THE RIETVELD REFINEMENT METHOD IN GSAS-II
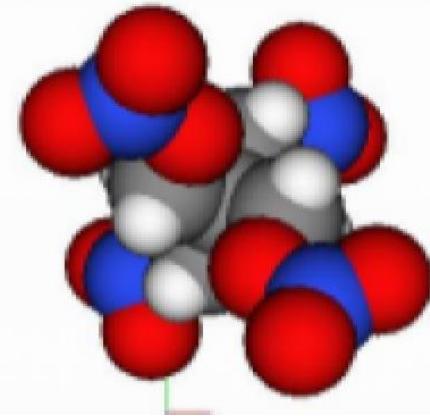
R. B. VON DREELE
ANL/APS (retired)
vondreele@anl.gov

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, <u>nonlinear LS curve fitting</u>

Exact overlaps
- symmetry
Incomplete overlaps
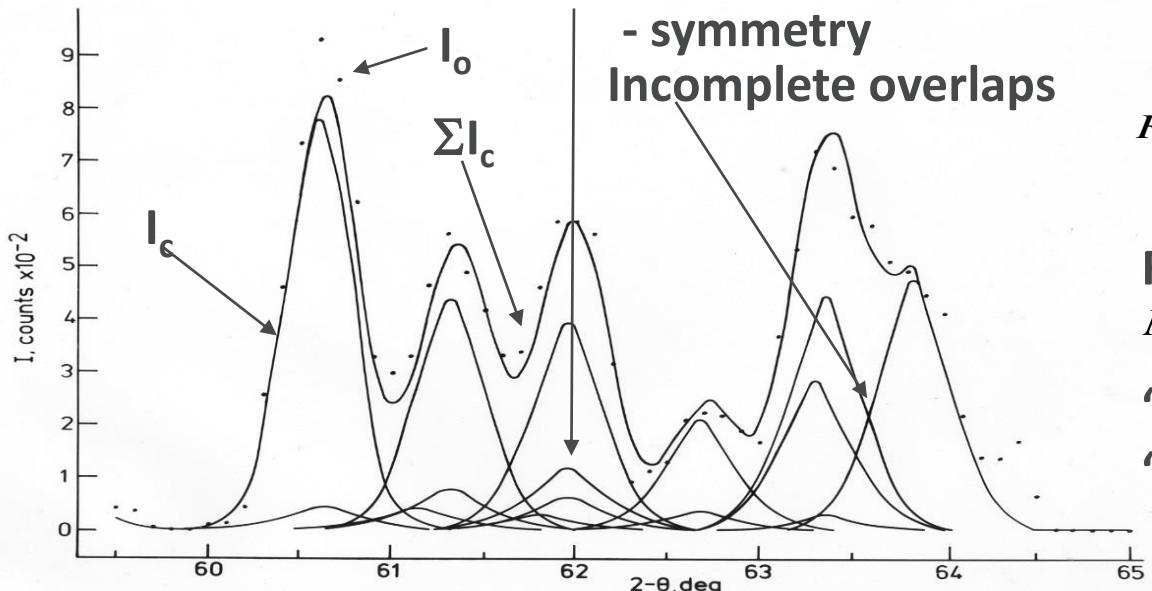
Residuals:

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

Rietveld Minimize

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

"chi-squared" or "goodness-of-fit"

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

LINEAR LEAST SQUARES THEORY

Given a set of observations I_{obs}

and a function

$$I_{calc} = f(p_1, p_2, p_3 ..., p_n)$$

then the best estimate of the values p_i is found by minimizing

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

This is done by setting the derivative to zero

$$\sum w(I_o - I_c) \frac{\partial I_c}{\partial p_j} = 0$$

Results in n "normal" equations (one for each variable) - solve for p_i

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NON-LINEAR LEAST SQUARES THEORY

Problem - I(p_i) is nonlinear & transcendental (sin, cos, etc.) so can't solve directly

Expand I(p_i) as Taylor series & toss high order terms

$$I_c(p_i) = I_c(a_i) + \sum_i \frac{\partial I_c}{\partial p_i} \Delta p_i$$

a_i - initial values of p_i

$\Delta p_i = p_i - a_i$ (shift)

Normal equations - one for each Δp_i

$$\sum w \left[\Delta I - \sum_i \frac{\partial I_c}{\partial p_i} \Delta p_i \right] \frac{\partial I_c}{\partial p_j} = 0 \qquad \Delta I = I_o - I_c(a_i)$$

Outer sum over observations

Solve for Δp_i - shifts of parameters, <u>NOT</u> values

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LEAST SQUARES THEORY - CONTINUED

Rearrange

$$\sum w \frac{\partial I_c}{\partial p_1} \left(\sum_{i=1}^{n} \frac{\partial I_c}{\partial p_i} \Delta p_i \right) = \sum w \Delta I \frac{\partial I_c}{\partial p_1}$$

$\vdots$

$$\sum w \frac{\partial I_c}{\partial p_n} \left(\sum_{i=1}^{n} \frac{\partial I_c}{\partial p_i} \Delta p_i \right) = \sum w \Delta I \frac{\partial I_c}{\partial p_n}$$

Matrix form: Ax=v

$$a_{i,j} = \sum w \frac{\partial I_c}{\partial p_i} \frac{\partial I_c}{\partial p_j} \quad x_j = \Delta p_j \quad v_i = \sum w (\Delta I) \frac{\partial I_c}{\partial p_i}$$

Solve: x = A⁻¹v = Bv; B = A⁻¹ This gives set of Δp$_i$ to apply to "old" set of a$_i$; repeat until Δp$_i$ small.

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GSAS-II ALGORITHM

GSAS – process point-by-point to make I_c (value) & $\partial I_c/\partial p_i$ (vector)
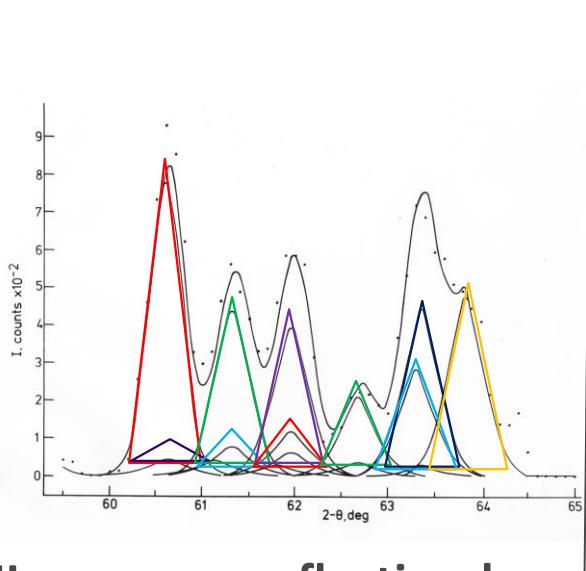
GSAS-II – process reflection-by-reflection to make I_c (vector) & $\partial I_c/\partial p_i$ (Jacobian matrix)

p_i

2Θ or TOF →

Jacobian matrix - J

x

2Θ or TOF

p_i →

Σ

$\partial I_c/\partial p_i$

$\partial I_c/\partial p_j$

$\Sigma w[\partial I_c/\partial p_i]\cdot[\partial I_c/\partial p_j]$

Hessian matrix - A

$$wJ^TJ = A$$
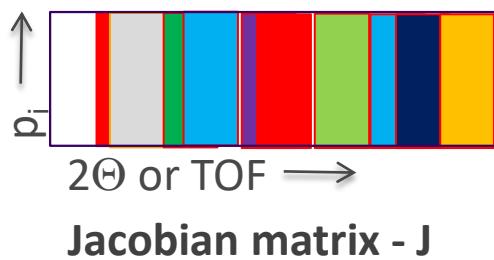
NB: GSAS-II – needs large memory!

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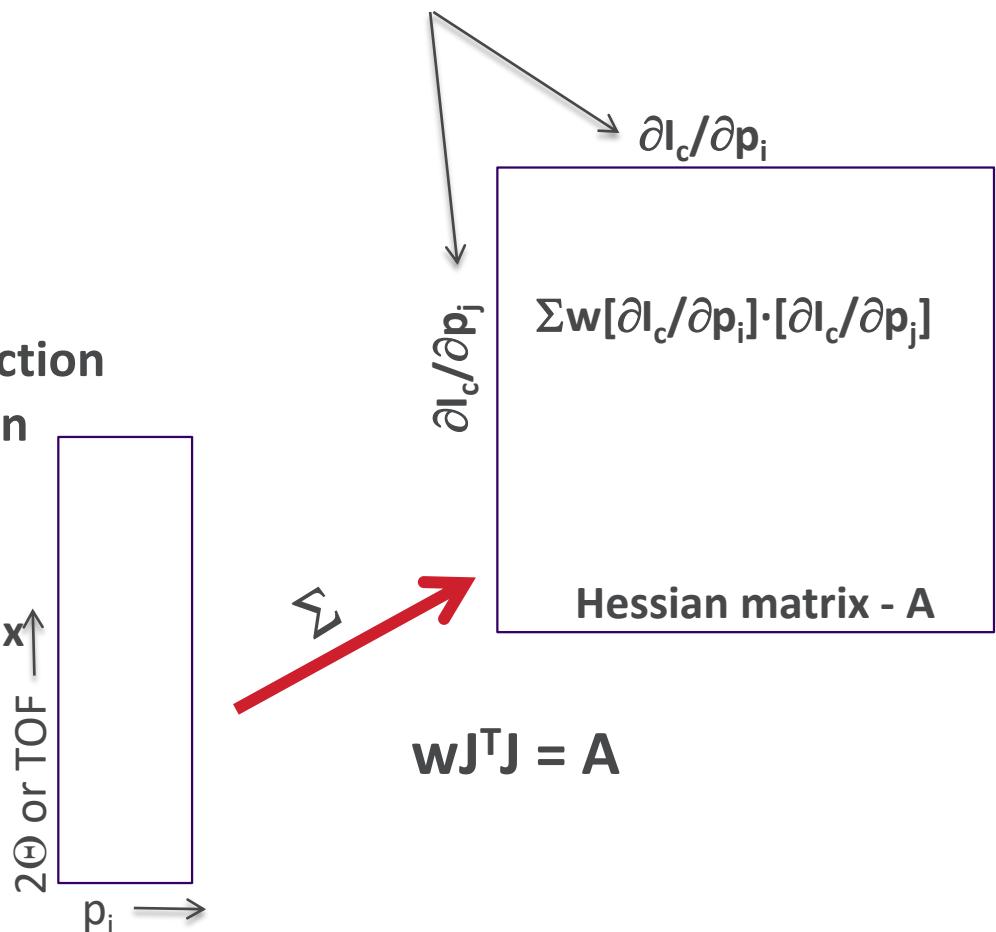
REFINEMENT VIA MODIFIED LEVENBERG/MARQUARDT-SVD ALGORITHM

Steps:

1. Compute $A_{ij} = \sum w \dfrac{\partial I_c}{\partial p_i}\dfrac{\partial I_c}{\partial p_j}$ **SLOW step**

2. Normalize $A'_{ij} = A_{ij}/\sqrt{A_{ii}A_{jj}}$

3. compute $\chi^2(p)$

4. Select λ (=0.001, "damping factor")

5. Modify $A''_{ii} = A'_{ii}(1 + \lambda)$

6. **Make SVD inversion of A"**

7. Solve for δp (unnormalized!) & compute $\chi^2(p+\delta p)$

8. If $\chi^2(p+\delta p) > \chi^2(p)$ then λ*10 go to 5

9. Else apply δp to p & go to 1 (new cycle)

10. Quit when $\chi^2(p) - \chi^2(p+\delta p) / \chi^2(p) < 0.0001$

FAST steps
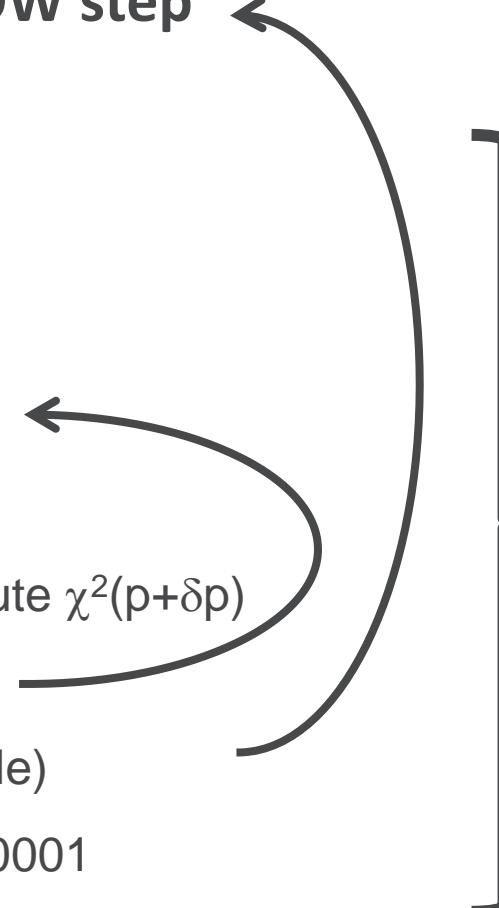
NB: all in ~40 lines of python; all double precision
NB^2: this thing is exceedingly robust – no user damping factors needed

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SVD – SINGULAR VALUE DECOMPOSITION

Singularities & near singularities – see Mathematical Recipes 2.9

LS matrix: solve for x   Ax=b   by $x = A^{-1}b$; x are the parameter shifts

SVD: replace $A = UwV$ where U & V are such that $U^{-1} = U^T$ & $V^{-1} = V^T$

          & w – diagonal matrix; all same size as A

Then: $A^{-1} = V(1/w_{ii})U^T$

The trick: what to do if $w_{ii} \sim 0$? (singularity) → make $1/w_{ii} = 0$! (instead of ∞)

Then: $x = V(1/w_{ii})U^Tb$ does away with ill-conditioned terms

Have to choose tolerance on $w_{ii} \sim 0$ (typically 10^{-6} but 10^{-3} for proteins works well)

SVD is in python library as numpy.linalg.svd

          & uses LAPACK _gesdd routine (fortran – code in MR 2.9)

NB: all double precision in python; downside is w_{ii} not 1:1 to parameters so id of failures difficult.

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LEAST SQUARES ALGORITHMS IN GSAS-II

Useful choices – found in Controls
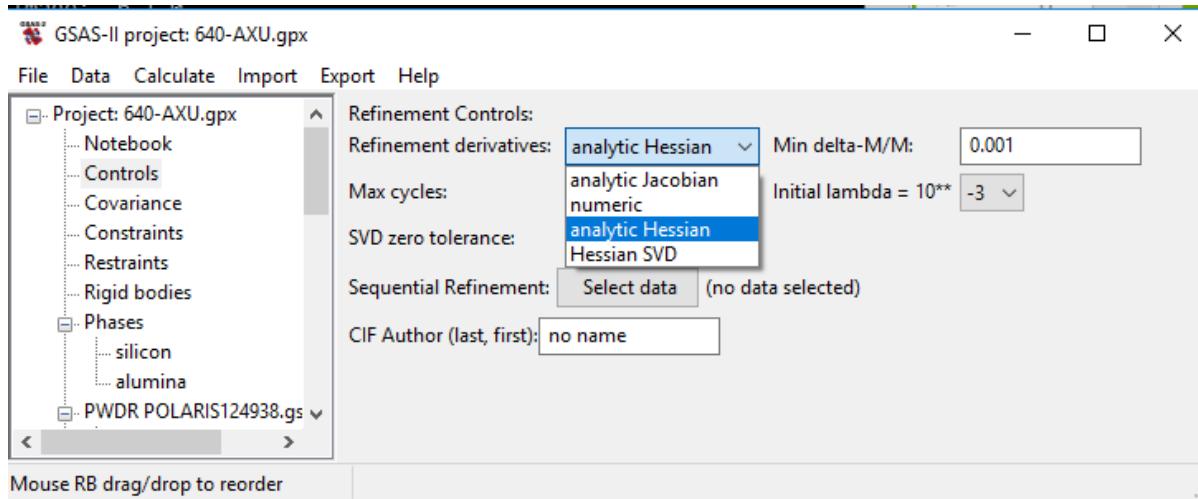
Analytic Hessian – **default** Levenberg-Marquardt SVD from Hessian & computed derivatives
Downside: hard singularities hard to find → "linear algebra errors" cause failures

Analytic Jacobian – uses Jacobian matrix (not Hessian) no SVD; identifies singularities & Removes them from LS refinement; always runs to convergence

Hessian SVD – no Levenberg-Marquardt (might be better for single crystal data)
Same downside as Analytic Hessian

Numeric – no derivatives & slow – mostly for testing purposes.

LEAST SQUARES THEORY - CONTINUED

Error estimates (mostly from W.C. Hamilton)
Given observations n > m parameters
with distributions that have finite 2nd moments
(no need to be "normal" although usually are for powders)
Then LS gives parameter estimates (shifts in our case)
with the minimum variance in any linear combination
The error estimates ("esd's") are

$$\sigma_i = \sqrt{b_{ii}\big/\chi^2} \qquad \chi^2 = \frac{\sum w(I_o - I_c)^2}{n-m}$$

b_{ii} - diagonal elements of the inverted A matrix
Note: There is little justification for additional scaling of the σ_i **NB: systematic errors will bias results beyond σ_i.**

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

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.

$P(\triangle_p)$ - 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

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PROFILE FUNCTIONS $P(\Delta_P)$ – 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

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

Voigt – convolution = G $\otimes$ 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
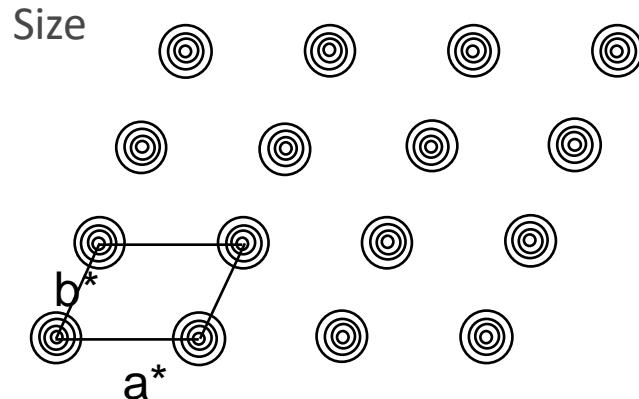
Size

μstrain

Small (<1μm) crystals → not δ-functions

Size distribution →

   superposition of sharp to broad spots

→ Shape ~Lorentzian

Width $\Delta d^* = $ 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

$$S = \frac{180k\lambda}{\pi p \cos\Theta}$$
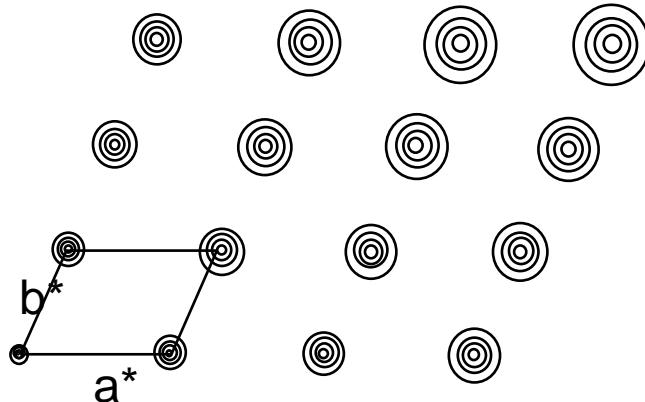
Unit cell variation (defects??)

Lorentzian distribution → shape

$\Delta d/d = $ constant $= \Delta d^*/d^* = \Delta\Theta\cot\Theta$

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

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

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)

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

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

- Normally m_s & m_μ = 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)

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CW PROFILE PEAK BROADENING IN GSAS-II

The split of sample broadening from instrumental contribution

Instrument – fixed from calibration
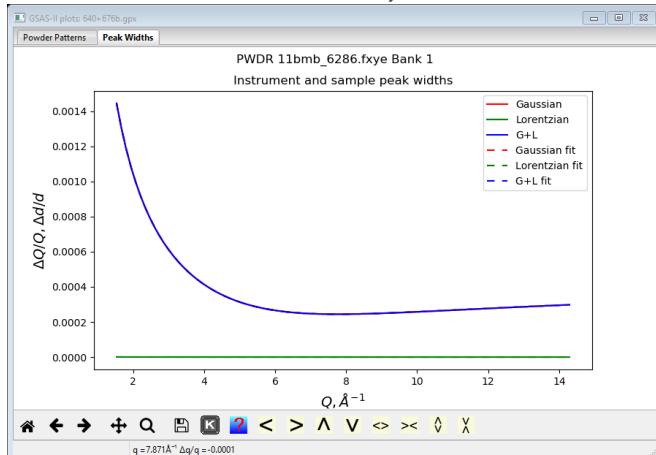
Sample – phase & histogram dependent
Refined & constrained as needed

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

Sample:
New NIST SRMS
640f & 676b

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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

$e^{\alpha\tau}$ $e^{-\beta\tau}$ $\otimes$ **(1-η)G(ΔT,Γ)**

$\otimes$ η**L(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

Peak position – not peak top

Empirical relationships to d-spacing

$\alpha = {}^{\infty_0}\!/_d$; $\beta = \beta_0 + {}^{\beta_1}\!/_{d^4} + {}^{\beta_q}\!/_{d^2}$

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

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

New terms for epithermal effects

Sample broadening terms - earlier slide; may be hkl dependent

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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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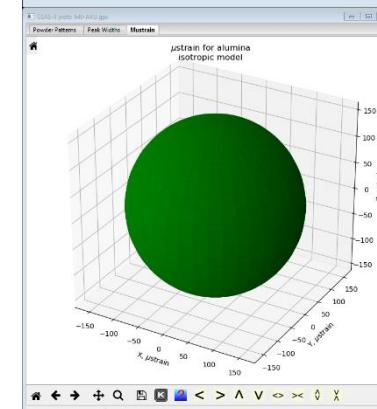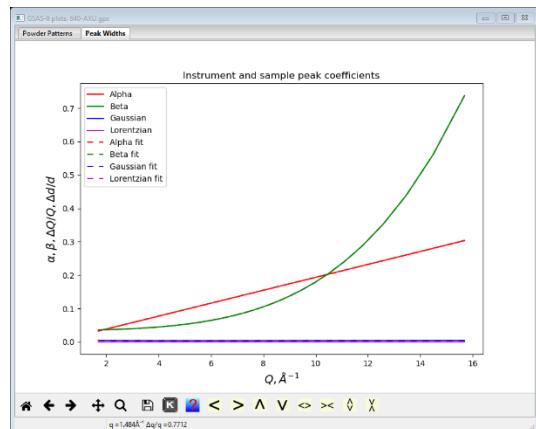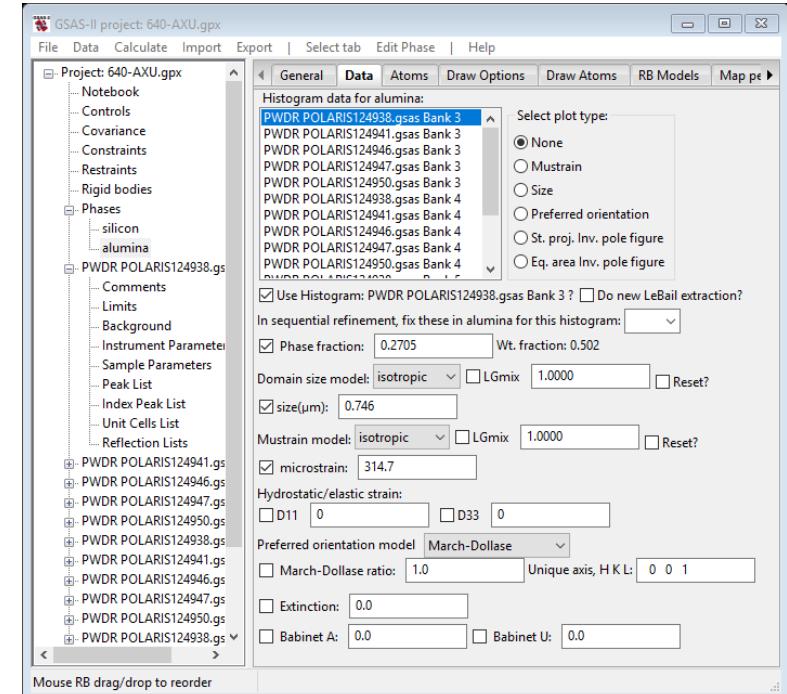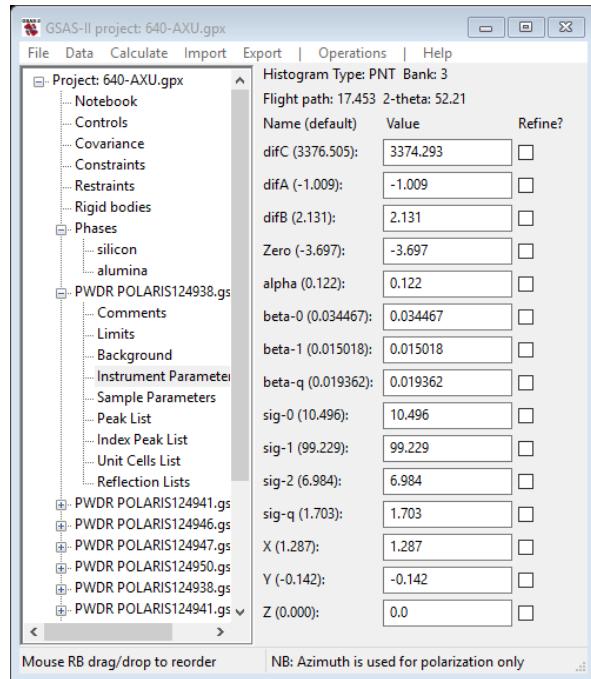
AXIAL BROADENING FUNCTION – CONST. WAVELENGTH

Finger, Cox & Jephcoat based on van Laar & Yelon

Debye-Scherrer cone

2Θ Scan

H

Slit

$2\Theta_{min}$ $2\Theta_i$ $2\Theta_{Bragg}$
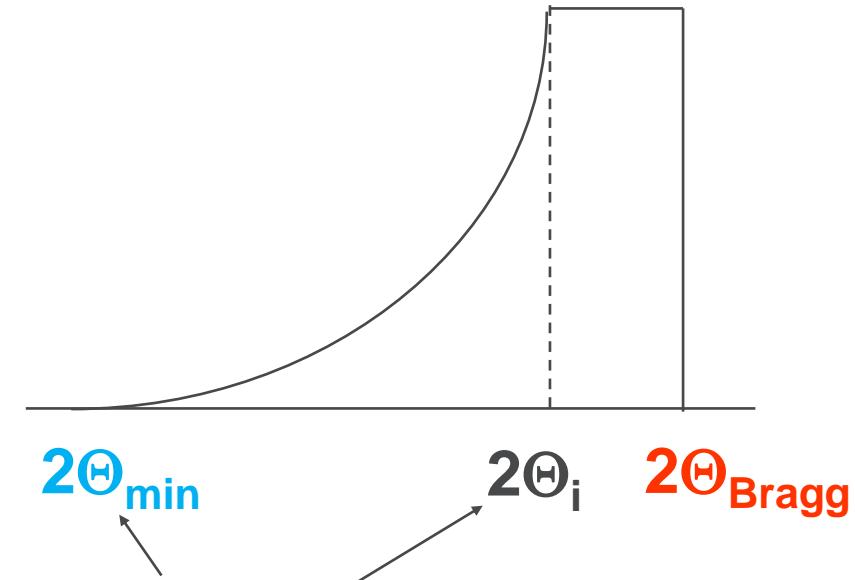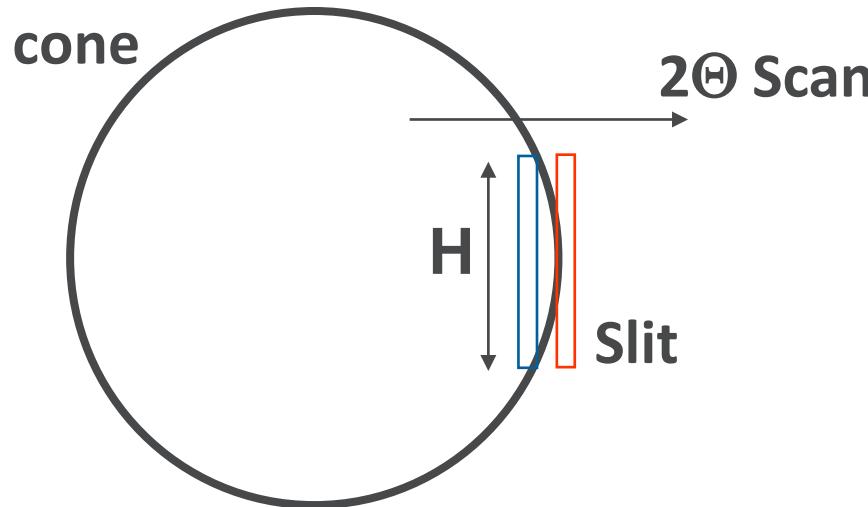
Depend on slit & sample "heights" wrt diffr. radius
H/L & S/L - parameters in function; combined as H+S/L in GSAS-II
(typically 0.005 - 0.020)

$\otimes$ **Pseudo-Voigt**
= profile function

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# HOW GOOD IS THIS FUNCTION?

lysozyme RT 0.70A   Hist   1
Lambda 1.1501 A, L-S cycle   542   Obsd. and Diff. Profiles
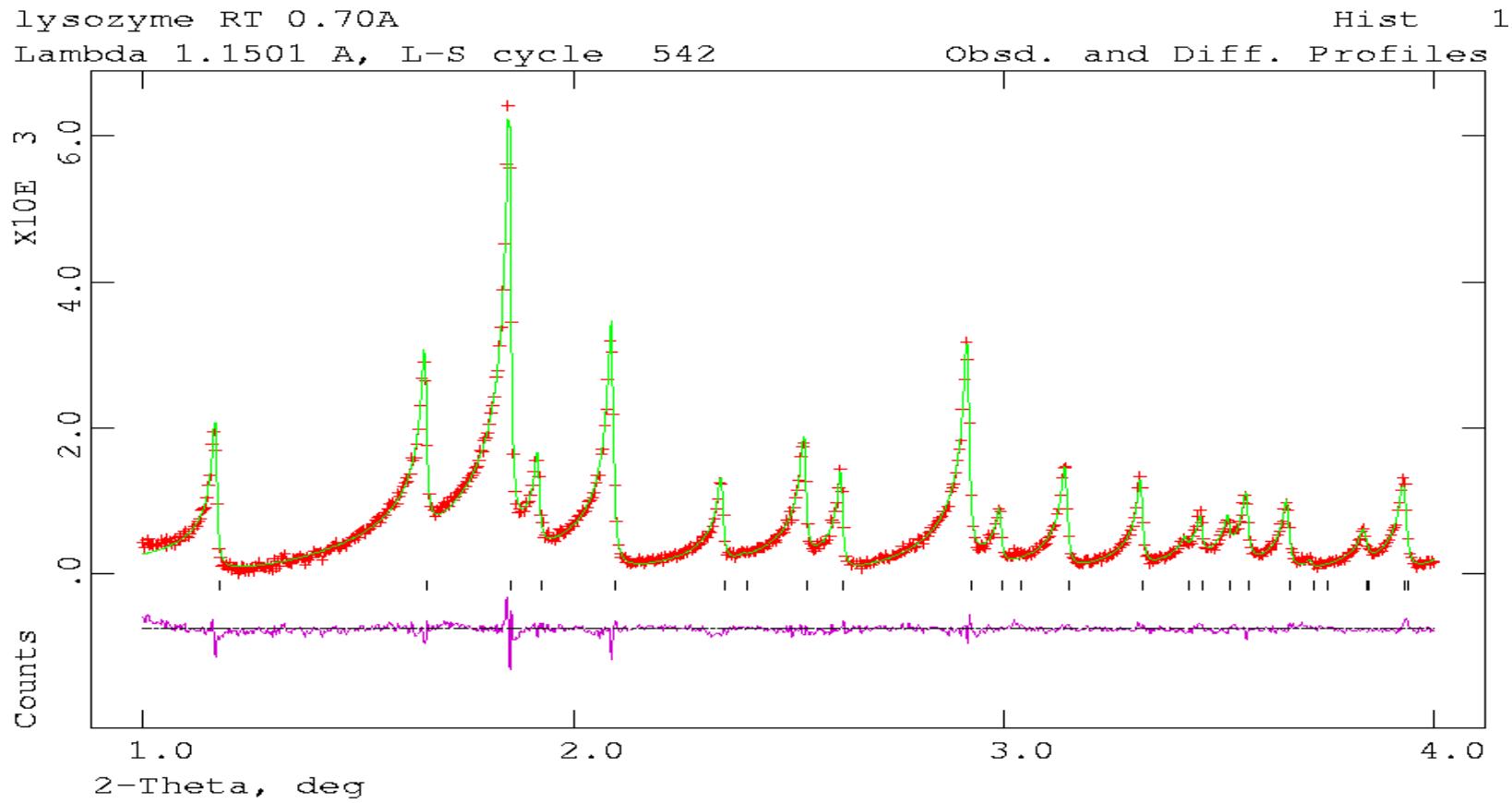
Protein Rietveld refinement - Very low angle fit

1.0-4.0° peaks - strong asymmetry

"perfect" fit to shape

PROFILE FUNCTION – COMPLEXITIES
AN EXAMPLE – UNUSUAL LINE BROADENING
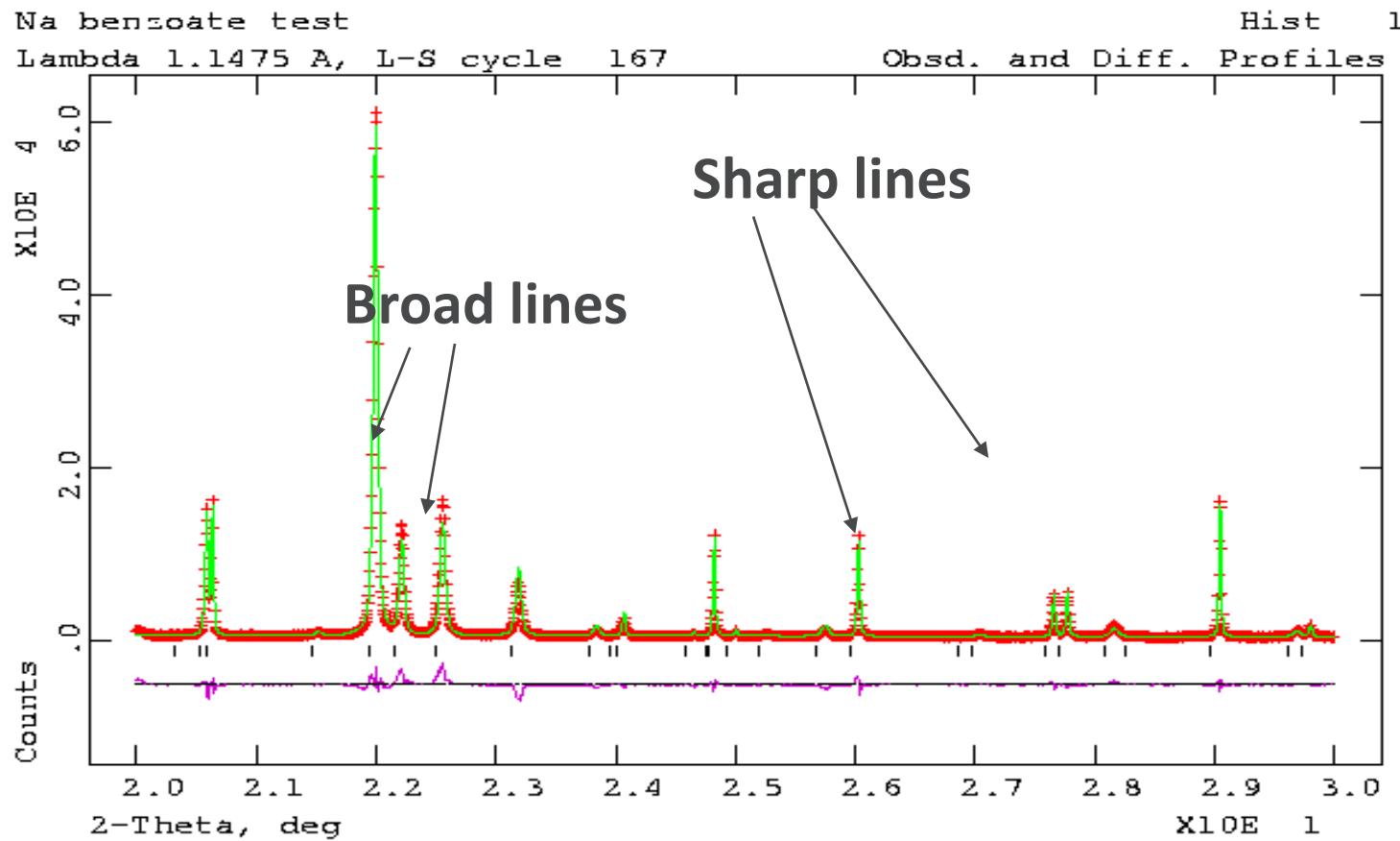
Seeming inconsistency in line broadening - hkl dependent

MICROSTRAIN BROADENING – PHYSICAL MODEL

Model – elastic deformation of crystallites

Stephens, P.W. (1999). *J. Appl. Cryst.* **32**, 281-289.
Also see Popa, N. (1998). *J. Appl. Cryst.* **31**, 176-180.

d-spacing expression

$$\frac{1}{d_{hkl}^2} = M_{hkl} = \alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk$$

Broadening – variance in M_{hkl}; refine C_{ij}

$$\sigma^2(M_{hkl}) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j}$$

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NA PARAHYDROXYBENZOATE

## *Unusual micostrain effects - peak broadening*
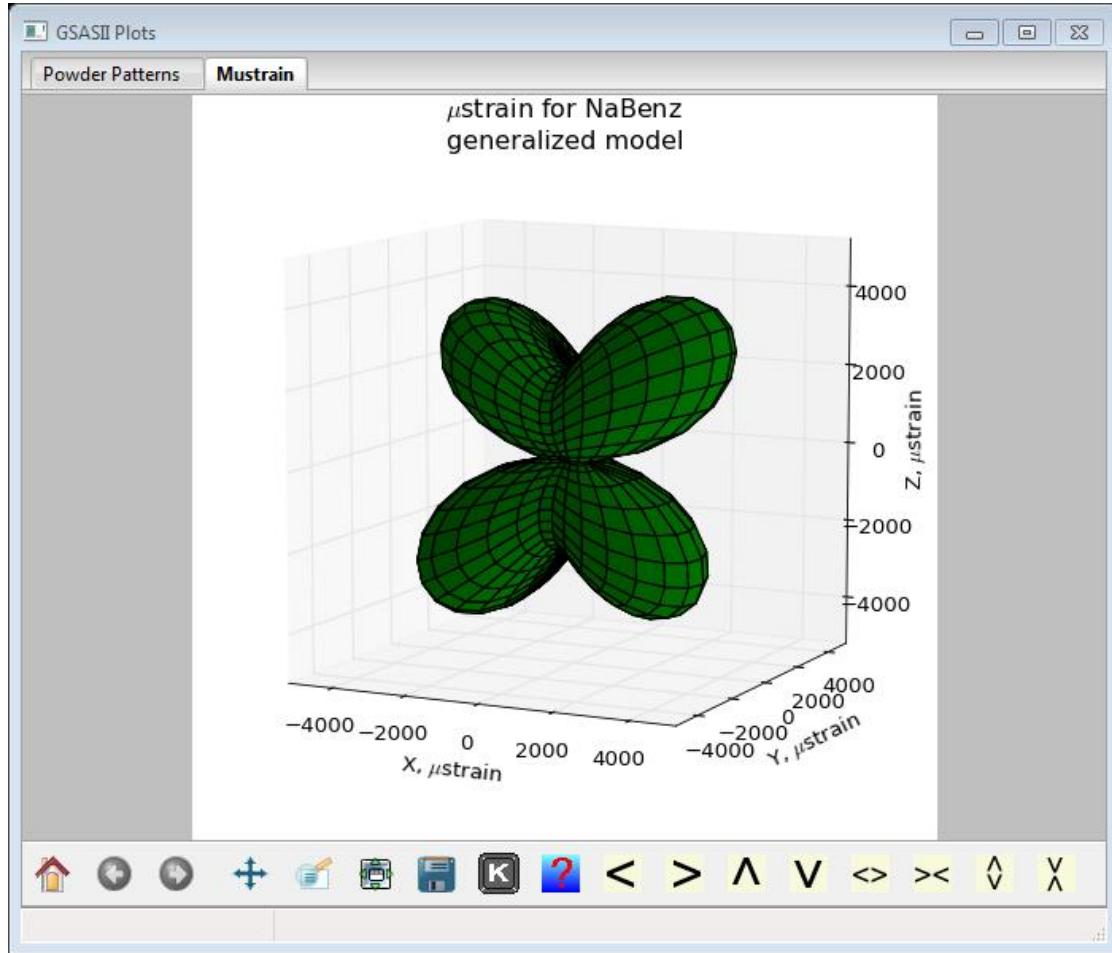
Directional dependence - Lattice defects? Inclusion allowed OH atom placement from ΔF map
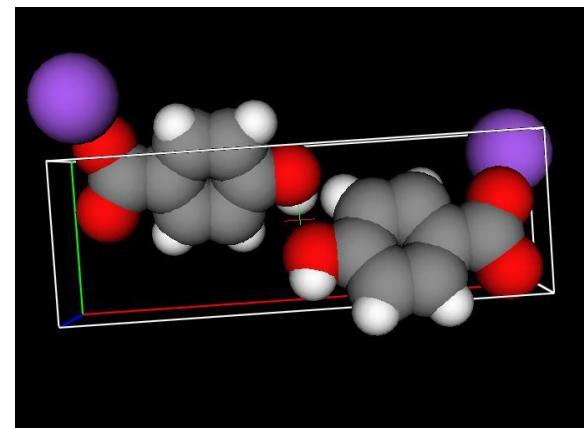
INTENSITY EXTRACTION

Structure factors from powder patterns? → structure solution
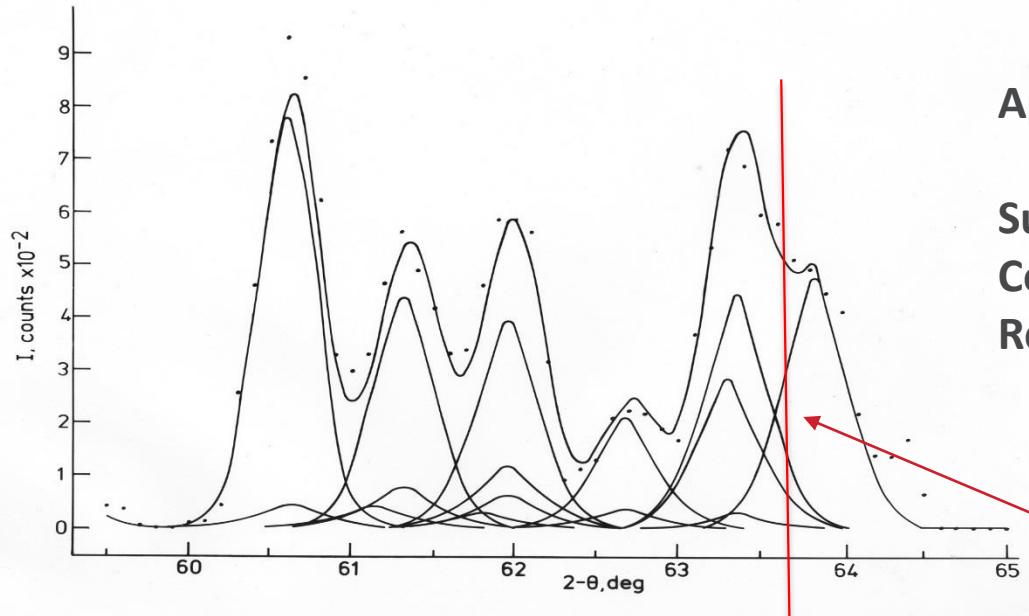
Apportion I_o by ratios of $I_c(H)$
    for contributing reflections →
Sum over all under peak profile
Correct for multiplicity & Lp, etc.
Result is $F^2(H)$

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

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AN EXAMPLE: FLUROAPATITE

Add atoms & do default initial refinement – scale & background
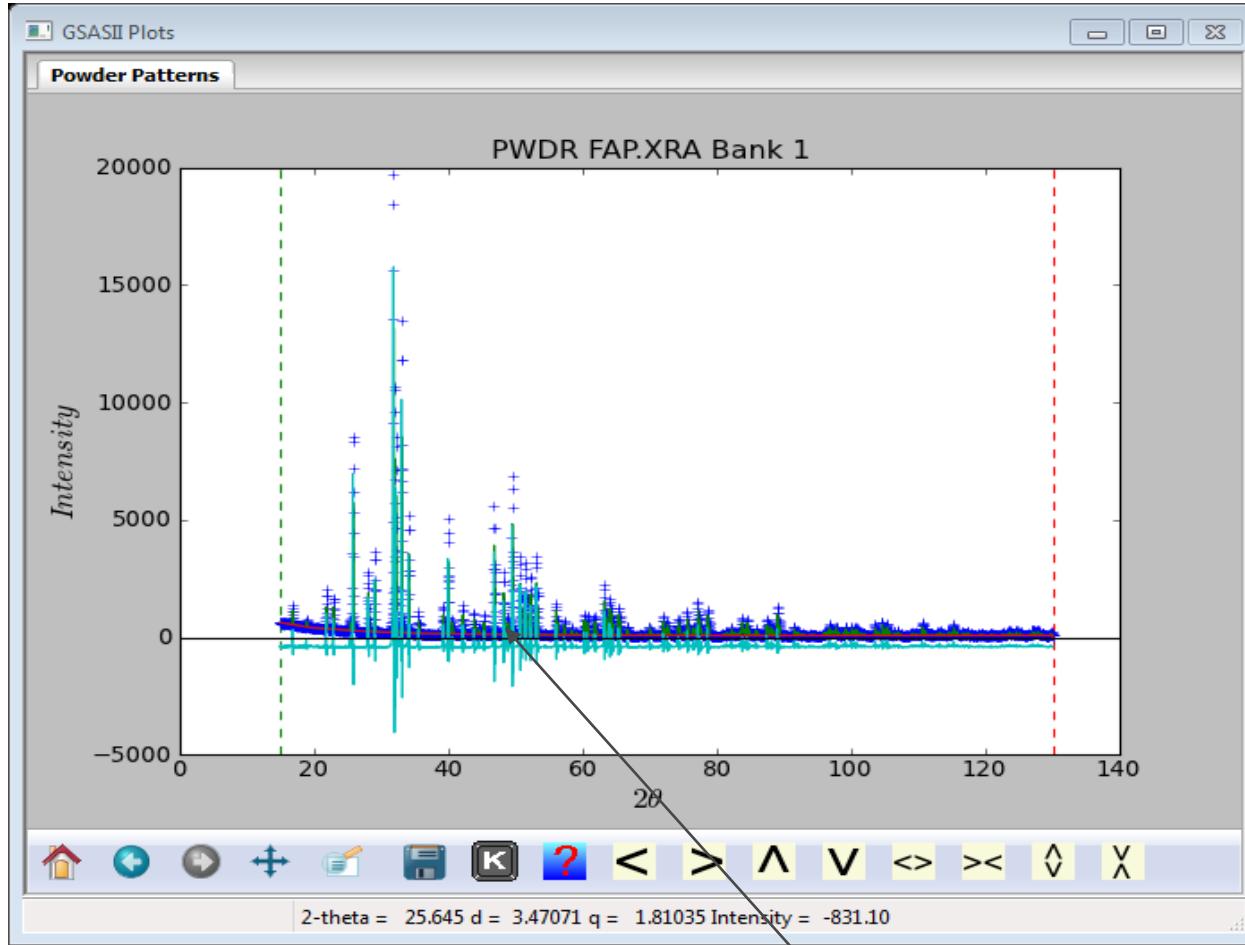

- **Notice shape of difference curve – position/shape/intensity errors**

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

peak shift

too sharp

wrong intensity

a – too small

size - too large

Ca2(x) – too small

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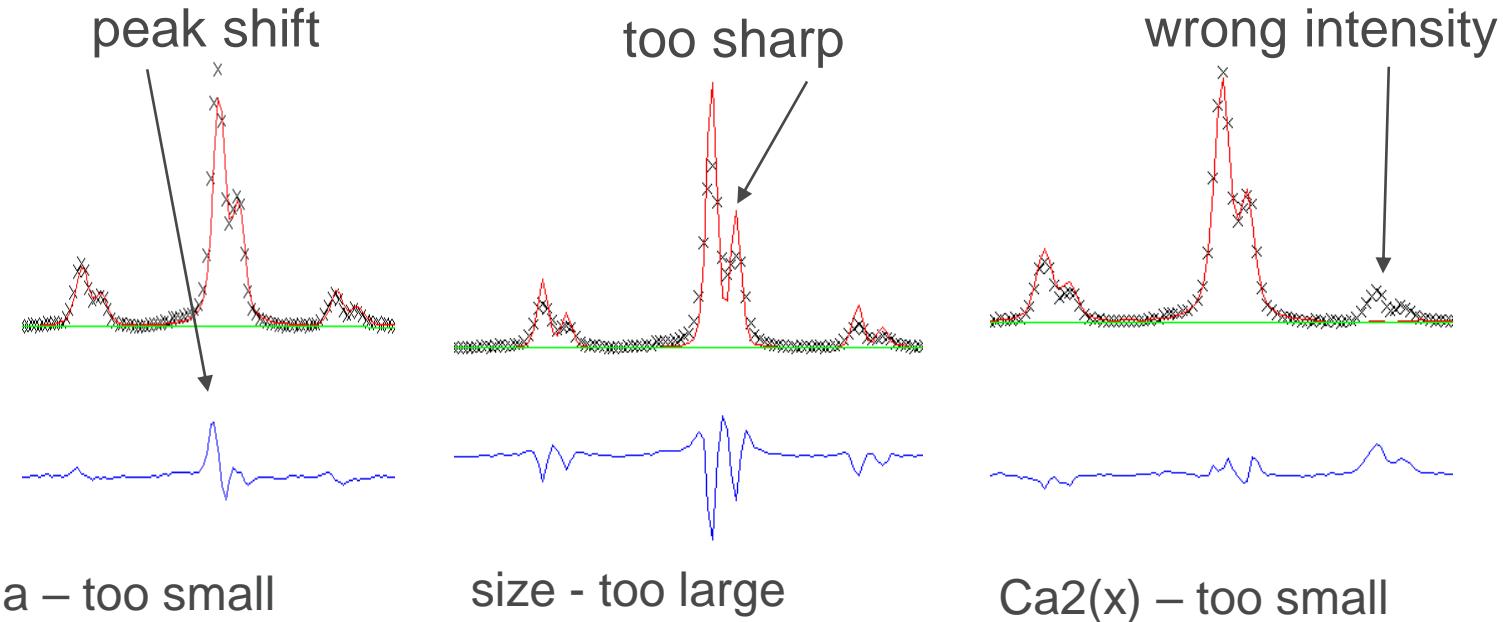
DIFFERENCE CURVE – WHAT TO DO NEXT?
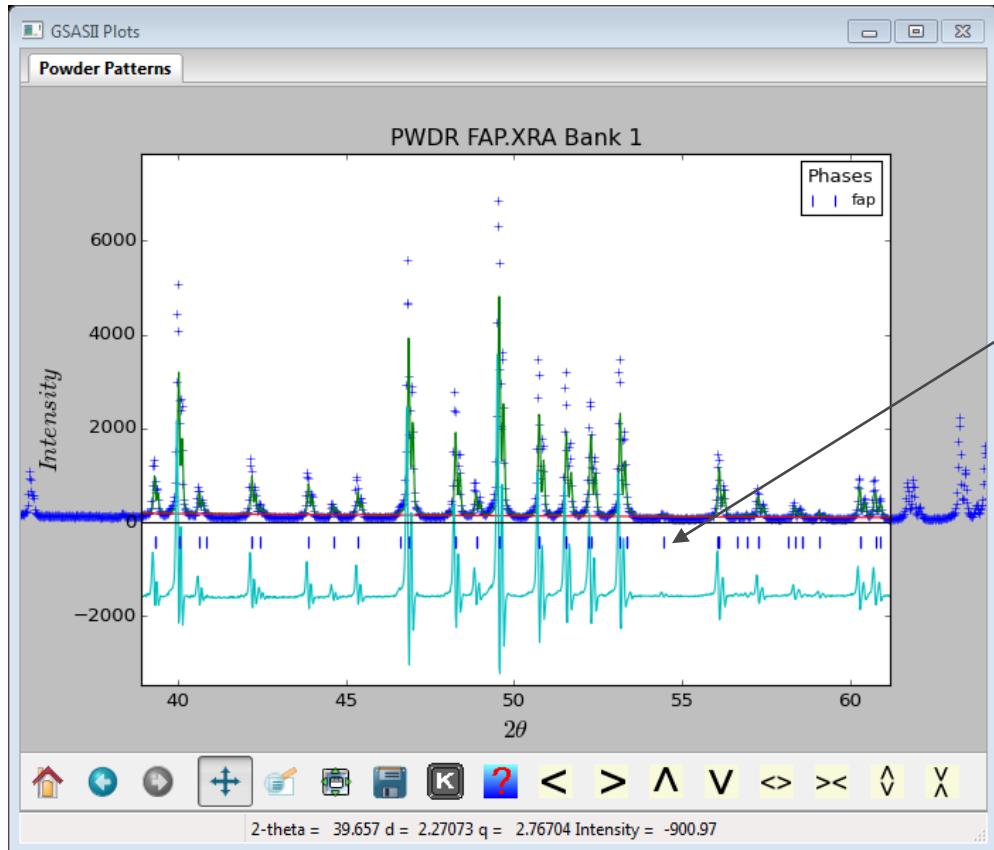
Characteristic "up-down-up"
→profile error
NB – can be "down-up-down" for too "fat" profile

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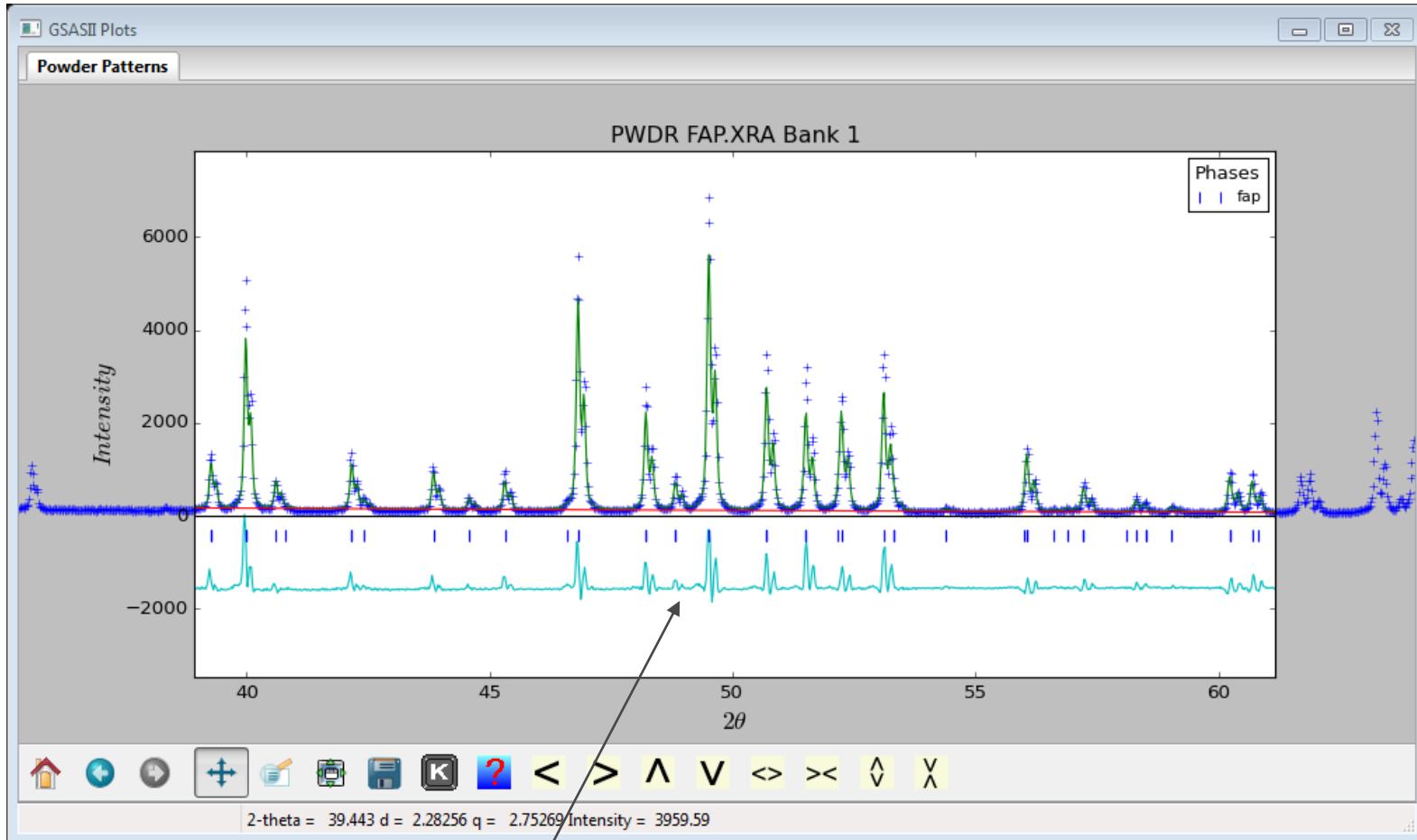
- **maybe intensity differences remain**
    - **– refine coordinates & thermal parms.**

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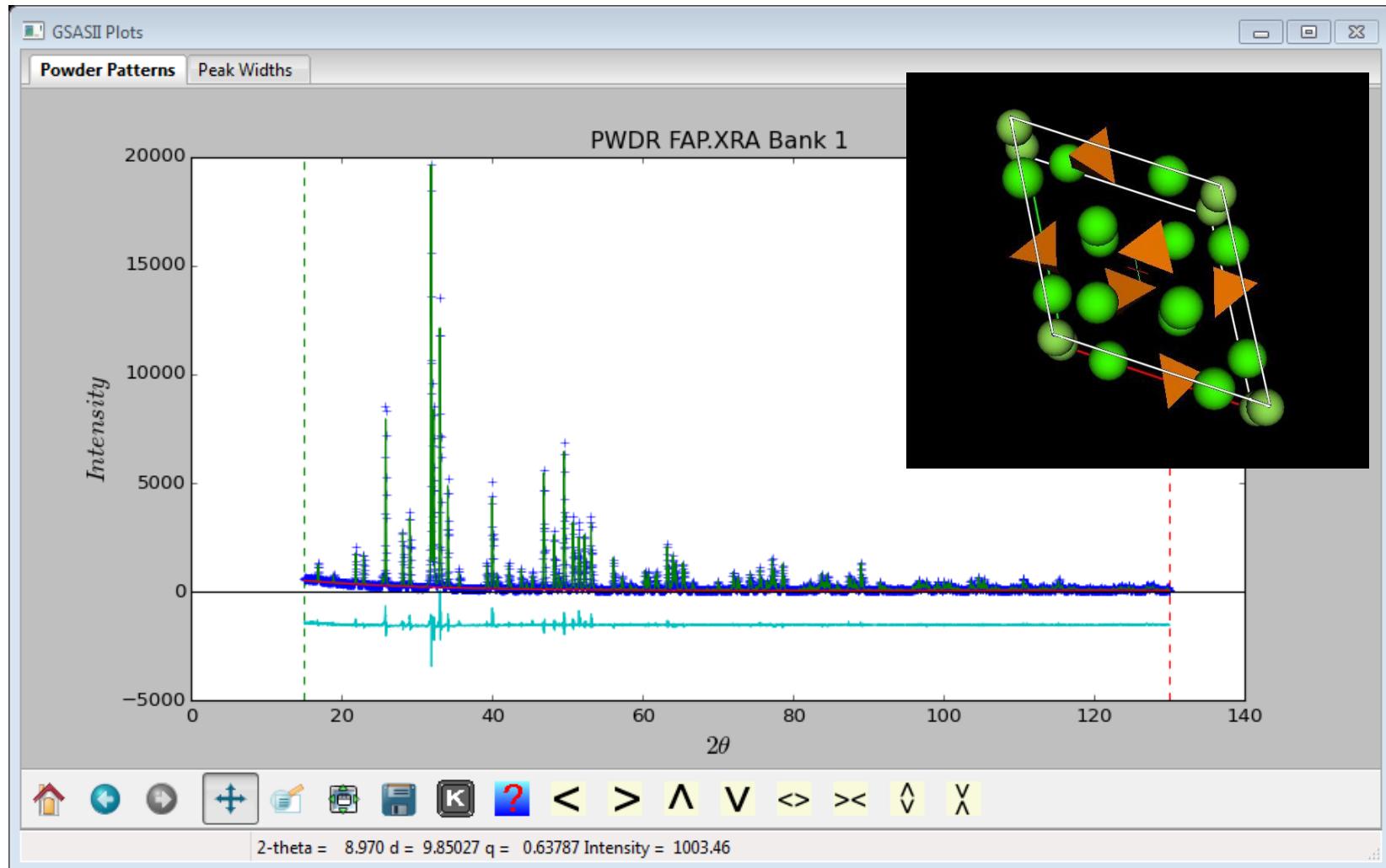
- Thus, major error in the initial model –
  peak shapes & sample displacement/lattice parameters

A USEFUL PLOT – COVARIANCE MATRIX
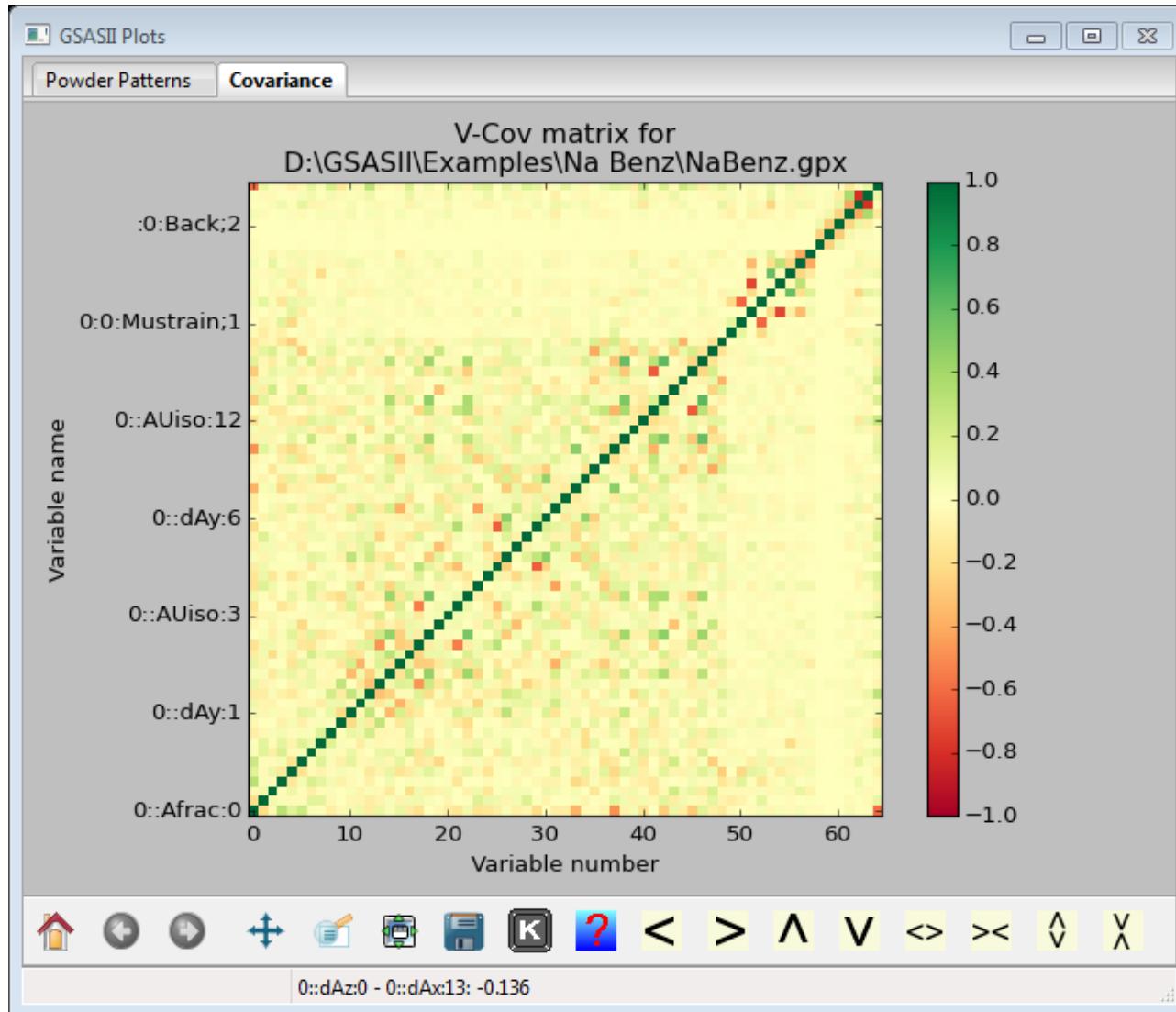
Green: cov>0
Red: cov<0
Yellow: cov~0
Cursor reports:
Cov or value(esd)
on diagonal
Can be zoomed!

Beware white
bands & nan:
Singularities!

A FEW FINAL WORDS

"A Rietveld refinement is never perfected, merely abandoned" (P. Stephens, 2000)

"Rietveld refinement is one of those few fields of intellectual endeavor wherein the more one does it, the less one understands." (Sue Kesson)

"A Rietveld refinement is done when you run out of parameters" (R. Von Dreele)

Books:

Modern Powder Diffraction, Eds. J. Post & D. Bish (1989)

The Rietveld Method, Ed. R.A. Young (1993)

Powder Diffraction: Theory & Practice, Eds. R. Dinnebier & S. Billinge (2008)

THANK YOU

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