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Neutron Rietveld Refinement

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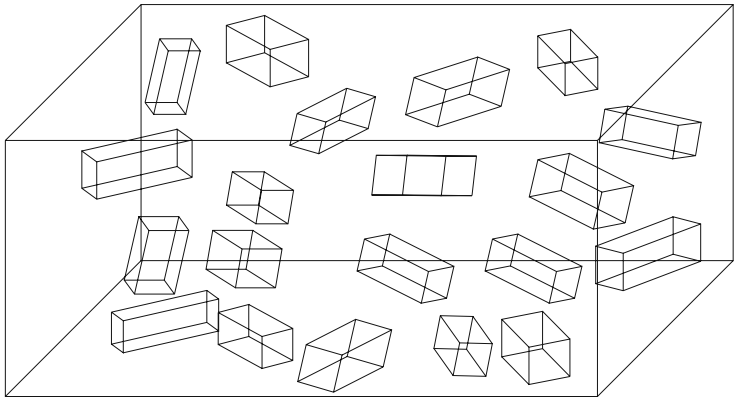
“Rietveld refinement is one of those few fields of intellectual endeavor wherein the more one does it, the less one understands.” (Sue Kesson)

Powder - polycrystalline mass

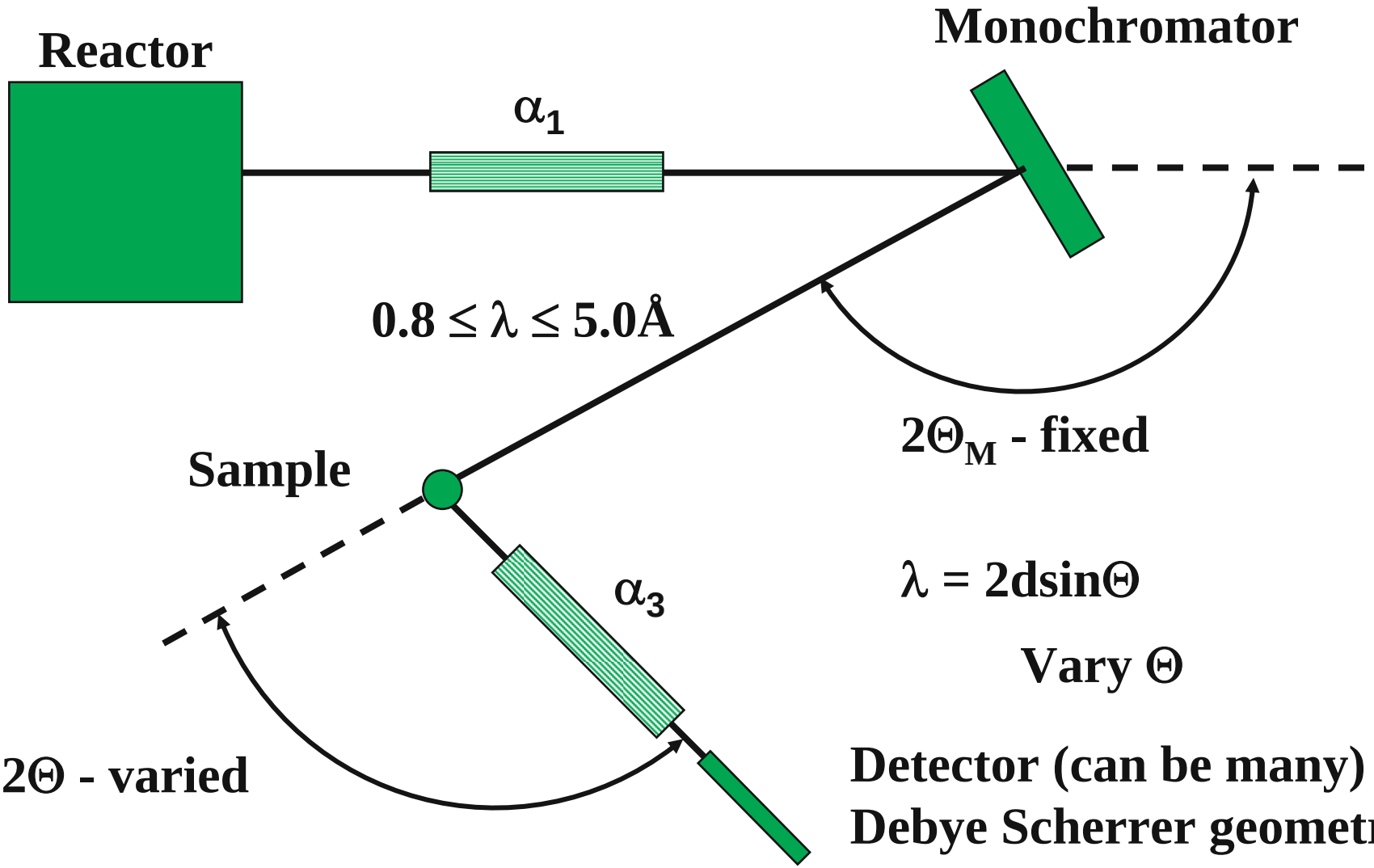


All orientations of crystallites possible

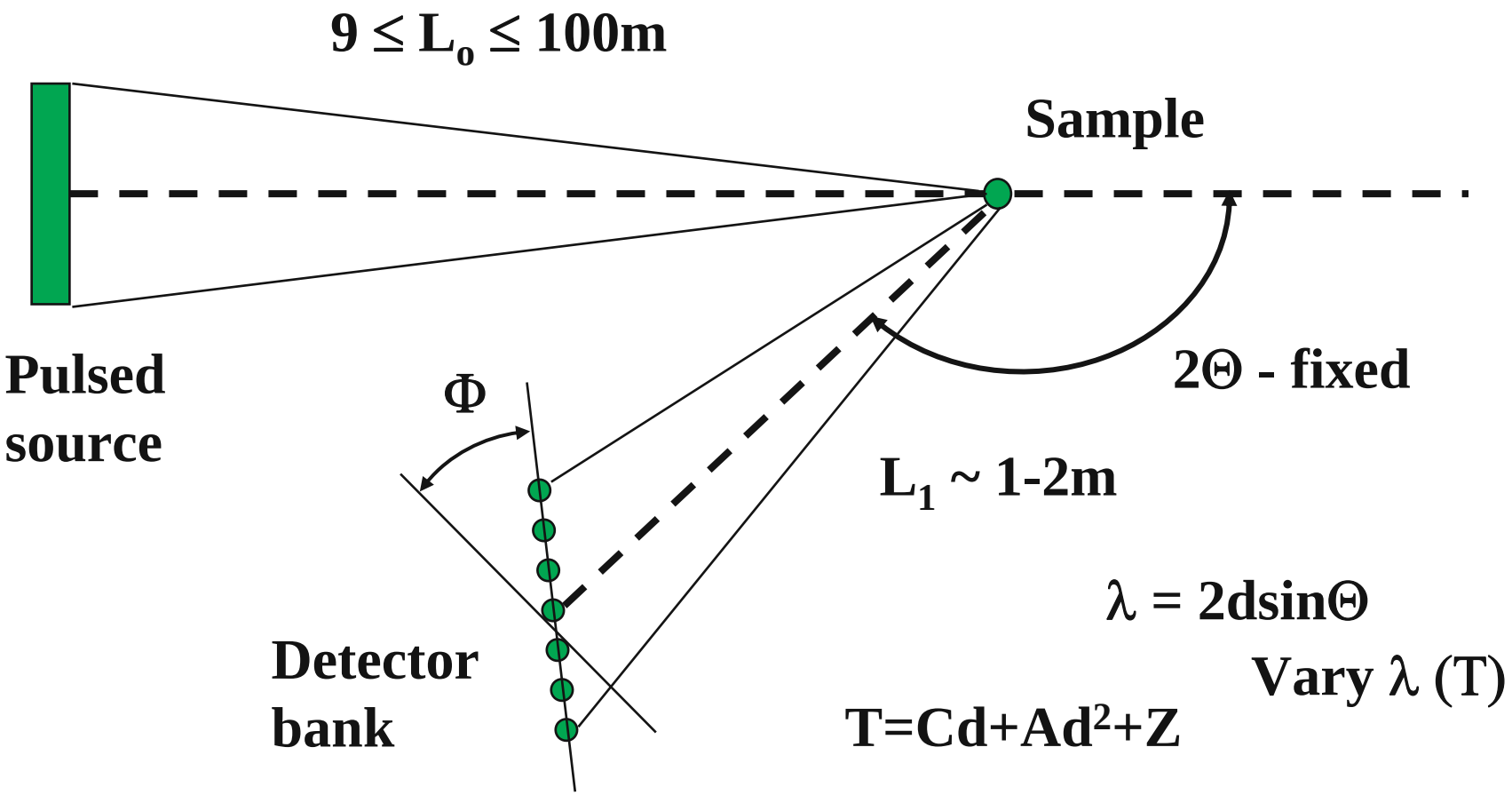
Sample: 1cc powder of 10μm crystallites - 10^9 particles
if 1μm crystallites - 10^{12} particles

Single crystal reciprocal lattice
- smeared into spherical shells
- broadened by instrumental & sample effects

Neutron Diffractometers - Constant Wavelength

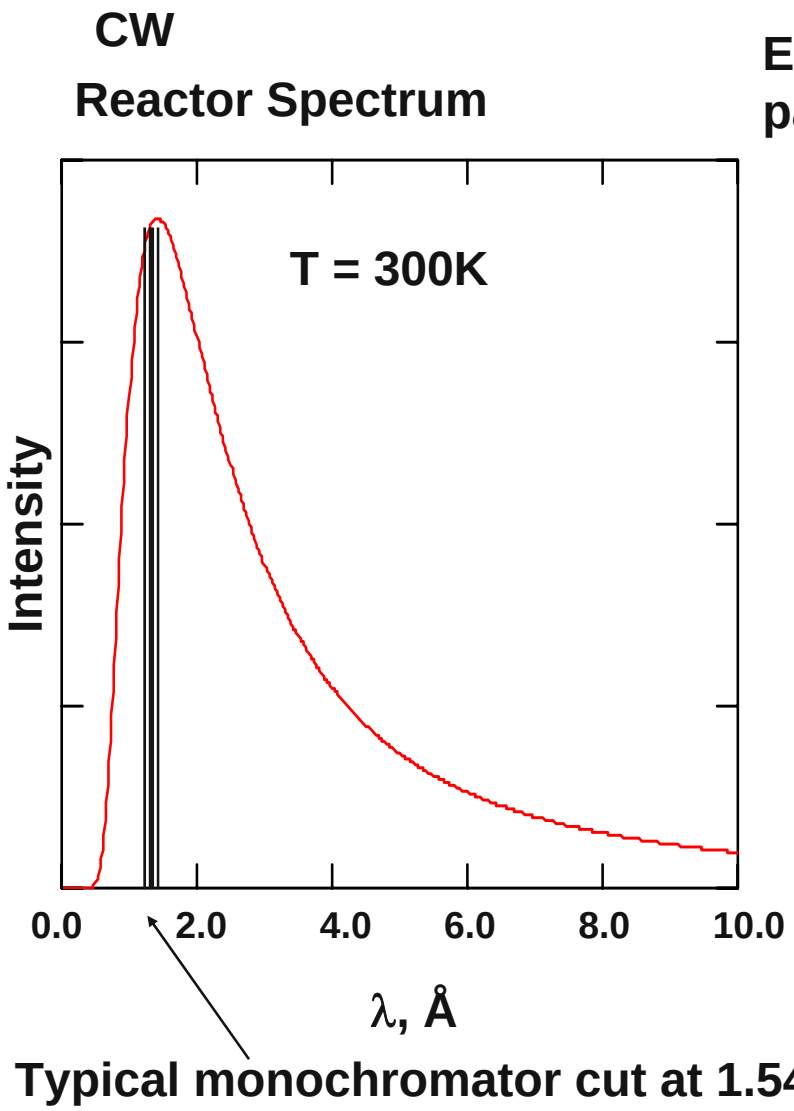


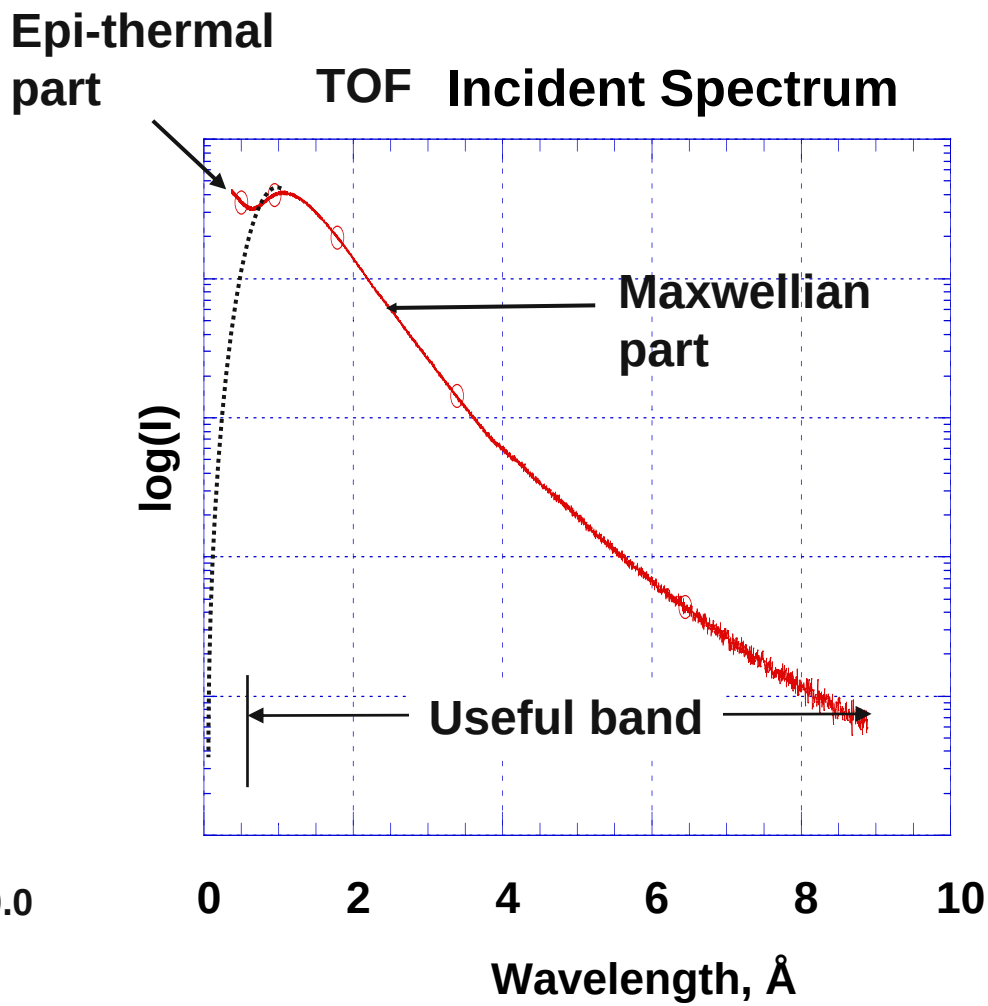
Neutron Diffractometers - Time-of-Flight



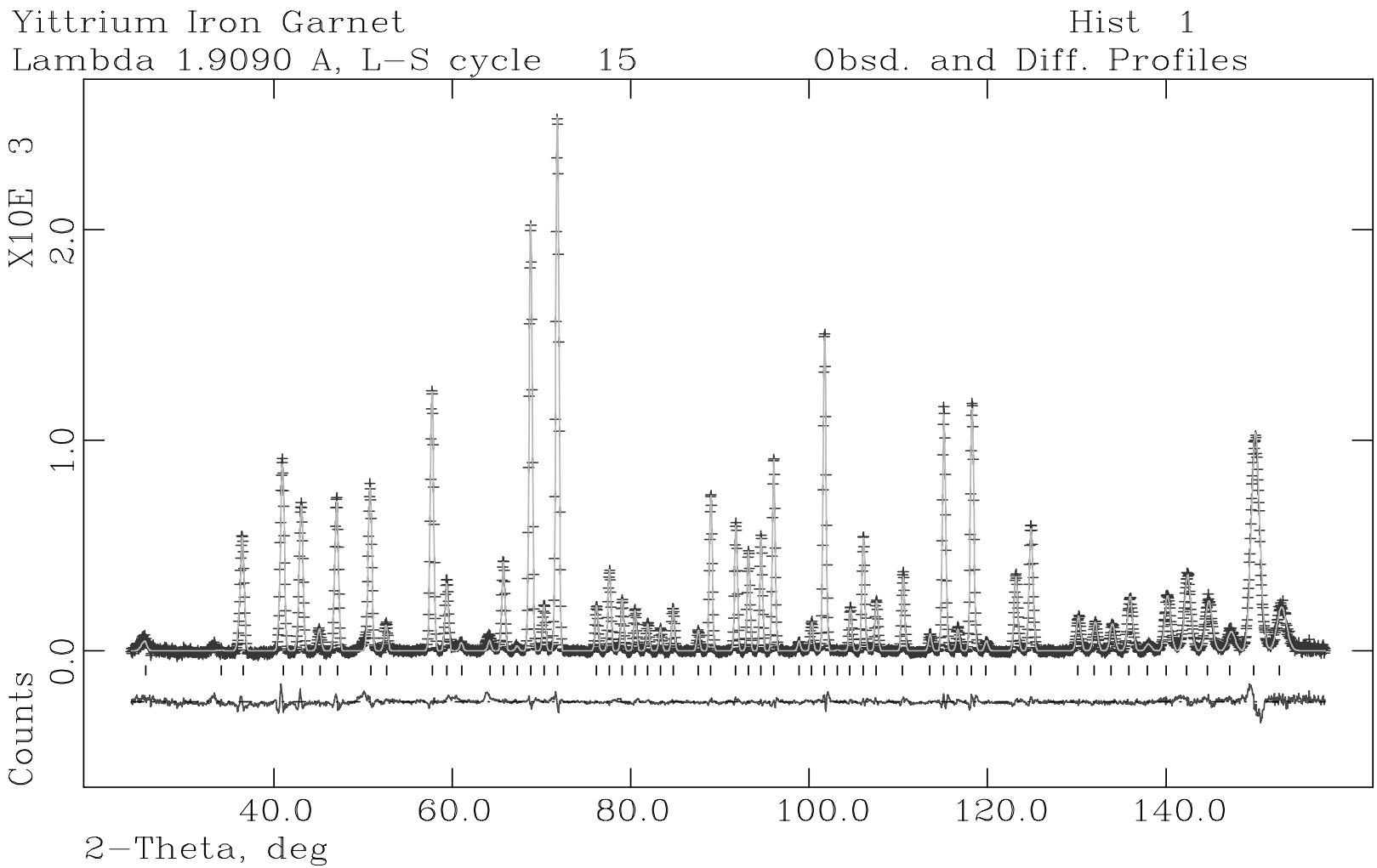
Also Debye Scherrer

Source comparison: CW vs TOF

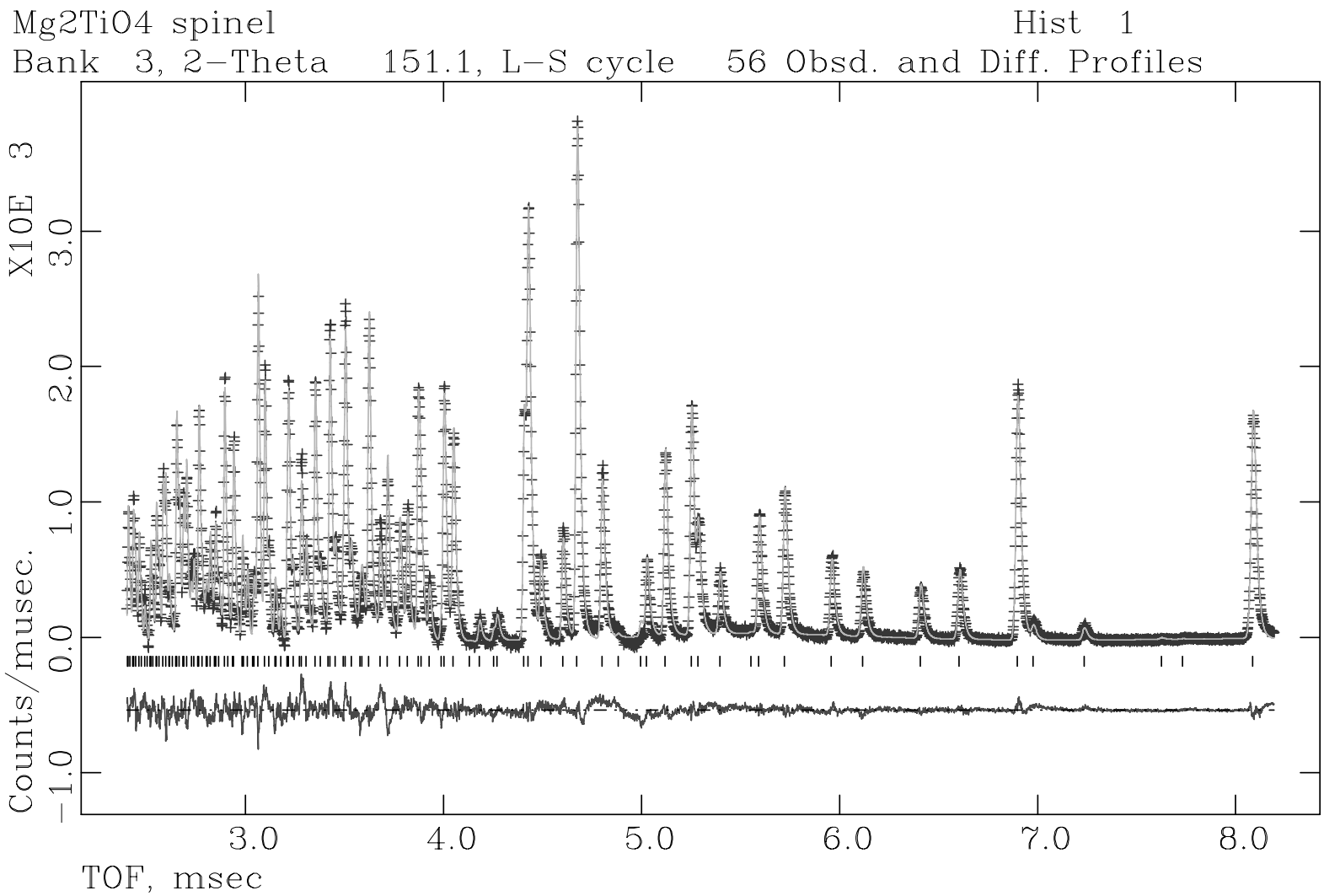




CW neutron pattern (& Rietveld refinement fit)



TOF neutron pattern (& Rietveld refinement fit)

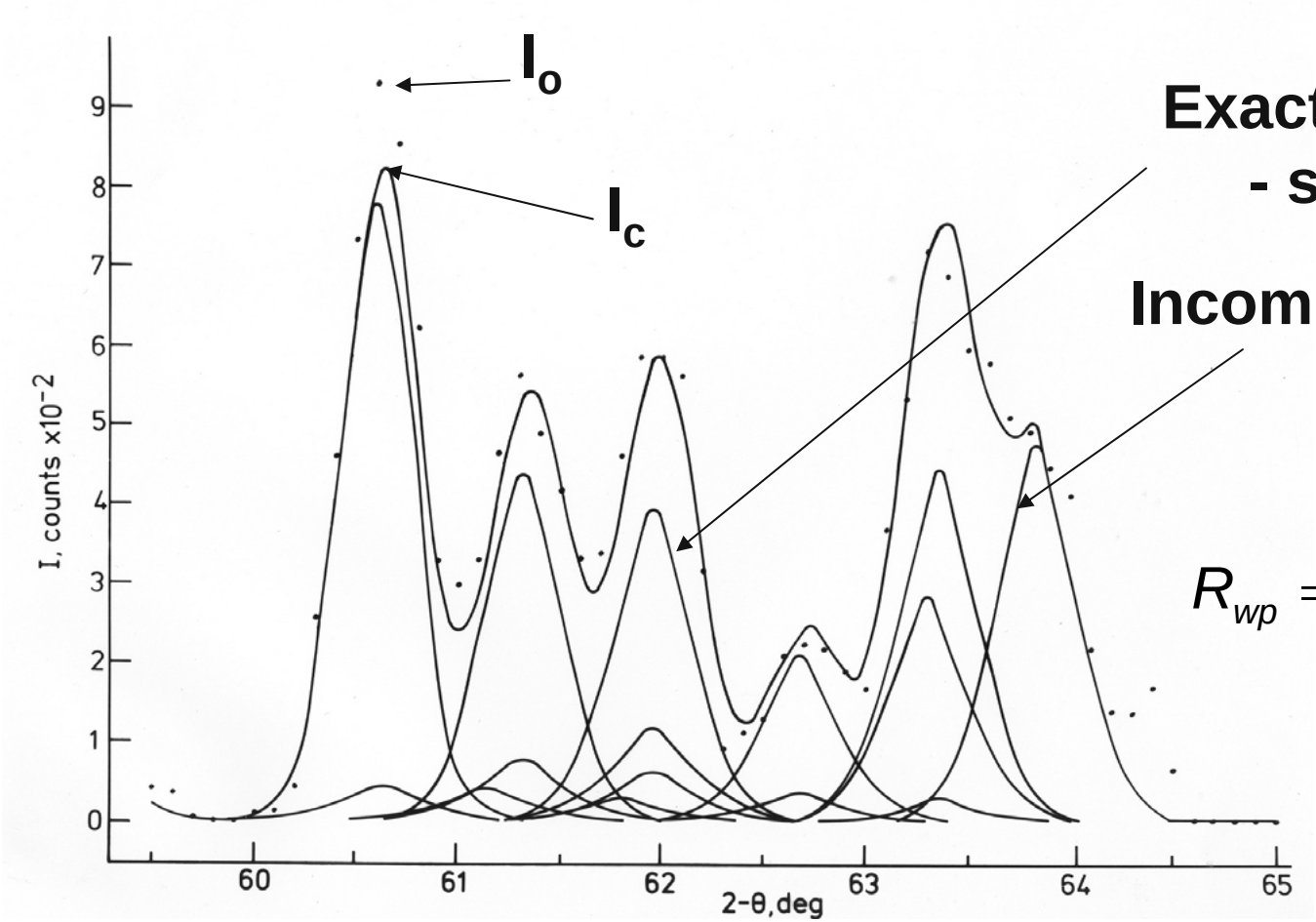


Rietveld refinement – multiparameter curve fitting

$$I_c = I_i \left[\sum_h k_h F_h^2 m_h L_h P(\Delta_h) + I_b \right]$$

Rietveld minimize

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



Exact overlaps - symmetry

Incomplete overlaps

Residual:

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

Least Squares Theory - simple

Given a set of observations: G_o

and a function: $G_c = g(p_1, p_2, p_3 \ldots, p_n)$

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

$$M = \sum w(G_o - G_c)^2$$

This is done by setting the derivative to zero

$$\sum w(G_o - G_c)\frac{\partial G_c}{\partial p_j} = 0$$

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

Least Squares Theory - continued

Problem - $g(p_i)$ is nonlinear & transcendental (sin, cos, etc.) for crystallography - so can't solve directly
Expand $g(p_i)$ 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)

Substitute above

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

Normal equations - one for each Δp_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

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

Least Squares Theory - continued

Matrix equation $Ax=v$

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 all $x_i \sim 0$ (i.e. no more shifts)

Rietveld refinement - this process applied to powder profiles – curve fitting!

Note: Starting model REQUIRED

I_o – observed powder profile (including background)

I_c - model function for the powder profile

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")
Then LS gives parameter estimates (shifts in our case)
with the minimum variance in any linear combination
The error estimates ("esd's" or "su'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

Rietveld refinement in GSAS - minimization function

$$M = \sum w_i \left(I_{oi} - I_{ci}\right)^2$$ **Powder profiles (Rietveld)**

$$+ f_a \sum w_i \left(a_{oi} - a_{ci}\right)^2$$ **Bond angles**

$$+ f_d \sum w_i \left(d_{oi} - d_{ci}\right)^2$$ **Bond distances**

$$+ f_t \sum w_i \left(t_{oi} - t_{ci}\right)^2$$ **Torsion angles**

$$+ f_p \sum w_i \left(- p_{ci}\right)^2$$ **Plane RMS displacements**

$$+ f_v \sum w_i \left(v_{oi} - v_{ci}\right)^4$$ **van der Waals distances**

$$+ f_h \sum w_i \left(h_{oi} - h_{ci}\right)^2$$ **Hydrogen bonds**

$$+ f_x \sum w_i \left(x_{oi} - x_{ci}\right)^2$$ **Chiral volumes**

$$+ f_R \sum w_i \left(-R_{ci}\right)^2$$ **"ϕ/ψ or χ_1/χ_2" pseudopotential**

$w_i = 1/\sigma^2$ weighting factor

f_x - weight multipliers (typically 0.1-3)

Model - represent each profile intensity

$$I_c = I_i \left[\sum_h k_h F_h^2 m_h L_h P(\Delta_h) + I_b \right]$$

I_i - incident intensity - variable for neutron TOF

k_h - scale factor for particular phase

F_h^2 - structure factor for particular reflection

m_h - multiplicity of the reflection

L_h - correction factors on intensity

$P(\Delta_h)$ - peak shape function

Minimize $\sum w(I_o - I_c)^2$ thus need all $\frac{\partial I_c}{\partial p_i}$

Profile Functions - Basics

$\Delta T = T_{reflection} - T_{profile}$

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

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

Constant Wavelength Profile Function - GSAS

Thompson, Cox & Hastings (with modifications)

Pseudo-Voigt

$$F(\Delta T) = \eta L(\Delta T, \Gamma) + (1-\eta) G(\Delta T, \Gamma)$$

Mixing coefficient

$$\eta = \sum_{j=1}^{3} k_j \left(\gamma / \Gamma\right)^j$$

FWHM parameter

$$\Gamma = \sqrt[5]{\sum_{i=1}^{5} c_i \Gamma_g^{5-i} \gamma^i}$$

CW Function Coefficients - GSAS

Asymmetry A_s or H/L & S/L

Sample shift $$s = \frac{-\pi R S_s}{36000}$$

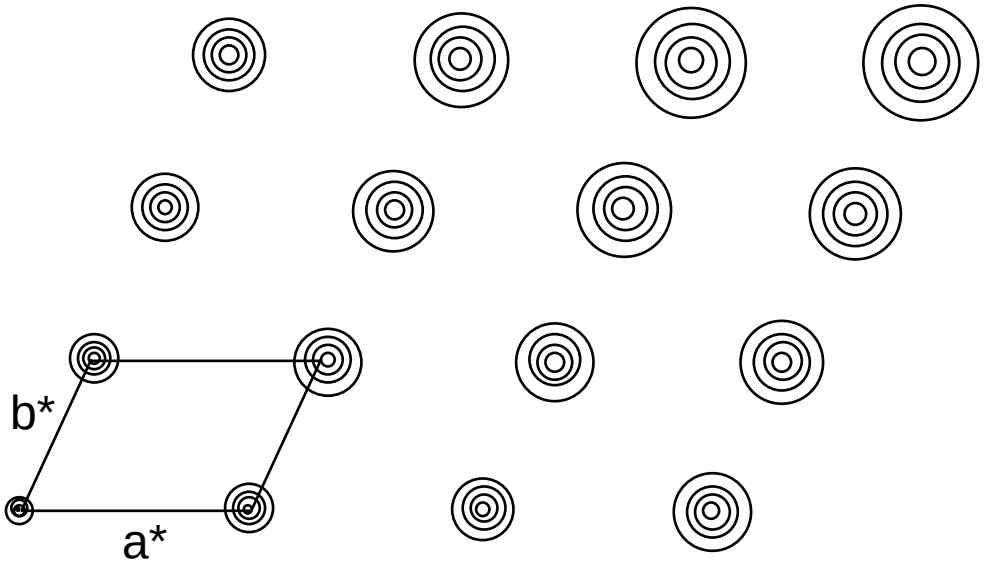
Sample transparency $$\mu_{eff} = \frac{-9000}{\pi R T_s}$$

Gaussian profile $$\Gamma_g^2 = U\tan^2\Theta + V\tan\Theta + W + P/\cos^2\Theta$$

Lorentzian profile $$\gamma = \frac{X}{\cos\Theta} + Y\tan\Theta$$

(plus anisotropic broadening terms)

Microstrain Broadening – simple model



$$\frac{\Delta d}{d} = cons\tan t$$

$$\frac{\Delta d}{d} = \frac{\Delta d^*}{d^*} = \Delta\Theta\cot\Theta$$

$$\Delta 2\Theta = \frac{2\Delta d}{d}\tan\Theta$$

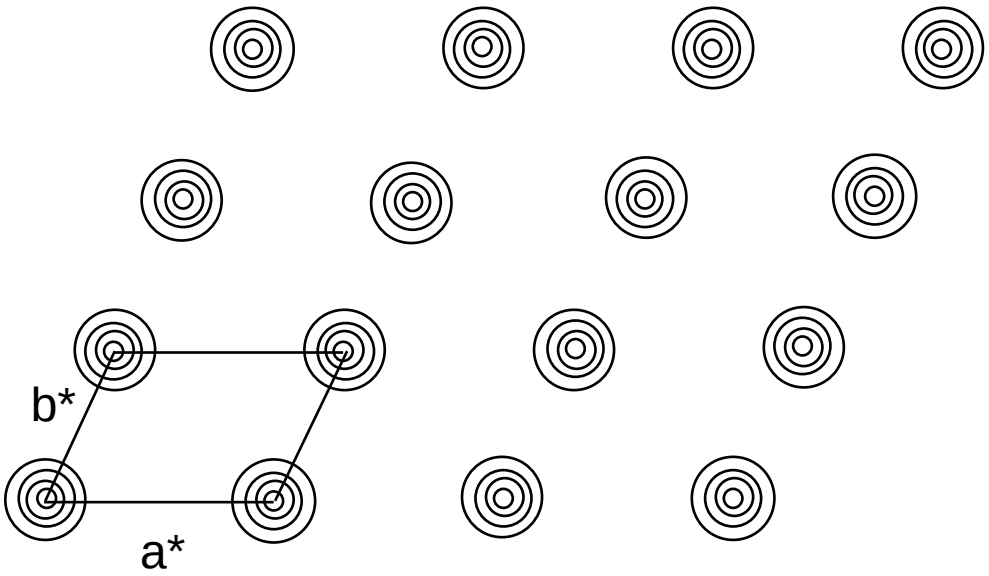
Lorentzian term - usual effect

$$S = 100\%\frac{\pi}{180}"LY"$$

Gaussian - Remove instrumental part

$$S = 100\%\frac{\pi}{180}\sqrt{\Delta"GU"}$$

Crystallite Size Broadening



$$\Delta d^* = \text{constant}$$

$$\Delta d^* = \frac{\Delta d}{d^2} = \frac{\Delta\Theta \cot\Theta}{d}$$

$$= \frac{\Delta 2\Theta \cot\Theta \sin\Theta}{\lambda}$$

$$\Delta 2\Theta = \frac{\lambda \Delta d}{d^2 \cos\Theta}$$

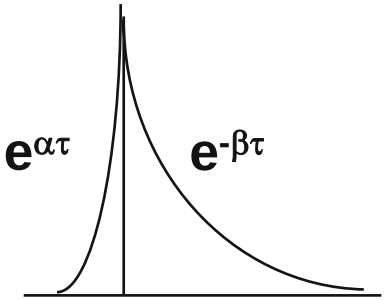
Lorentzian term - usual
K - Scherrer const.

$$p = \frac{180K\lambda}{\pi \text{"LX"}}$$

Gaussian term - rare particles same size?

$$p = \frac{180K\lambda}{\pi\sqrt{\text{"GP"}}}$$

Neutron TOF Neutron Profile Function



$\otimes$

$G(\Delta T,\sigma)$

Von Dreele, Jorgenson & Windsor (with modifications)
Convolution of paired exponentials and a Gaussian

$$H(\Delta T) = N\,[e^{u}\,\mathrm{erfc}(y) + e^{v}\,\mathrm{erfc}(z)]$$

where u, v, y & z are functions of profile coefficients

$\alpha = \alpha_o + \alpha_1/d$ **exponential rise**

$\beta = \beta_0 + \beta_1/d^4$ **exponential decay**

microstrain

$$\sigma^2 = \sigma_0^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 + (\sigma_{1e}^2 d^2 + \sigma_{2e}^2 d^4)\cos^2\phi$$

macrostrain

Gaussian variance - also anisotropic terms

$$\Delta T = (T - T_{p,hkl}) - \varepsilon_i d - \varepsilon_a d\cos\phi - \varepsilon_A d\,\frac{(hk)^2+(hl)^2+(kl)^2}{(h^2+k^2+l^2)^2}$$

peak displacement - macrostress

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}

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

Microstrain broadening - continued

Terms in variance

$$\frac{\partial M}{\partial \alpha_1} = h^2 \,,\; \frac{\partial M}{\partial \alpha_2} = k^2 \,,\; \frac{\partial M}{\partial \alpha_3} = l^2 \,,\; \frac{\partial M}{\partial \alpha_4} = kl \,,\; \frac{\partial M}{\partial \alpha_5} = hl \,,\; \frac{\partial M}{\partial \alpha_6} = hk$$

Substitute – note similar terms in matrix

$$\frac{\partial M}{\partial \boldsymbol{\alpha}_i}\frac{\partial M}{\partial \boldsymbol{\alpha}_j} = \begin{bmatrix} h^4 & h^2k^2 & h^2l^2 & h^2kl & h^3l & h^3k \\ h^2k^2 & k^4 & k^2l^2 & k^3l & hk^2l & hk^3 \\ h^2l^2 & k^2l^2 & l^4 & kl^3 & hl^3 & hkl^2 \\ h^2kl & k^3l & kl^3 & k^2l^2 & hkl^2 & hk^2l \\ h^3l & hk^2l & hl^3 & hkl^2 & h^2l^2 & h^2kl \\ h^3k & hk^3 & hkl^2 & hk^2l & h^2kl & h^2k^2 \end{bmatrix}$$

Microstrain broadening - continued

Broadening – as variance

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L \quad , H + K + L = 4$$

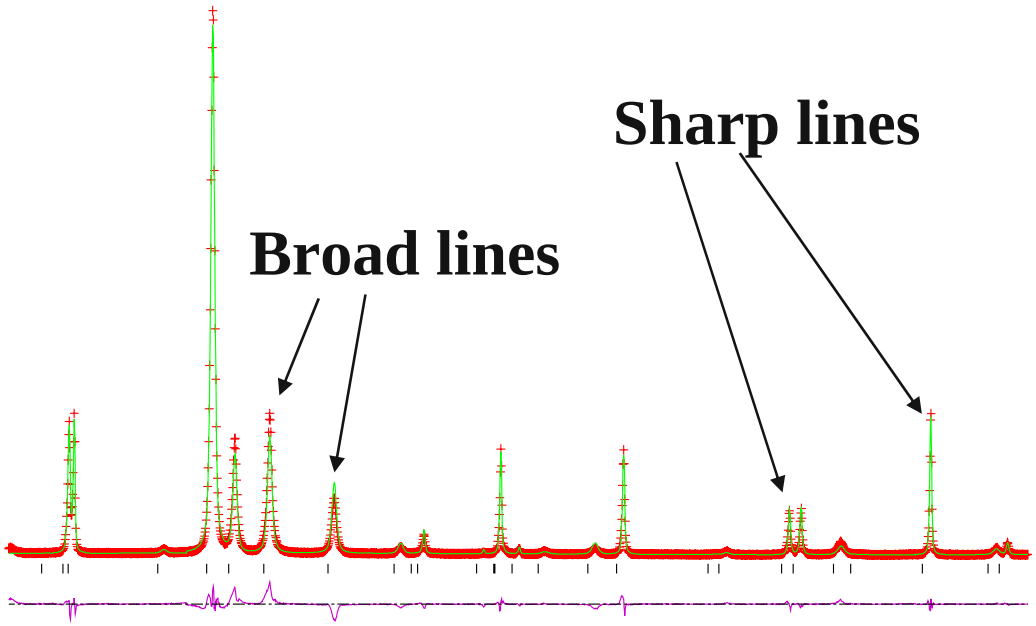
General expression – triclinic – 15 terms

$$\sigma^2(M_{hkl}) = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3\left(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2\right) +$$
$$2\left(S_{310}h^3k + S_{103}hl^3 + S_{031}k^3l + S_{130}hk^3 + S_{301}h^3l + S_{013}kl^3\right) +$$
$$4\left(S_{211}h^2kl + S_{121}hk^2l + S_{112}hkl^2\right)$$

Symmetry effects – monoclinic (b unique) – 9 terms

$$\sigma^2(M_{hkl}) = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3S_{202}h^2l^2 + 3(S_{220}h^2k^2 + S_{022}k^2l^2) +$$
$$2\left(S_{301}h^3l + S_{103}hk^3\right) + 4S_{121}hk^2l$$

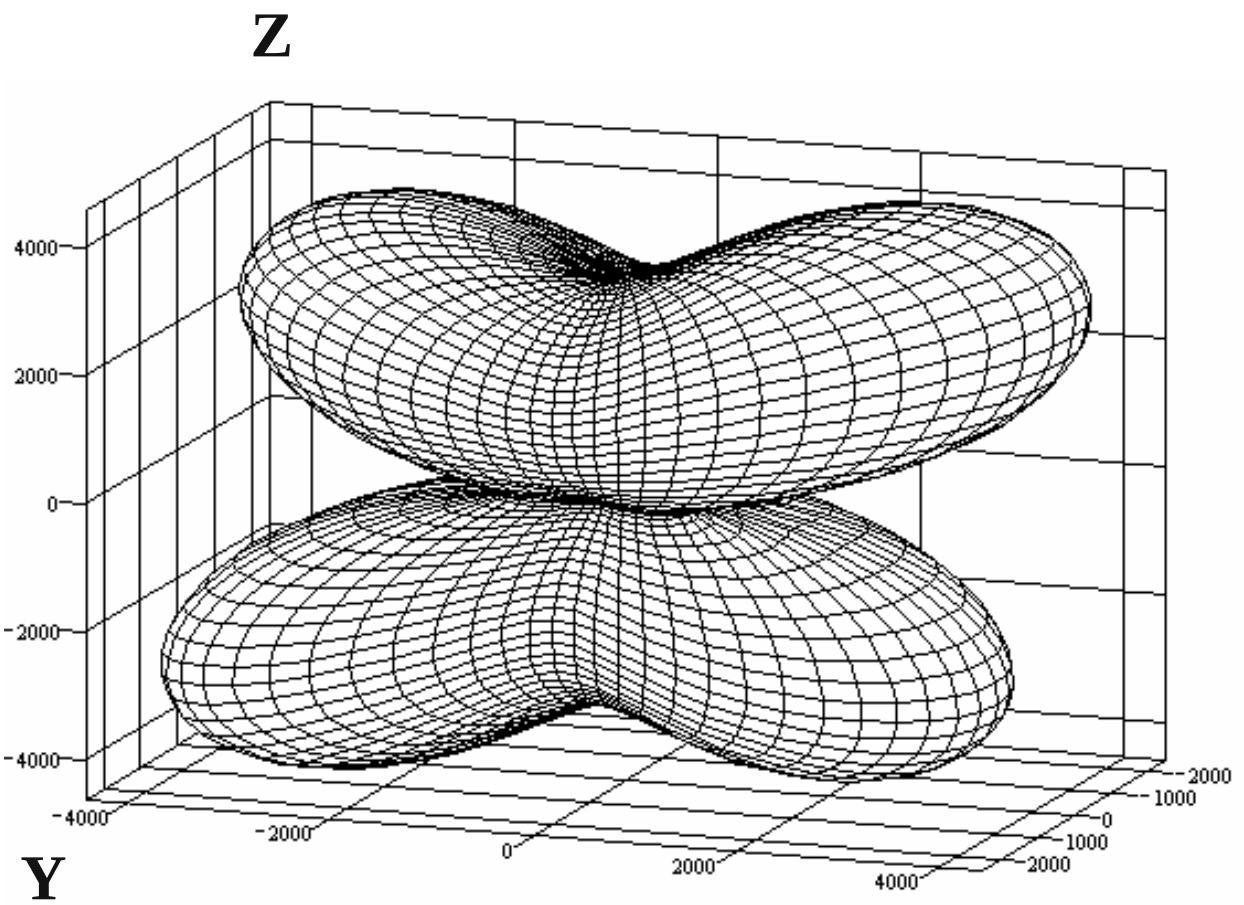
Unusual line broadening effects



Seeming inconsistency in line broadening
- hkl dependent

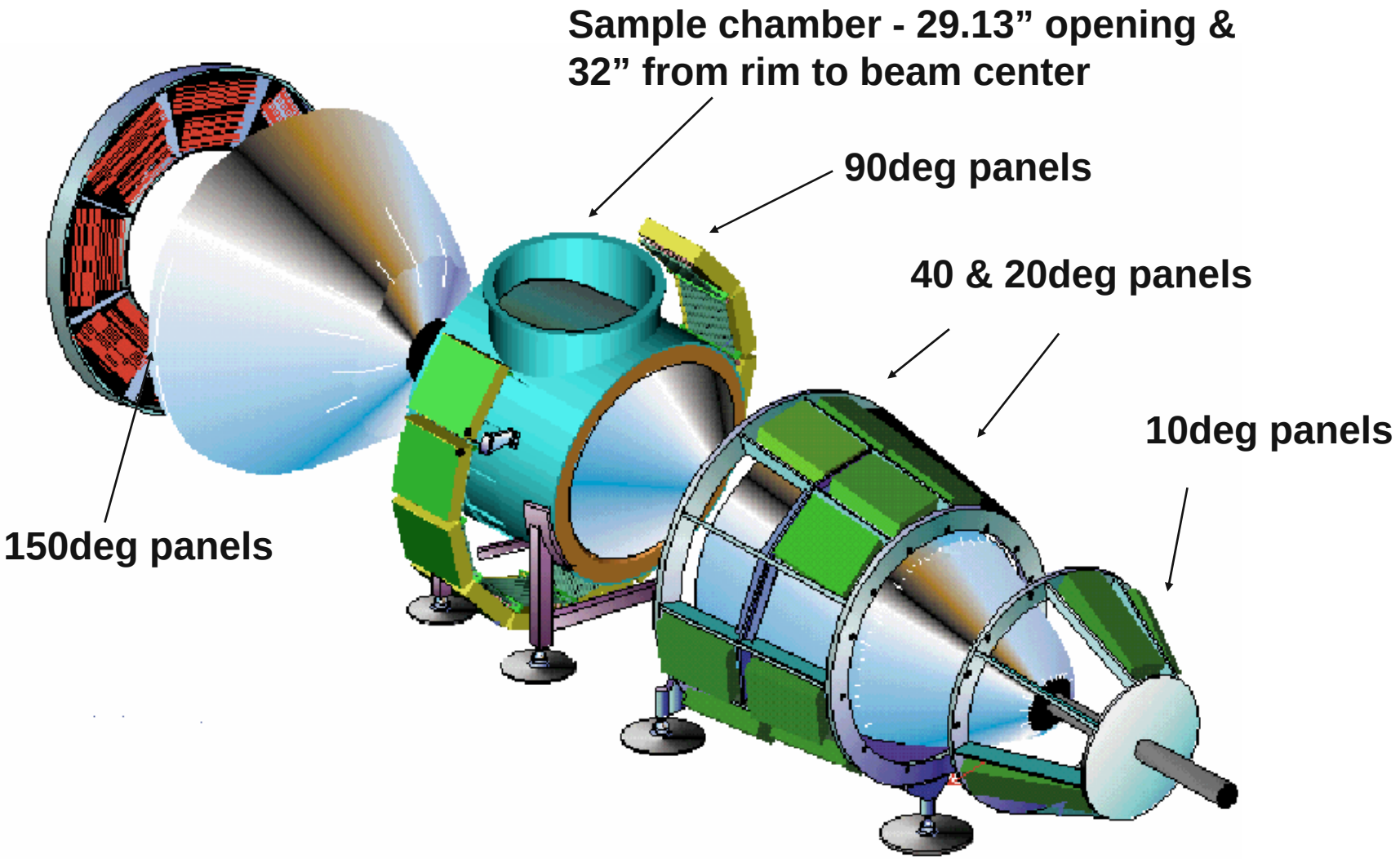
Na parahydroxybenzoate

Unusual micostrain effects - peak broadening



Directional dependence - Lattice defects?

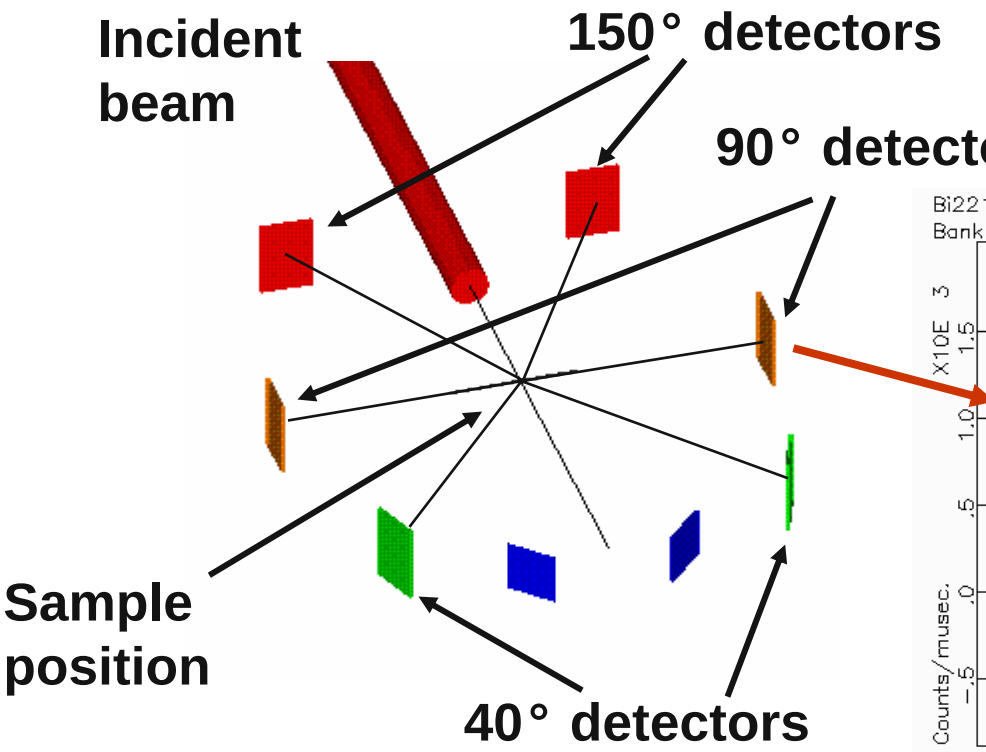
Exploded view of HIPPO Diffractometer



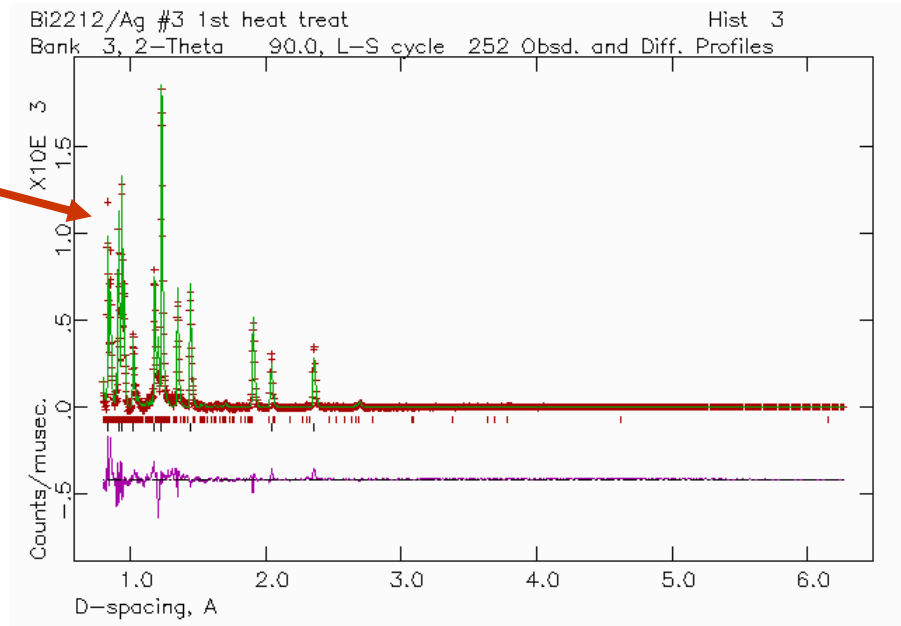
Neutron TOF Diffractometer - multiple detectors

High to low scattering angles
λ = 0.4Å to 10Å; d = 0.2Å to 30Å
Δd/d = 0.3% to 5%(other instr. <0.1%)

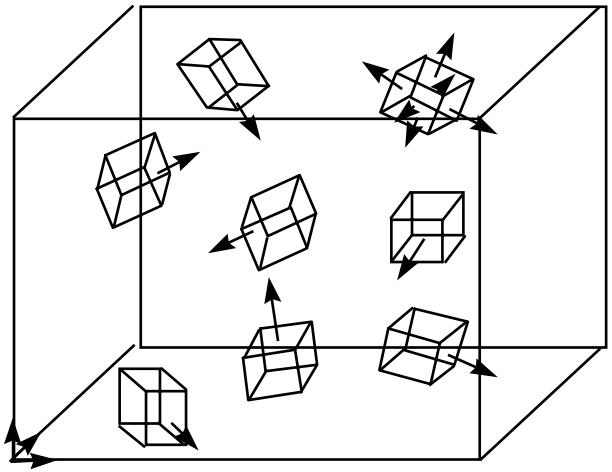
E.g. HIPD & HIPPO at LANSCE; POWGEN3 at SNS



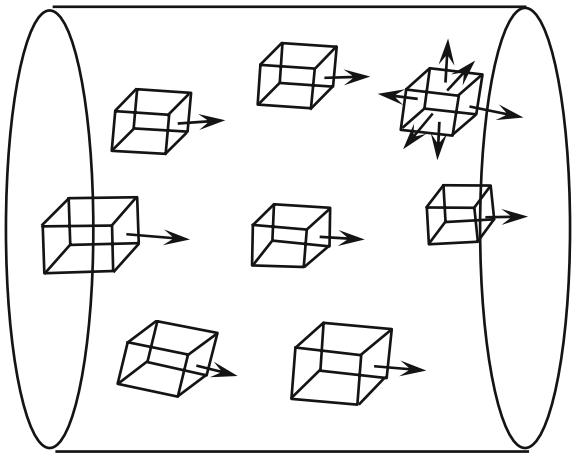
Fixed 2Θ, TOF $\propto \lambda \propto$ d



What is texture? "Interesting Preferred Orientation"



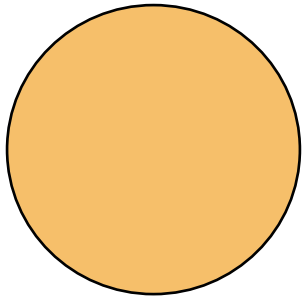
Loose powder



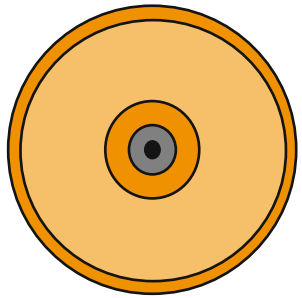
Metal wire

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



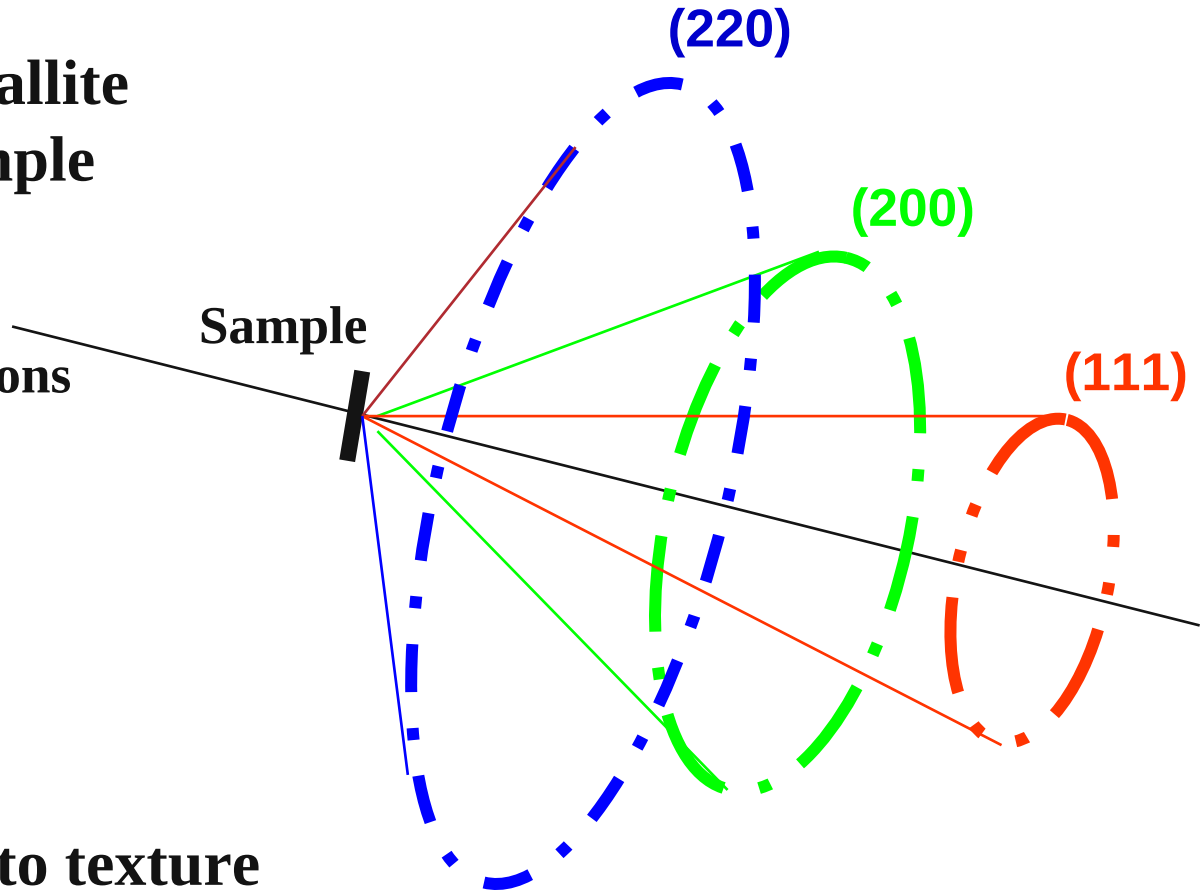
(100) wire texture

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 - measurement by diffraction

Non-random crystallite orientations in sample



Debye-Scherrer cones

- **uneven intensity due to texture**
- **also different pattern of unevenness for different hkl's**
- **Intensity pattern changes as sample is turned**

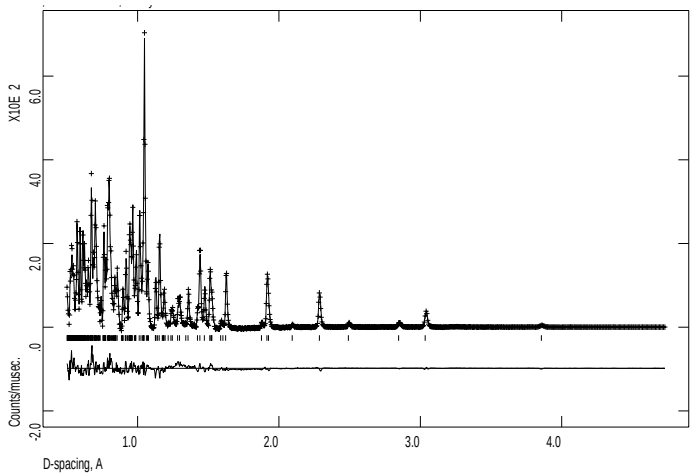
Texture effect on reflection intensity - Rietveld model

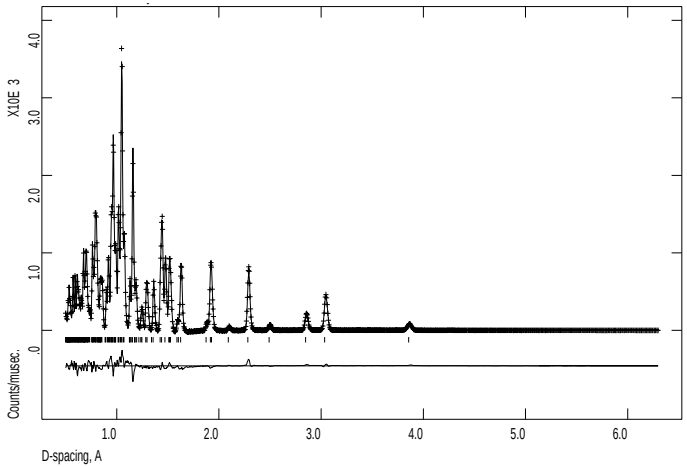
$$A(h,y) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \sum_{n=-l}^{l} C_l^{mn} K_l^m(h) K_l^n(y)$$

- 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

Example: $CaCO_3$ calcite - “Standard Round Robin Sample”

[H.R. Wenk, J. Appl. Cryst.(1991). 24, 920-927]

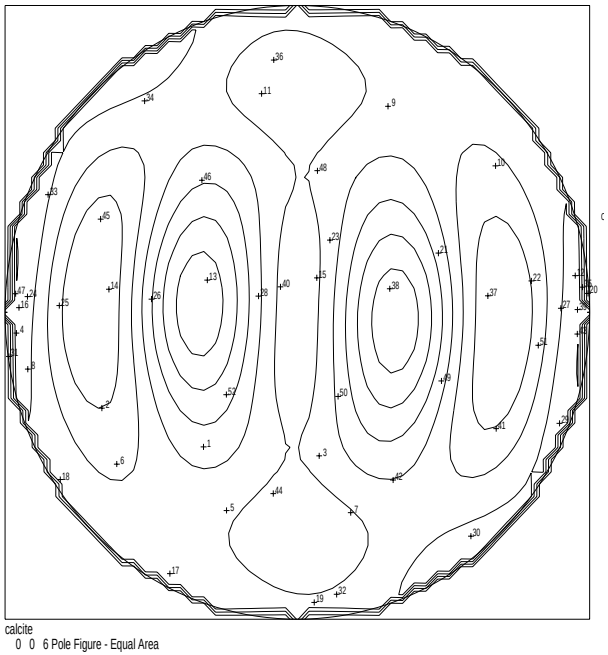


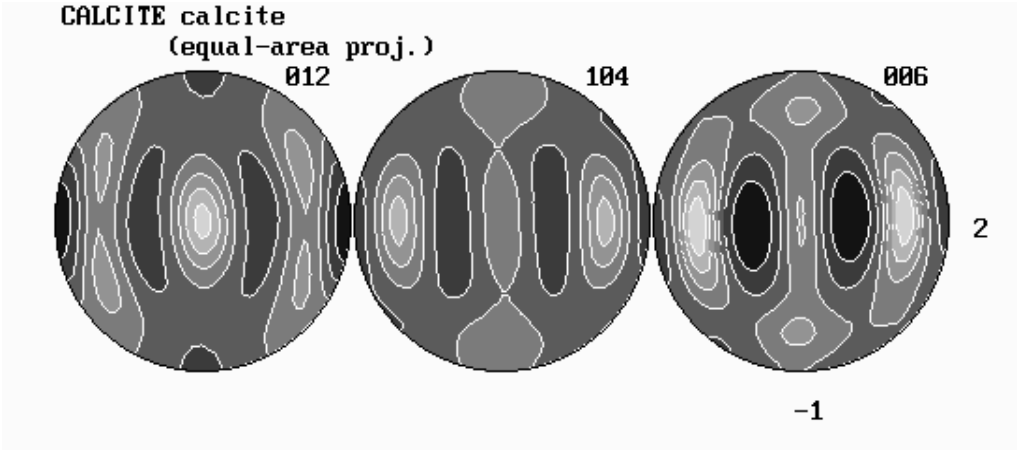


- **Two patterns from different sample orientations and different detector banks**
- **Very different reflection intensities from texture**
- **Any one pattern useless for Rietveld due to texture variation**
- **But all 52 combined in single LS gives texture and crystal structure**

Calcite pole figures - compute from C_l^{mn}

006 pole figure for calcite - shows sampling orientations

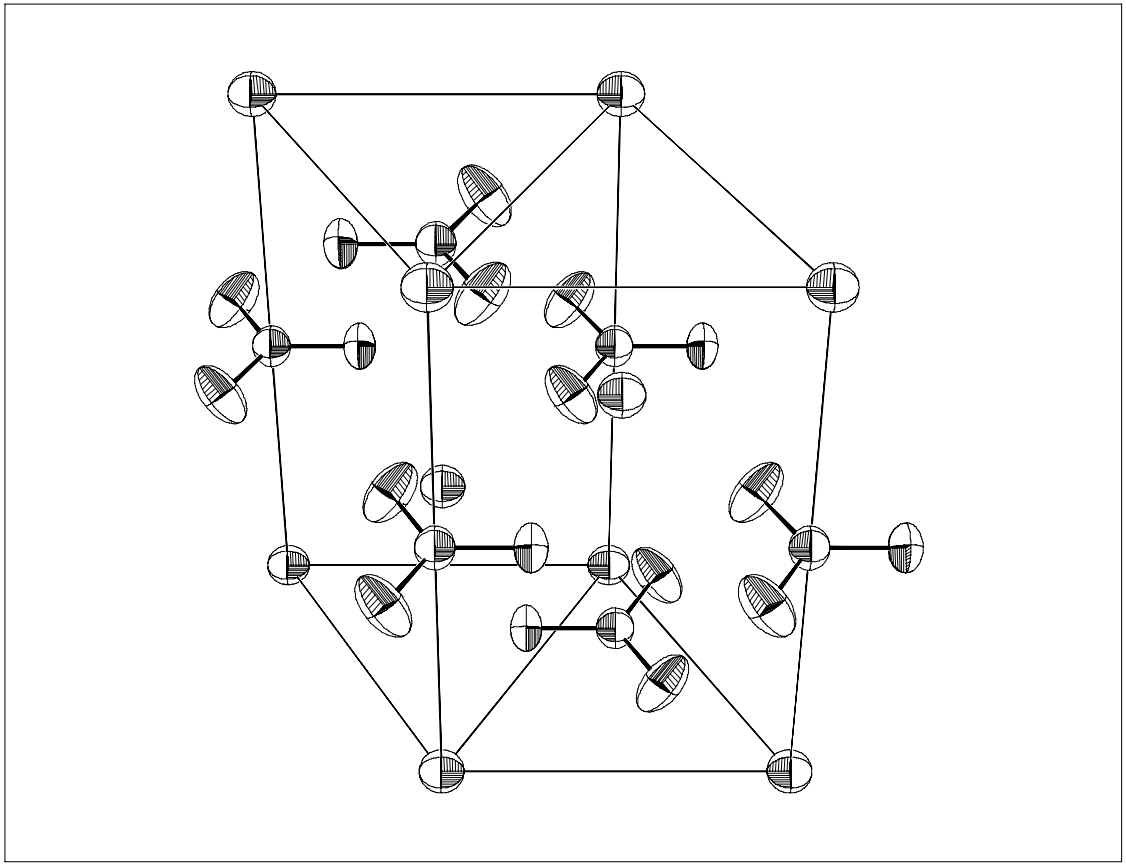




Other pole figures generated from harmonic coefficients

Match those from neutron measurements given by Wenk

Crystal structure of calcite - refined with texture



1/2 calcite unit cell

Result – matches “best” single crystal X-ray result

A final word

**“A Rietveld refinement is never perfected,
merely abandoned”**

(P. Stephens, 2000)