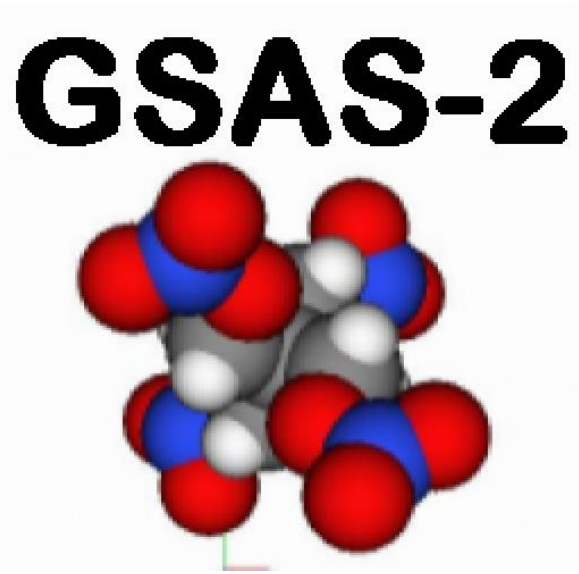
THE RIETVELD REFINEMENT METHOD IN GSAS-II



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Acknowledgements: DOE/SC

HISTORY – H.M. RIETVELD

Hugo Rietveld; neutron powder diffractometer, Petten, Netherlands

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

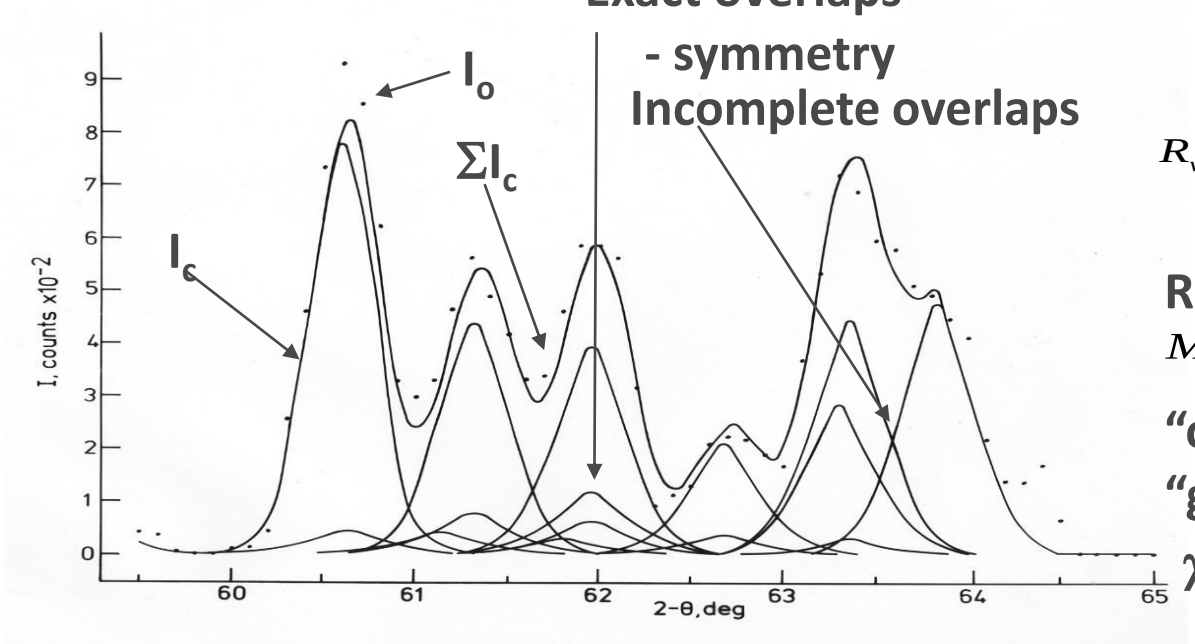
H.M. Rietveld, J. App. Cryst., 2, 65-71 (1969)

Multi-parameter, nonlinear LS curve fitting

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

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

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

LEAST SQUARES THEORY - CONTINUED

Rearrange

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

$$\vdots$$

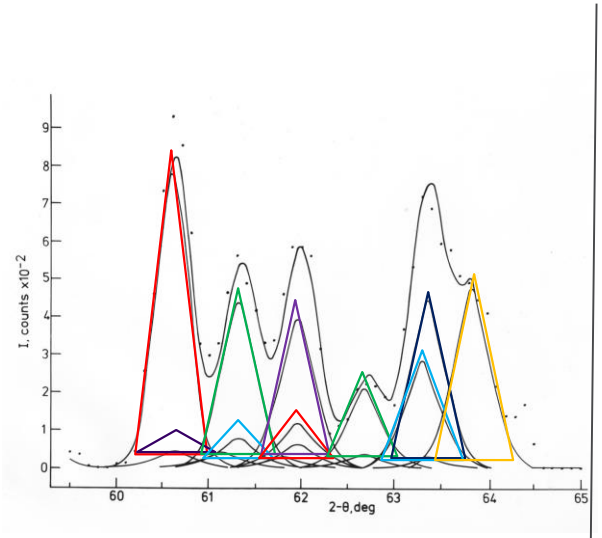
$$\sum w \frac{\partial I_c}{\partial p_n}\left(\sum_{i=1}^{n} \frac{\partial I_c}{\partial p_i}\Delta p_i\right) = \sum w \Delta I \frac{\partial I_c}{\partial p_n}$$

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: $x = A^{-1}v = Bv$; $B = A^{-1}$ This gives set of Δp_i to apply to "old" set of a_i; repeat until Δp_i small.

GSAS-II ALGORITHM



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

$\partial I_c/\partial p_i$

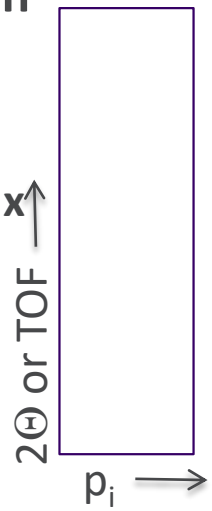
$\partial I_c/\partial p_j$

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

Hessian matrix - A

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

Jacobian matrix - J



Σ

$wJ^TJ = A$

NB: GSAS-II – needs large memory!

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REFINEMENT VIA MODIFIED LEVENBERG/MARQUARDT-SVD ALGORITHM

Steps:

1. Compute $A_{ij} = \sum w \frac{\partial I_c}{\partial p_i} \frac{\partial I_c}{\partial p_j}$
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 $\lambda * 10$ go to 5
9. Else apply δp to p & go to 1 (new cycle)
10. Quit when $\chi^2(p) - \chi^2(p+\delta p) / \chi^2(p) < 0.0001$

SLOW step

FAST steps

NB: all in ~40 lines of python; all double precision

NB^2: this thing is exceedingly robust – no user damping factors needed

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)

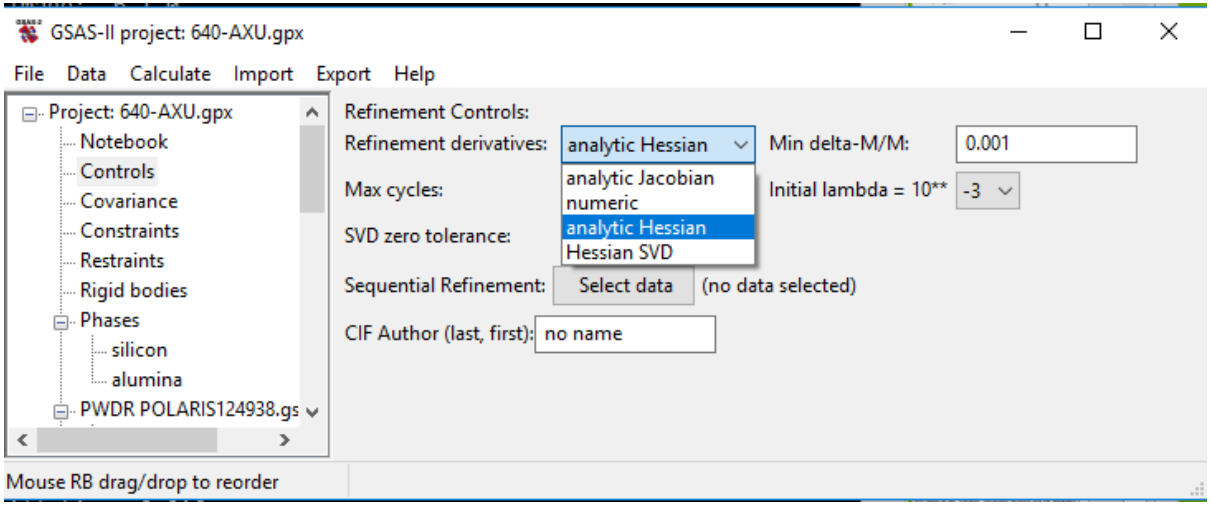
SVD is in python library as numpy.linalg.svd

& 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.

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

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

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.**

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

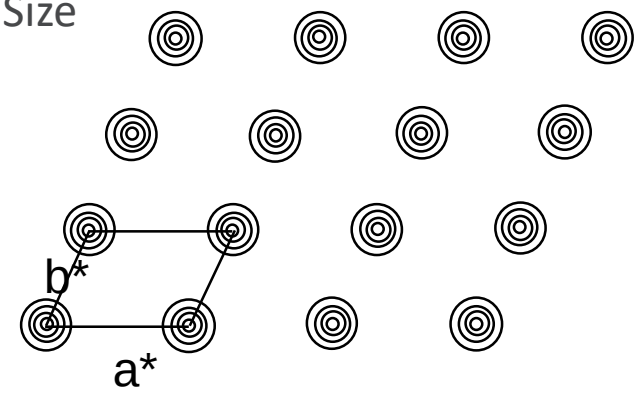
CW Asymmetry from axial divergence – Finger, Cox & Jephcoat

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

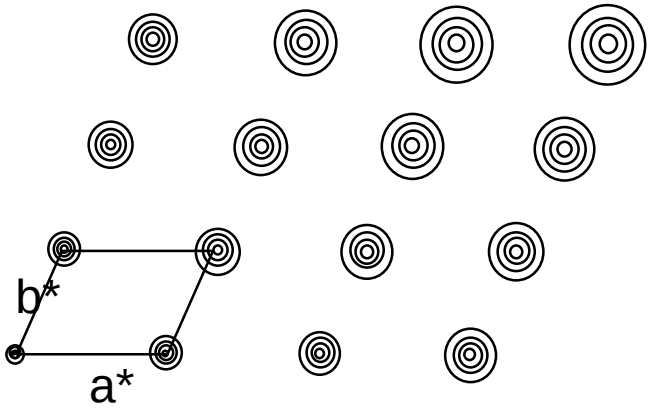
Bragg's Law: $\Delta 2\Theta = \lambda\Delta d/d^2\cos\Theta$ (= $X/\cos\Theta$)

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

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

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:

$$S_\gamma = S + M$$

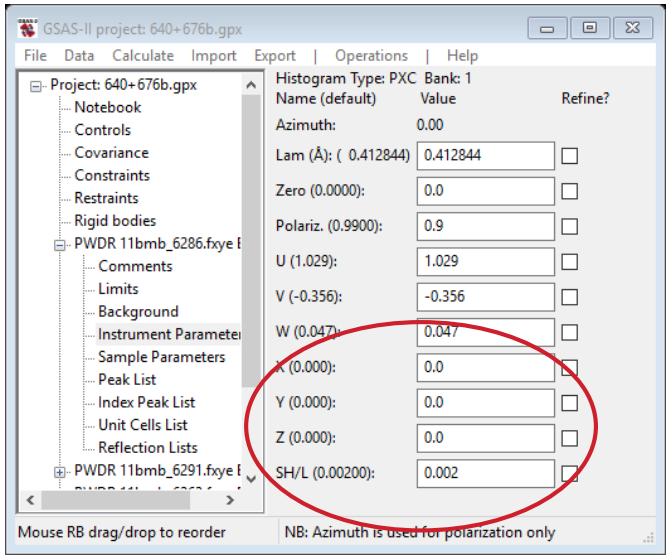
$S_\Gamma = 0$ (no Gaussian sample broadening)

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

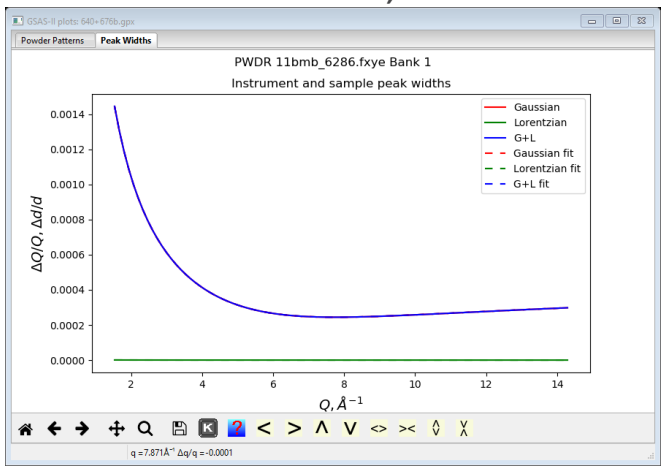
CW PROFILE PEAK BROADENING IN GSAS-II

The split of sample broadening from instrumental contribution

Instrument – fixed from calibration

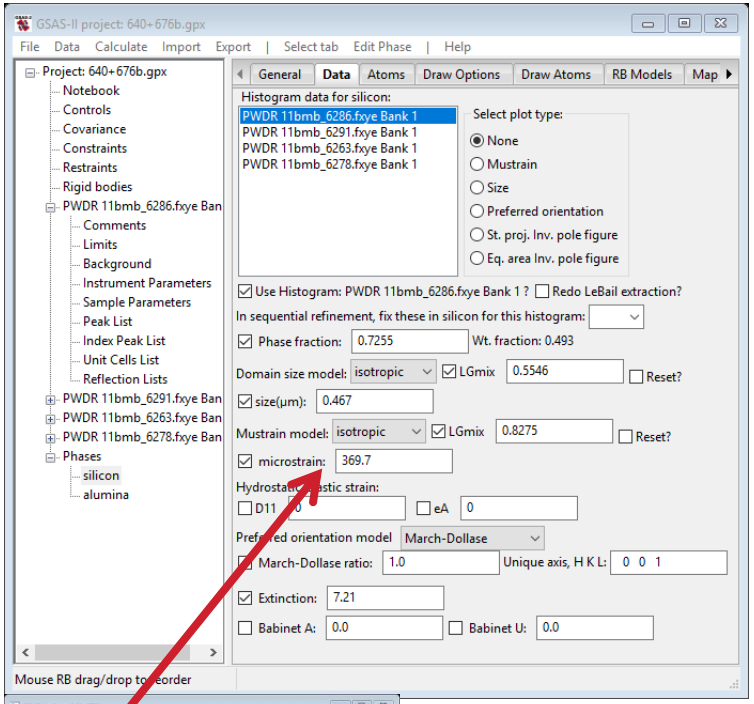


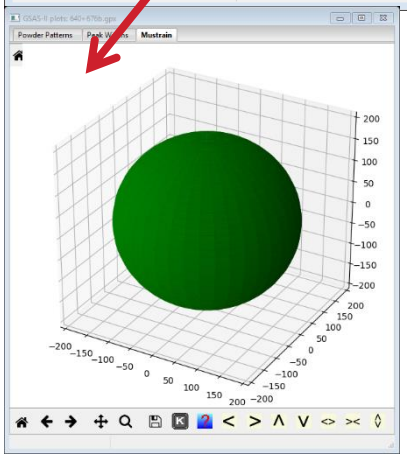
NB: for APS 11BM X,Y & Z = 0



Sample – phase & histogram dependent

Refined & constrained as needed

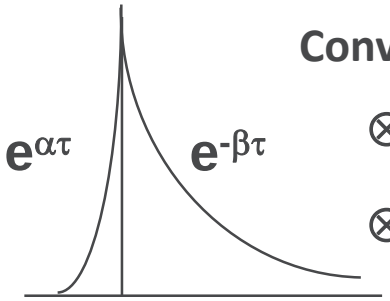




Sample:
New NIST SRMS
640f & 676b

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

⊗ (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

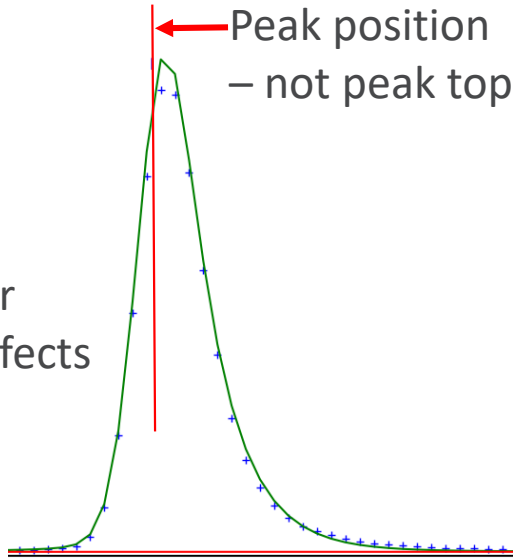
$$\alpha = {}^{\propto_0}/_{d};\ \beta = \beta_0 + {}^{\beta_1}/_{d^4} + {}^{\beta_q}/_{d^2}$$

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

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

New terms for epithermal effects

Sample broadening terms - earlier slide; may be hkl dependent



MIXING

Lorentzian vs Gaussian sample broadening?

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

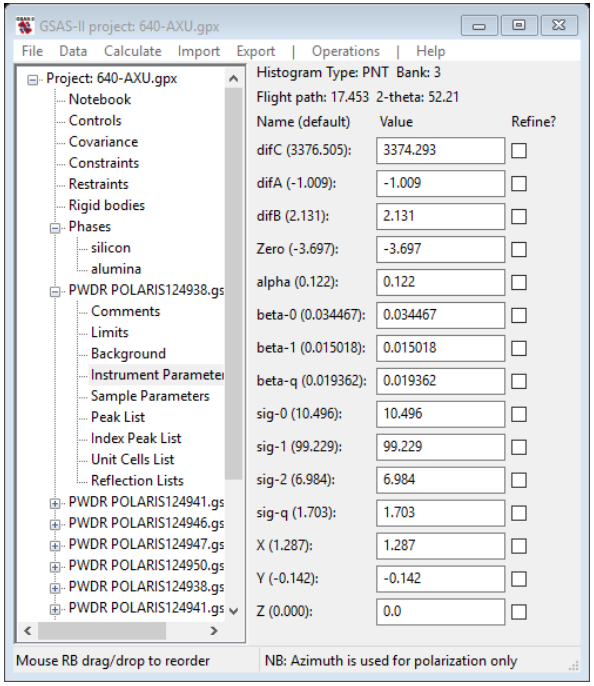
- X,Y,Z = 0 (no Lorentzian instrument broadening)

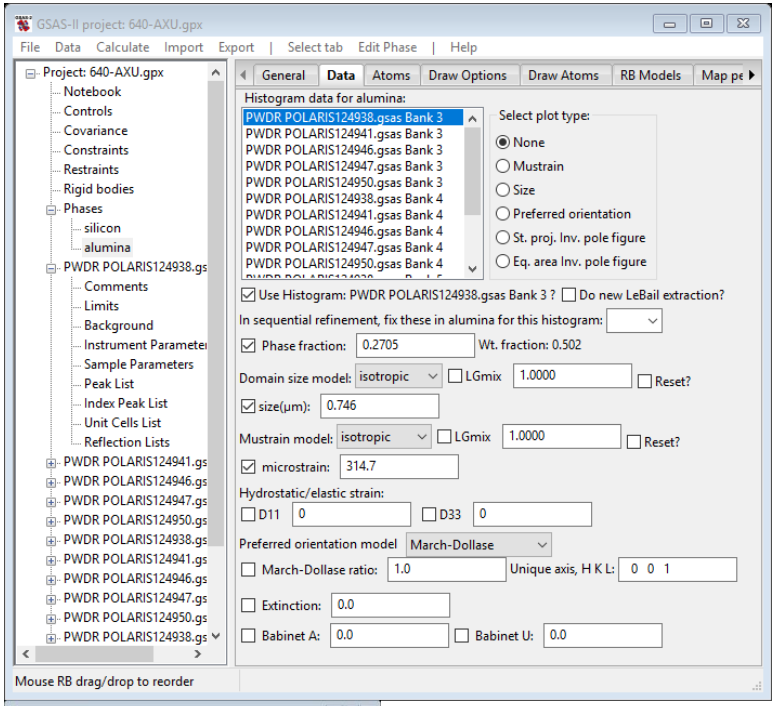
TOF PROFILE PEAK BROADENING IN GSAS-II

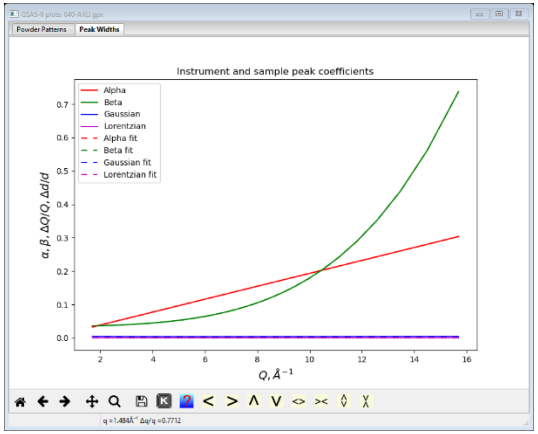
The split of sample broadening from instrumental contribution

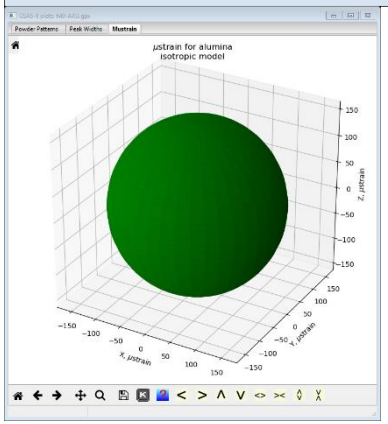
Instrument – fixed from calibration

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









Sample:
New NIST SRMS
640f & 676b

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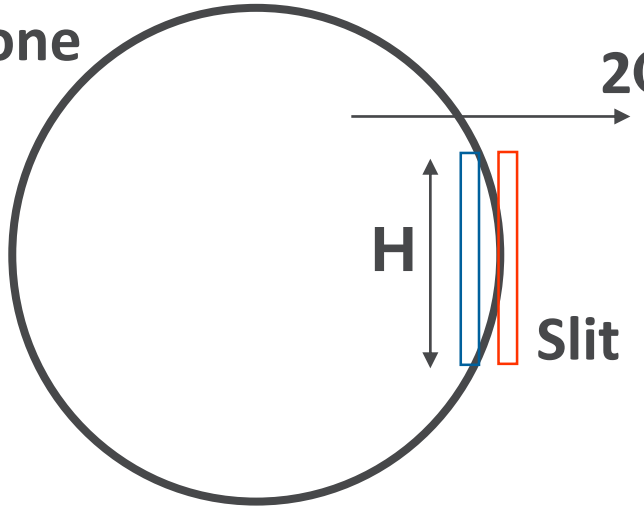
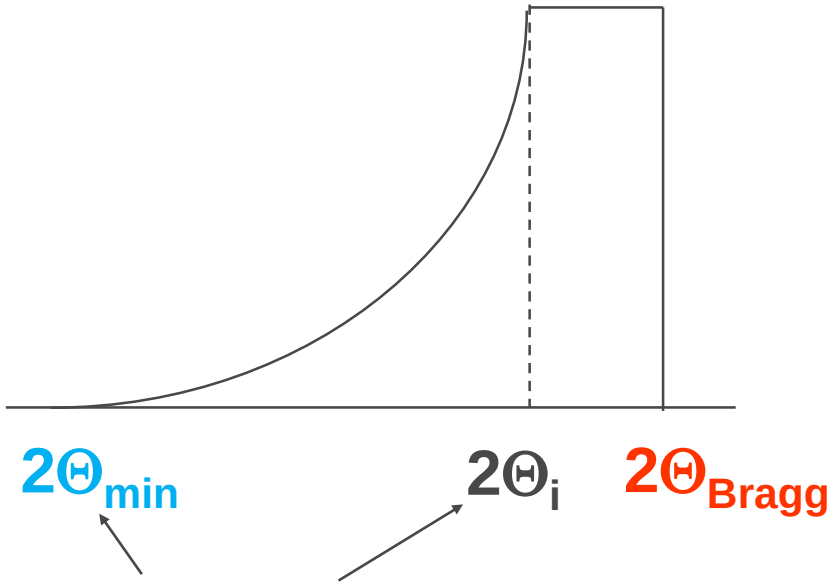
AXIAL BROADENING FUNCTION – CONST. WAVELENGTH

Finger, Cox & Jephcoat based on van Laar & Yelon

Debye-Scherrer cone





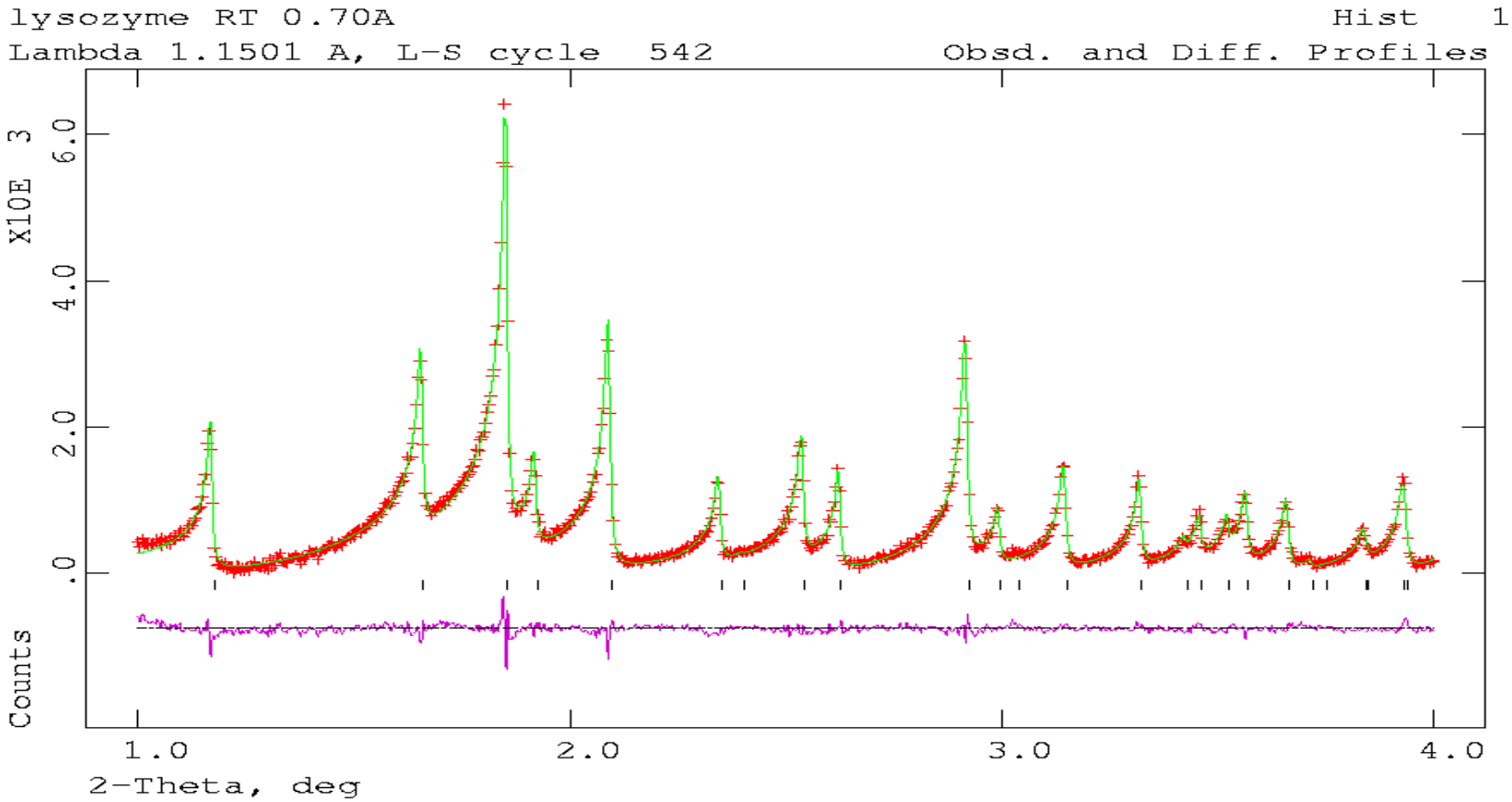
Depend on slit & sample "heights" wrt diffr. radius

H/L & S/L - parameters in function; combined as H+S/L in GSAS-II (typically 0.005 - 0.020)

⊗ Pseudo-Voigt

= profile function

HOW GOOD IS THIS FUNCTION?

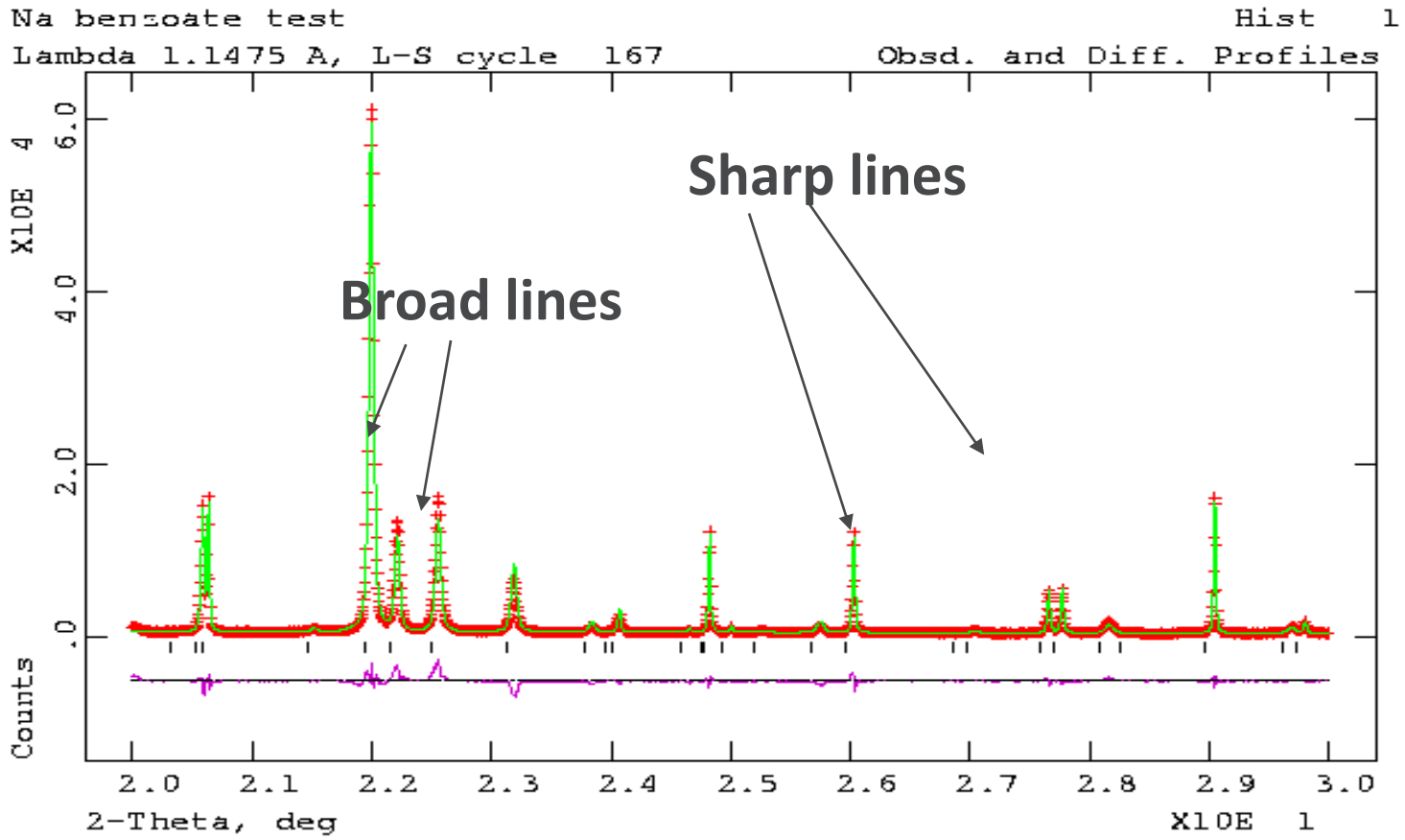


Protein Rietveld refinement - Very low angle fit

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

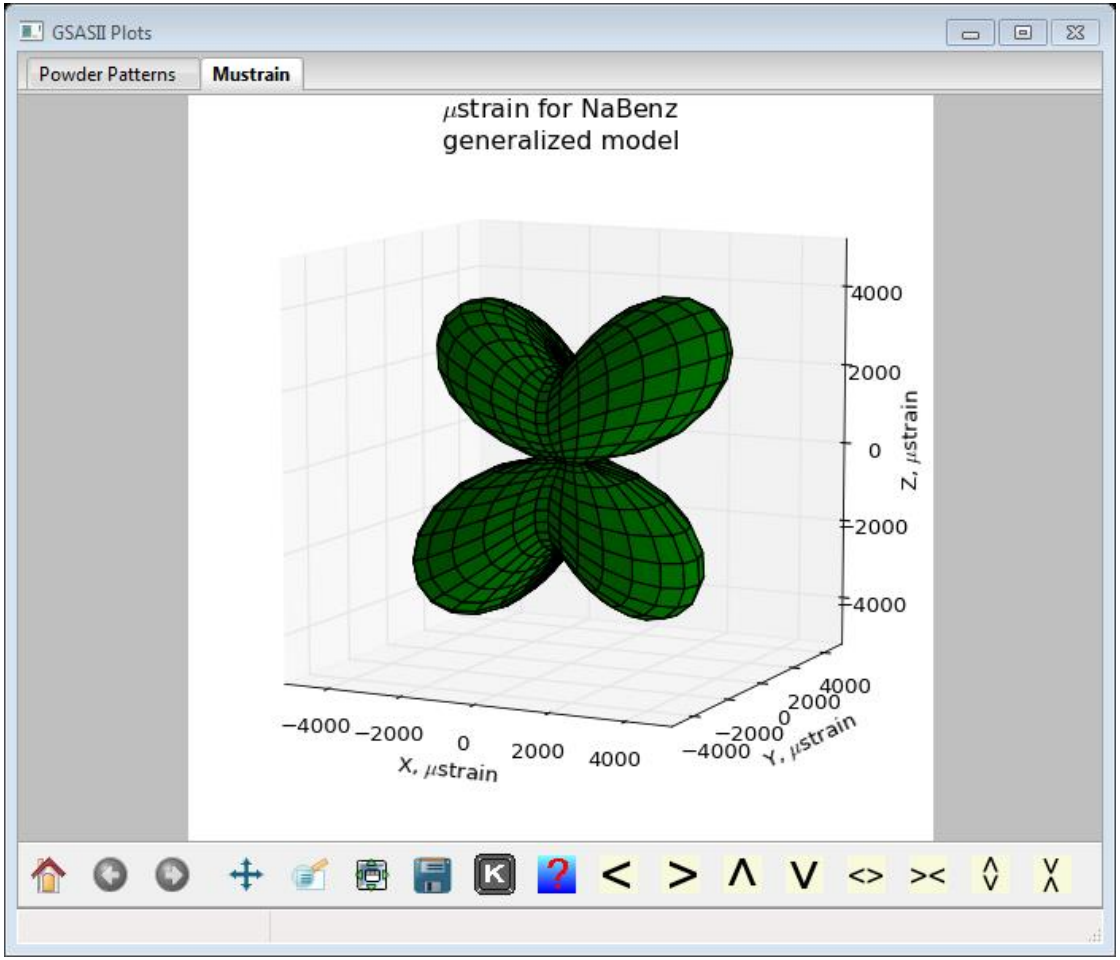
$$\frac{1}{d_{hkl}^2} = M_{hkl} = \alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk$$

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

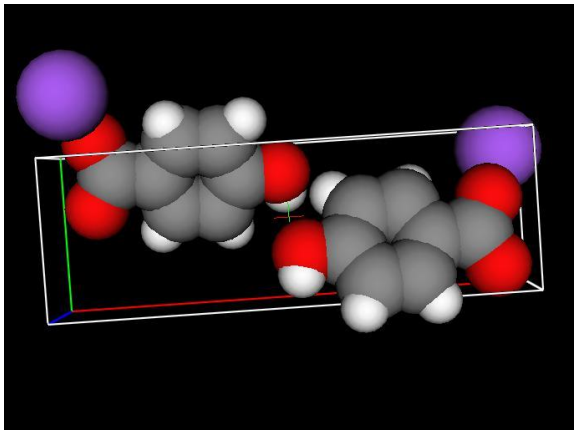
$$\sigma^2\left(M_{hkl}\right) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j}$$

NA PARAHYDROXYBENZOATE

Unusual micostrain effects - peak broadening

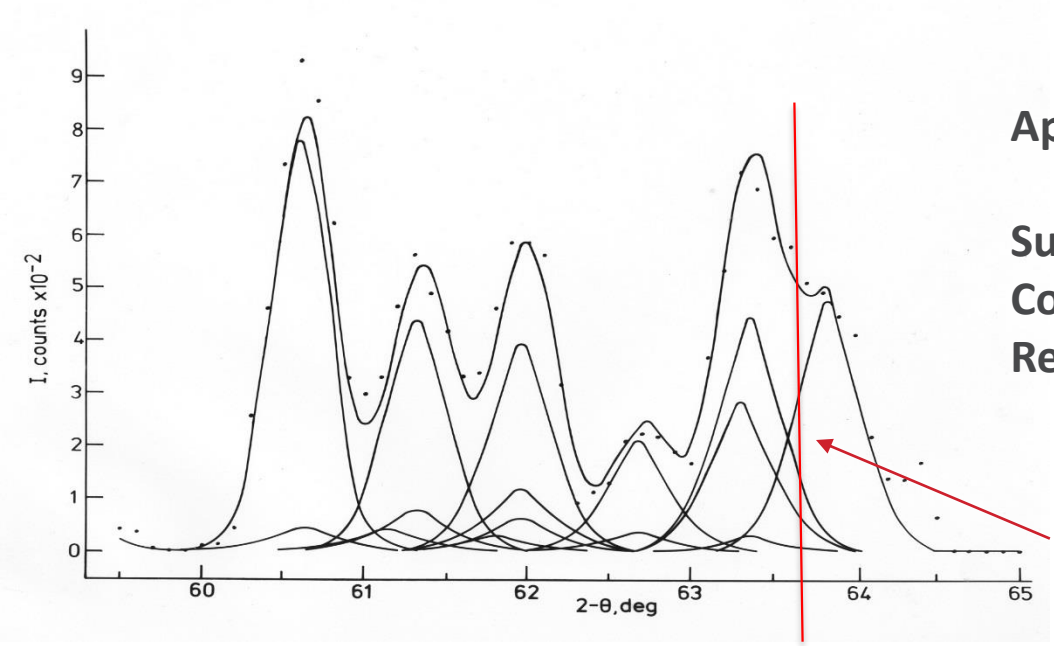


Directional dependence - Lattice defects? Inclusion allowed OH atom placement from ΔF map



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

THANK YOU

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