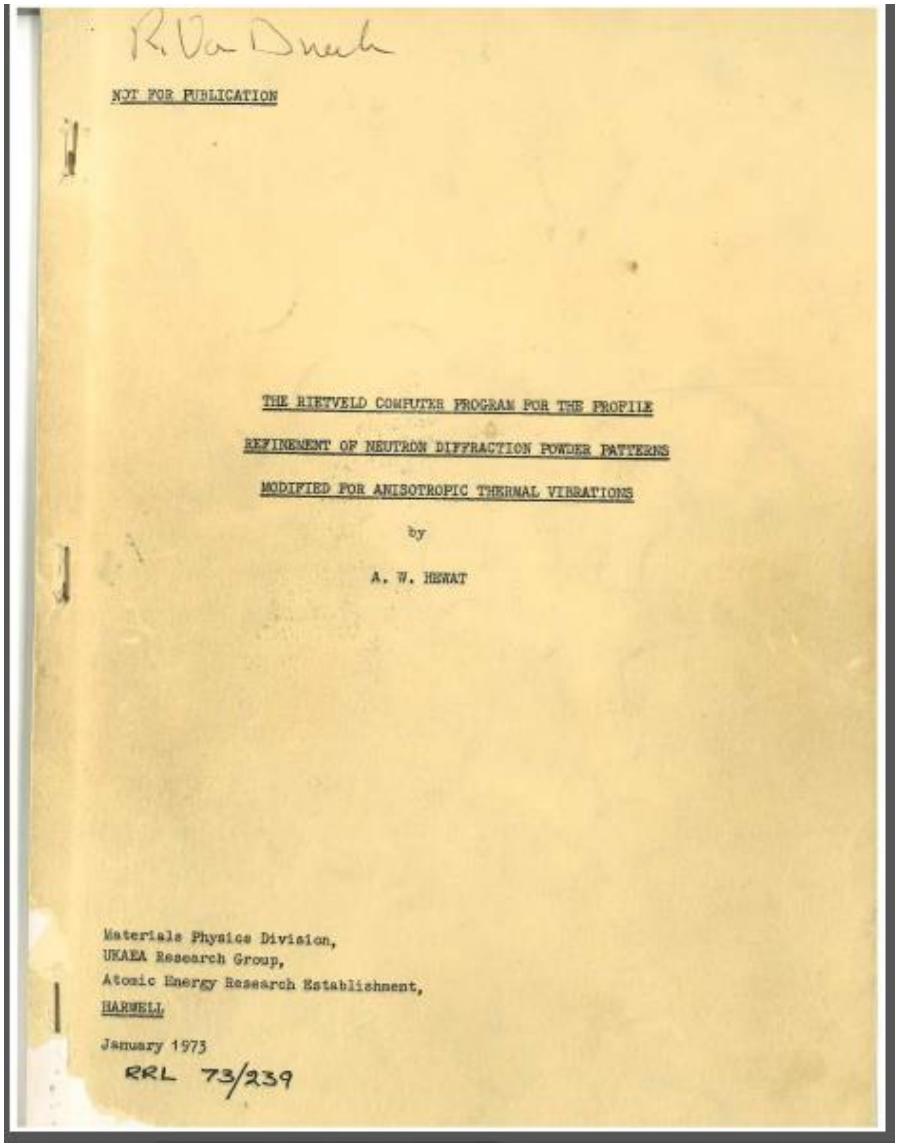
Fig. 2. A schematic diagram of a neutron powder diffractometer named PANDA which is installed at A.E.R.E. Harwell.

?



AKC & RBVD experiments: $2\Theta_m$ 92°,
λ=1.57&1.61Å, 2-2.5x10^5 n/scm^2, scan @50m/deg!

This is where it starts - Alan's Manual



R. Va Dreele

NOT FOR PUBLICATION

THE RIETVELD COMPUTER PROGRAM FOR THE PROFILE

REFINEMENT OF NEUTRON DIFFRACTION POWDER PATTERNS

MODIFIED FOR ANISOTROPIC THERMAL VIBRATIONS

by

A. W. HEWAT

Materials Physics Division,
UKAEA Research Group,
Atomic Energy Research Establishment,
HARWELL.

January 1973

RRL 73/239

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: GeorgeIII & 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.

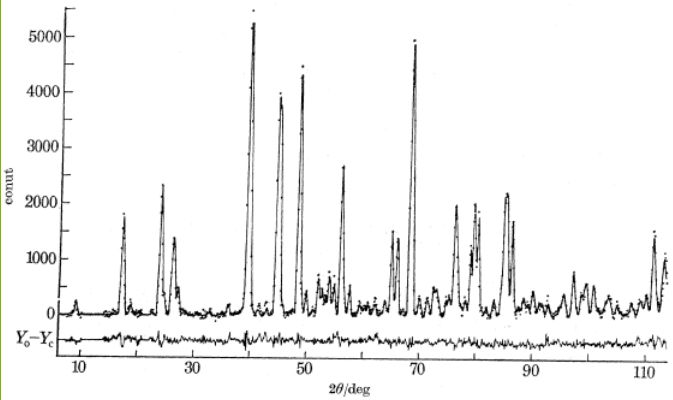
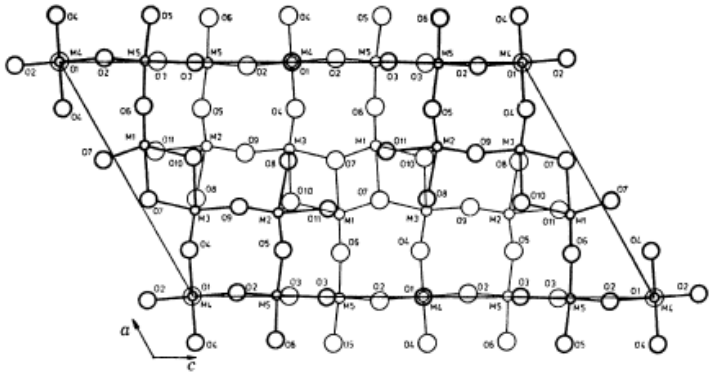


FIGURE 3. Neutron powder diffraction profile for $TiNb_2O_7$. Lines and points represent calculated and observed profiles, respectively. A difference curve is shown.



$TiNb_2O_7$;A2/m,a=11.89,b=3.80,c=20.37,β=120.2º
603 refl.,1077 data points

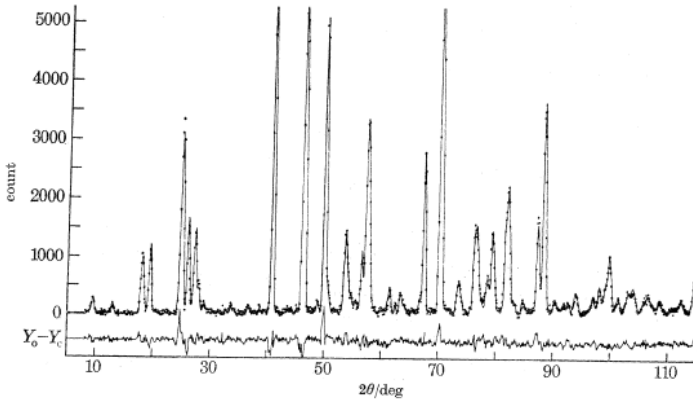
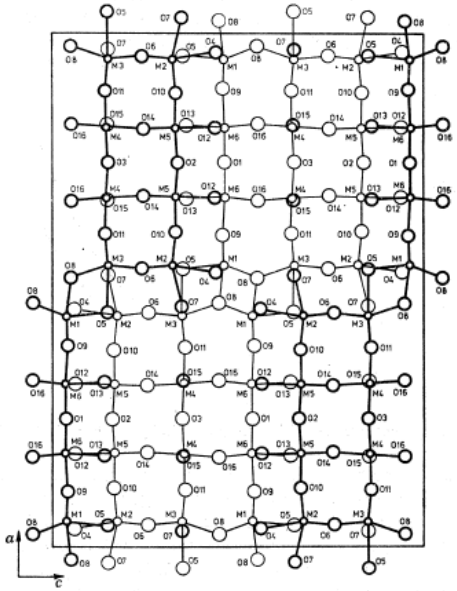


FIGURE 4. Neutron powder diffraction profile for ortho-$Ti_2Nb_{10}O_{29}$. Lines and points represen calculated and observed profiles, respectively. A difference curve is also shown.



o-$Ti_2Nb_{10}O_{29}$, 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.

Argonne NATIONAL LABORATORY

HUGO'S PROGRAM FAMILY TREE

pref & profls
Hugo Rietveld – 1967, 1969 Petten

Algol & Fortran

pref & profls
Alan Hewat – 1973 Harwell

add U_{ij} refinement
Chilton ICL 1906a

pref & profls
Von Dreele – 1973 Oxford

Bigger structures & add X-rays (didn't work!)
Oxford ICL1906a

tofpref & tofls
Von Dreele – 1982 RAL

Neutron TOF, IPNS adopt.
by Rotella for VAX

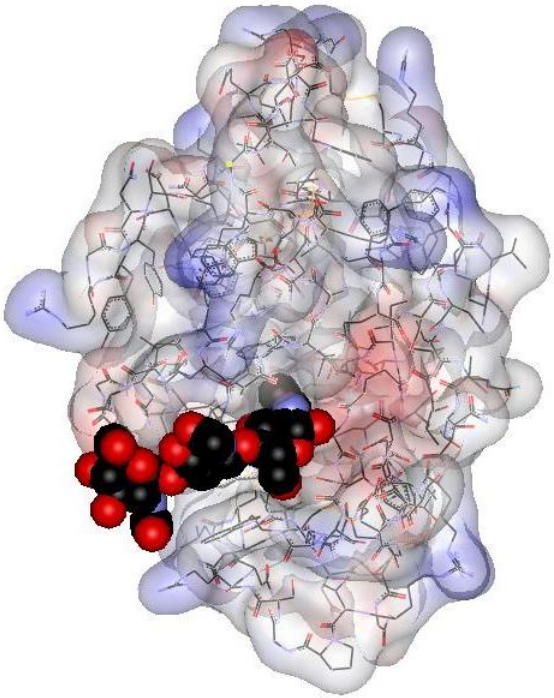
DBW2.9 – 1981-94
DBWS-9006PC
Ga. Tech.
Young & Wiles

Original, x-ray profiles - Young &
Mackie Wiles rewrite – single pgm
Sakthivel revised; Run on IBM PC

LPHM – Hunter & Howard – Australia
FullProf – J. Rodriguez-Carvajal (now revised but same "pcr" file)
Phillips – instrument pkg.
– might be other descendants from DBW/DBWS

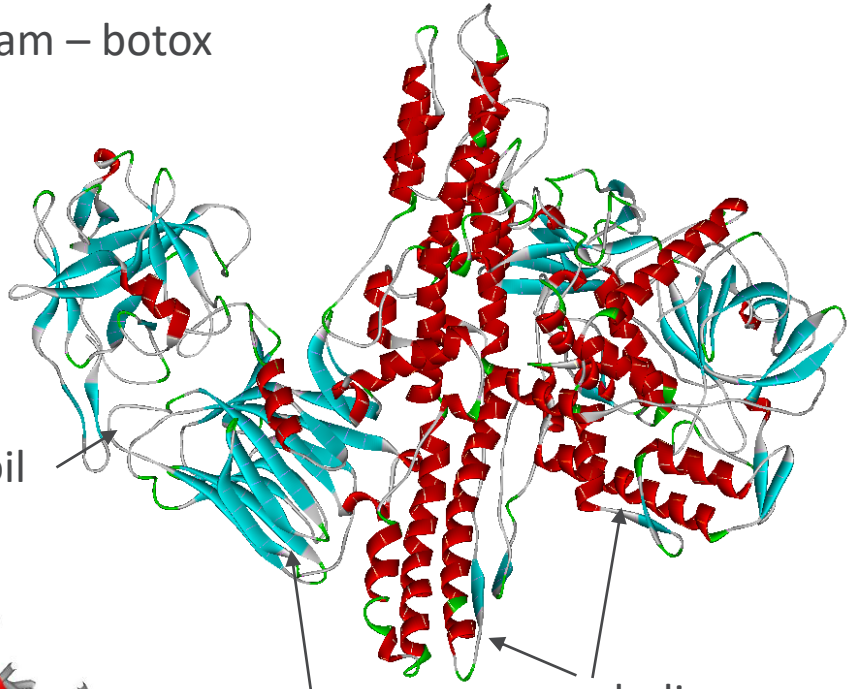
A FEW MORE RIETVELD REFINEMENT EXAMPLES – BIGGEST & FASTEST

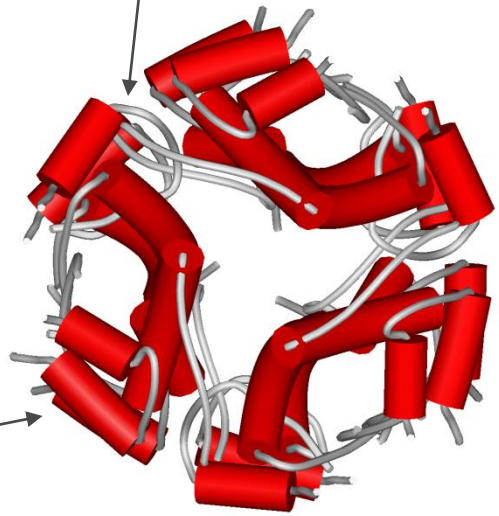
Biggest: Proteins – polymers of amino acids - representations



Space filling (HEWL+NAG_3)
129 AA

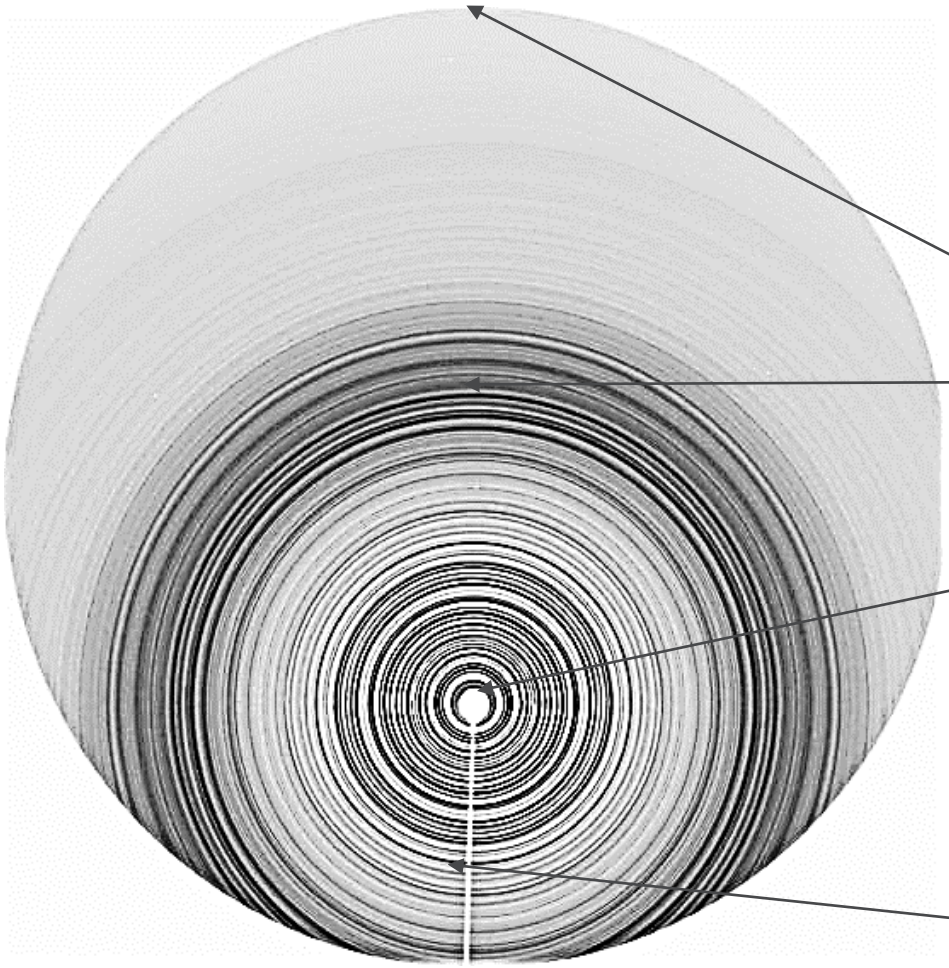
Ribbon diagram – botox
~1100AA





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 –
1μm "perfect" powder

Resolution limit – 1.85Å

Residual solvent scattering – background

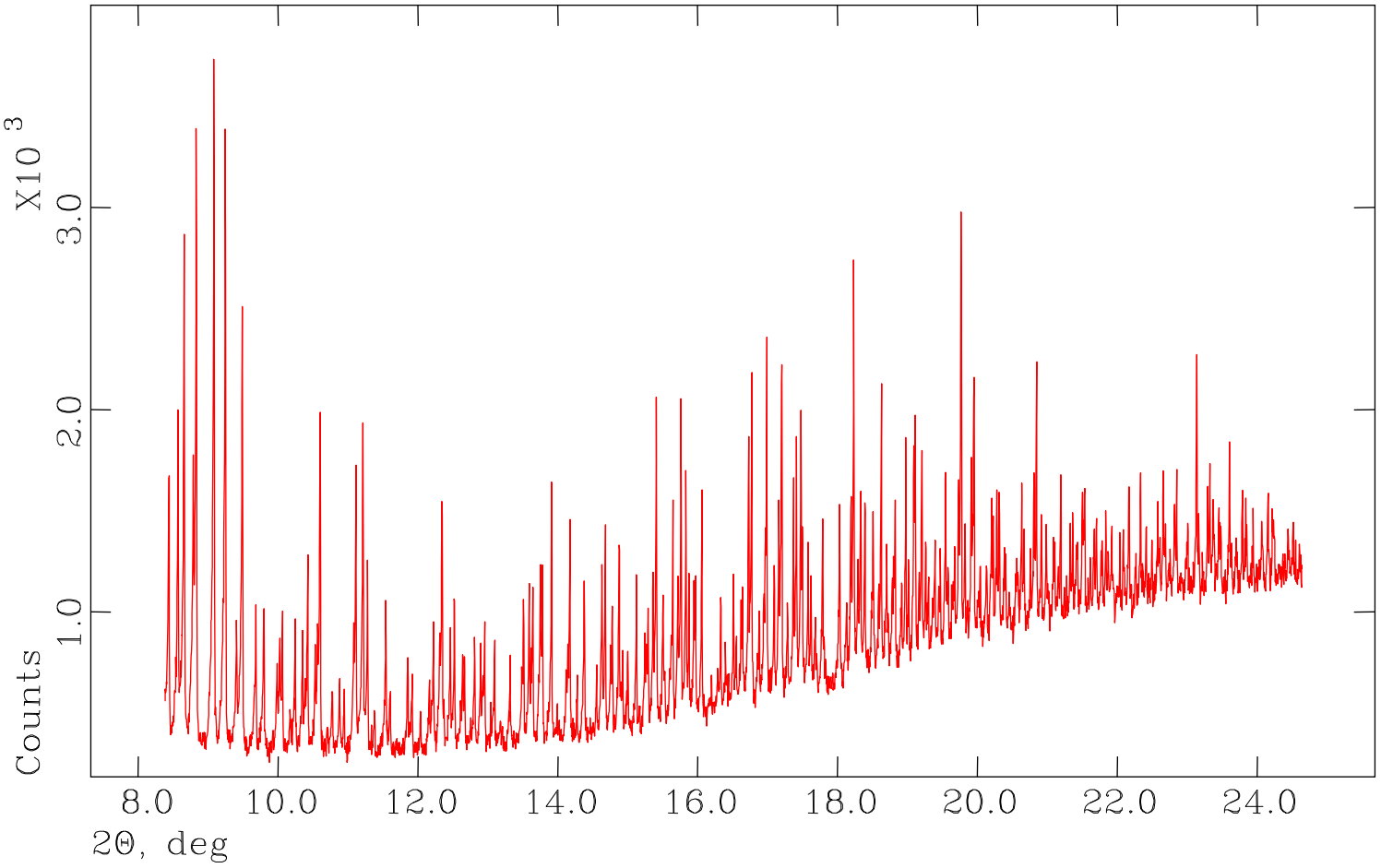
Inner most ring – d~55Å
(110) Reflection, lowest order for tetragonal lysozyme
$2\Theta \sim 0.67$deg

Beam stop holder

~9000 F_{hkl} for HEWL >2Å

Protein powders – "ideal" (1μm & no μstrain)

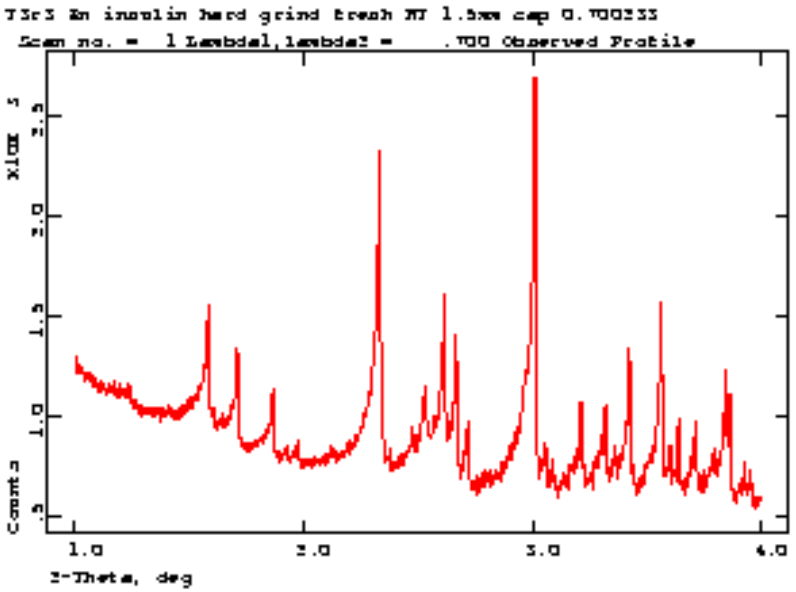
T_6 Zn insulin; NSLS X3b1; λ=1.401Å

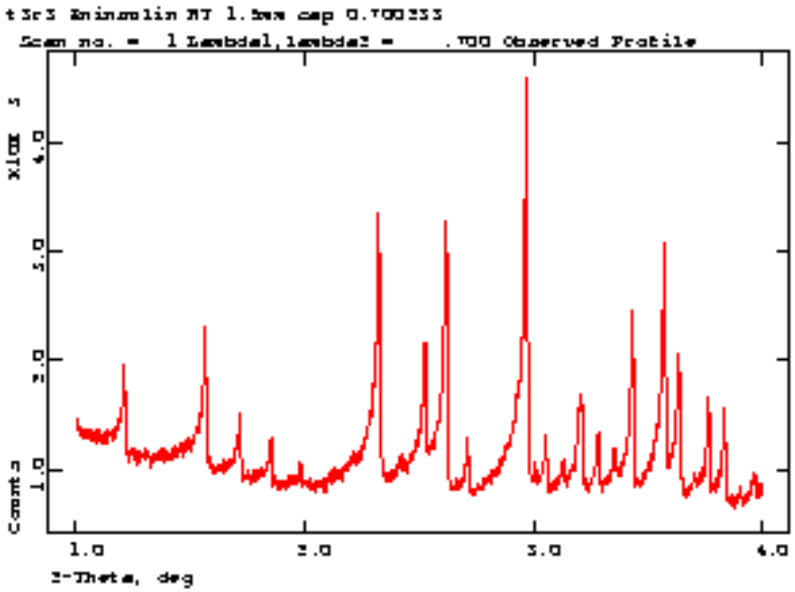


- Sharp peaks! (better than NIST SRM's!)

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

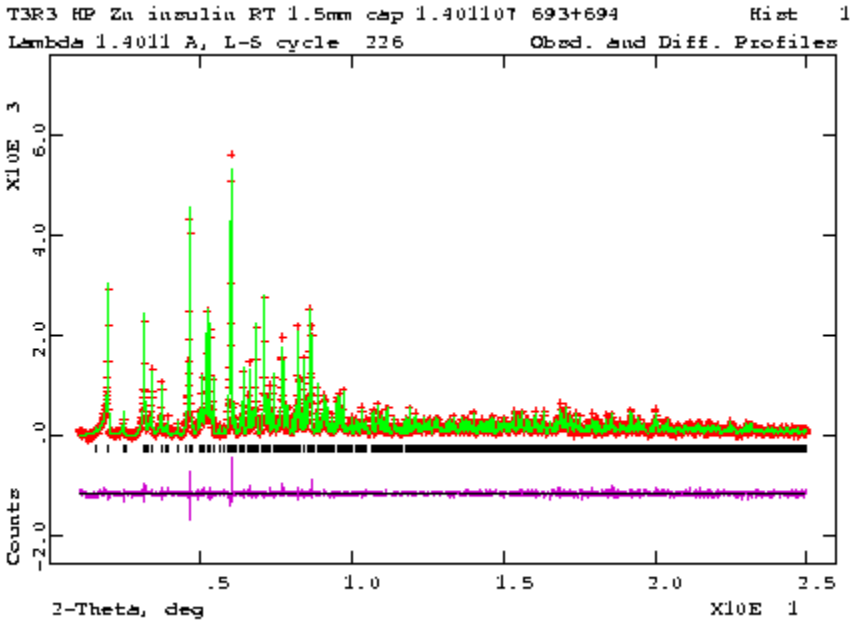
Indexed – R3
a=81.275Å, c=73.024Å
New phase – T_3R_3DC

After 2 days rest

Indexed – R3
a=81.084Å, c=37.537Å
same as single xtal

X3b1/NSLS in Oct. 1999

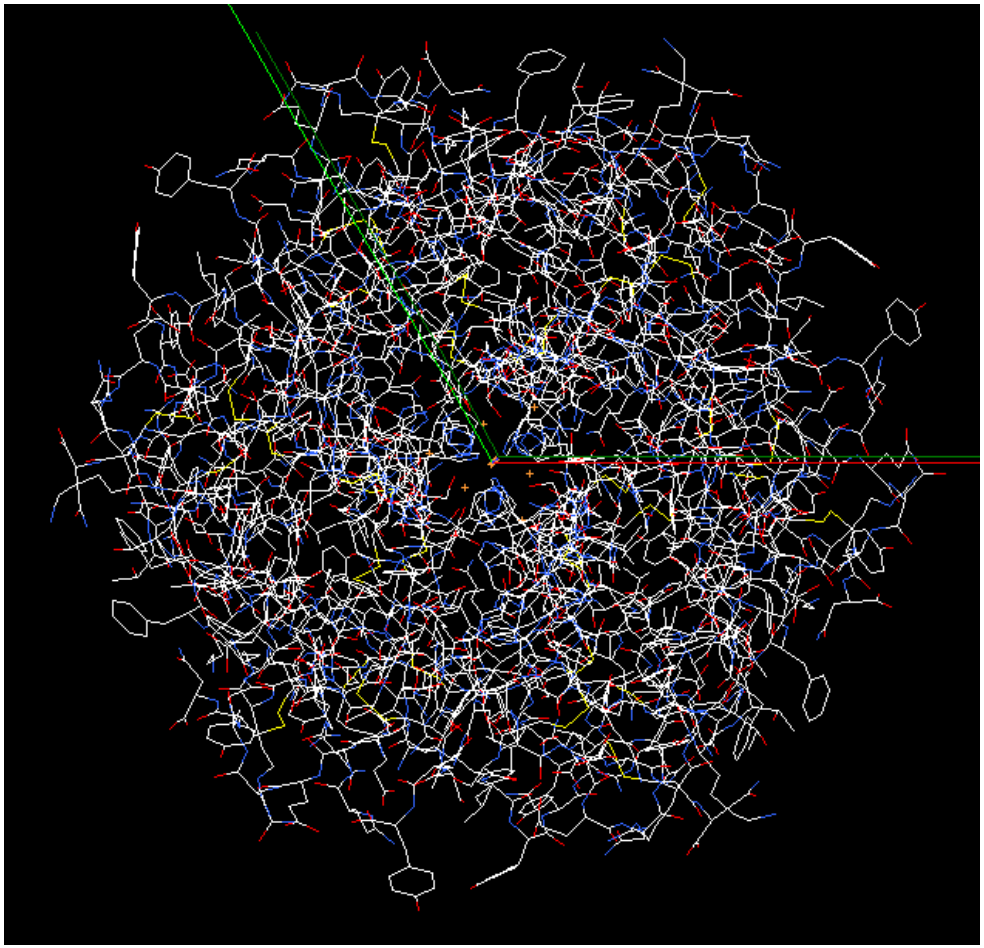
High Resolution X-ray Powder Diffraction on Proteins



Zn insulin structure determined from powder diffraction data

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

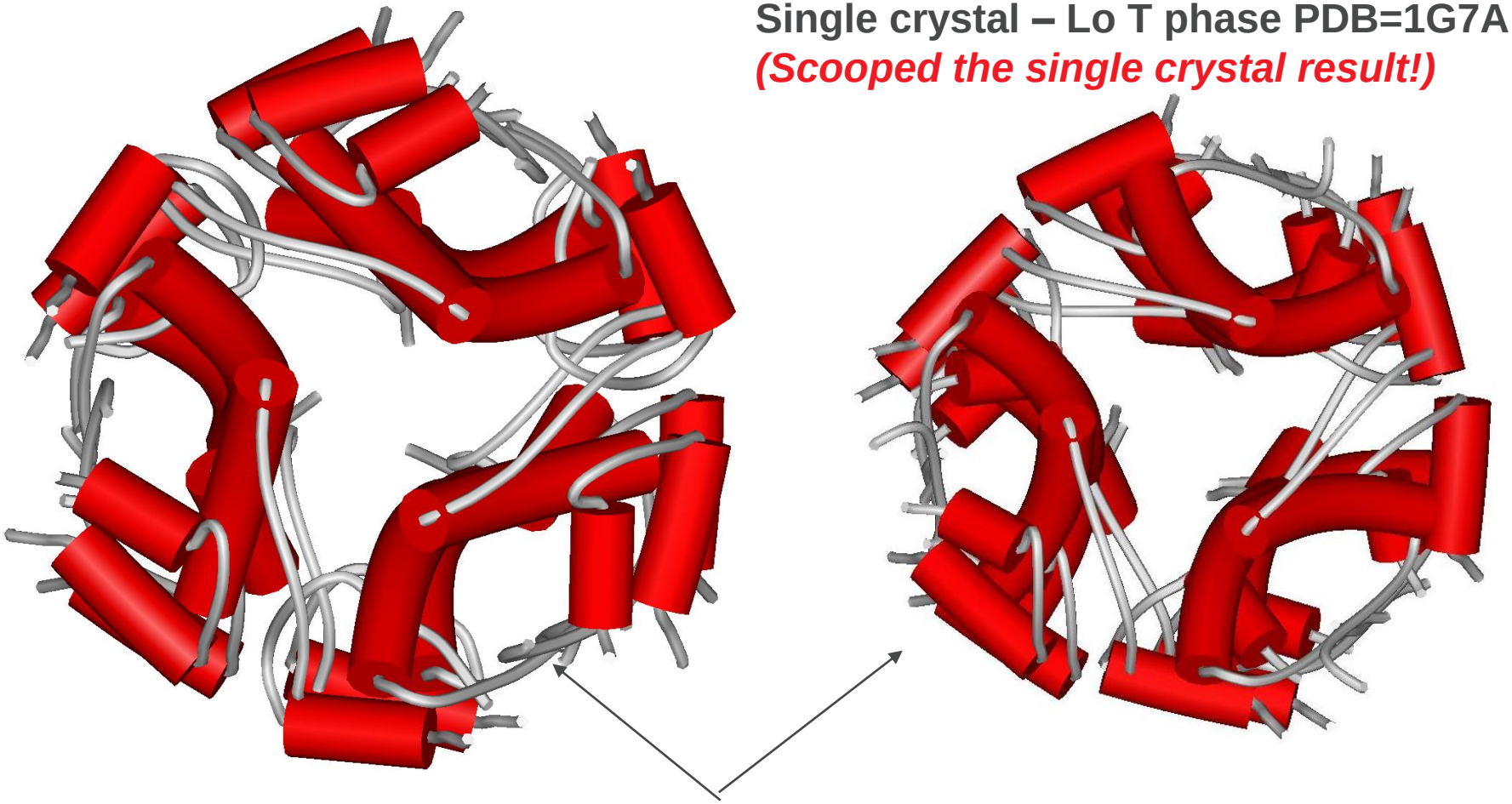
1st Molecular replacement solution!!
3 parameter problem



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!)

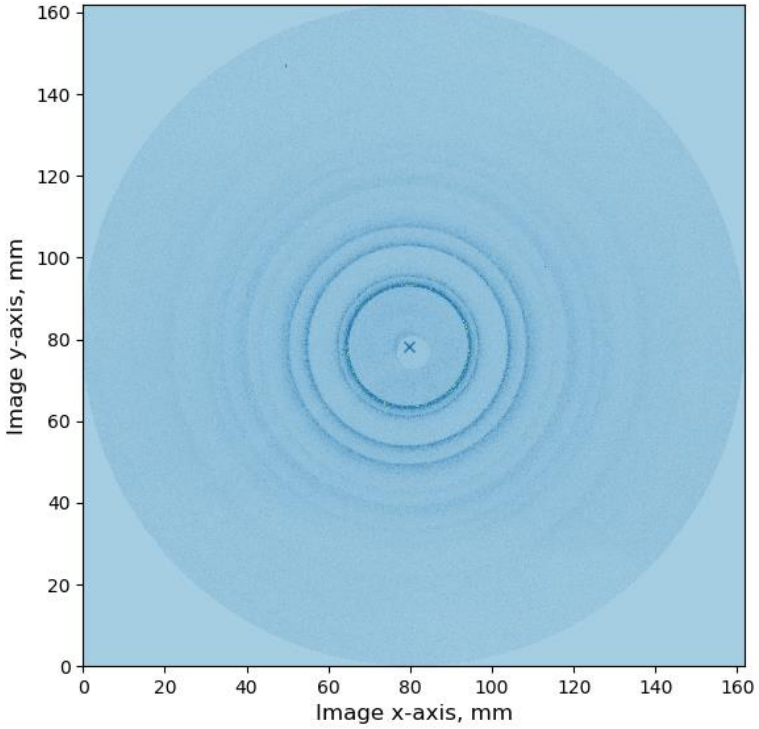


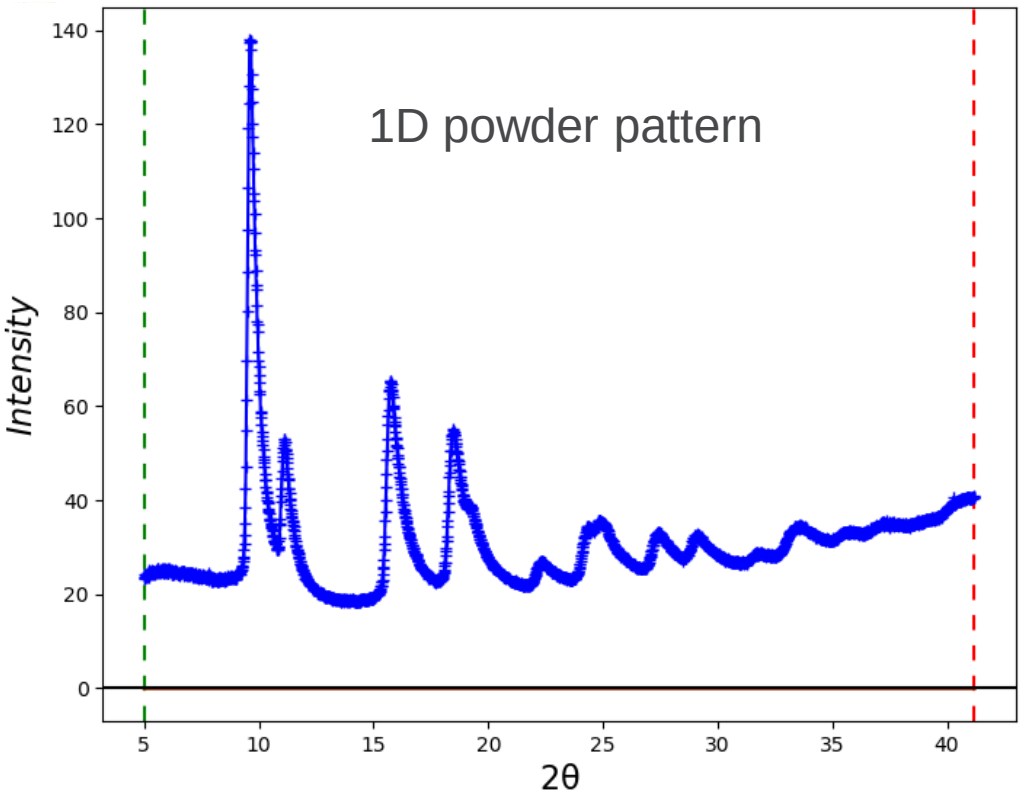
View down 3-fold axis - front T_3R_3 turned 9º wrt back T_3R_3

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. D**57**, 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 τ=0

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

Convolute with Gaussian

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

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

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

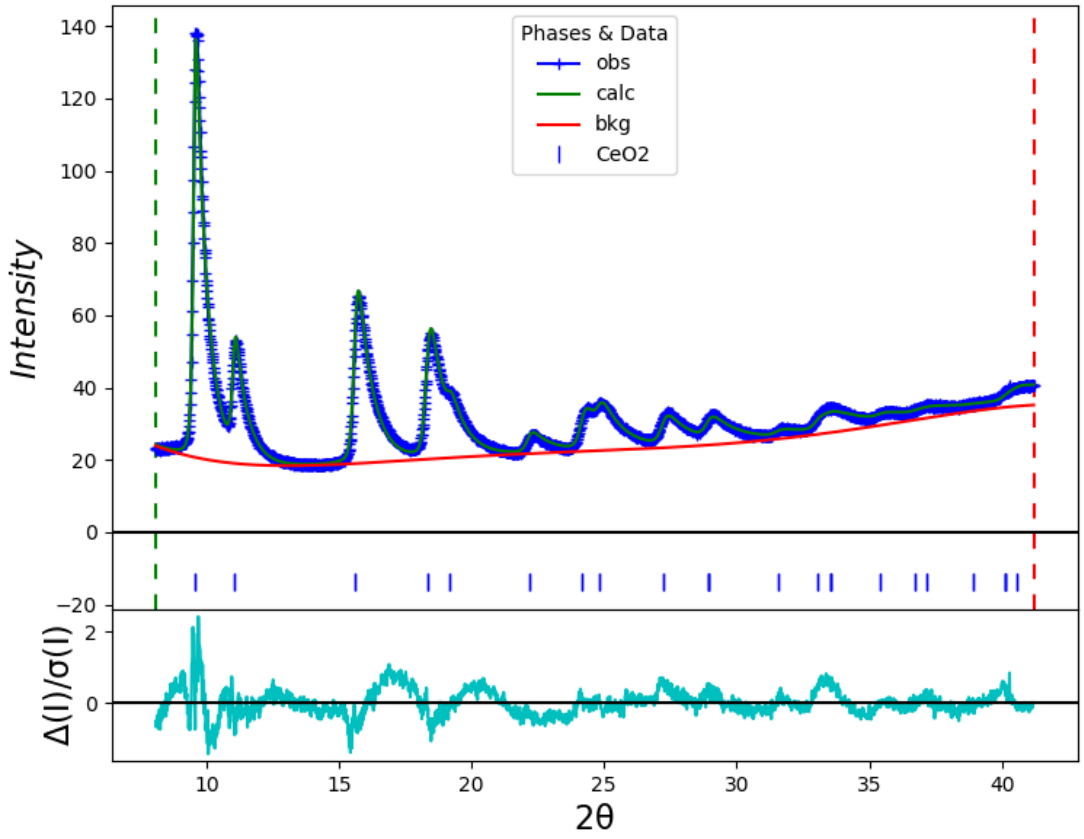
where

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

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 sinΘ

Good fit; R_{wp} = 2.08%

∴ Crystal structures at very high pressures can be refined

RIETVELD REFINEMENT IN GSAS-II

RIETVELD MODEL: $I_C = I_I\{\Sigma K_P F^2_P M_P L_P P(\Delta_P) + I_B\}$

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

k_p - scale factor for particular phase

F^2_p - 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(Δ_P) – BASICS

$\Delta_p = T_{reflection} - T_{profile}$ (T = 2Θ 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

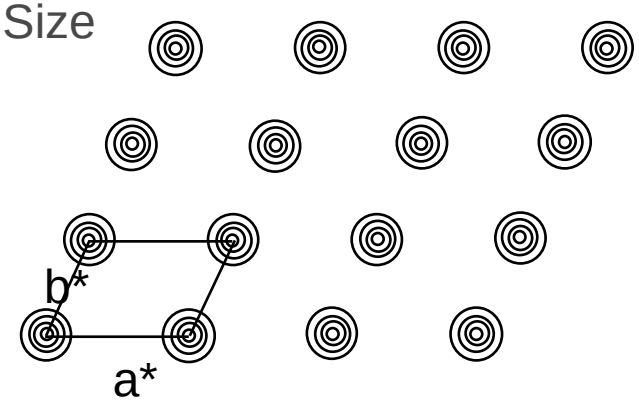
$$L(\Delta T, \gamma) = \frac{2}{\pi\gamma} \frac{1}{1+\left(\frac{2\Delta T}{\gamma}\right)^2}$$

Voigt – convolution = G ⊗ L
Pseudo-Voigt – linear combination = ηL+(1-η)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 & μstrain broadening

Size



Small (<1μm) crystals → not δ-functions
Size distribution →
superposition of sharp to broad spots
→ Shape ~Lorentzian

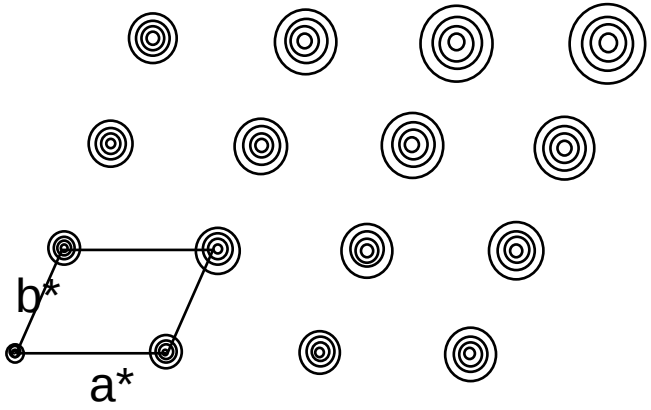
Width $\Delta d^* = \text{constant} = \Delta d/d^2 = \Delta\Theta\cot\Theta/d$

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

→Scherrer equation
k=1,p = size

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

μstrain



Unit cell variation (defects??)

Lorentzian distribution → shape

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

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

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

μ – μstrain (x10^6) parameter

CW PROFILE COEFFICENTS

Lorentzian vs Gaussian sample broadening?

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

$$\Gamma_g^2 = 8ln2(Utan^2\Theta + Vtan\Theta + W + S_\Gamma)$$

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

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

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

$$S_\Gamma = [(1 - m_s)^2 S^2 + (1 - m_\mu)^2 M^2]/8ln2$$

- Normally m_s & m_μ = 1 (all Lorentzian sample broadening) so:

$$S_\gamma = S + M$$

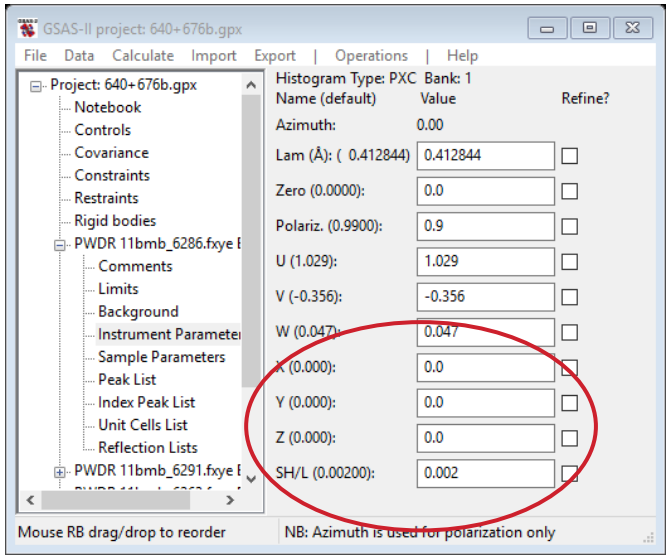
$S_\Gamma = 0$ (no Gaussian sample broadening)

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

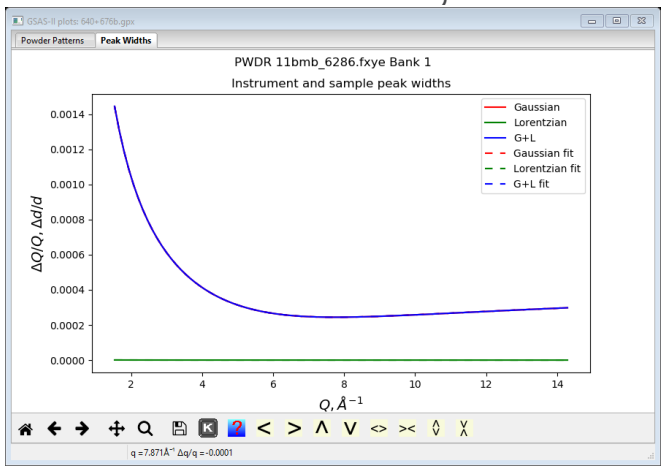
CW PROFILE PEAK BROADENING IN GSAS-II

The split of sample broadening from instrumental contribution

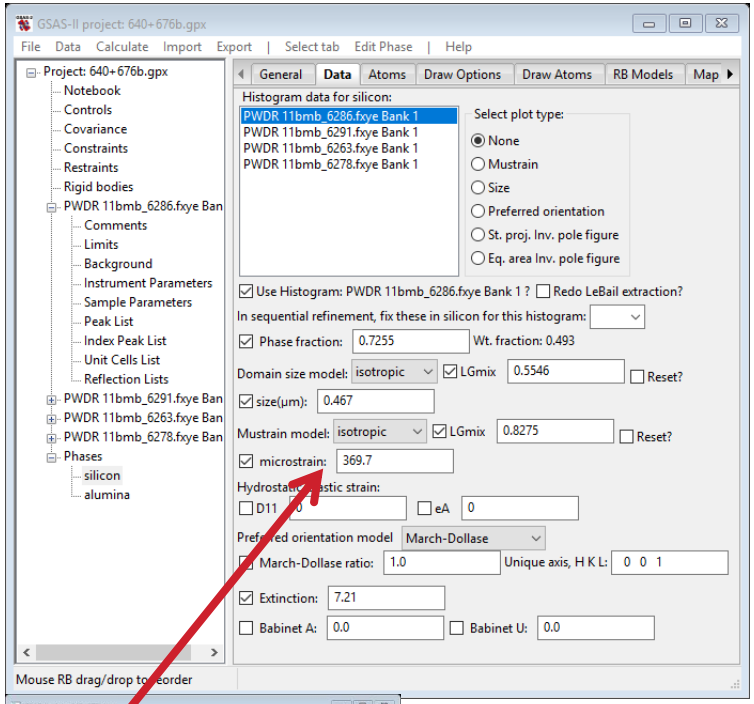
Instrument – fixed from calibration

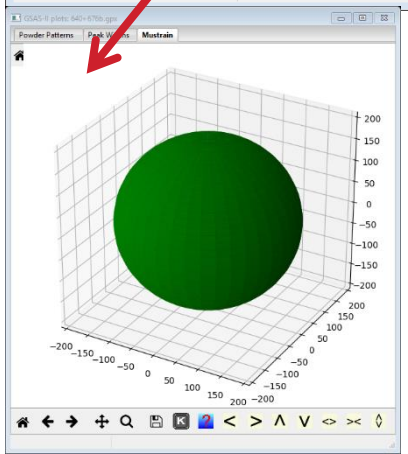


NB: for APS 11BM X,Y & Z = 0



Sample – phase & histogram dependent
Refined & constrained as needed

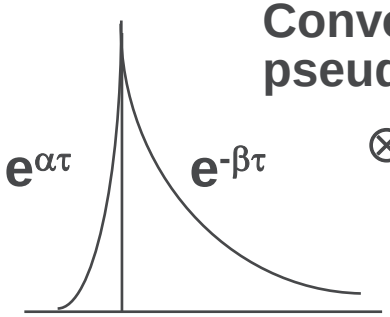




Sample:
New NIST SRMS
640f & 676b

TOF PROFILE FUNCTION IN GSAS-II

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



Convolution of paired exponentials and a pseudoVoigt

$\otimes$ (1-η)G(ΔT,Γ)+ηL(ΔT,γ)

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

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

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

Empirical relationships to d-spacing

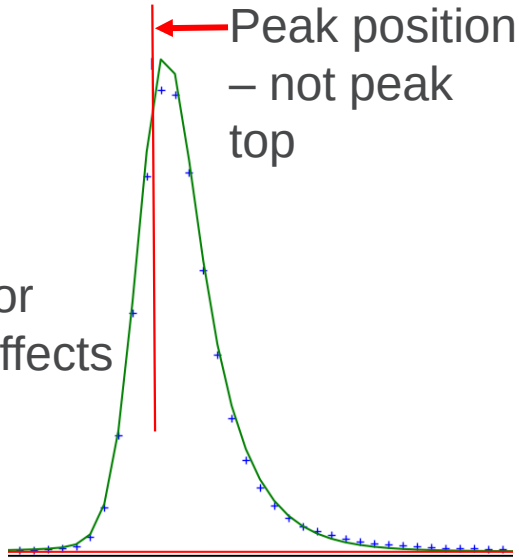
$$\alpha = {}^{\alpha_0}/_{d};\ \beta = \beta_0 + {}^{\beta_1}/_{d^4} + {}^{\beta_q}/_{d^2}$$

$$\sigma^2 = s_0 + s_1 d^2 + s_2 d^4 + S_q d + S_\Gamma$$

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

New terms for epithermal effects

Sample broadening terms - earlier slide; may be hkl dependent



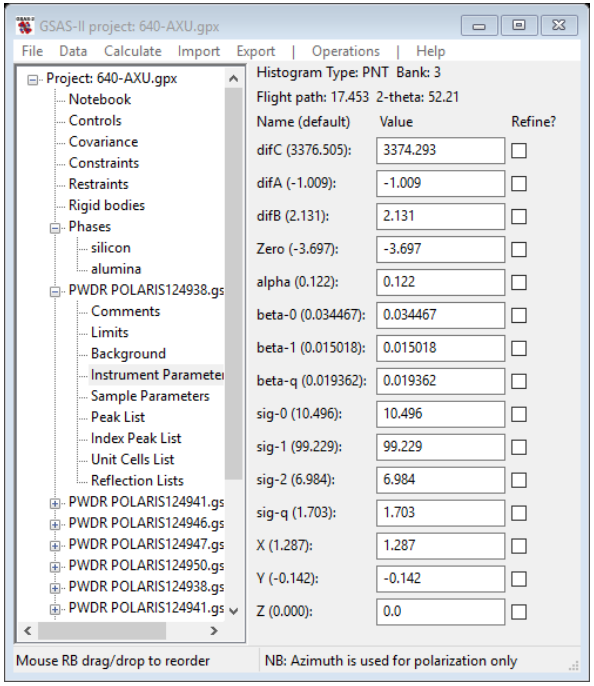
Peak position – not peak top

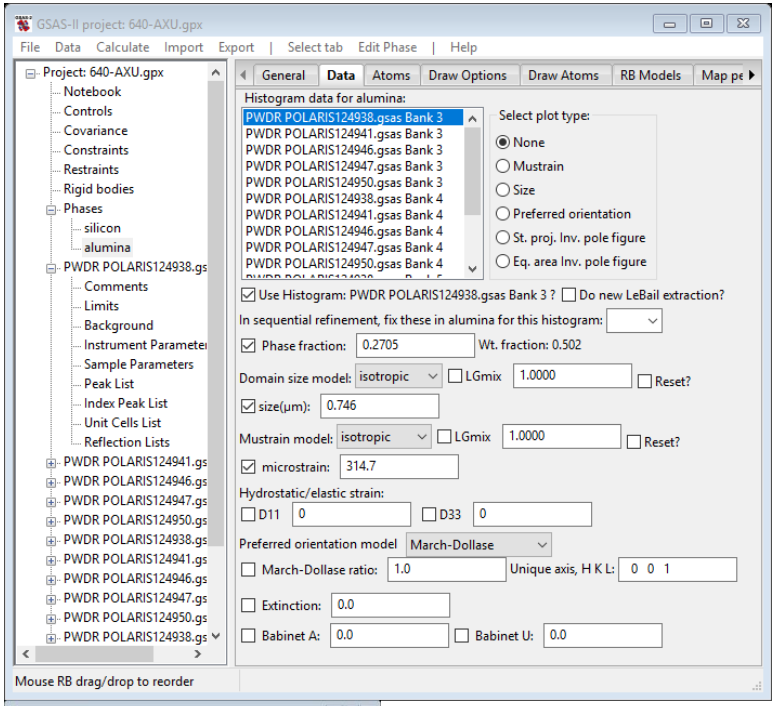
TOF PROFILE PEAK BROADENING IN GSAS-II

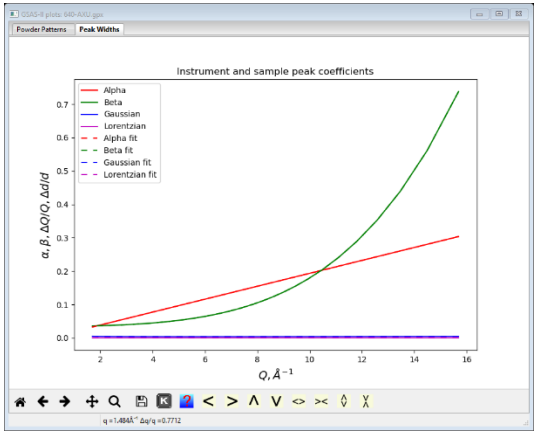
The split of sample broadening from instrumental contribution

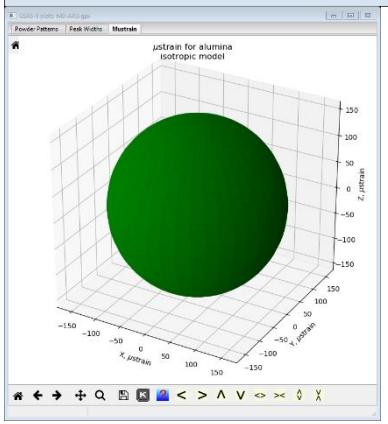
Instrument – fixed from calibration

Sample – phase & histogram dependent
Independent of experiment (e.g. CW or TOF)









Sample:
New NIST SRMS
640f & 676b

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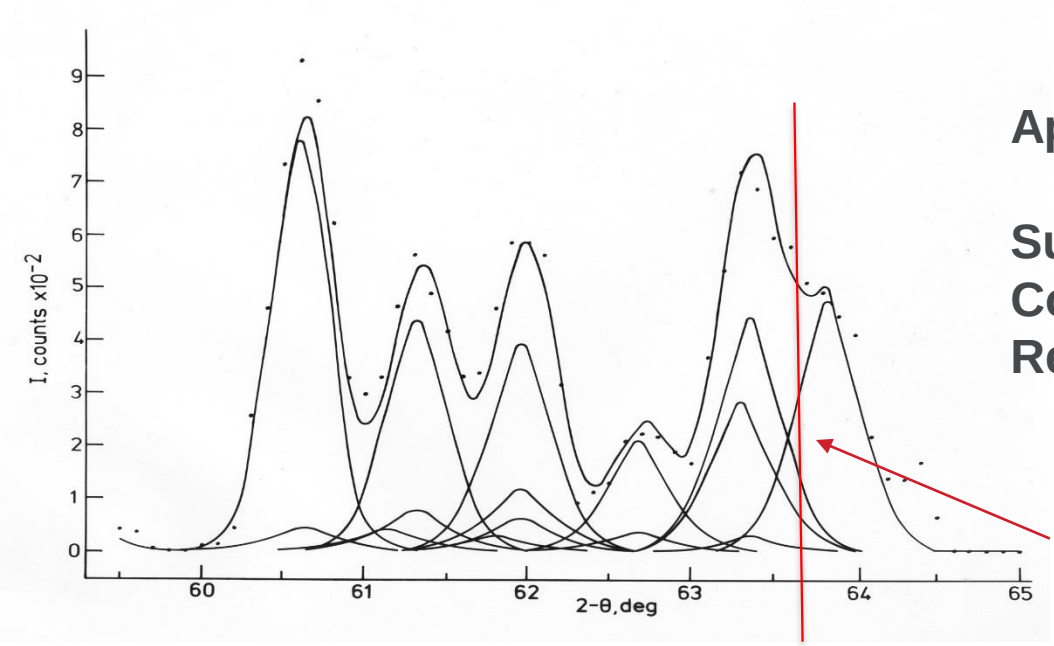
INTENSITY EXTRACTION

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 & Lp, etc.
Result is $F^2(H)$

Here 4 reflections contribute

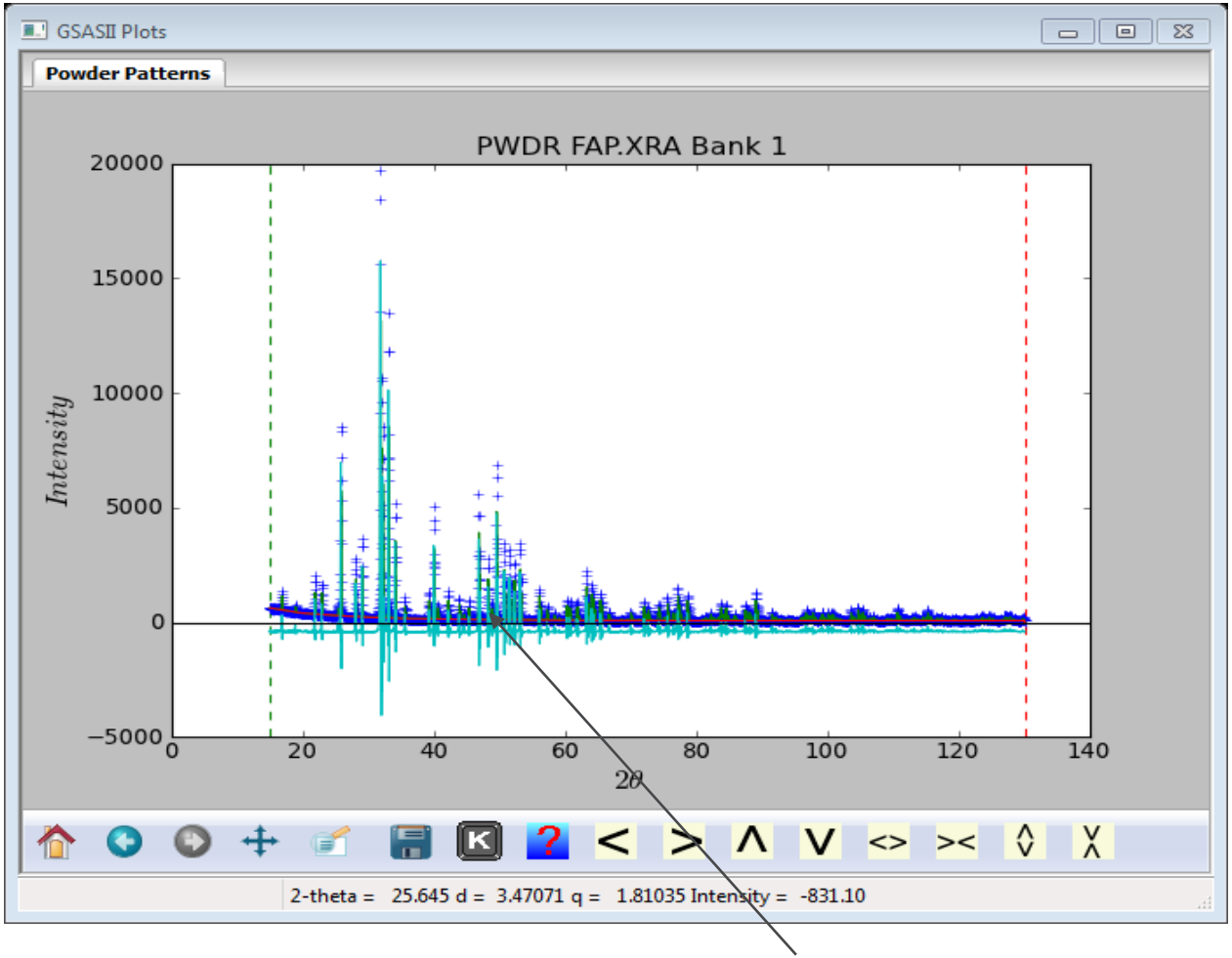
LeBail algorithm – extracted F^2_o → new F^2_c then next cycle;
refine only background, peak shapes & positions – few parameters
No constraints needed for overlaps – Simple

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



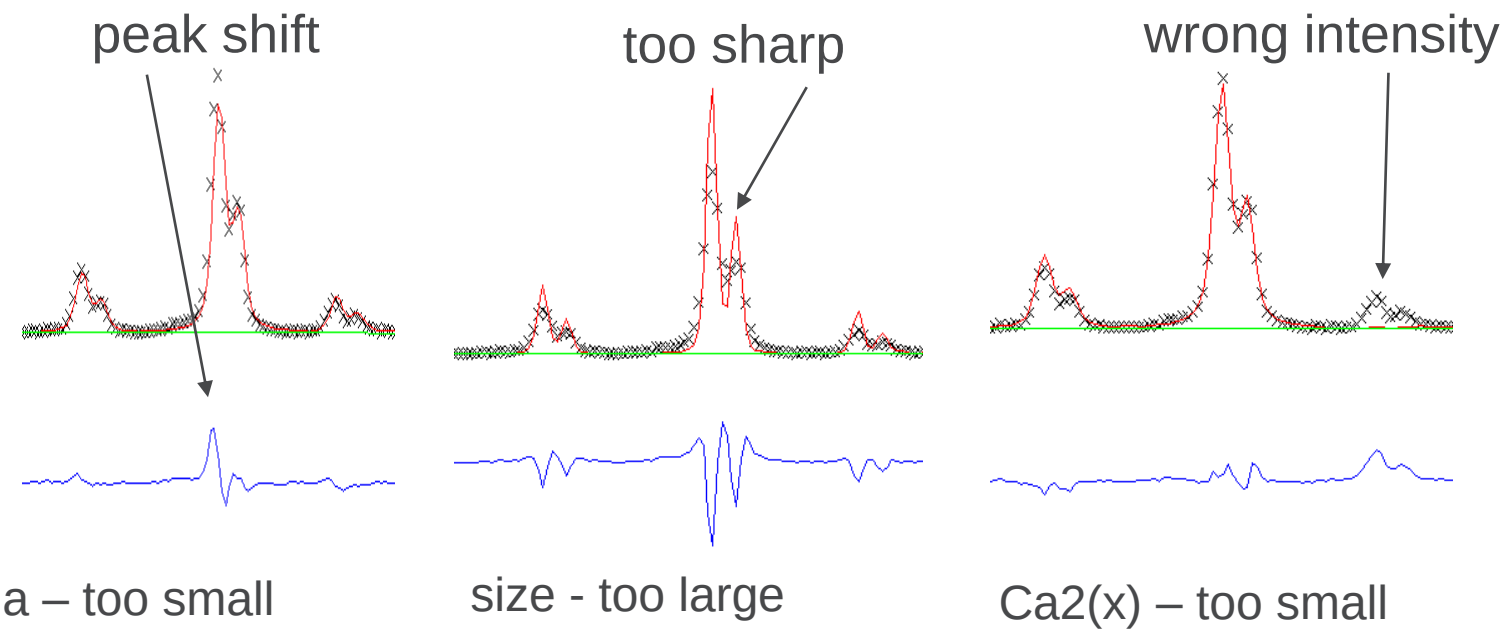
- **Notice shape of difference curve – position/shape/intensity errors**

ERRORS & PARAMETERS?

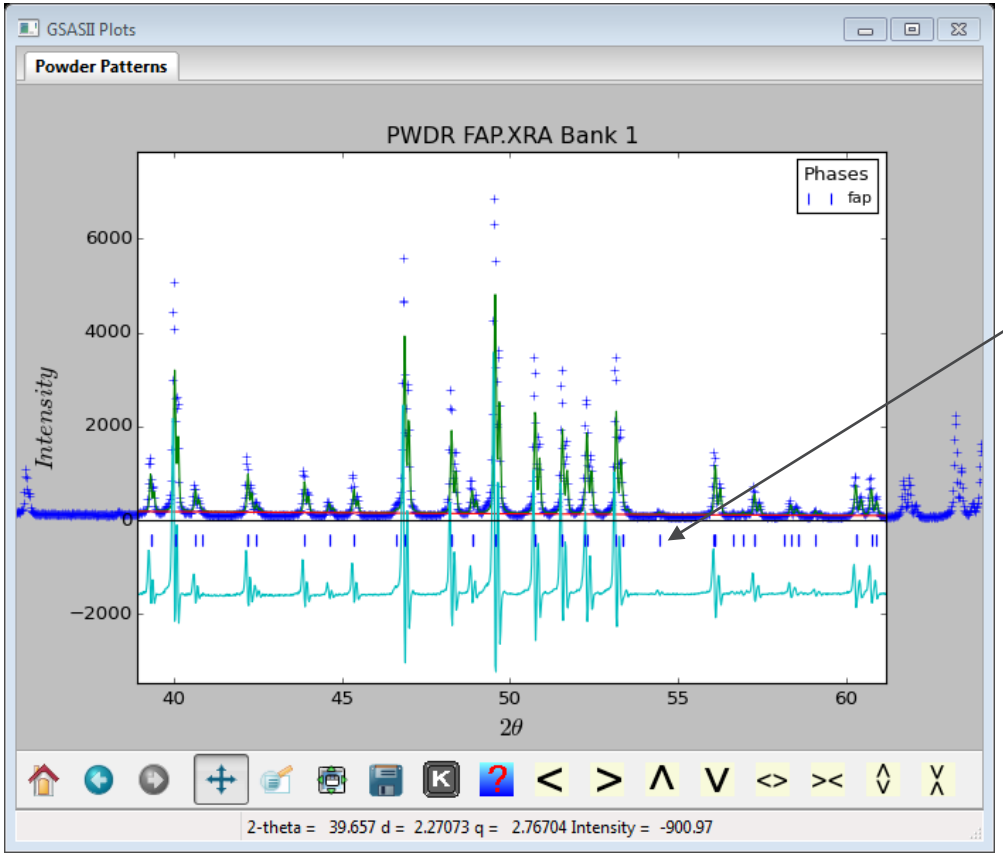
- position – lattice parameters, zero point (not common)
  - other systematic effects – sample shift/offset
- shape – profile coefficients – sample size/μstrain

  (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^2 – trend with 2Θ (or TOF) important



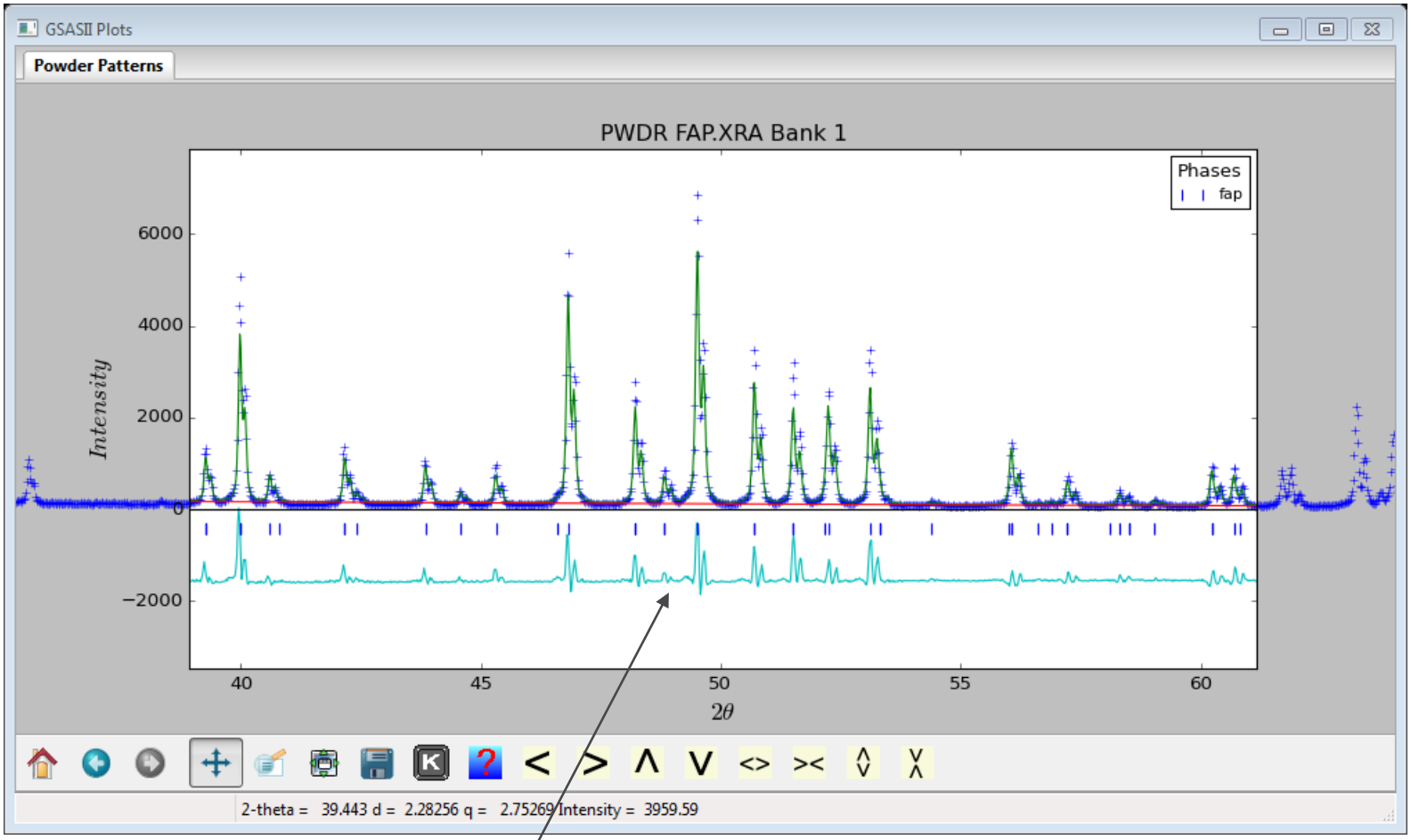
DIFFERENCE CURVE – WHAT TO DO NEXT?



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

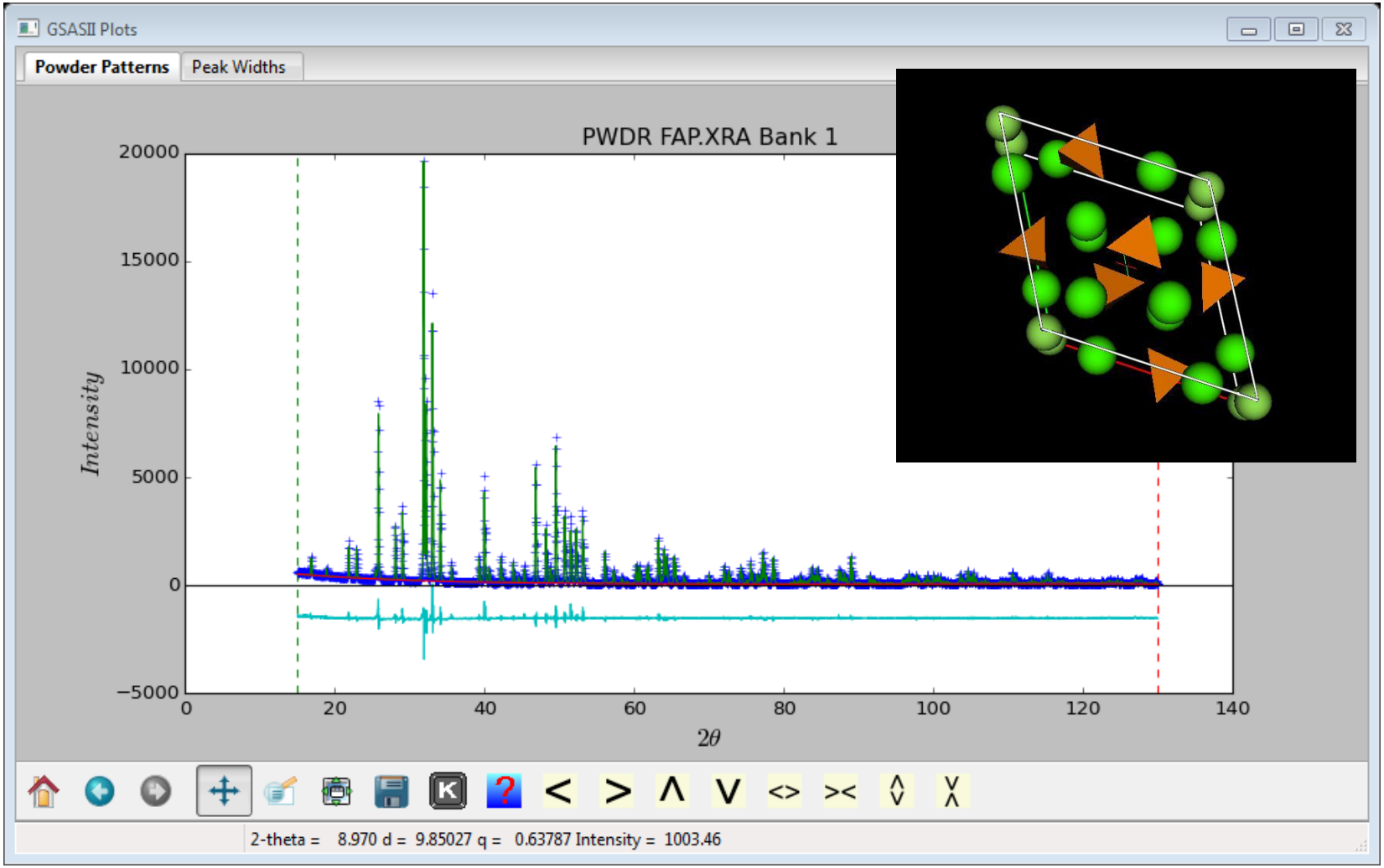
- Dominant error – peak positions? peak shapes - too sharp?
- Refine sample μstrain parameter next & include lattice parameters
- **NB - EACH CASE IS DIFFERENT – no magic recipe**

RESULT – MUCH IMPROVED!



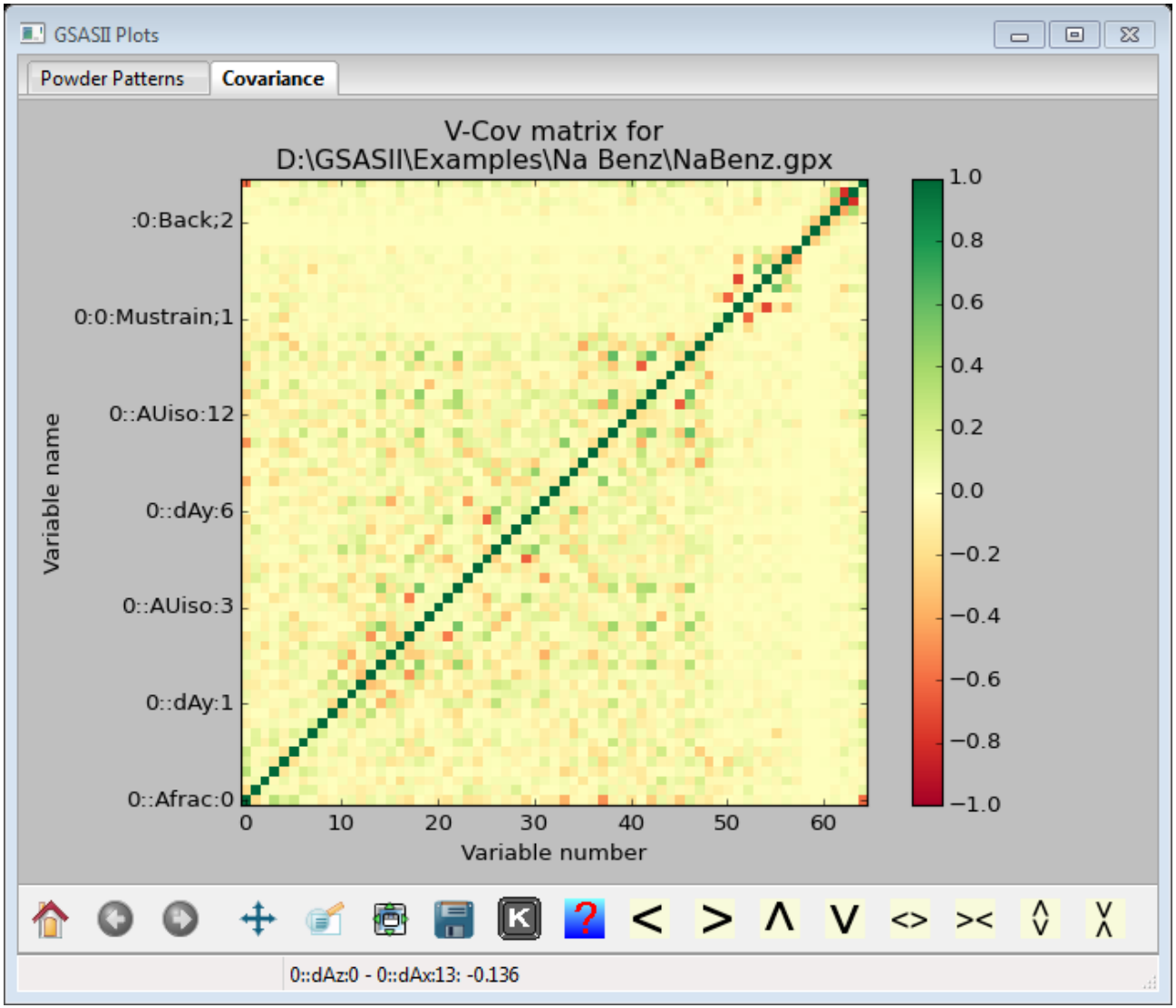
- **maybe intensity differences remain**
  - **refine coordinates & thermal parms.**

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

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