

INTRODUCTION TO THE RIETVELD METHOD AND THE PROGRAM MAUD



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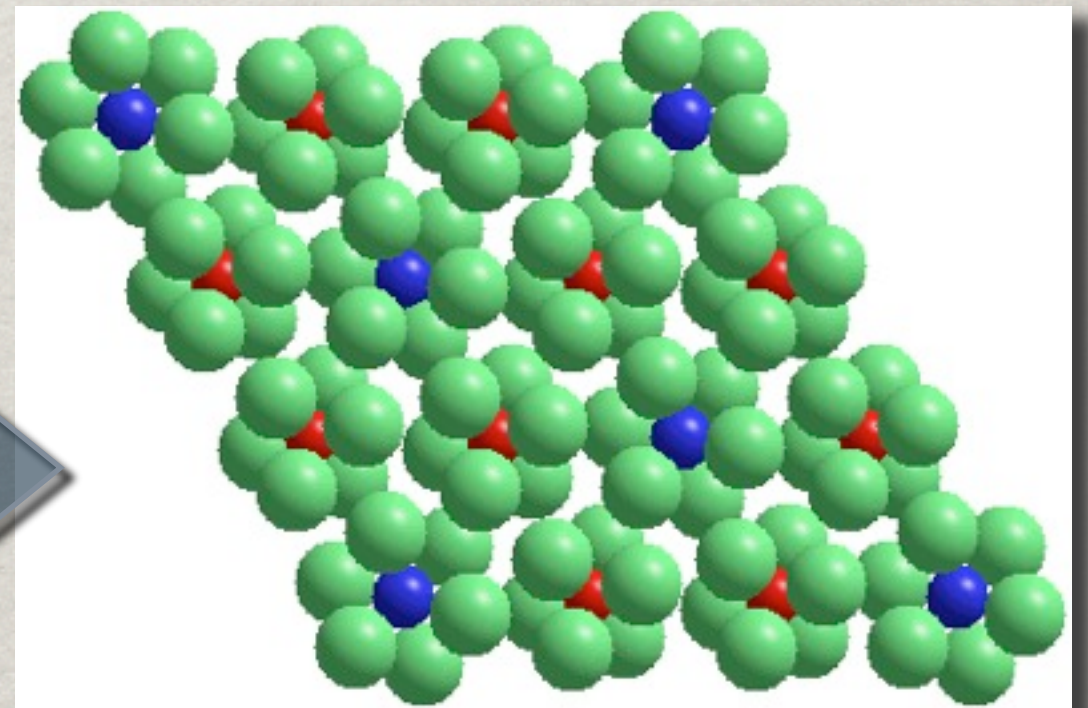
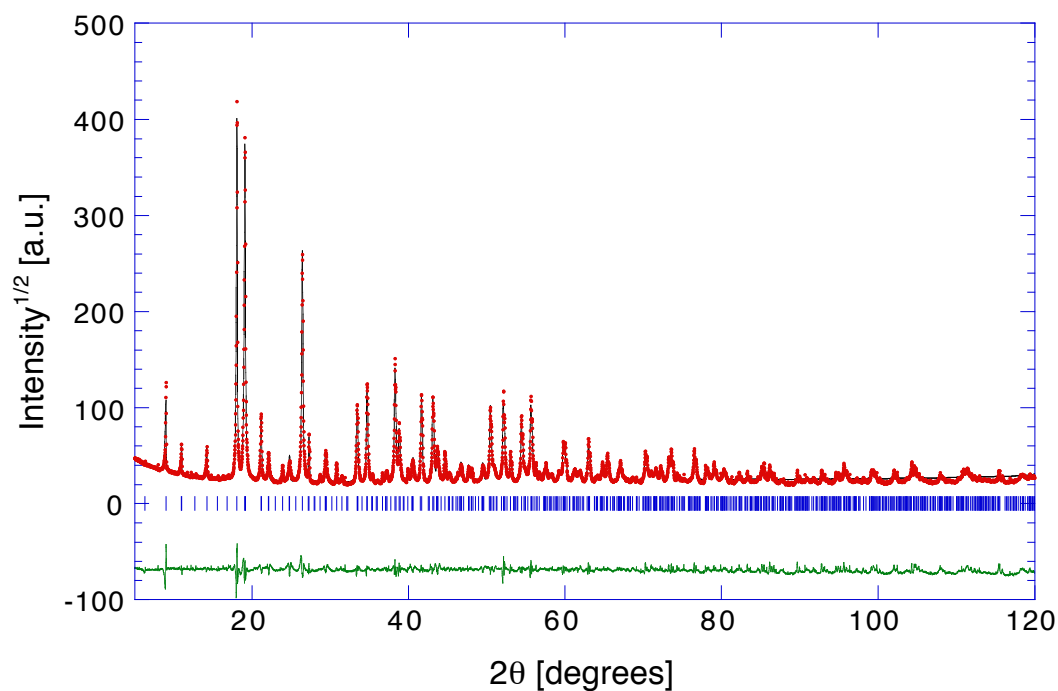
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GOAL OF THE RIETVELD METHOD

- ✿ To minimize the residual function using a non-linear least squares algorithm

$$WSS = \sum_i w_i \left(I_i^{\text{exp}} - I_i^{\text{calc}} \right)^2, w_i = \frac{1}{I_i^{\text{exp}}}$$

- ✿ and thus refine the crystal structure of a compound (cell parameters, atomic positions and Debye-Waller factors)



DIFFRACTION INTENSITIES

✻ The intensity in a powder diffractometer

$$I_i^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

✻ The structure factor:

$$|F_{k,j}|^2 = m_k \left| \sum_{n=1}^N f_n e^{-B_n \frac{\sin^2 \theta}{\lambda^2}} \left(e^{2\pi i(hx_n + ky_n + lz_n)} \right) \right|^2$$

DIFFRACTION ANALYSES

- ✻ Phase identifications (crystalline and amorphous)
- ✻ Crystal structure determination
- ✻ **Crystal structure refinements**
- ✻ Quantitative phase analysis (and crystallinity determination)
- ✻ Microstructural analyses (crystallite sizes - microstrain)
- ✻ Texture analysis
- ✻ Residual stress analysis
- ✻ Order-disorder transitions and compositional analyses
- ✻ Thin films

GOAL OF THE RIETVELD METHOD

- ✿ To minimize the residual function:

$$WSS = \sum_i w_i (I_i^{\text{exp}} - I_i^{\text{calc}})^2, w_i = \frac{1}{I_i^{\text{exp}}}$$

- ✿ where:

$$I_i^{\text{calc}} = S_F \sum_k L_k |F_k|^2 S(2\theta_i - 2\theta_k) P_k A + bkg_i$$

P_k = preferred orientation function

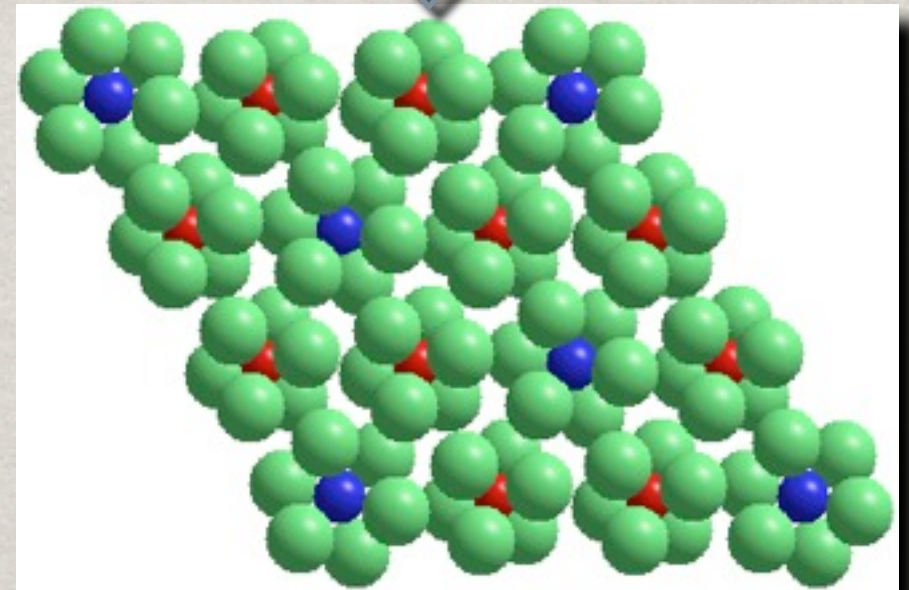
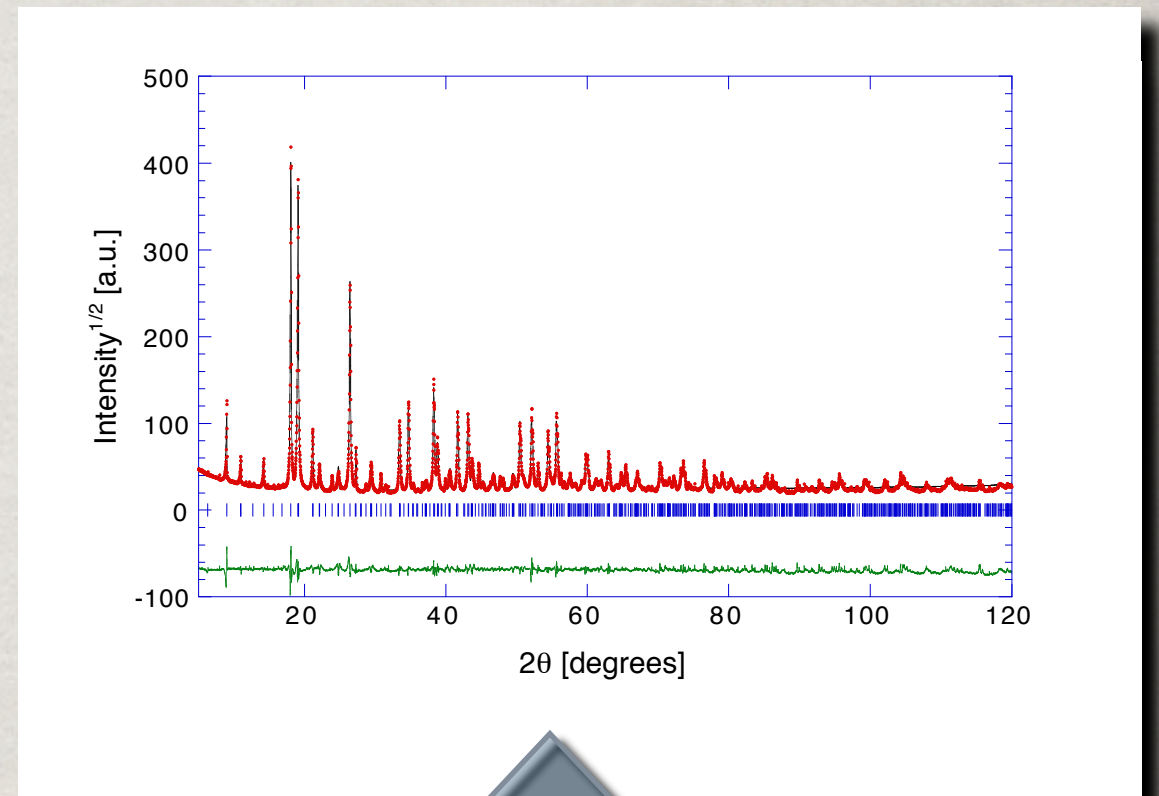
$S(2\theta_i - 2\theta_k)$ = profile shape function

(PV : η , HWHM)

$$HWHM^2 = U \tan^2 \theta + V \tan \theta + W$$

$$P_k = \left(r^2 \cos^2 \alpha + \frac{\sin^2 \alpha}{r} \right)^{-3/2}$$

- ✿ using a non-linear least squares algorithm



THE CLASSICAL RIETVELD METHOD

- ✿ The function to minimize by a least squares method (non linear):

$$WSS = \sum_i w_i \left(I_i^{\text{exp}} - I_i^{\text{calc}} \right)^2, w_i = \frac{1}{I_i^{\text{exp}}}$$

- ✿ the spectrum is calculated by the classical intensity equation:

$$I_i^{\text{calc}} = S_F \sum_{j=1}^{N_{\text{phases}}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{\text{peaks}}} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- ✿ The spectrum depends on
 - ✿ phases: crystal structure, microstructure, quantity, cell volume, texture, stress, chemistry etc.
 - ✿ instrument geometry characteristics: beam intensity, Lorentz-Polarization, background, resolution, aberrations, radiation etc.
 - ✿ sample: position, shape and dimensions, orientation.
- ✿ Each of the quantity can be written in term of parameters that can be refined (optimized).

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

✱ The spectrum (at a 2θ point i) is determined by:

➡ ✱ a background value

➡ – some reflection peaks that can be described by different terms:

➡ ✱ Diffraction intensity (determines the “height” of the peaks)

➡ • Line broadening (determines the shape of the peaks)

➡ • Number and positions of the peaks

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- ✱ The more used background in Rietveld refinements is a polynomial function in 2θ :

$$bkg(2\theta_i) = \sum_{n=0}^{N_b} a_n (2\theta_i)^n$$

- ✱ N_b is the polynomial degree
- ✱ a_n the polynomial coefficients
- ✱ For more complex backgrounds specific formulas are available
- ✱ It is possible to incorporate also the TDS in the background

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- ✻ Starting with the “Diffraction Intensities”, the factors are:
 - ✻ A scale factor for each phase
 - ✻ A Lorentz-Polarization factor
 - ✻ The multiplicity
 - ✻ The structure factor
 - ✻ The temperature factor
 - ✻ The absorption
 - ✻ The texture
- ✻ Problems: extinctions, absorption contrast, graininess, sample volume and beam size, inhomogeneity, etc.

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k |F_{k,j}|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- ✻ The scale factor (for each phase) is written in classical Rietveld programs as:

$$S_j = S_F \frac{f_j}{V_j^2}$$

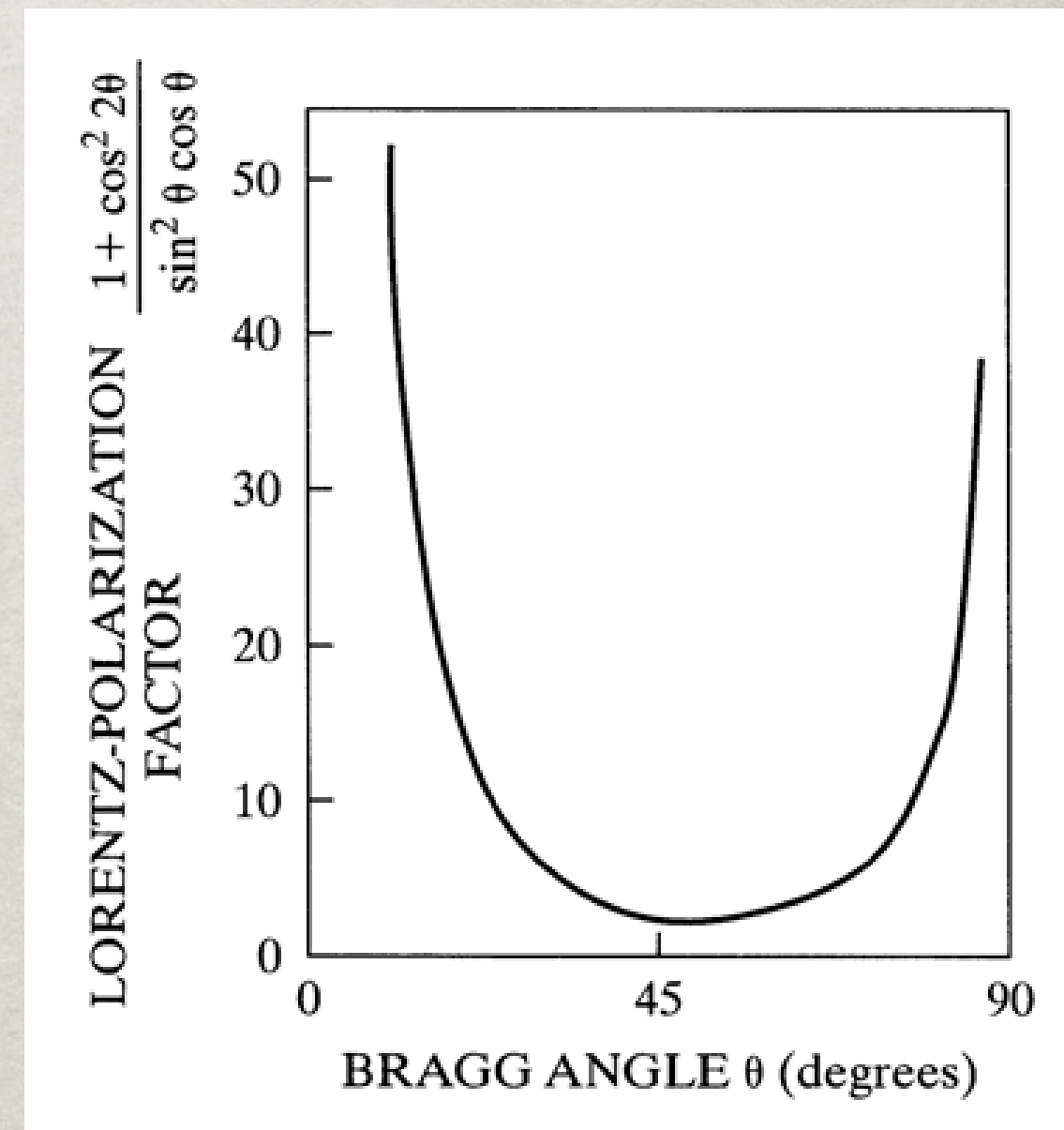
- ✻ S_j = phase scale factor (the overall Rietveld generic scale factor)
- ✻ S_F = beam intensity (it depends on the measurement)
- ✻ f_j = phase volume fraction
- ✻ V_j = phase cell volume (in some programs it goes in the F factor)
- ✻ In Maud the last three terms are kept separated.

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- ✱ The Lorentz-Polarization factor:
 - ✱ it depends on the instrument
 - ✱ geometry
 - ✱ monochromator (angle α)
 - ✱ detector
 - ✱ beam size/sample volume
 - ✱ sample positioning (angular)
- ✱ For a Bragg-Brentano instrument:

$$L_p = \frac{1 + P_h \cos^2(2\theta)}{2(1 + P_h) \sin^2 \theta \cos \theta} \quad P_h = \cos^2(2\alpha)$$



THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

✱ Under a generalized structure factor we include:

✱ The multiplicity of the k reflection (with h, k, l Miller indices): m_k

✱ The structure factor

✱ The temperature factor: B_n

$$|F_{k,j}|^2 = m_k \left| \sum_{n=1}^N f_n e^{-B_n \frac{\sin^2 \theta}{\lambda^2}} \left(e^{2\pi i(hx_n + ky_n + lz_n)} \right) \right|^2$$

✱ N = number of atoms

✱ x_n, y_n, z_n coordinates of the n^{th} atom

✱ f_n , atomic scattering factor

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

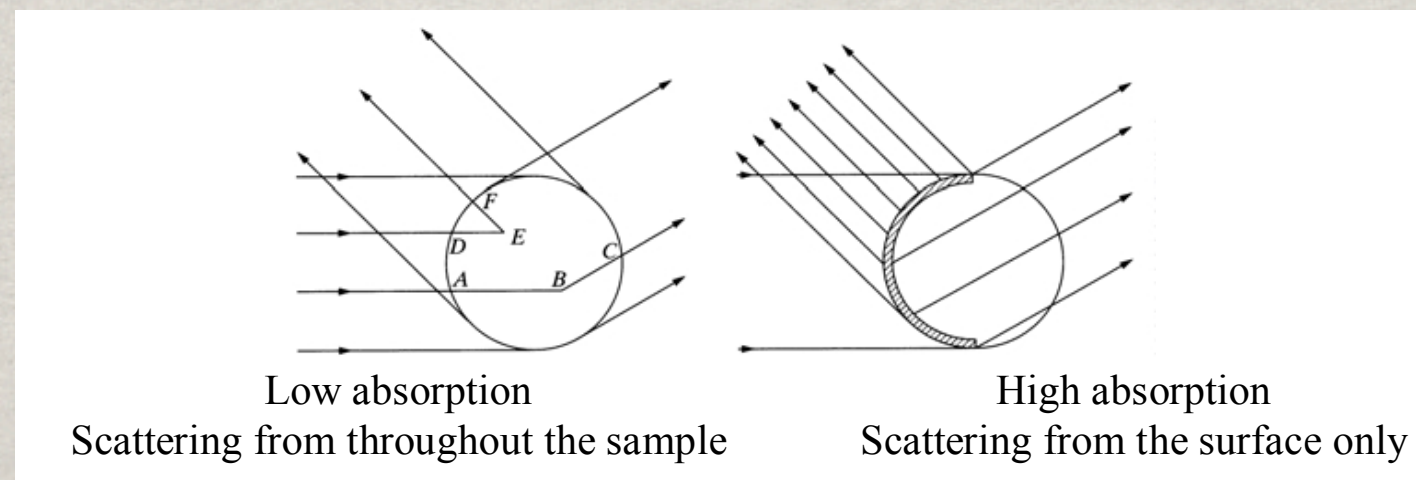
✻ The absorption factor:

✻ in the Bragg-Brentano case (thick sample):

$$A_j = \frac{1}{2\mu}, \quad \mu \text{ is the linear absorption coefficient of the sample}$$

✻ For the thin sample or films the absorption depends on 2θ

✻ For Debye-Scherrer geometry the absorption is also not constant



✻ There could be problems for microabsorption (absorption contrast)

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- ✱ The texture (or preferred orientations):

- ✱ The March-Dollase formula is used:

$$P_{k,j} = \frac{1}{m_k} \sum_{n=1}^{m_k} \left(P_{MD}^2 \cos^2 \alpha_n + \frac{\sin^2 \alpha_n}{P_{MD}} \right)^{-\frac{3}{2}}$$

- ✱ P_{MD} is the March-Dollase parameter

- ✱ summation is done over all equivalent hkl reflections (m_k)

- ✱ α_n is the angle between the preferred orientation vector and the crystallographic plane hkl (in the crystallographic cell coordinate system)

- ✱ The formula is intended for a cylindrical texture symmetry (observable in B-B geometry or spinning the sample)

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

✱ The profile shape function:

✱ different profile shape function are available:

✱ Gaussian (the original Rietveld function for neutrons)

✱ Cauchy

✱ Voigt and Pseudo-Voigt (PV)

✱ Pearson VII, etc.

✱ For example the PV:

$$PV(2\theta_i - 2\theta_k) = I_n \left[\eta_k \left(\frac{1}{1 + S_{i,k}^2} \right) + (1 - \eta_k) e^{-S_{i,k}^2 \ln 2} \right] \quad S_{i,k} = \frac{2\theta_i - 2\theta_k}{\omega_k}$$

✱ the shape parameters are:

Caglioti formula: $\omega^2 = W + V \tan \theta + U \tan^2 \theta$

Gaussianity: $\eta = \sum_{n=0}^{N_g} c_n (2\theta)^n$

THE CLASSICAL RIETVELD METHOD

$$I_i^{calc} = S_F \sum_{j=1}^{N_{phases}} \frac{f_j}{V_j^2} \sum_{k=1}^{N_{peaks}} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

- ✱ The number of peaks is determined by the symmetry and space group of the phase.
- ✱ One peak is composed by all equivalent reflections m_k
- ✱ The position is computed from the d-spacing of the hkl reflection (using the reciprocal lattice matrix):

$$d_{hkl} = \frac{V_C}{\sqrt{s_{11}h^2 + s_{22}k^2 + s_{33}l^2 + 2s_{12}hk + 2s_{13}hl + 2s_{23}kl}}$$

$$S = \begin{pmatrix} a^{*2} & a^* b^* \cos \gamma^* & a^* c^* \cos \beta^* \\ a^* b^* \cos \gamma^* & b^{*2} & b^* c^* \cos \alpha^* \\ a^* c^* \cos \beta^* & b^* c^* \cos \alpha^* & c^{*2} \end{pmatrix}$$

QUALITY OF THE REFINEMENT

✻ Weighted Sum of Squares:

$$WSS = \sum_{i=1}^N \left[w_i \left(I_i^{\text{exp}} - I_i^{\text{calc}} \right) \right]^2, \quad w_i = \frac{1}{\sqrt{I_i^{\text{exp}}}}$$

✻ R indices (N=number of points, P=number of parameters):

$$R_{wp} = \sqrt{\frac{\sum_{i=1}^N \left[w_i \left(I_i^{\text{exp}} - I_i^{\text{calc}} \right) \right]^2}{\sum_{i=1}^N \left[w_i I_i^{\text{exp}} \right]^2}}, \quad w_i = \frac{1}{\sqrt{I_i^{\text{exp}}}}$$

$$R_{\text{exp}} = \sqrt{\frac{(N - P)}{\sum_{i=1}^N \left[w_i I_i^{\text{exp}} \right]^2}}, \quad w_i = \frac{1}{\sqrt{I_i^{\text{exp}}}}$$

✻ The goodness of fit: $GofF = \frac{R_{wp}}{R_{\text{exp}}}$

THE R INDICES

- ✱ The R_{wp} factor is the more valuable. Its absolute value does not depend on the absolute value of the intensities. But it depends on the background. With a high background is more easy to reach very low values. Increasing the number of peaks (sharp peaks) is more difficult to get a good value.
 - ✱ $R_{wp} < 0.1$ correspond to an acceptable refinement with a medium complex phase
 - ✱ For a complex phase (monoclinic to triclinic) a value < 0.15 is good
 - ✱ For a highly symmetric compound (cubic) with few peaks a value < 0.08 start to be acceptable
- ✱ With high background better to look at the R_{wp} background subtracted.
- ✱ The R_{exp} is the minimum R_{wp} value reachable using a certain number of refineable parameters. It needs a valid weighting scheme to be reliable.

WSS AND GOFF (OR SIGMA)

- ✱ The weighted sum of squares is only used for the minimization routines. Its absolute value depends on the intensities and number of points.
- ✱ The goodness of fit is the ratio between the R_{wp} and R_{exp} and cannot be lower than 1 (unless the weighting scheme is not correctly valuable: for example in the case of detectors not recording exactly the number of photons or neutrons).
- ✱ A good refinement gives GofF values lower than 2.
- ✱ The goodness of fit is not a very good index to look at as with a noisy pattern is quite easy to reach a value near 1.
- ✱ With very high intensities and low noise patterns is difficult to reach a value of 2.
- ✱ The GofF is sensible to model inaccuracies.

WHY THE RIETVELD REFINEMENT IS WIDELY USED?

✻ Pro

- ✻ It uses directly the measured intensities points
- ✻ It uses the entire spectrum (as wide as possible)
- ✻ Less sensible to model errors
- ✻ Less sensible to experimental errors

✻ Cons

- ✻ It requires a model
- ✻ It needs a wide spectrum
 - Rietveld programs are not easy to use
 - Rietveld refinements require some experience (1-2 years?)

✻ Can be enhanced by:

- ✻ More automatic/expert mode of operation
- ✻ Better easy to use programs

RIETVELD PROCEDURE

- ✱ Experiment:

- ✱ choose the correct instrument/s
- ✱ select the experiment conditions
- ✱ prepare the sample and collect the pattern/s

- ✱ Analysis:

- ✱ verify the data quality and perform the qualitative analysis

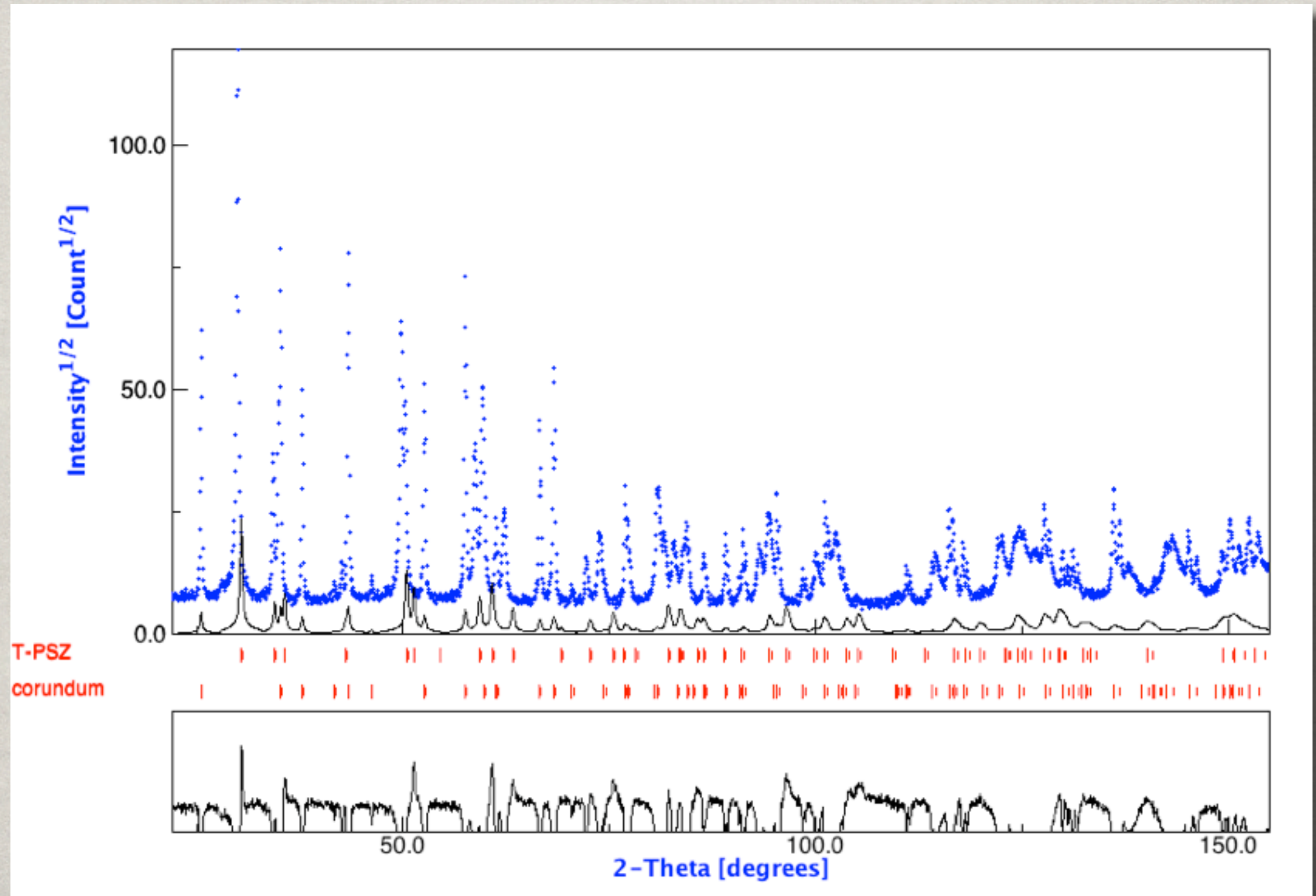
- ✱ Rietveld refinement:

- ✱ load or input the phases in the sample
- ✱ adjust manually some parameters (cell, intensities, background)
- ✱ refine overall intensities and background
- ✱ refine peaks positions
- ✱ refine peaks shapes
- ✱ refine structures

- ✱ Assess the results

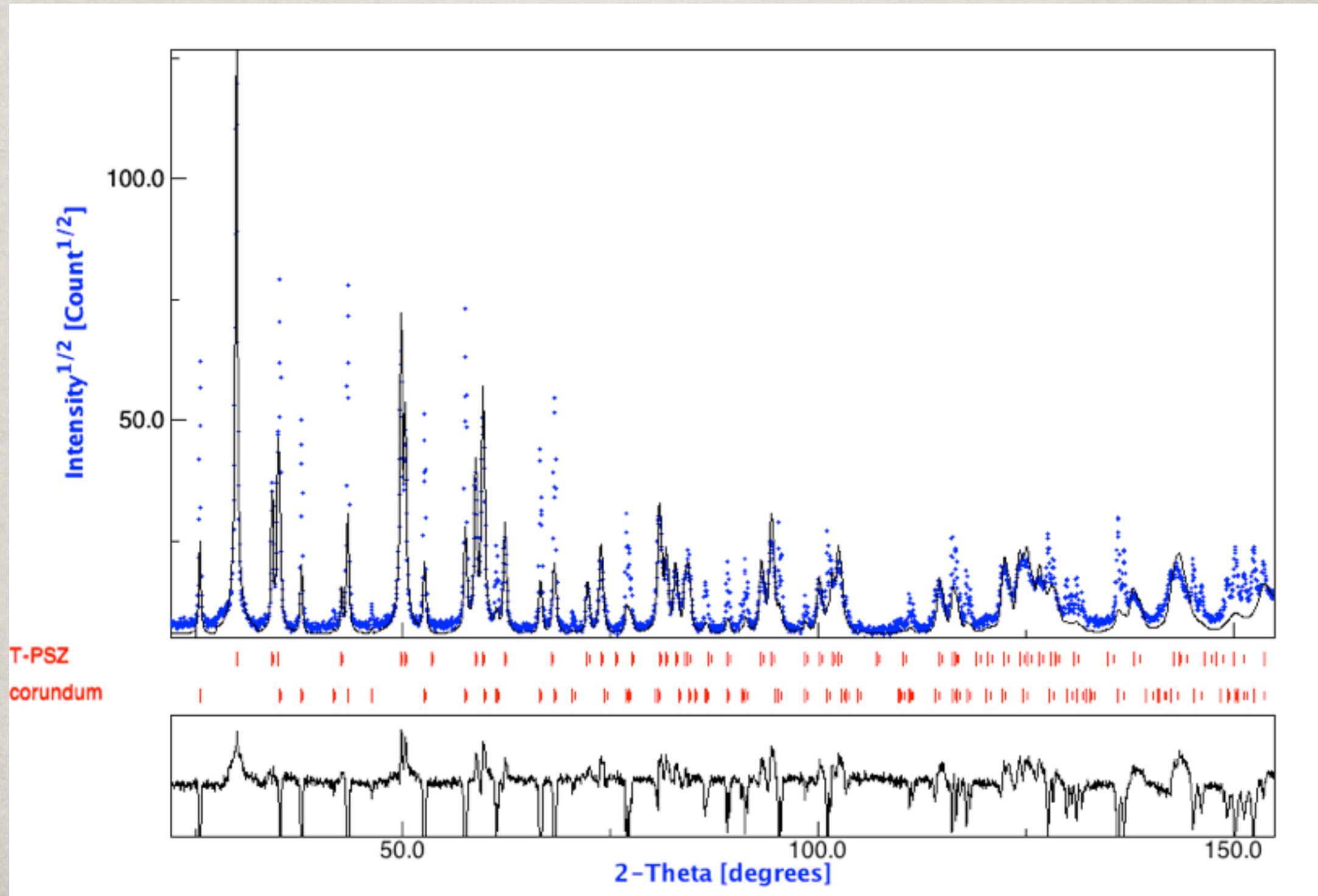
STARTING POINT: DEFINING THE PHASES

- ✱ We need to specify which phases we will work with (databases)



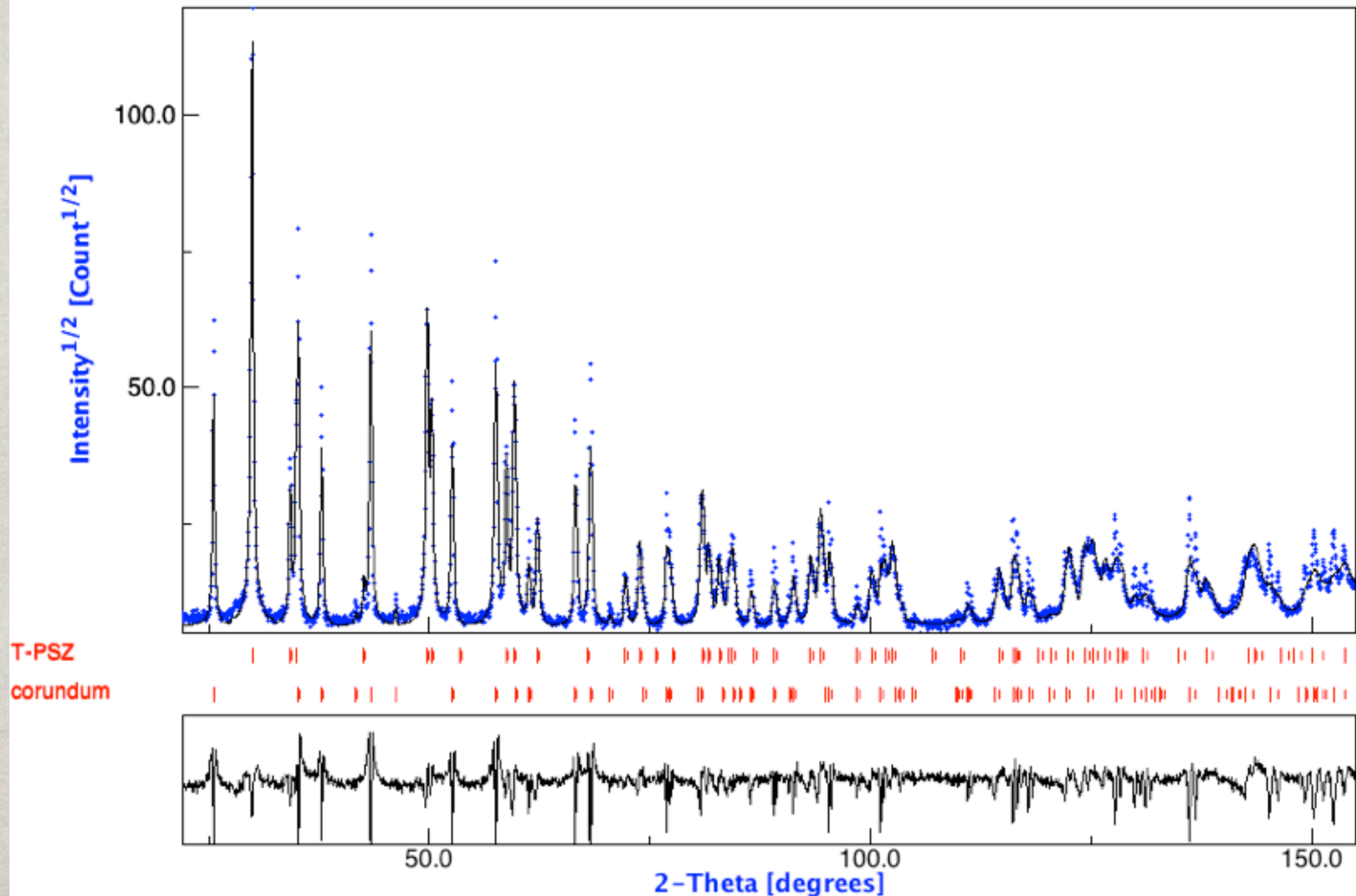
ADJUSTING MANUALLY: CELL PARAMETERS, INTENSITIES

- ✱ The peaks positions must be sufficiently correct for a good start; better also to adjust scale factors and background



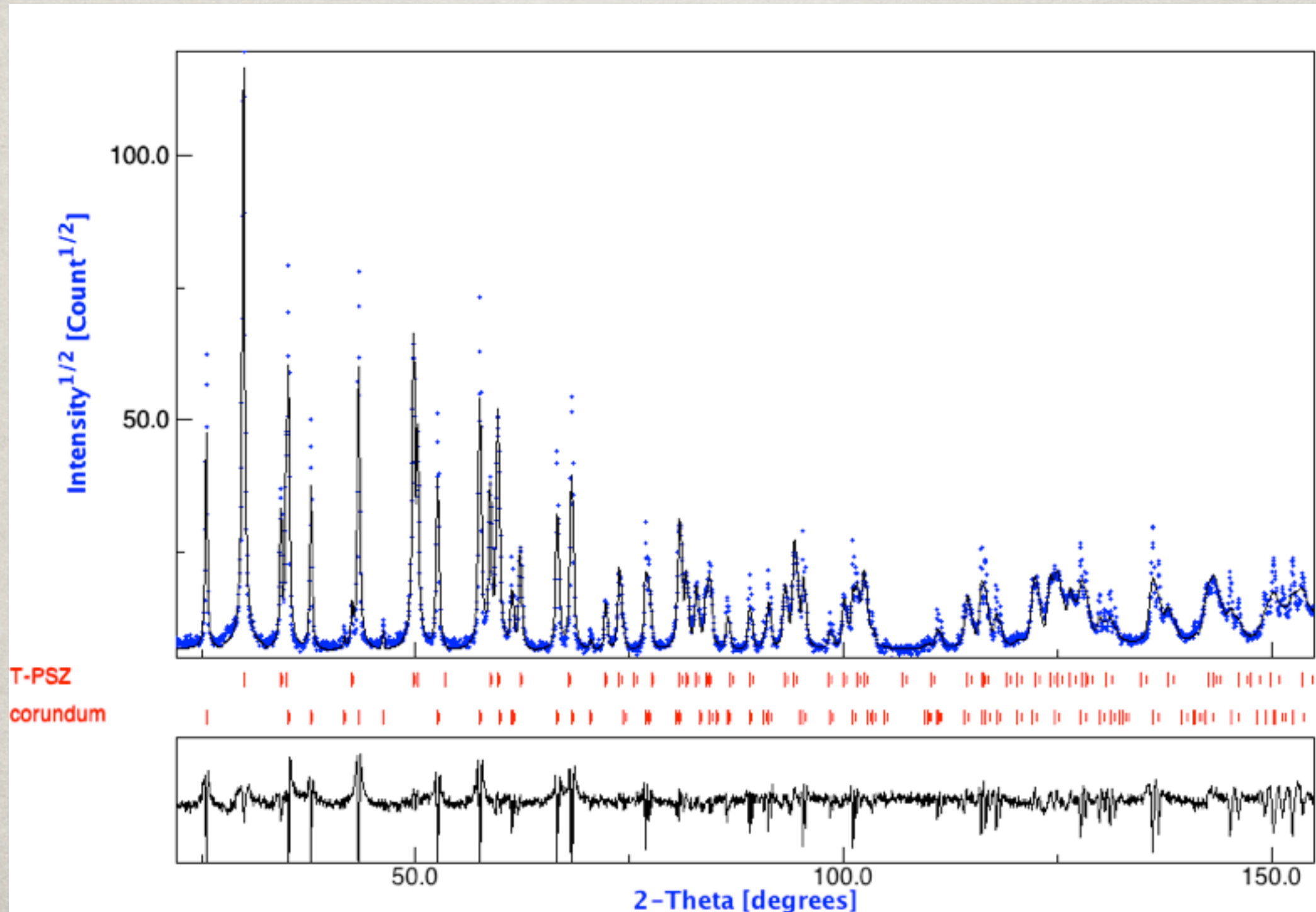
STEP 1: REFINING SCALE FACTORS AND BACKGROUND

- ✿ After 5 iterations the R_{wp} is 26.5 %; intensities look better; we use only one overall B factor for all atoms.



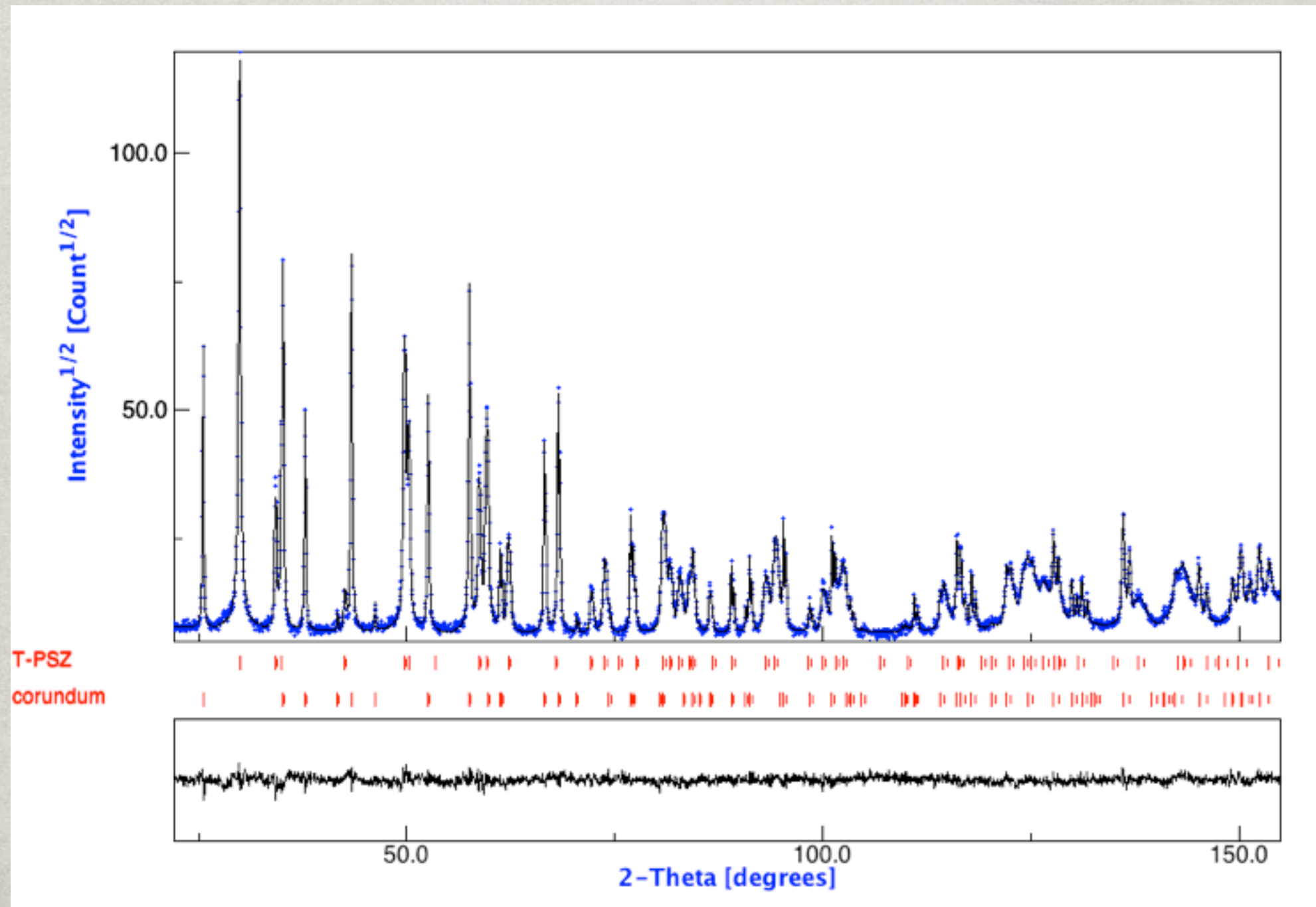
STEP 2: PEAKS POSITIONS

- ✿ Adding to refinement cell parameters and 2Θ displacement; R_{wp} now is at 24.8%; major problems are now peaks shapes



STEP 3: PEAKS SHAPES

- ✿ We add to the refinement also peaks shapes parameters; either the Caglioti parameters (classical programs) or crystallite sizes and microstrains; Rwp is now at 9.18 %



STEP 4: CRYSTAL STRUCTURE REFINEMENT

- ✻ Only if the pattern is very good and the phases well defined. We refine separated B factors and only the coordinates that can be refined. Final Rwp at 8.86%

