



UNIVERSITÀ
DI TRENTO

Dipartimento di
Ingegneria Industriale

Rietveld Analysis

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DIFFRACTION ANALYSES

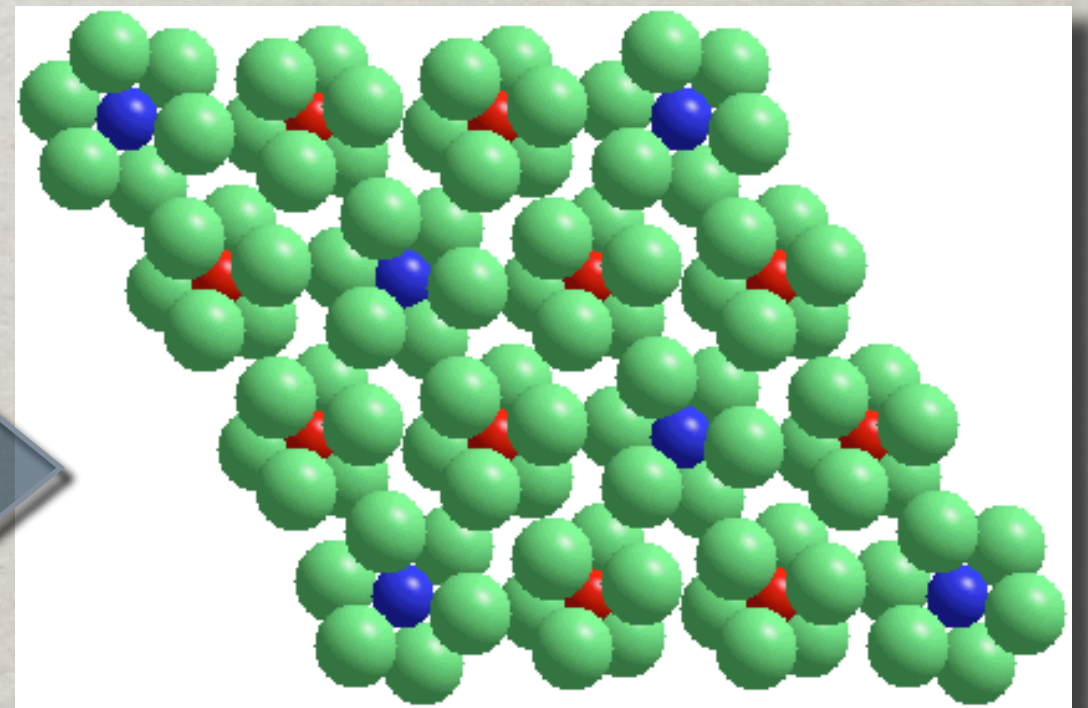
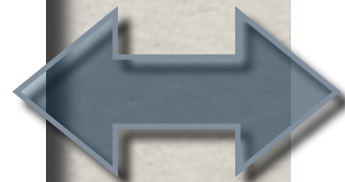
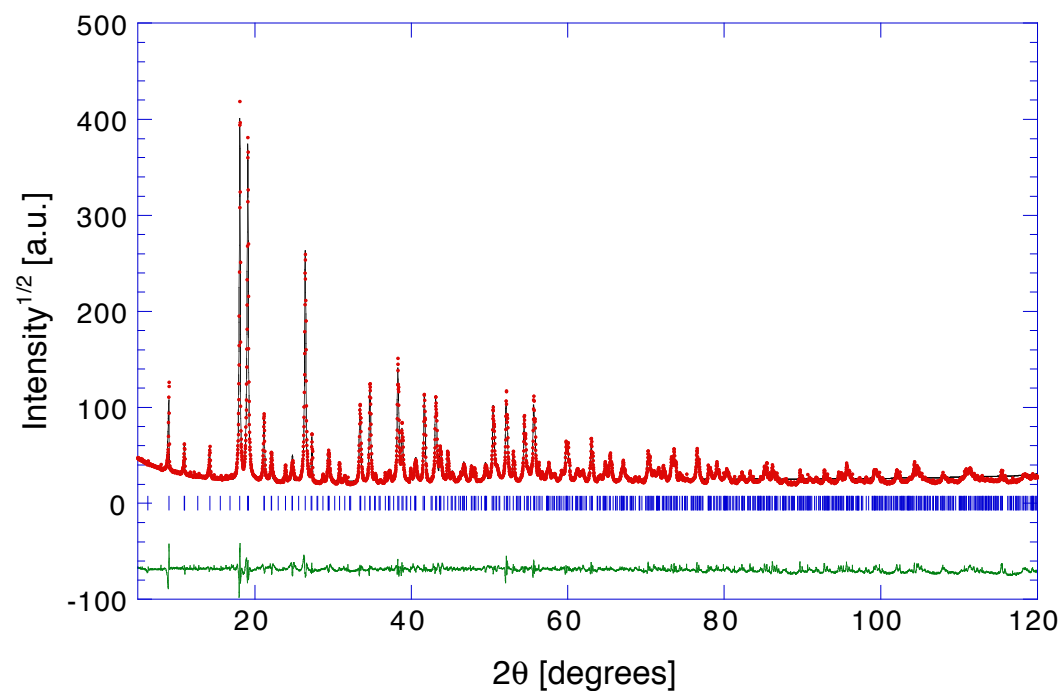
- ✻ Phase identifications (crystalline and amorphous)
- ✻ Crystal structure determination
- ✻ **Crystal structure refinements**
- ✻ Quantitative phase analysis (and crystallinity determination)
- ✻ Microstructural analyses (crystallite sizes - microstrain)
- ✻ Texture analysis
- ✻ Residual stress analysis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

GOAL OF THE RIETVELD METHOD

- ✿ To minimize the residual function 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:

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

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

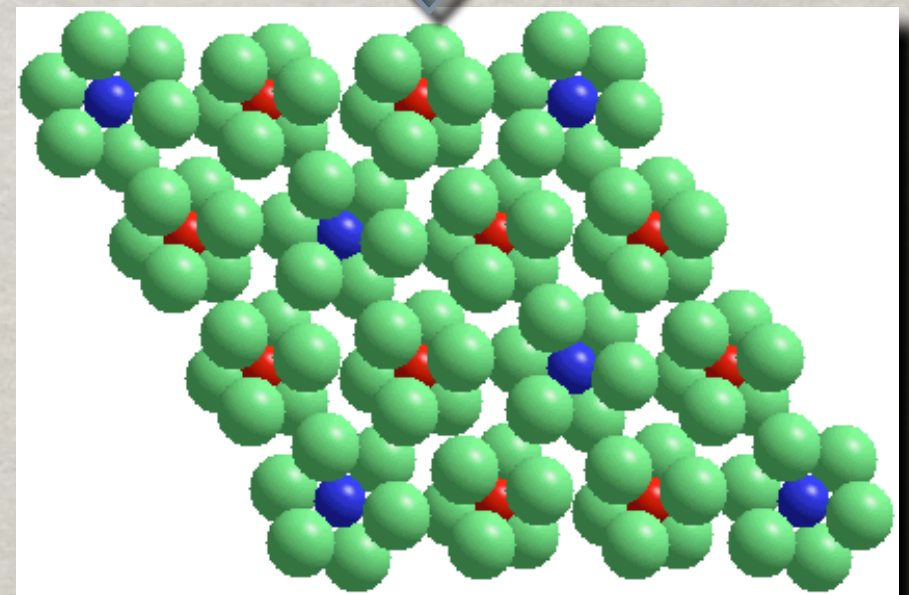
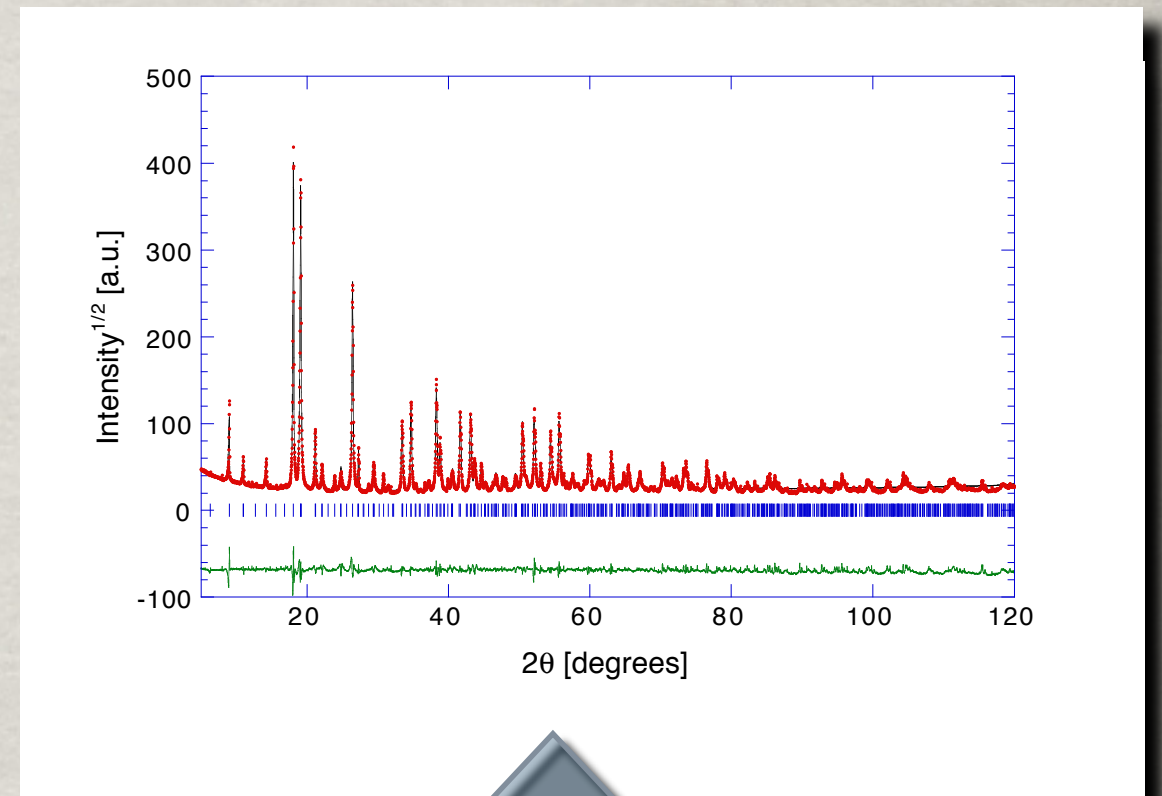
$S(2\theta_i - 2\theta_k)$ = profile shape function

(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 minimise by a least squares method (non linear):

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

- ✱ 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 (optimised).

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

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

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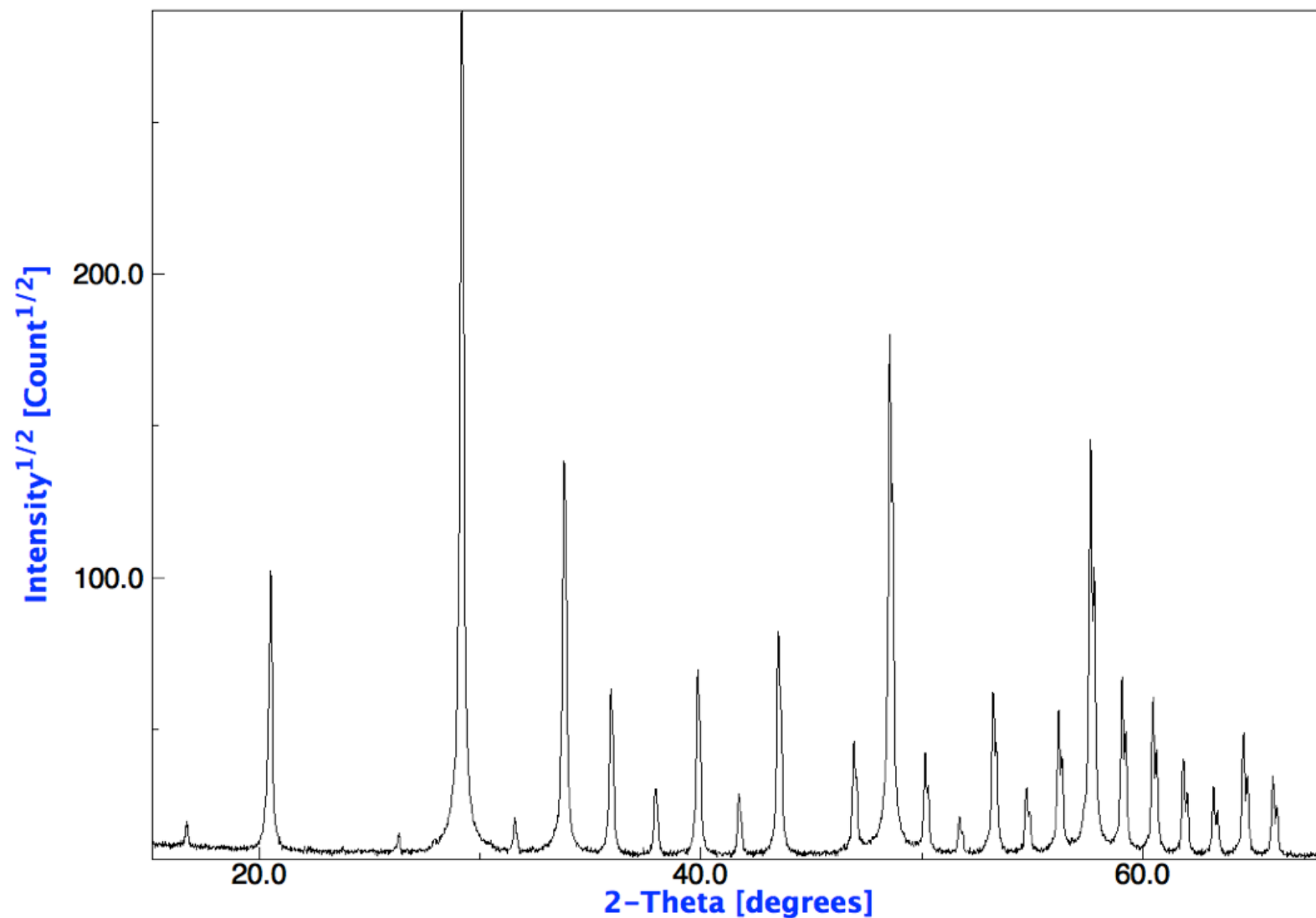
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rent terms:

(the peaks)

(aks)

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 (compose by the volume fraction, beam intensity and cell volume)
 - ✱ A Lorentz-Polarization factor
 - ✱ The multiplicity
 - ✱ The structure factor
 - ✱ The temperature factor
 - ✱ The absorption
 - ✱ The texture
- ✱ Problems: extinctions, absorption contrast, graininess, sample

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:

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

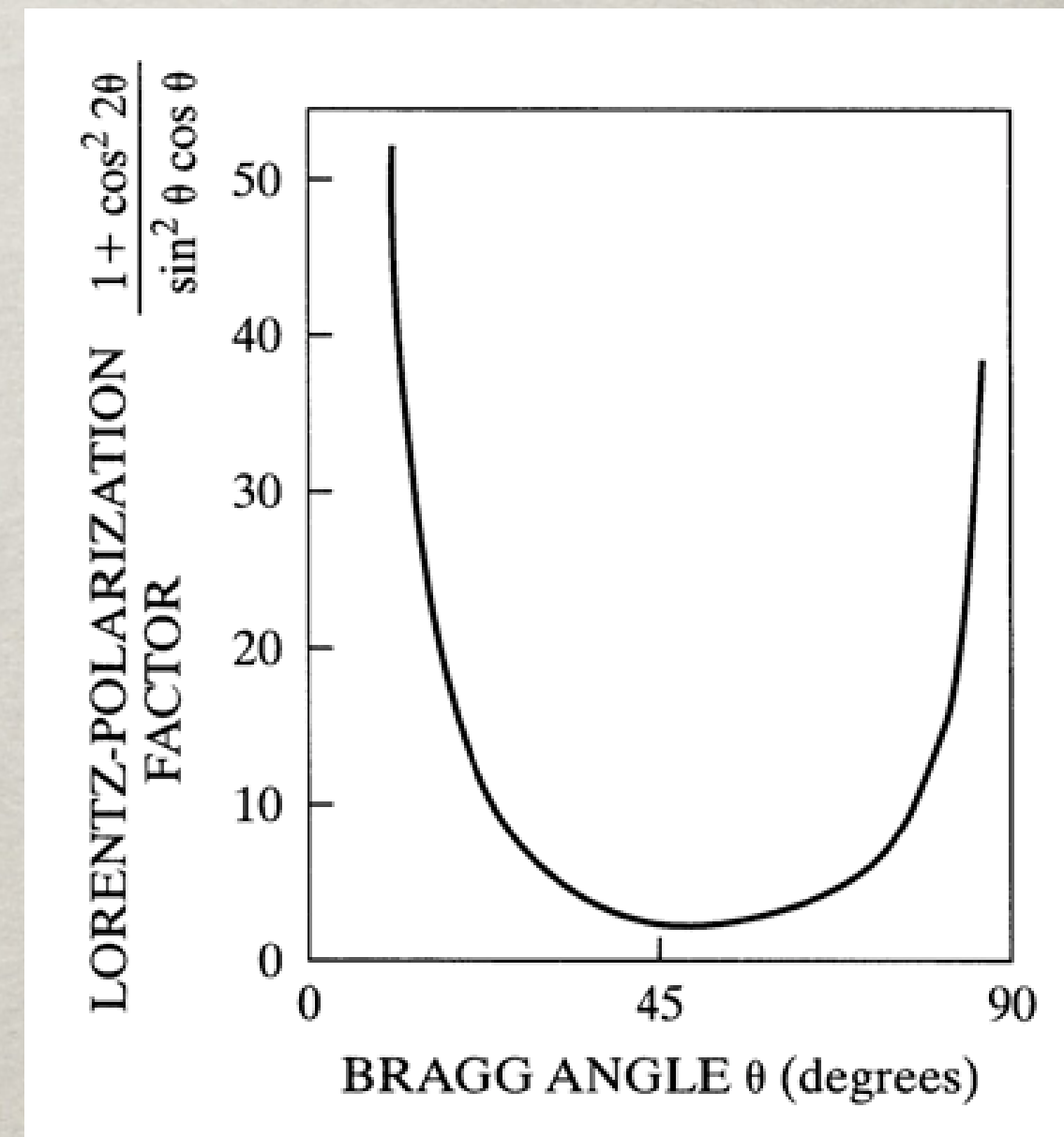
- ✻ H_j = phase scale factor (the overall Rietveld generic scale factor)
- ✻ S_F = beam intensity (it depends on the measurement)
- ✻ f_j = phase volume fraction
- ✻ V_j = phase cell volume (in some programs it goes in the F factor)
- ✻ In Maud the last three terms are kept separated.

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

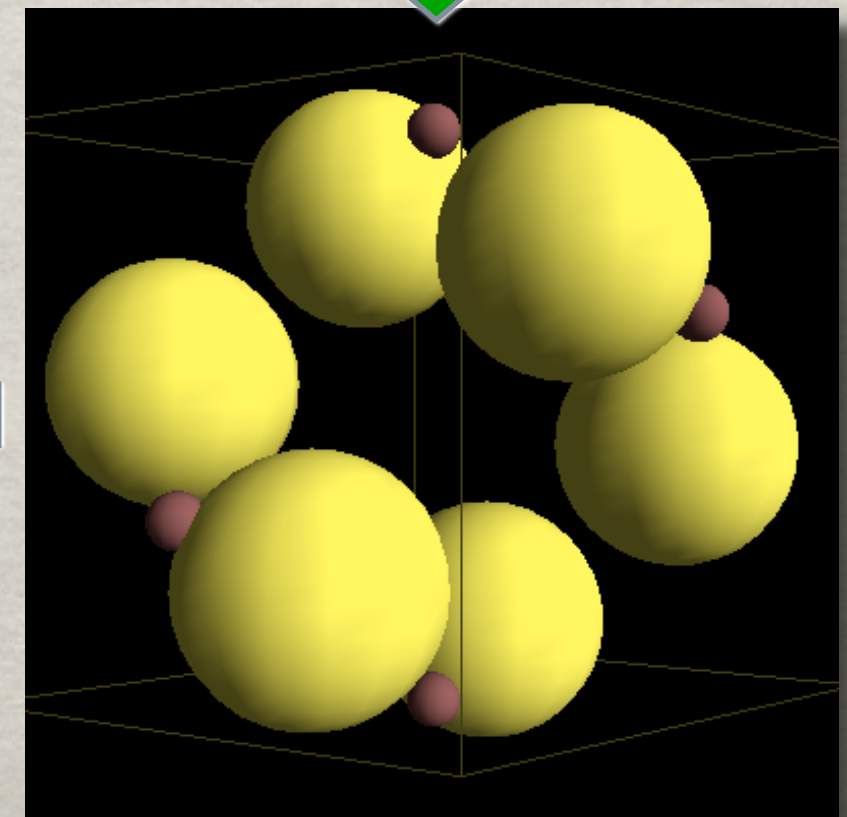
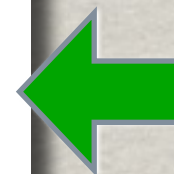
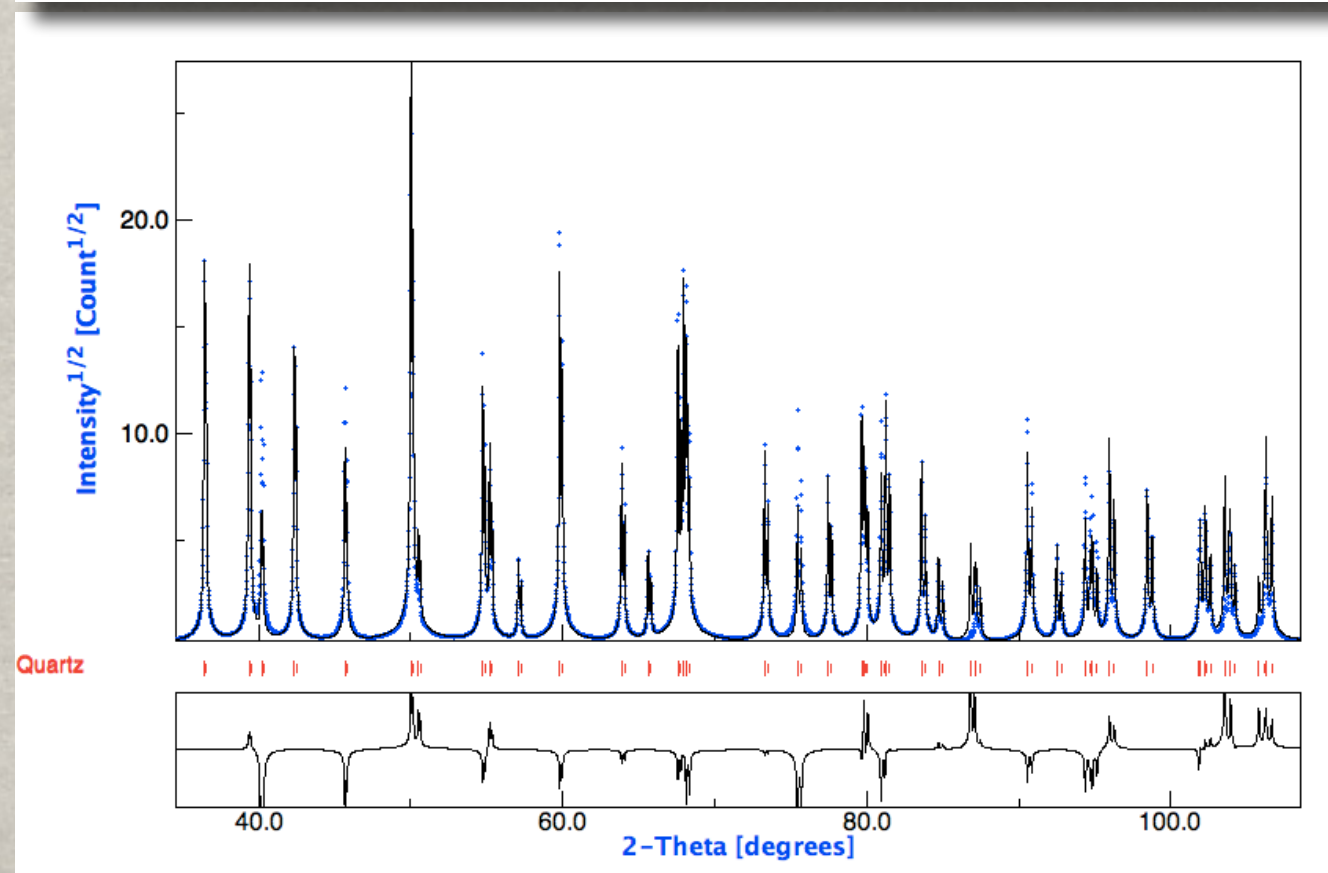
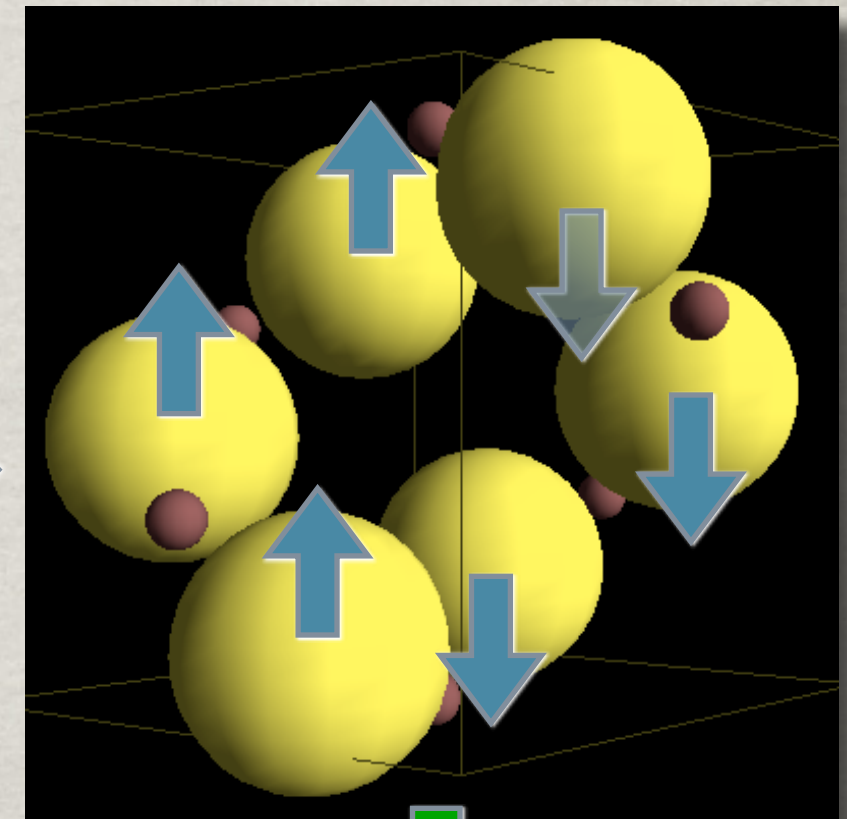
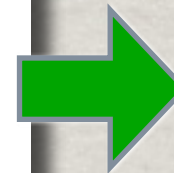
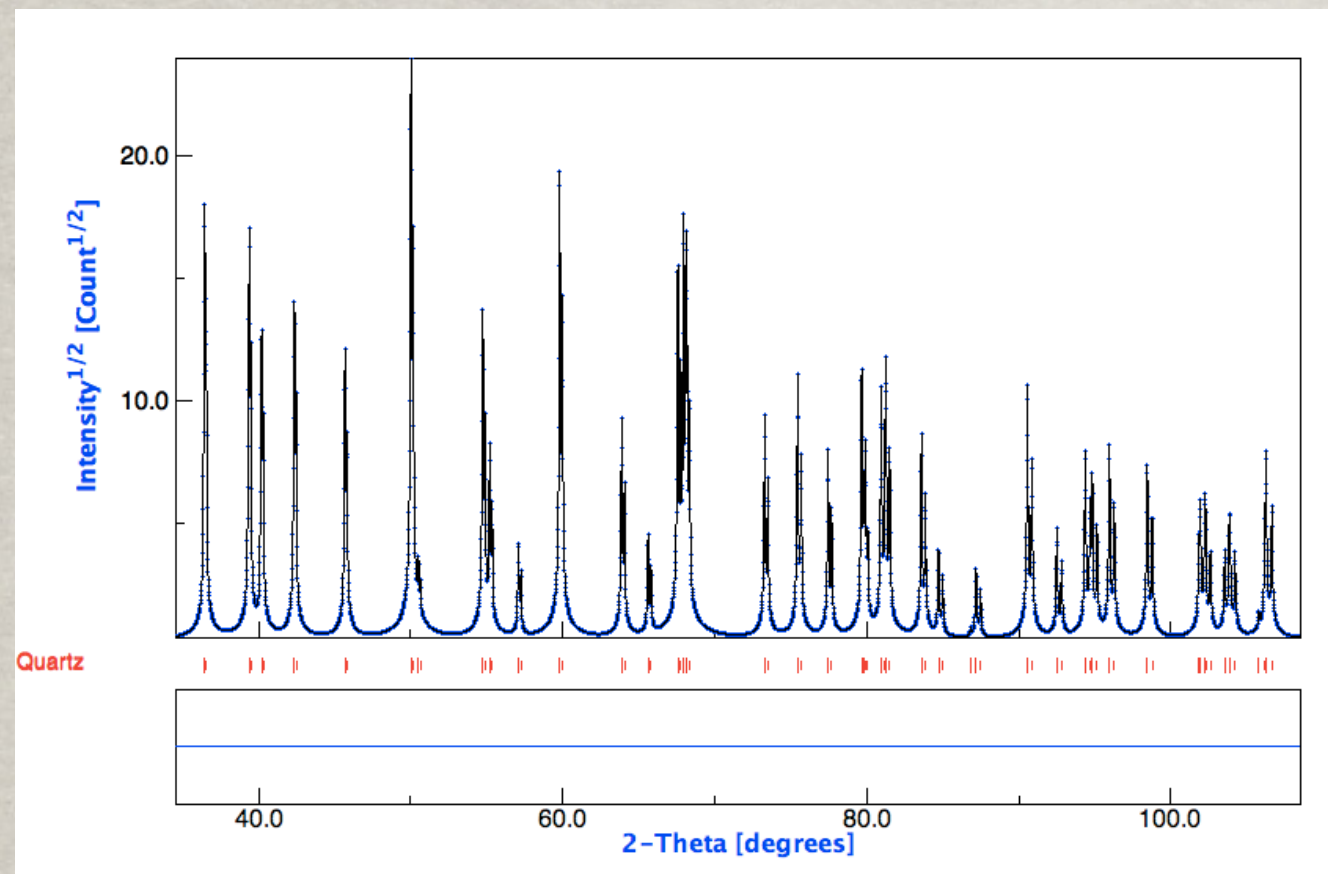
$$|F_{k,j}|^2 = m_k \left| \sum_{n=1}^N f_n e^{-B_n \frac{\sin^2 \theta}{\lambda^2}} \left(e^{2\pi i(hx_n + ky_n + lz_n)} \right) \right|^2$$

✱ N = number of atoms

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

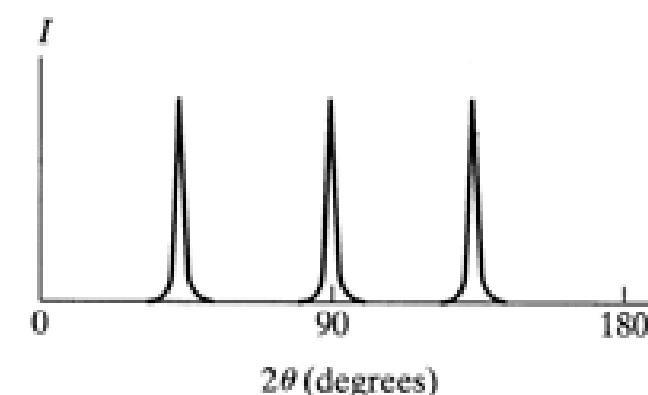
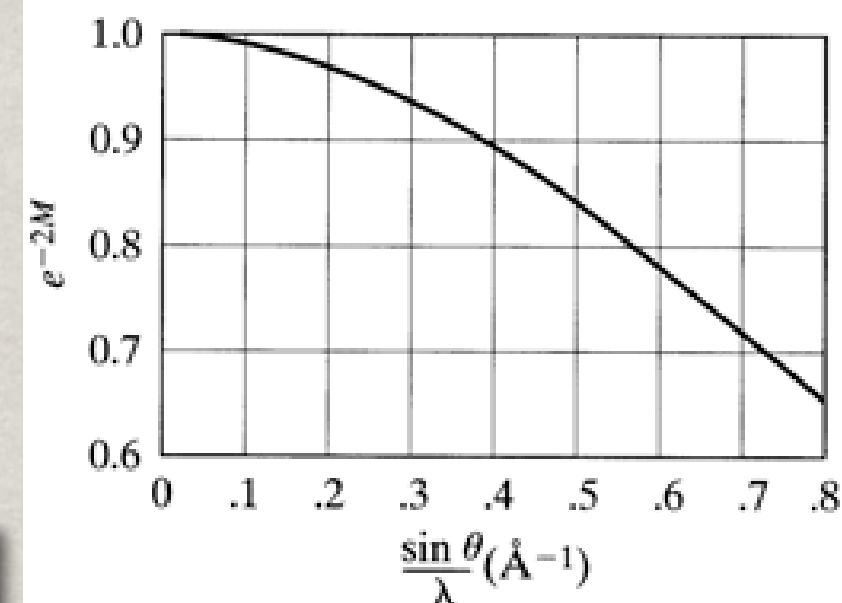
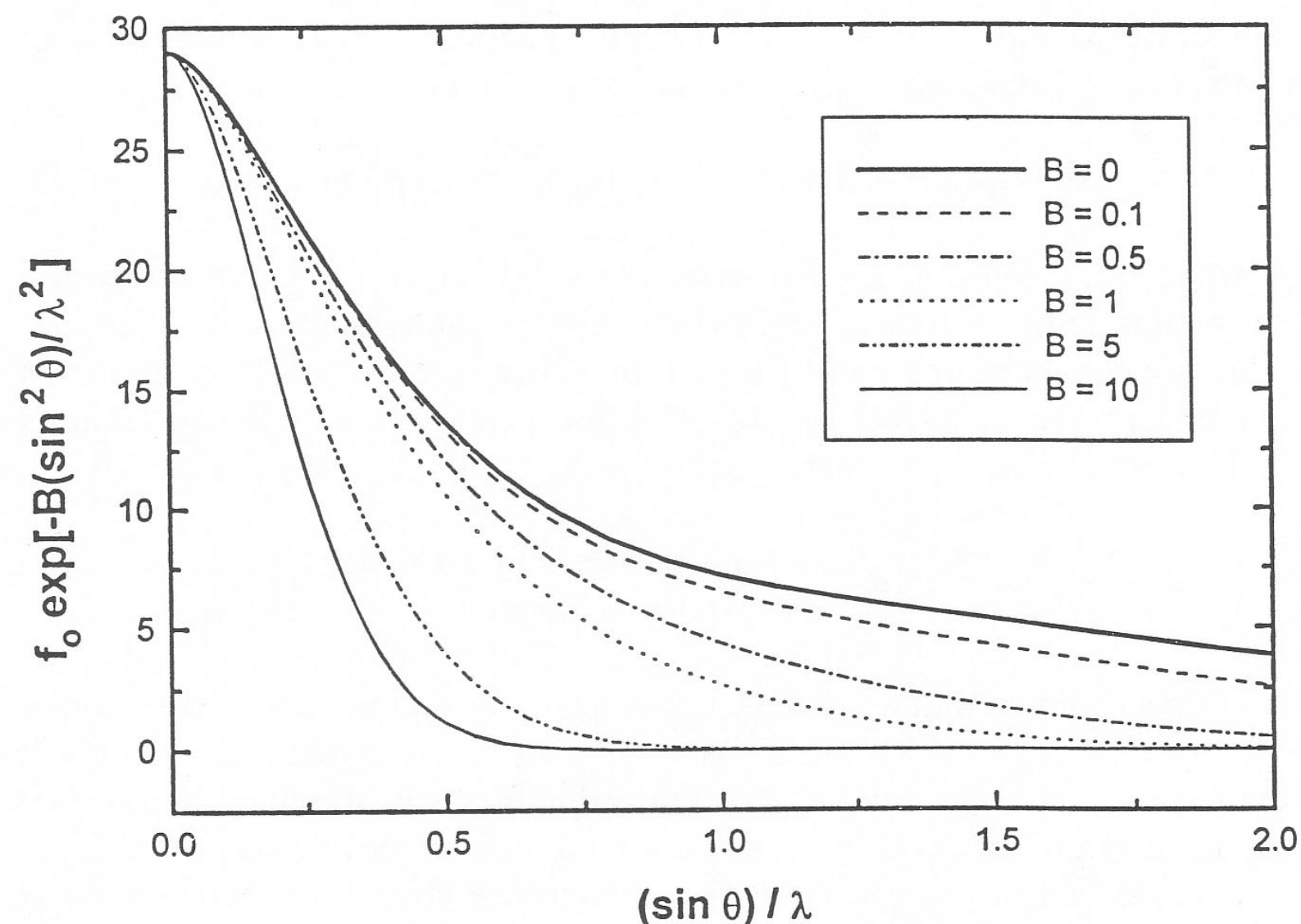
✱ f_n , atomic scattering factor

ATOM POSITIONS AND STRUCTURE FACTORS

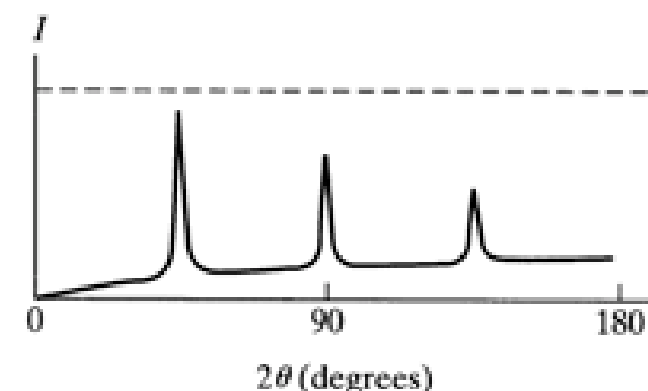


ATOMIC SCATTERING FACTOR AND DEBYE-WALLER

- ✿ The atomic scattering factor for X-ray decreases with the diffraction angle and is proportional to the number of electrons.
- ✿ The temperature factor (Debye-Waller, B) accelerates the decrease.

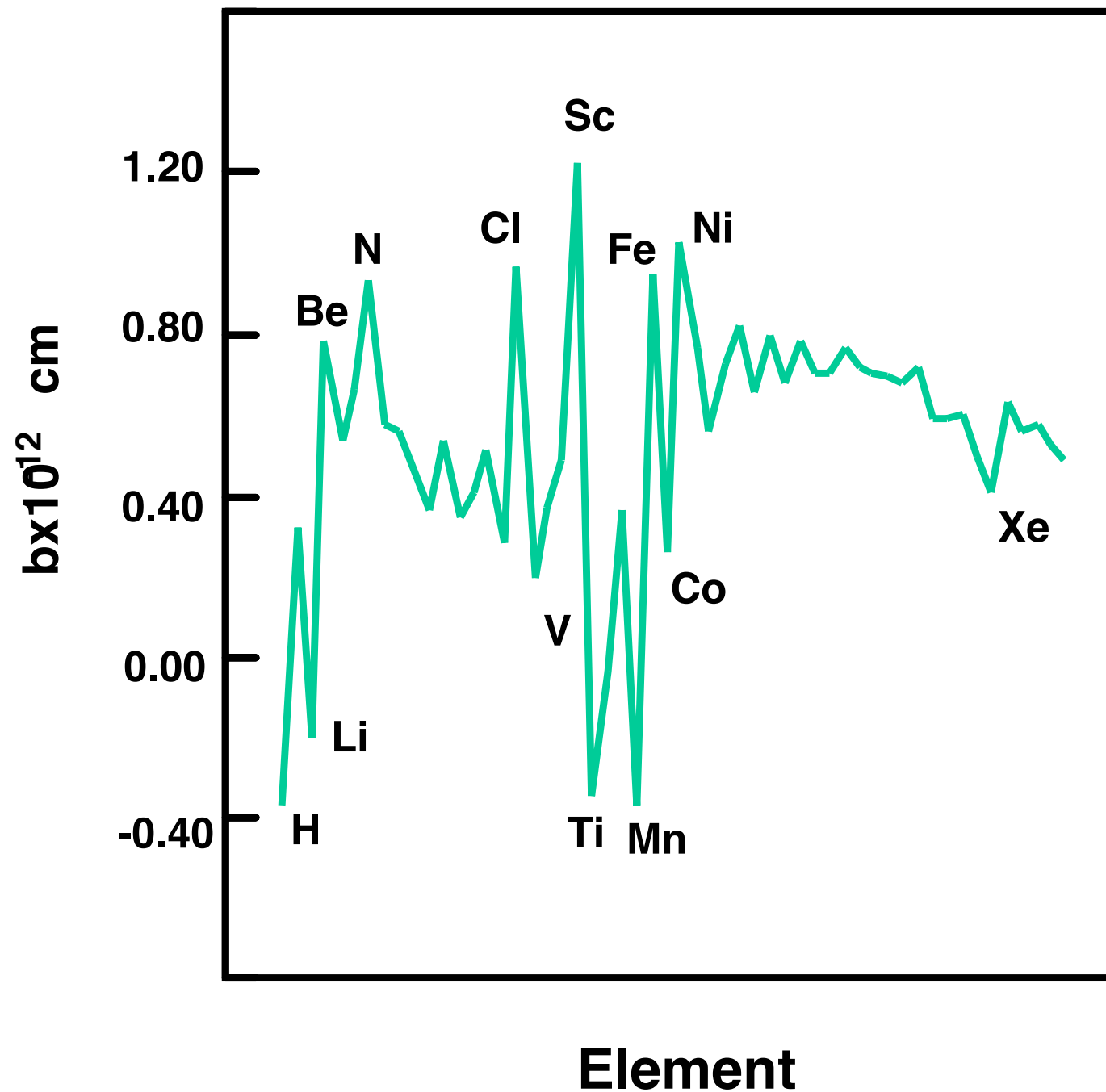


(a) No thermal vibration



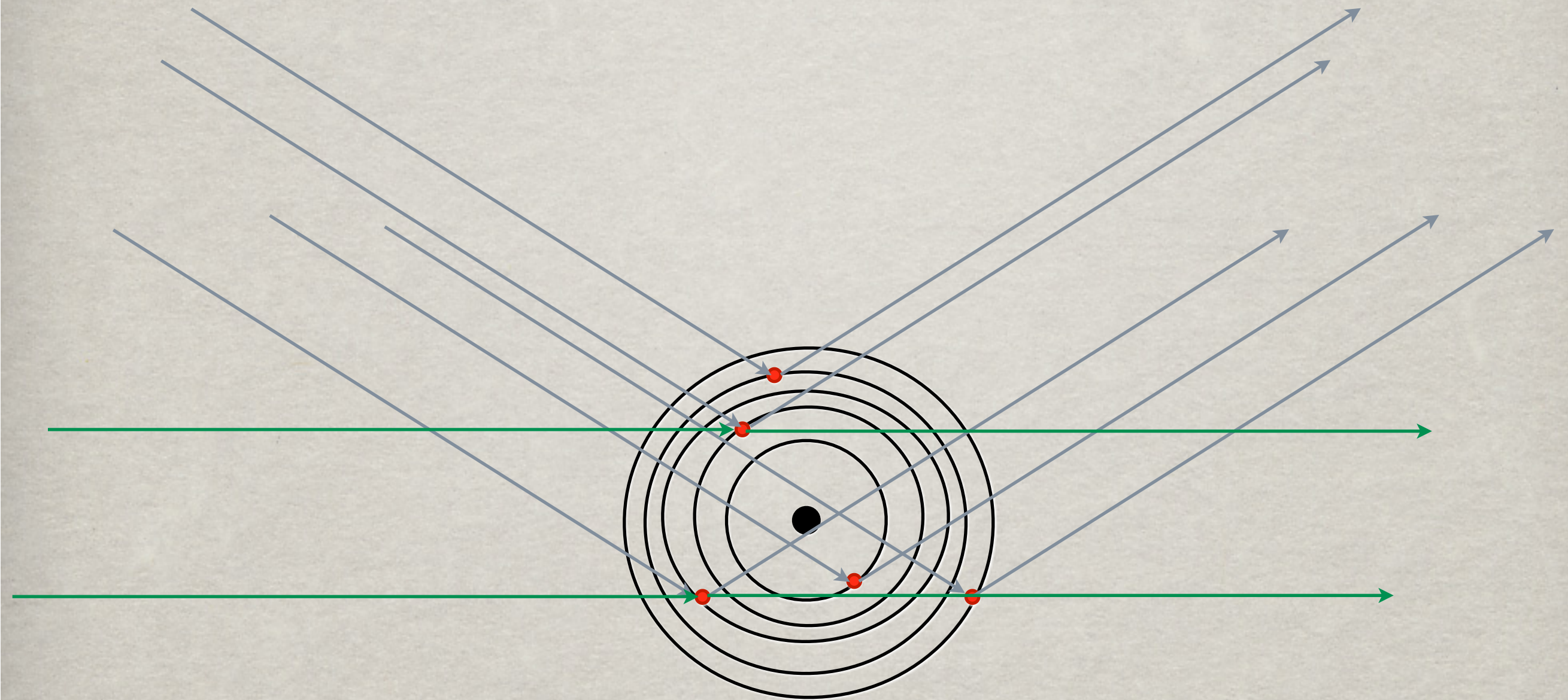
(b) Thermal vibration

NEUTRON SCATTERING FACTORS



- ✱ For light atoms neutron scattering has some advantages, since the scattering factor is not correlated to the atomic number.
- ✱ The scattering factor is constant with the diffraction angle
- ✱ For atoms very close in the periodic table, neutron scattering may help distinguish them.

WHY X-RAY SCATTERING FALL OFF AT HIGH ANGLE?

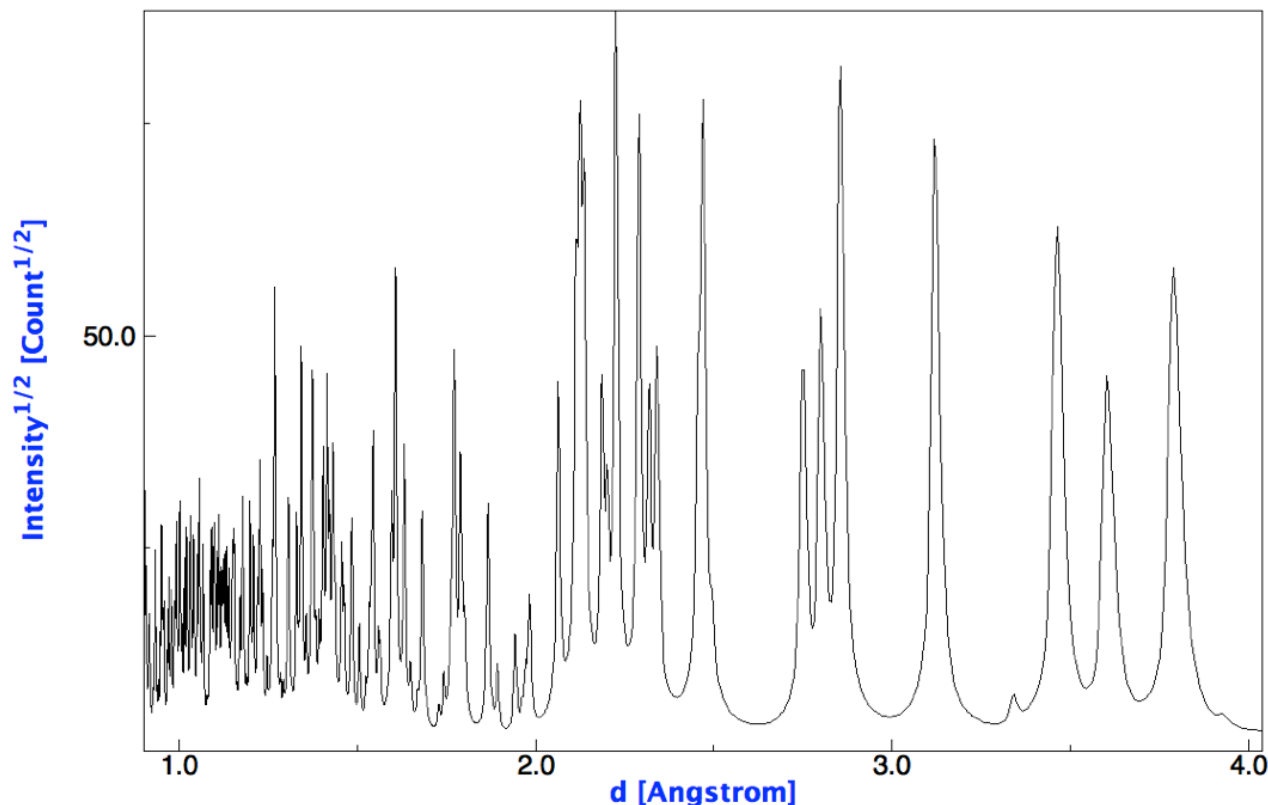


- ✱ At low angle all paths are the same (constructive interference)
- ✱ At high angle the path between different electron is different (destructive interference)

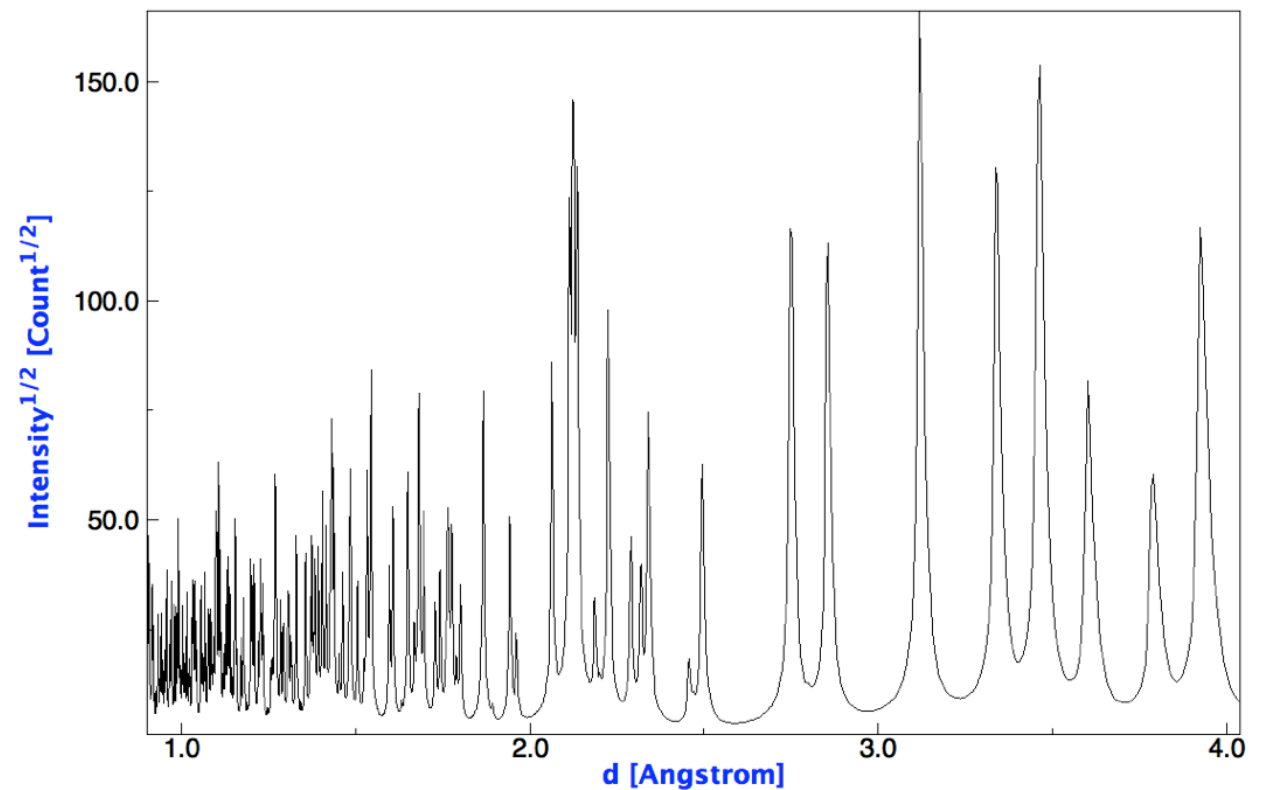
X-RAY AND NEUTRON DIFFRACTION

X-ray Diffraction - CuK α Phillips PW1710

- Higher resolution
- Intensity falloff at small d spacings
- Better at resolving small lattice distortions



Barite



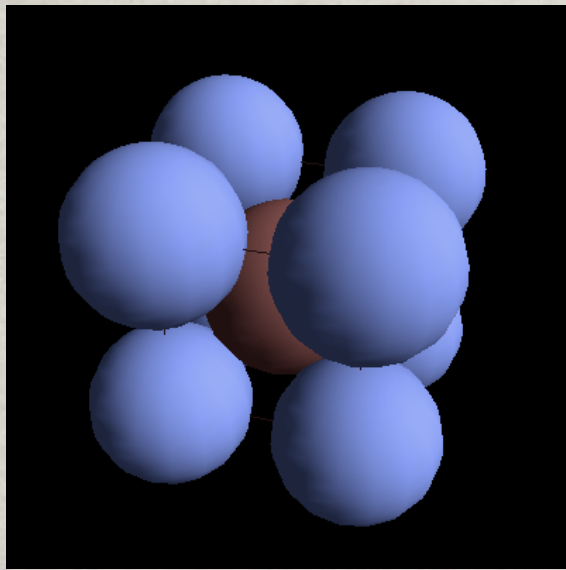
Barite

Neutron Diffraction - D1a, ILL $\lambda=1.909$ Å

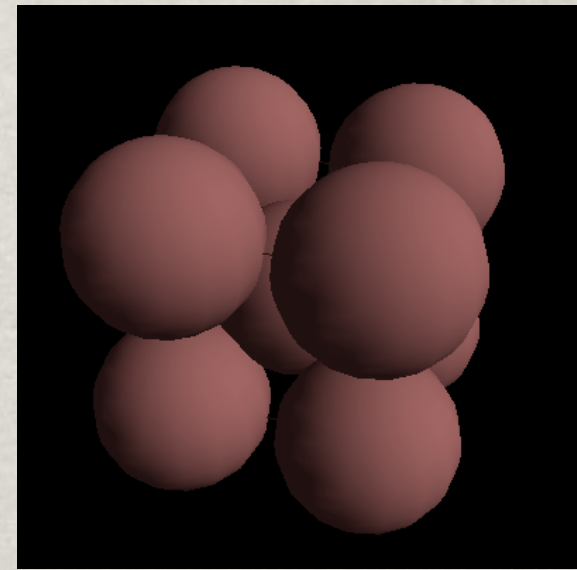
- Lower resolution
- Much higher intensity at small d-spacings
- Better atomic positions/thermal parameters



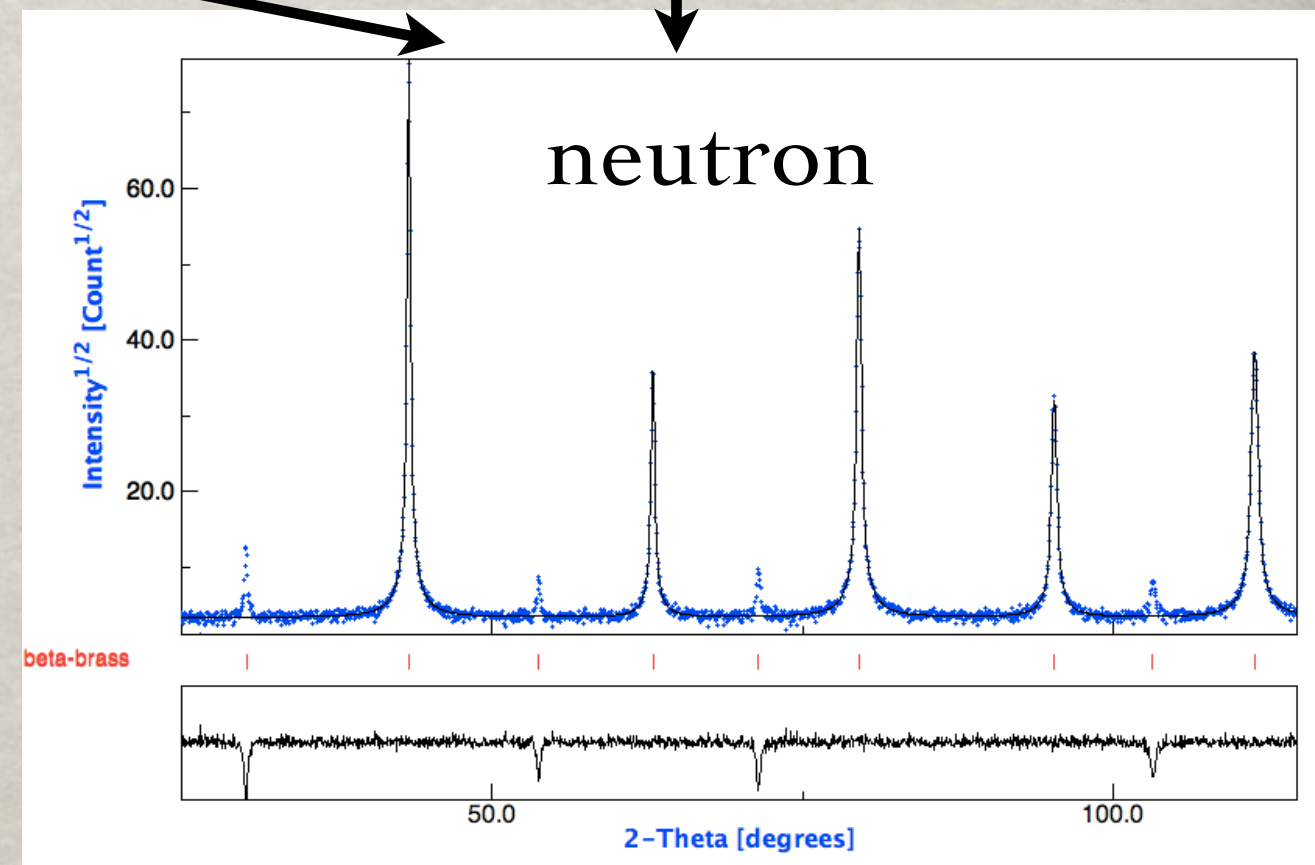
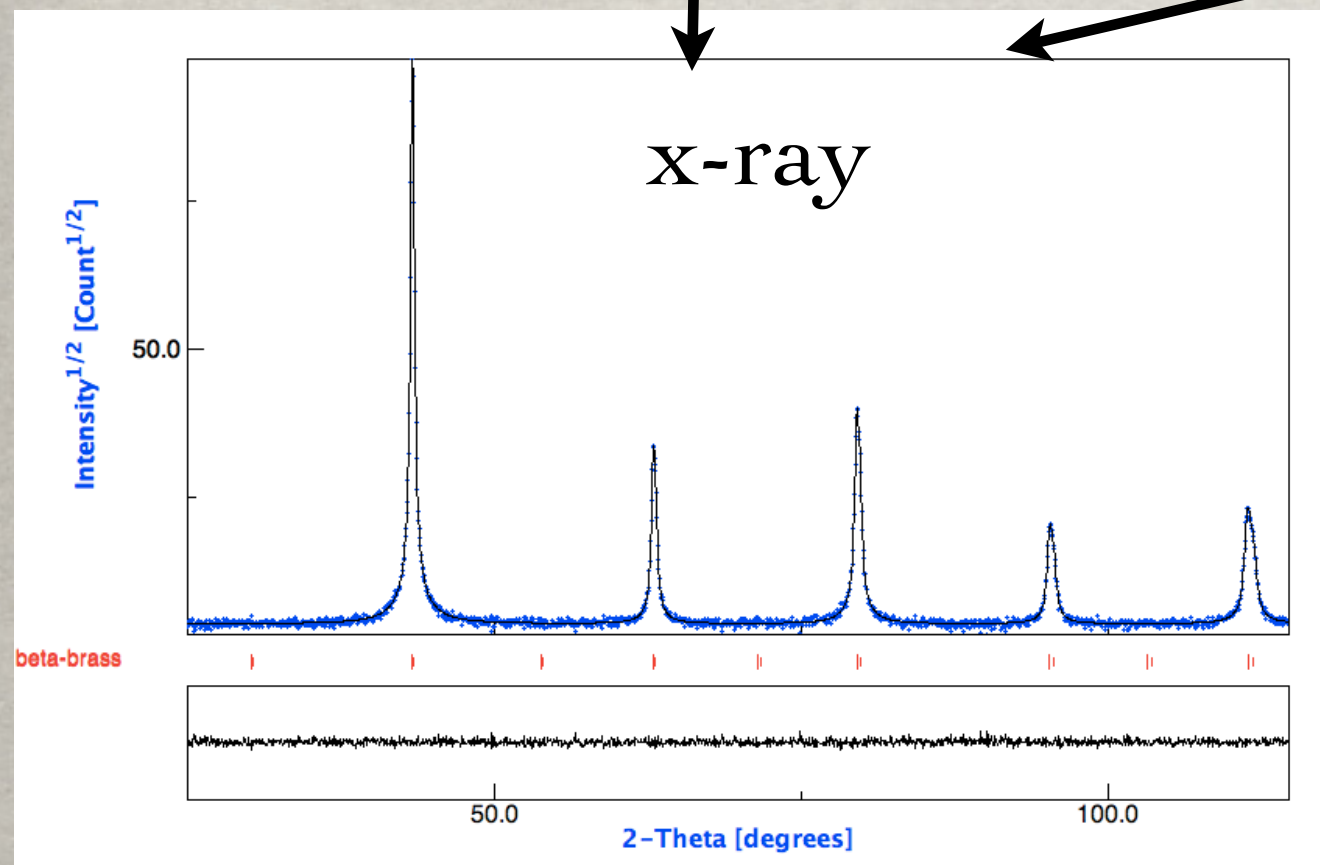
ORDER-DISORDER AND SCATTERING FACTORS: B-BRASS



ordered β -brass (blue, dots)



disordered β -brass (black, continuous line)



THE CLASSICAL RIETVELD METHOD

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

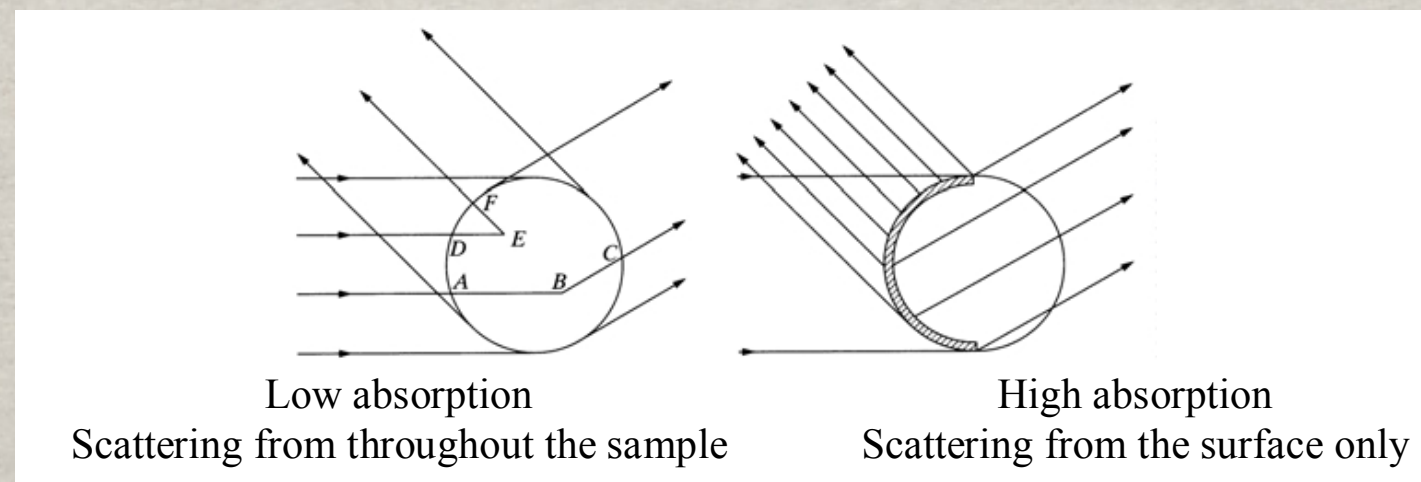
✻ The absorption factor:

✻ 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:

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

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

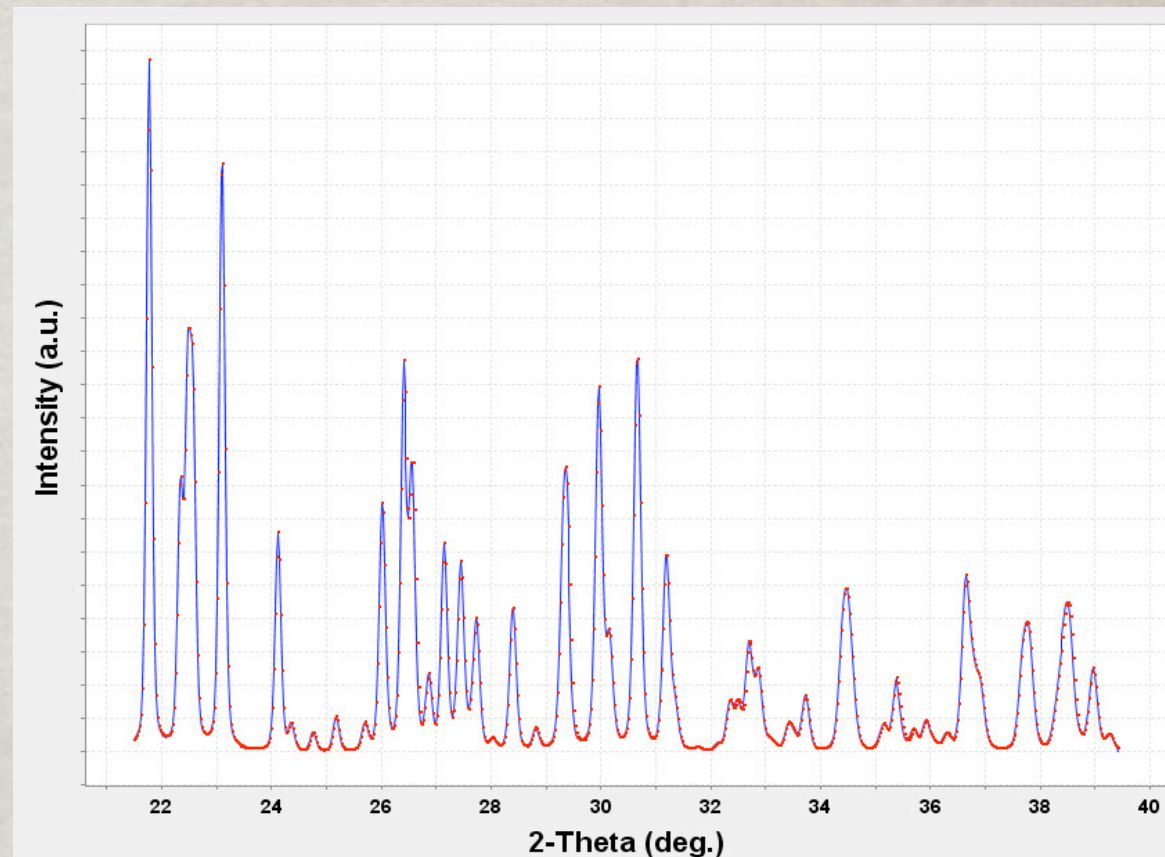
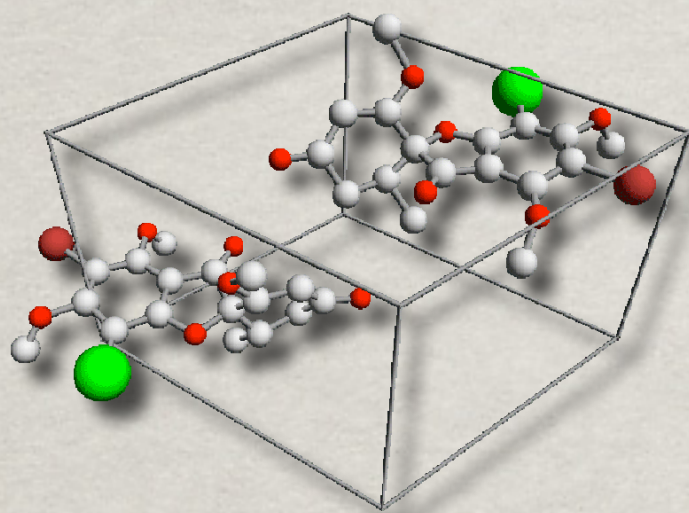
$$R_{wp} = \sqrt{\frac{\sum_{i=1}^N \left[w_i (I_i^{\text{exp}} - I_i^{\text{calc}}) \right]^2}{\sum_{i=1}^N \left[w_i I_i^{\text{exp}} \right]^2}}, \quad w_i = \frac{1}{\sqrt{I_i^{\text{exp}}}}$$

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

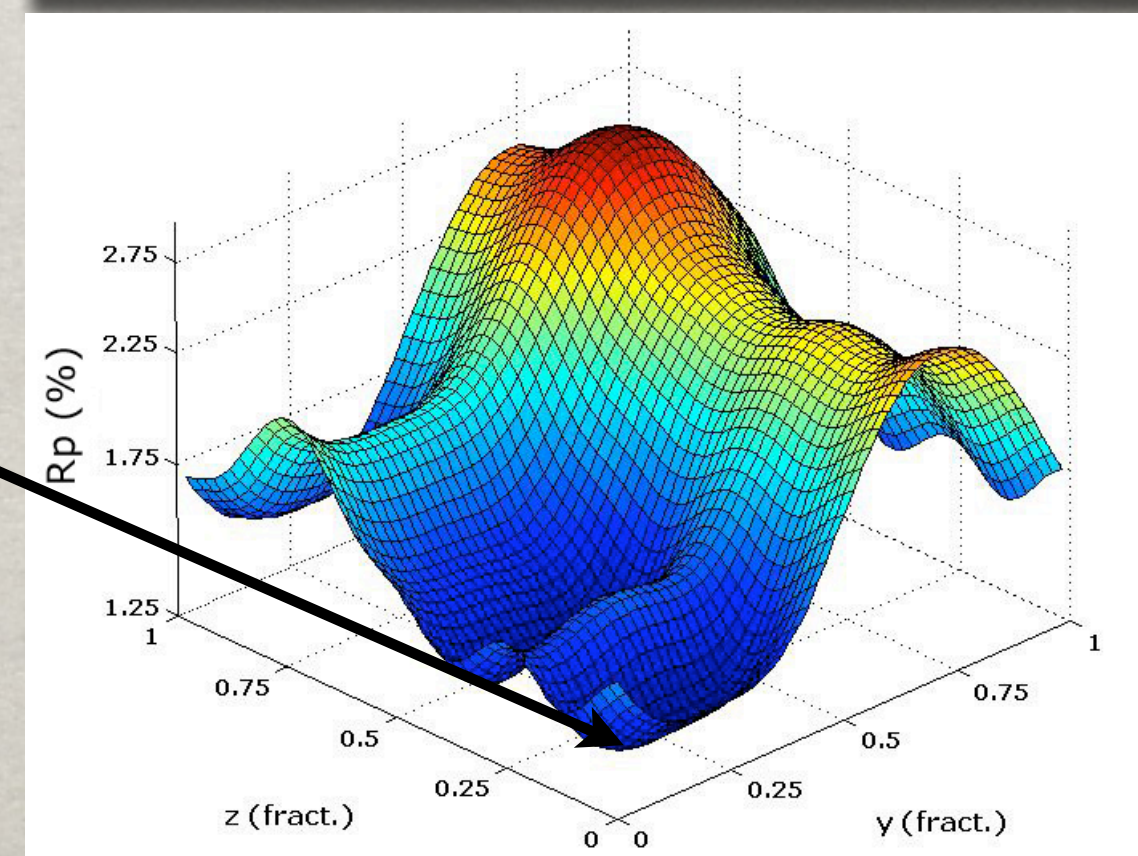
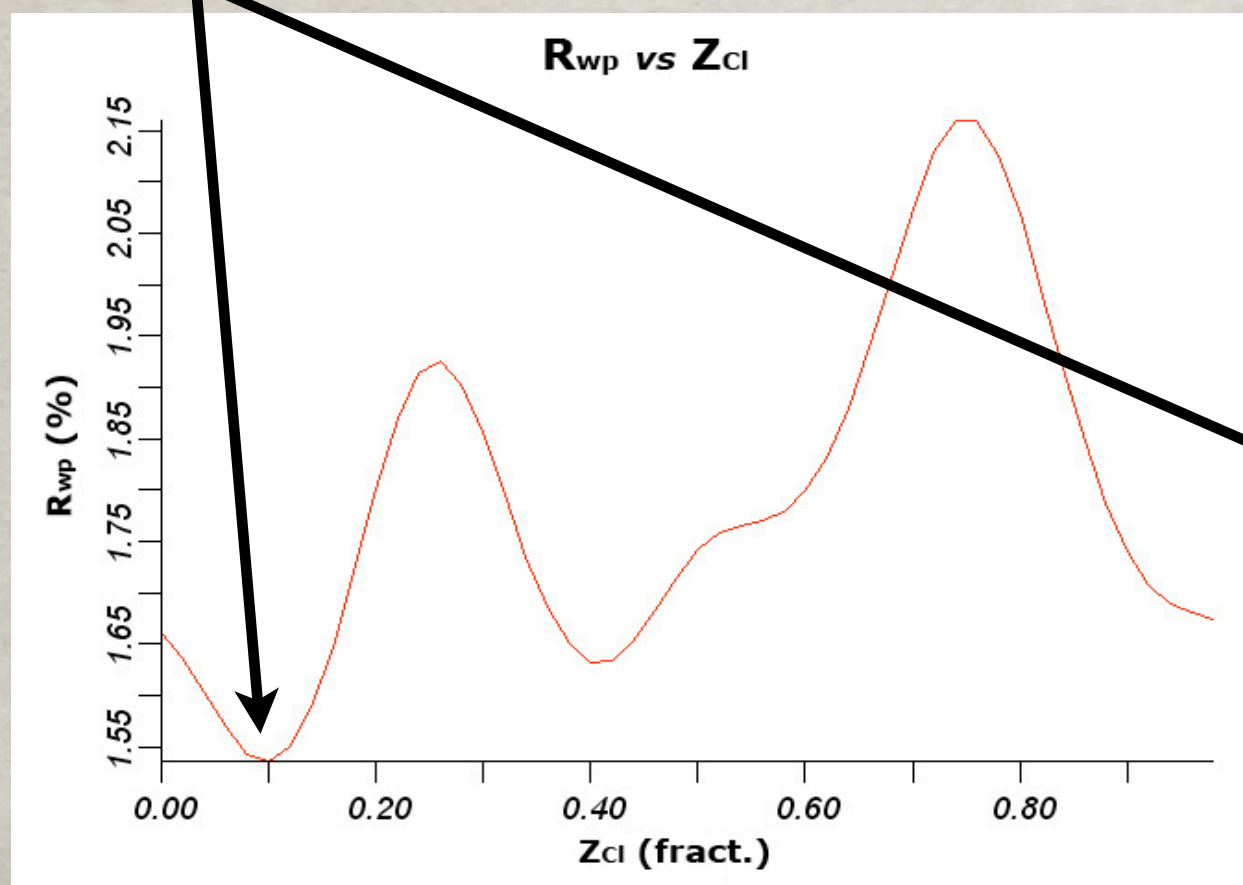
✻ The goodness of fit: $GofF = \frac{R_{wp}}{R_{\text{exp}}}$

LOCAL MINIMA: BROMO-GRISEOFULVIN

M. Bortolotti, PhD thesis,
Trento, 2007



Correct solution



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 sensitive 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 sensitive to model errors
- ✻ Less sensitive 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

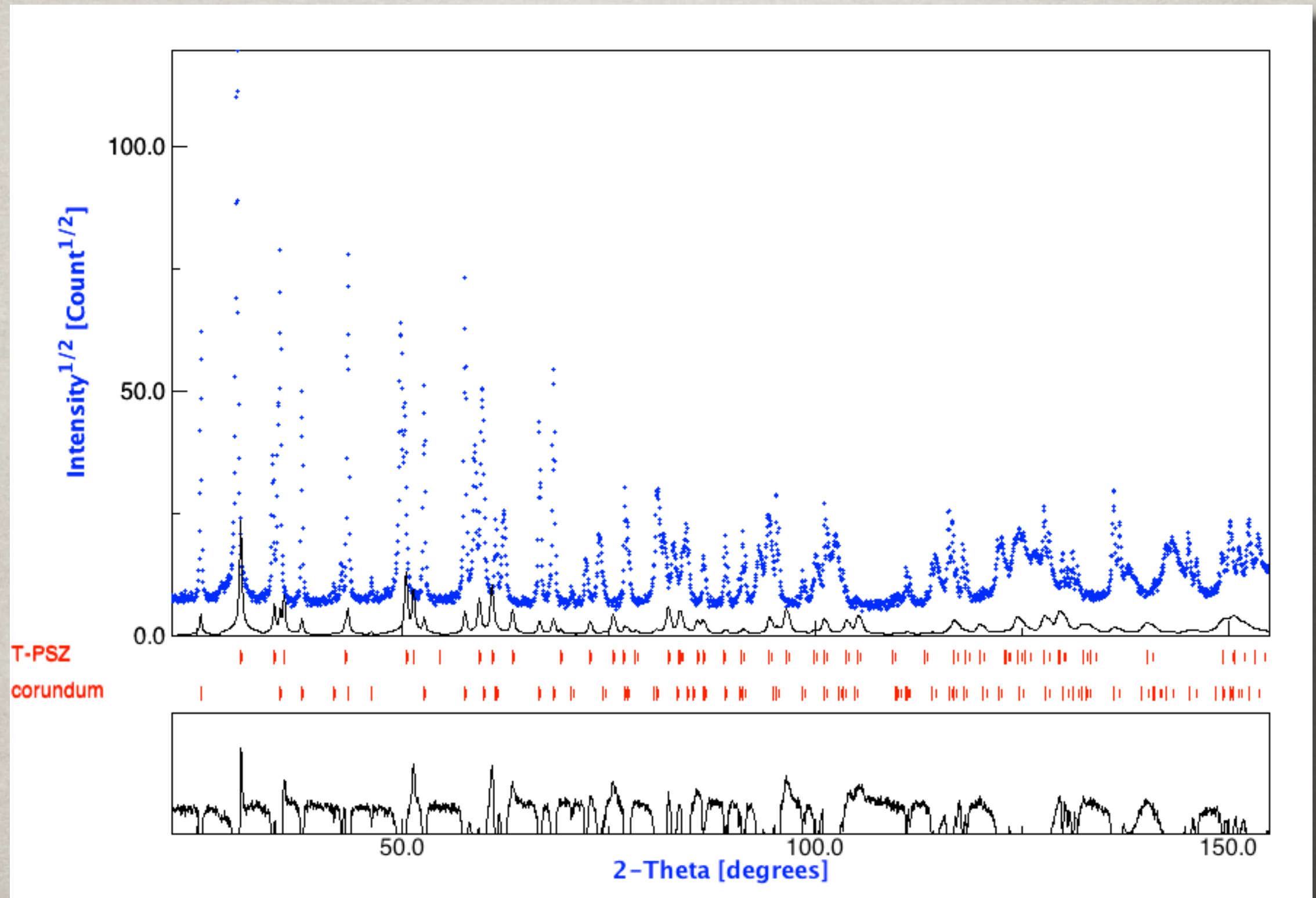
- ✱ Analysis:

- ✱ 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

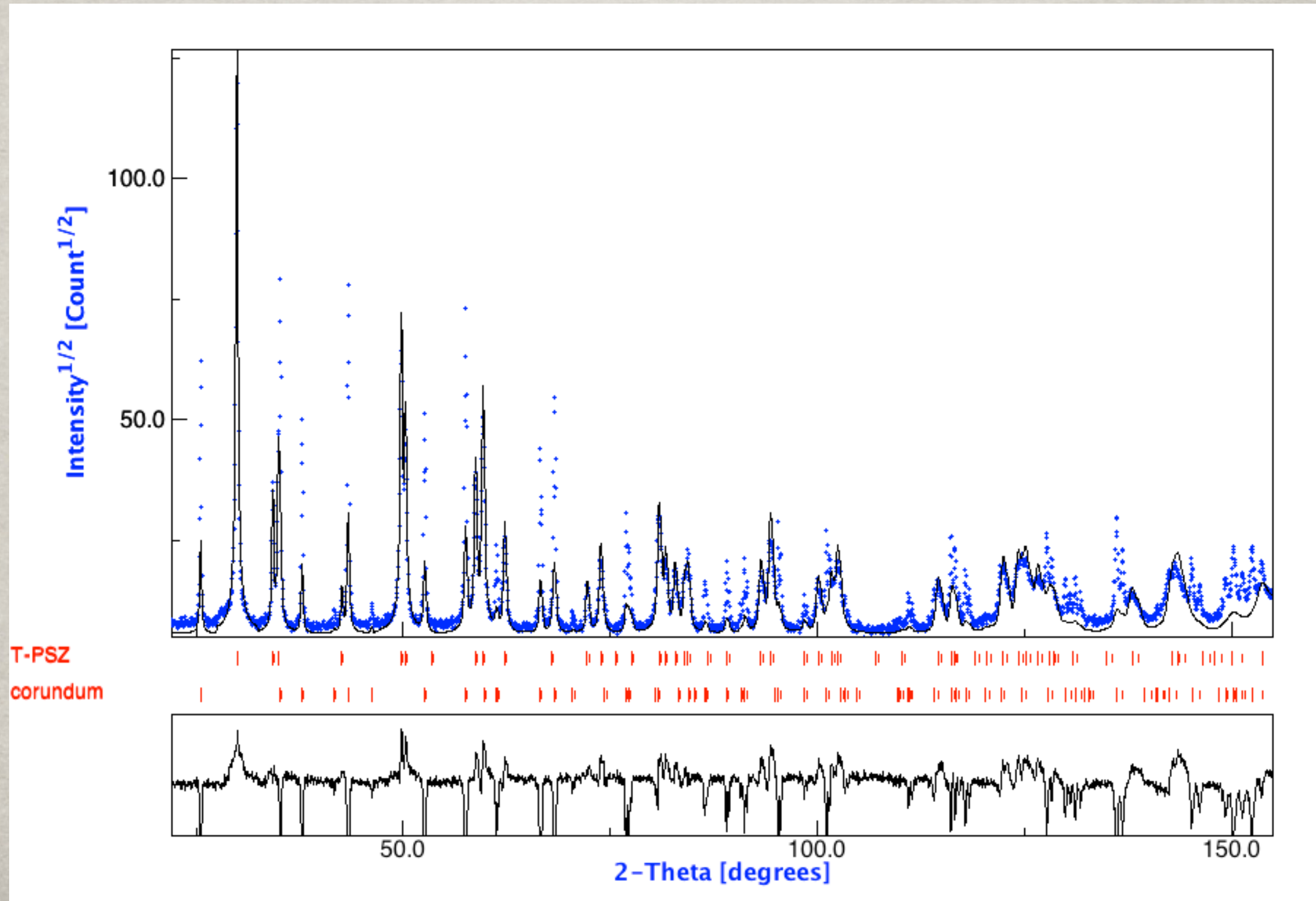
STARTING POINT: DEFINING THE PHASES

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



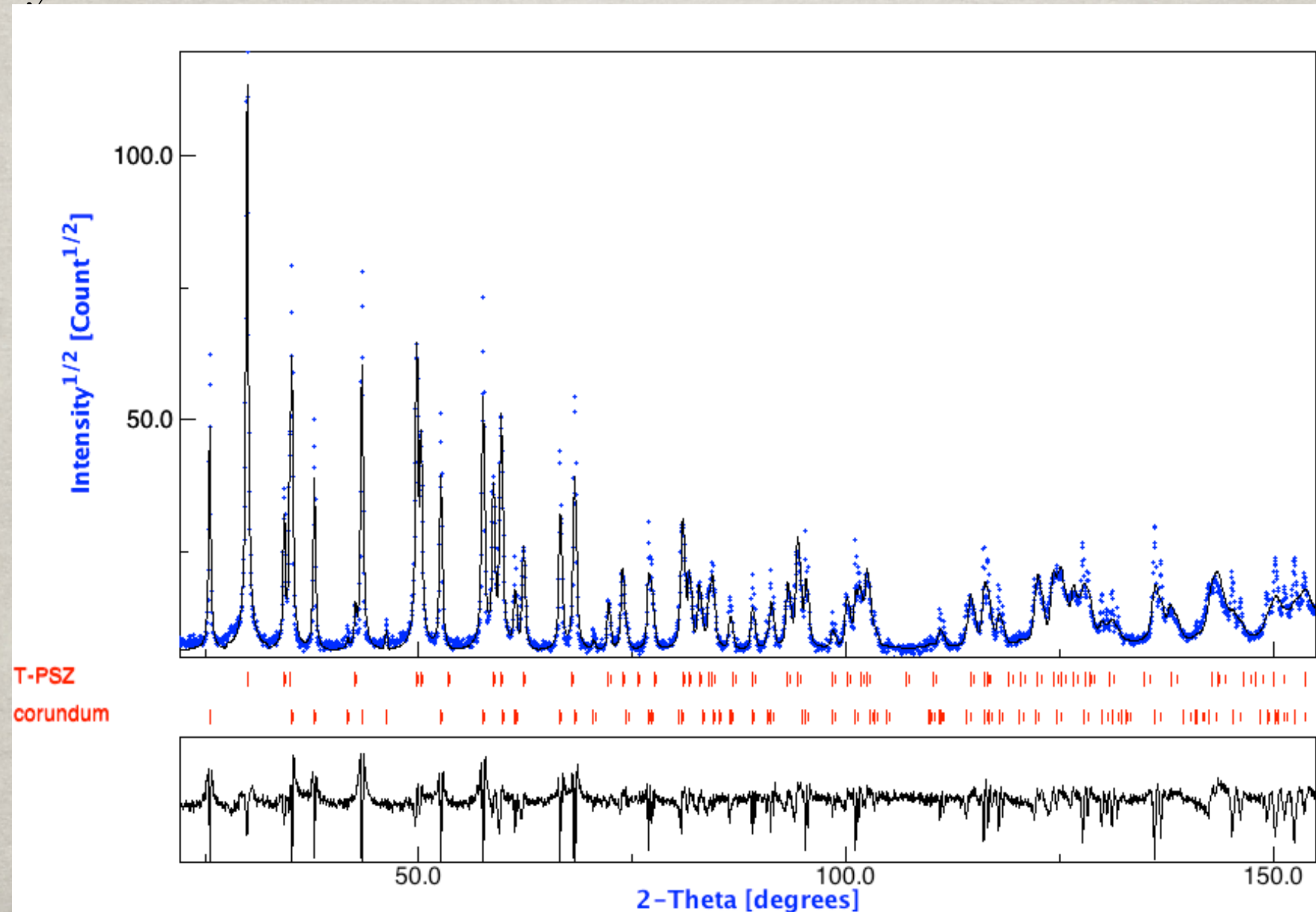
ADJUSTING MANUALLY: CELL PARAMETERS, INTENSITIES

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



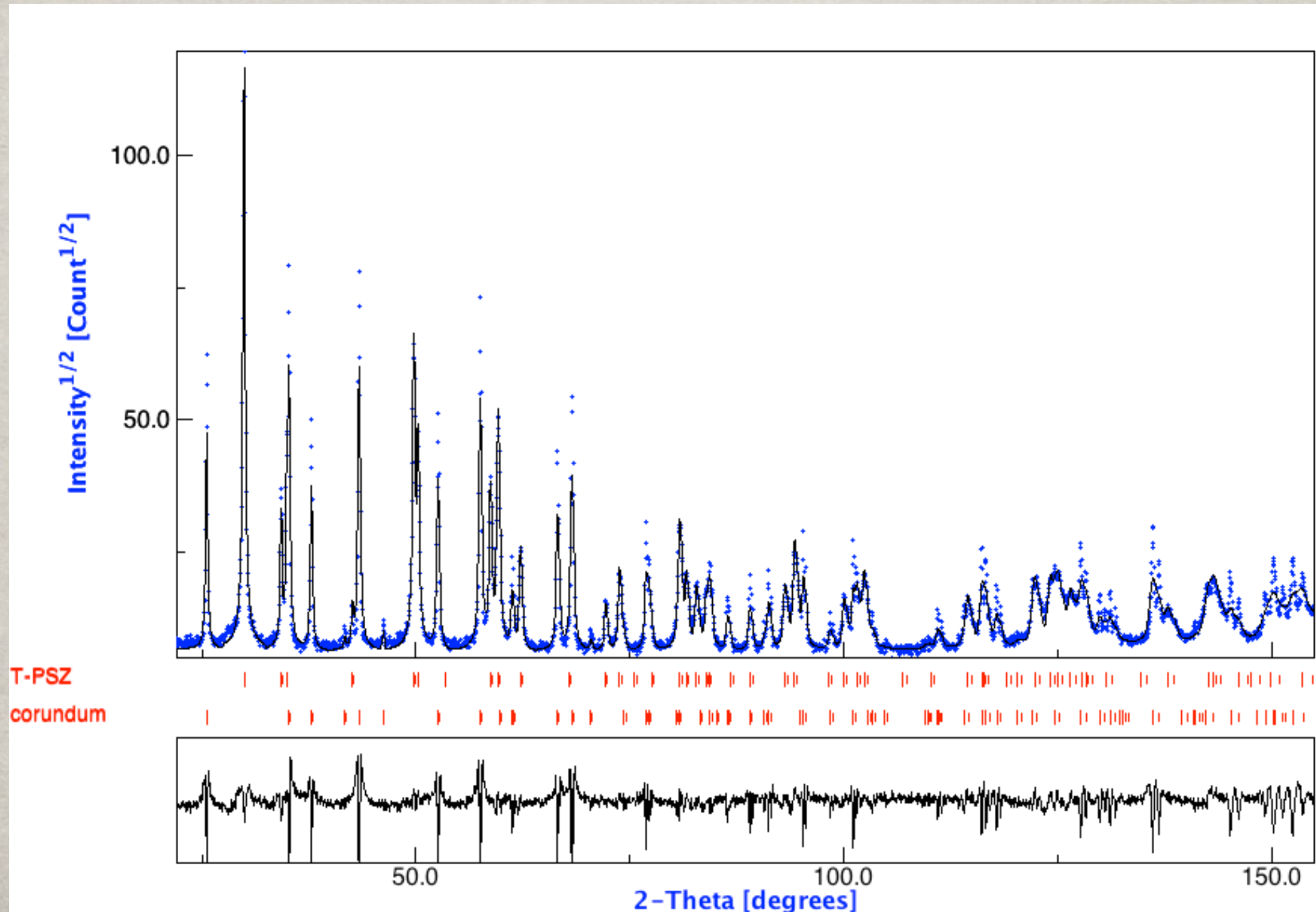
STEP 1: REFINING SCALE FACTORS AND BACKGROUND

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



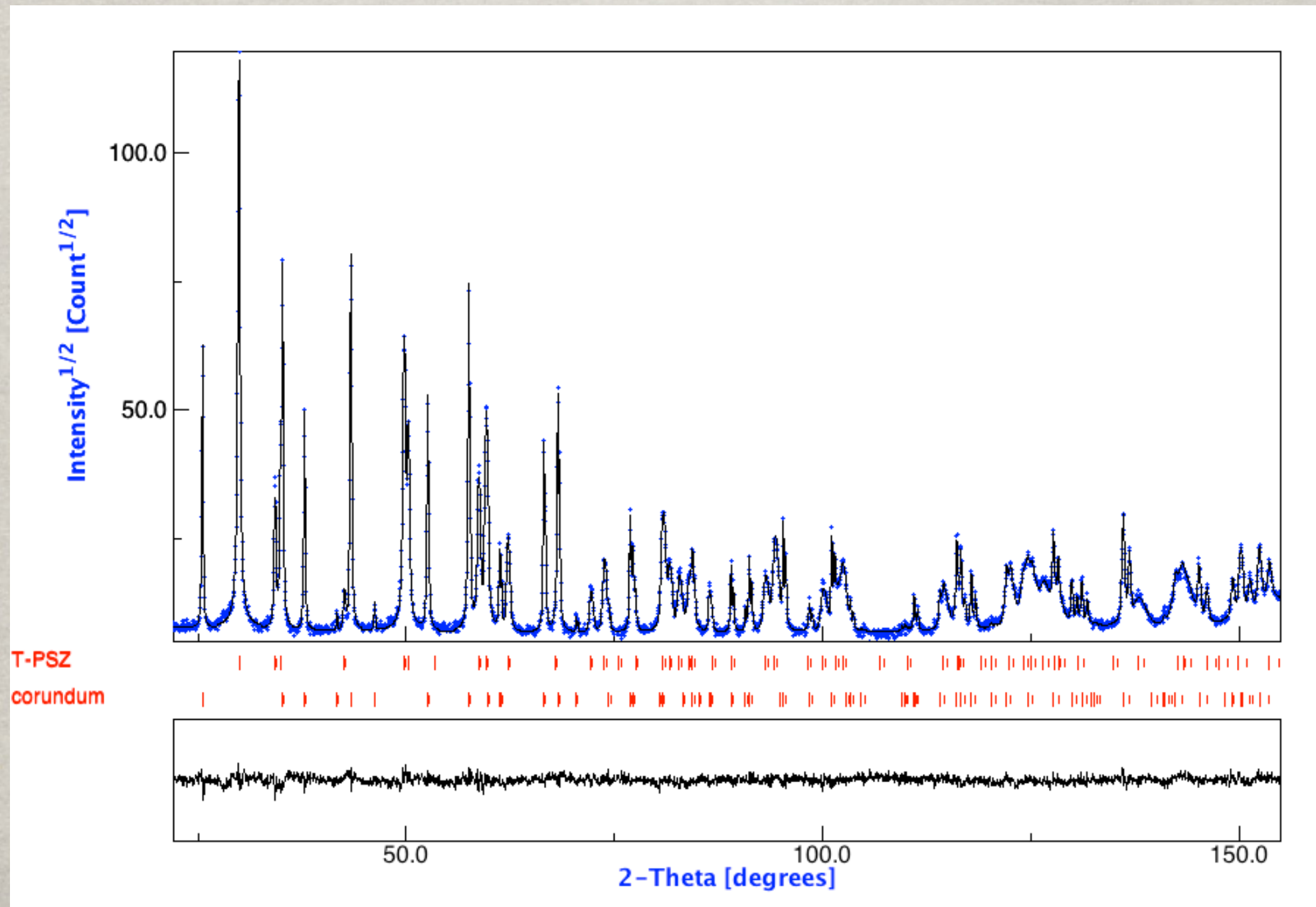
STEP 2: PEAKS POSITIONS

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



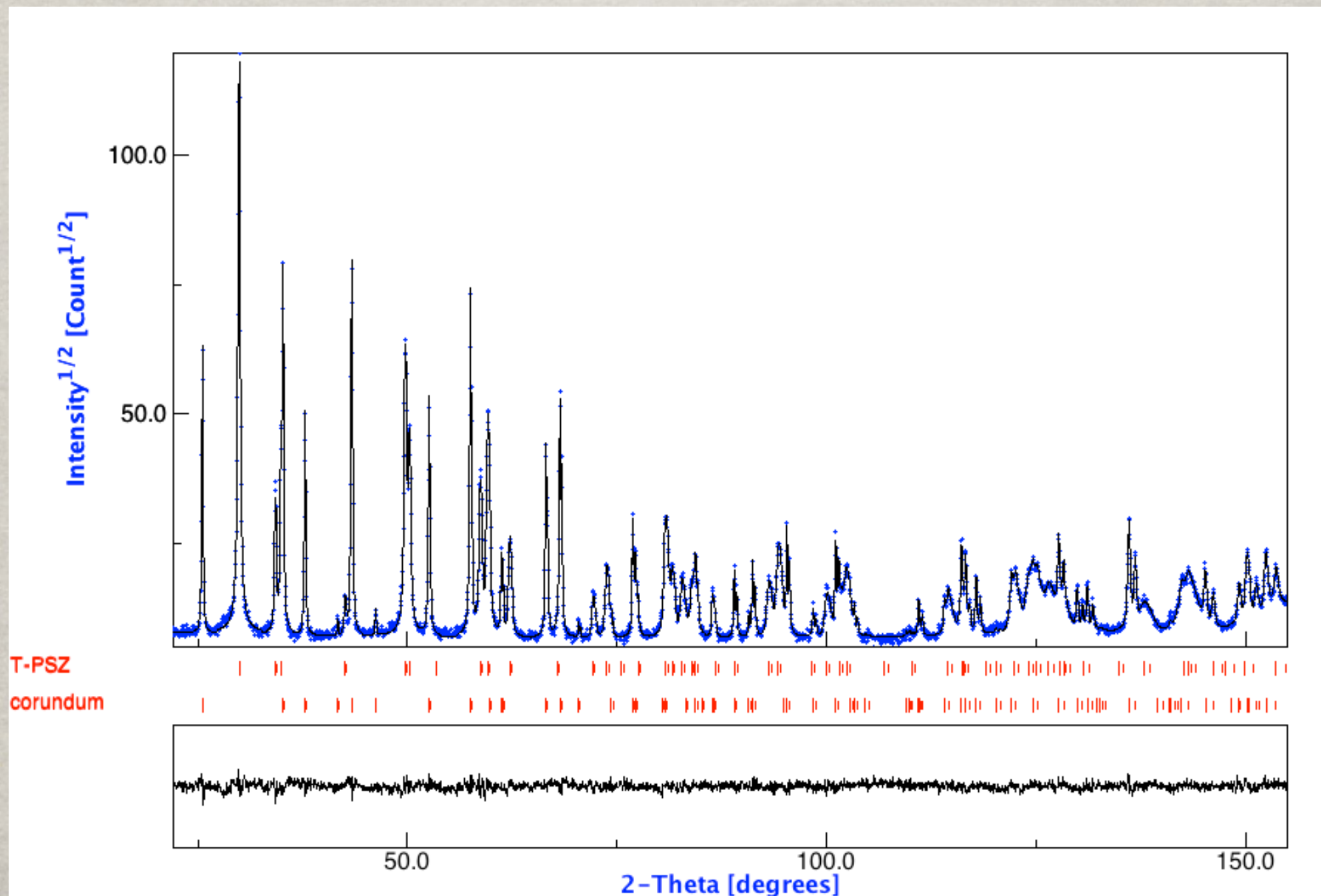
STEP 3: PEAKS SHAPES

- ✱ 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%



QUALITY OF THE EXPERIMENT

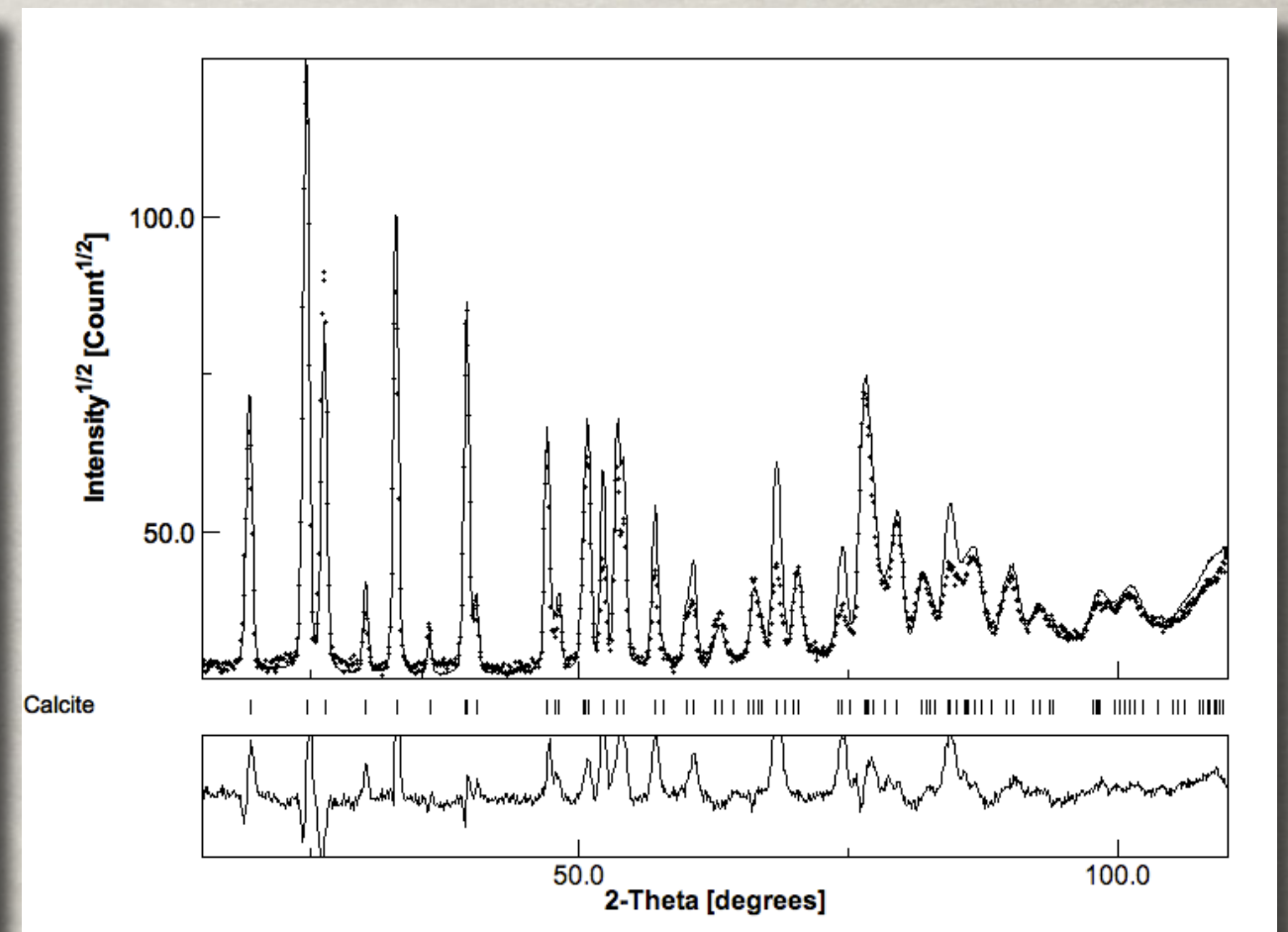
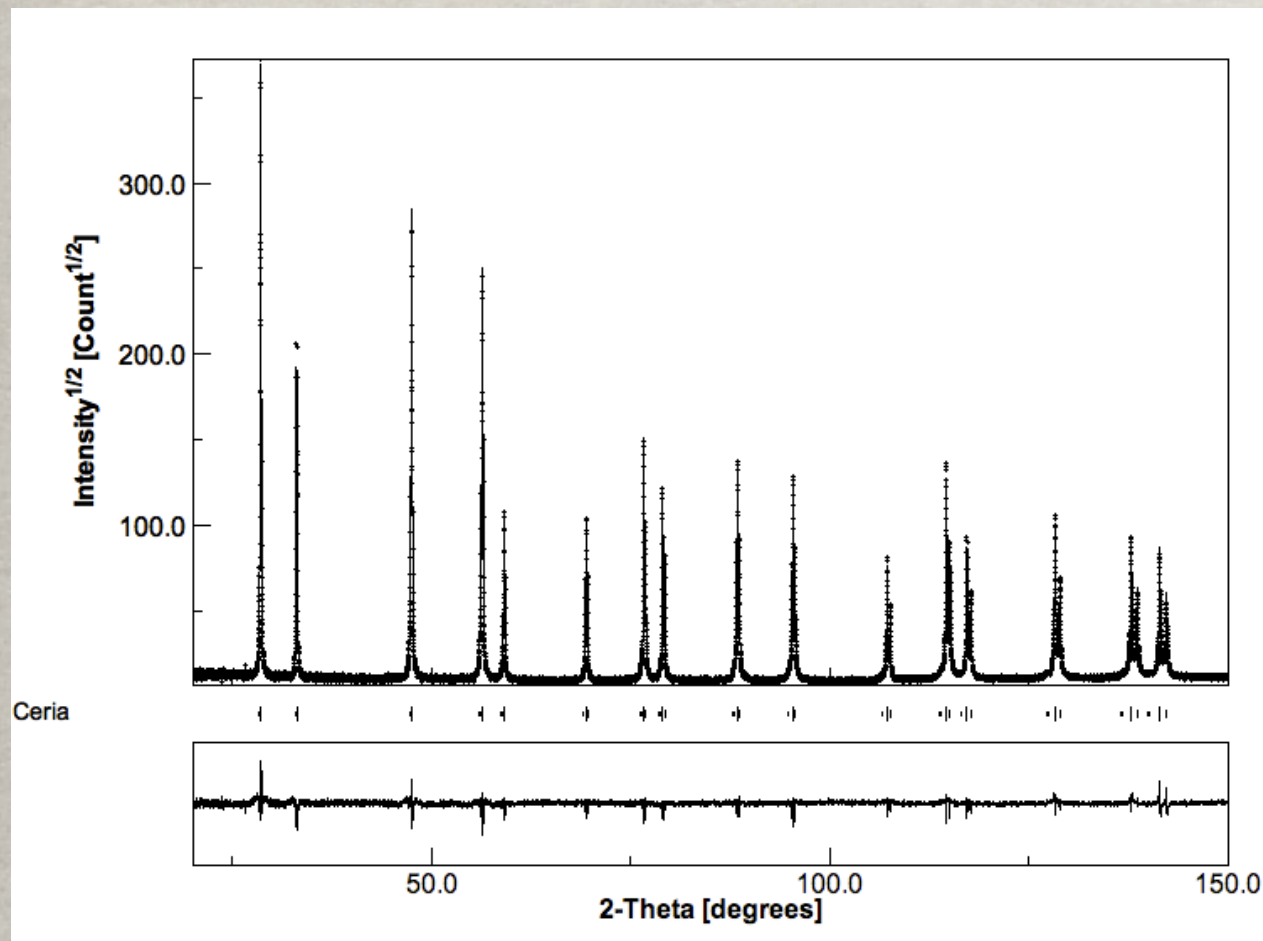
- ✱ A good diffraction fitting, a successful Rietveld analysis, they depend strongly on the quality of the experiment:
 - ✱ Instrument:
 - ✱ instrument characteristics and assessment
 - ✱ choice of instrument options
 - ✱ Collection strategies
 - ✱ range
 - ✱ step size
 - ✱ collection time
 - ✱ etc.
 - ✱ sample
 - ✱ sample size
 - ✱ sample preparation
 - ✱ sample condition

INSTRUMENT ASSESSMENT

- ✱ In most cases (or always) the instrument alignment and setting is more important than the instrument itself
- ✱ Be paranoid on alignment, the beam should pass through the unique rotation center and hits the detector at zero 2θ
- ✱ The background should be linear, no strange bumps, no additional lines and as low as possible
- ✱ Check the omega zero
- ✱ Collect regularly a standard for line positions and check if the positions are good both at low and high diffraction angle (check also the rest)

THE DATA COLLECTION

- ✱ The range should always be the widest possible compatible with the instrument and collection time (no need to waste time if no reliable informations are coming from a certain range)



- ✱ How much informations from $> 90^\circ$ for the pattern on the right?

THE STEP SIZE

- ✻ The step size should be compatible with the line broadening characteristics and type of analysis.
- ✻ In general 5-7 points in the half upper part of a peak are sufficient to define its shape.
- ✻ Slightly more points are preferred in case of severe overlapping.
- ✻ A little more for size-strain analysis.
- ✻ Too much points (too small step size) do not increase our resolution, accuracy or precision, but just increase the noise at equal total collection time.
- ✻ The best solution is to use the higher step size possible that do not compromise the information we need.
- ✻ Normally highly broadened peaks => big step size => less noise as we can increase the collection time per step (> 0.05)
- ✻ very sharp peaks => small step size (from 0.02 to 0.05 for Bragg-Brentano)

TOTAL COLLECTION TIME

- ✱ Ensure the noise is lower than the intensity of small peaks.
- ✱ If the total collection time is limited, better a lower noise than a smaller step size.
- ✱ Better to collect a little bit more than to have to repeat an experiment.
- ✱ If collection time is a problem go for line or 2D detectors:
 - ✱ CPS 120: 2 to 5 minutes for a good spectrum of 120 degrees (good for quantitative analyses or follow reactions, transformations, analyses in temperature)
 - ✱ Image plate or CCDs: very fast collection times when texture is needed or is a problem
- ✱ Data quality (not related to intensity) of these detectors is a little bit lower than the one from good point detectors. But sometimes intensity rules!

RESPECTING STATISTICS

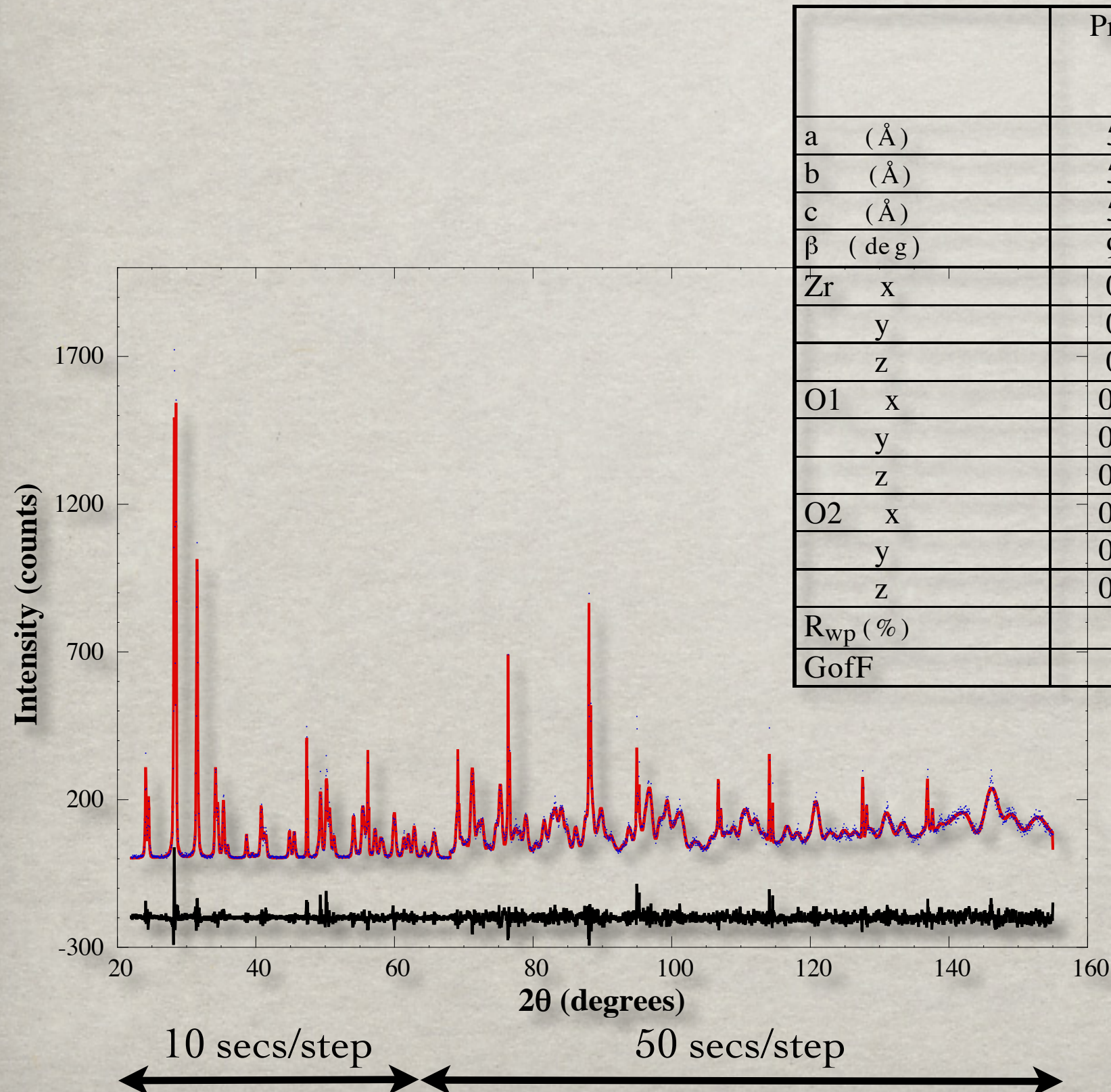
- ✻ In principle the measurement should be done at iso-statistical values:

$$\frac{1}{\sqrt{I_i}}$$

- ✻ For practical reasons this is not always possible.
- ✻ Scattering factors and L-P effects decrease the intensity at high angle.
- ✻ In most cases, peaks at low angle are more sensitive to heavy atoms (in high symmetric positions) and peaks at high angle to light atoms (in low symmetry sites).
- ✻ A good strategy is to divide the pattern in different parts and use a different collection time for each range reducing the noise for the high angle part (higher counting time at high angle).

MONOCLINIC ZIRCONIA: TWO RANGES

COLLECTION

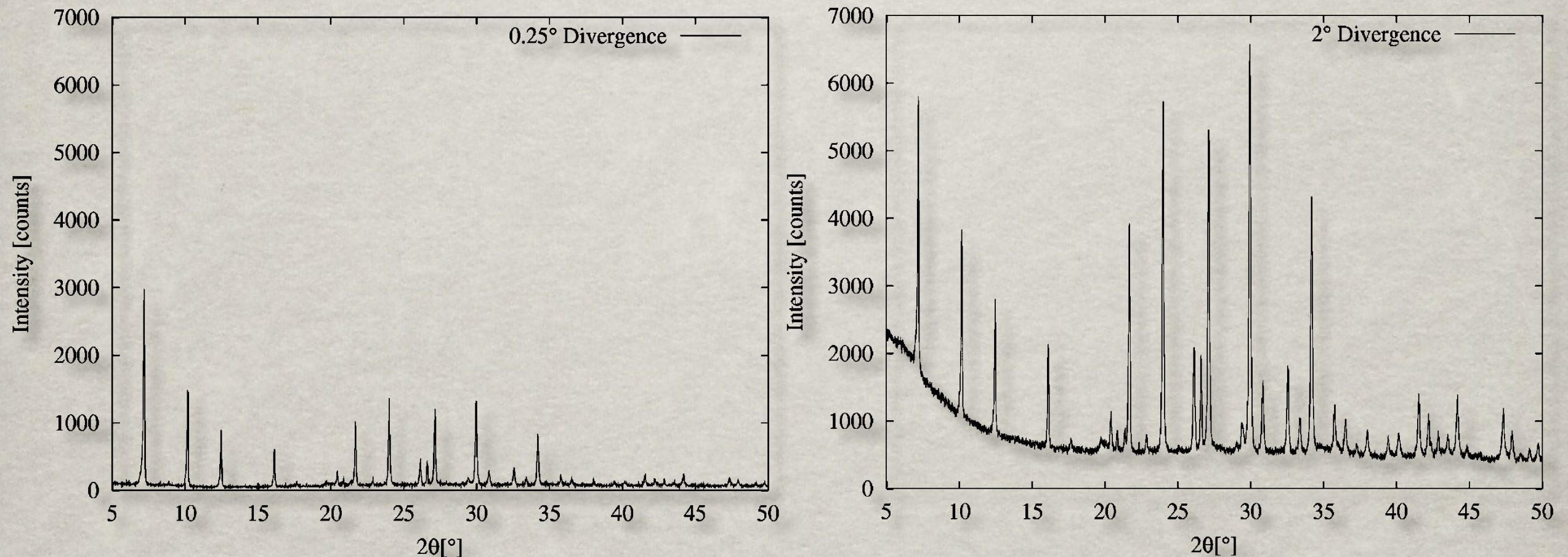


	Present work (XRPD)	Howard, Hill & Reichert (NPD)*	Smith & Newkirk (SCXRD)*
a (Å)	5.1511 (2)	5.1505 (1)	-
b (Å)	5.2027 (2)	5.2116 (1)	-
c (Å)	5.1387 (3)	5.3173 (1)	-
β (deg)	99.215 (4)	99.230 (1)	-
Zr x	0.2752 (3)	0.2754 (2)	0.2758 (2)
y	0.0402 (3)	0.0395 (2)	0.0411 (2)
z	0.2081 (3)	0.2083 (2)	0.2082 (2)
O1 x	0.0699 (22)	0.0700 (3)	0.0703 (15)
y	0.3317 (21)	0.3317 (3)	0.3359 (14)
z	0.3422 (19)	0.3447 (3)	0.3406 (13)
O2 x	0.4512 (20)	0.4496 (3)	0.4423 (15)
y	0.7536 (20)	0.7569 (3)	0.7549 (14)
z	0.4818 (24)	0.4792 (3)	0.4789 (13)
R _{wp} (%)	13.15	4.66	-
GofF	1.28	1.85	-

SAMPLE CHARACTERISTICS (1)

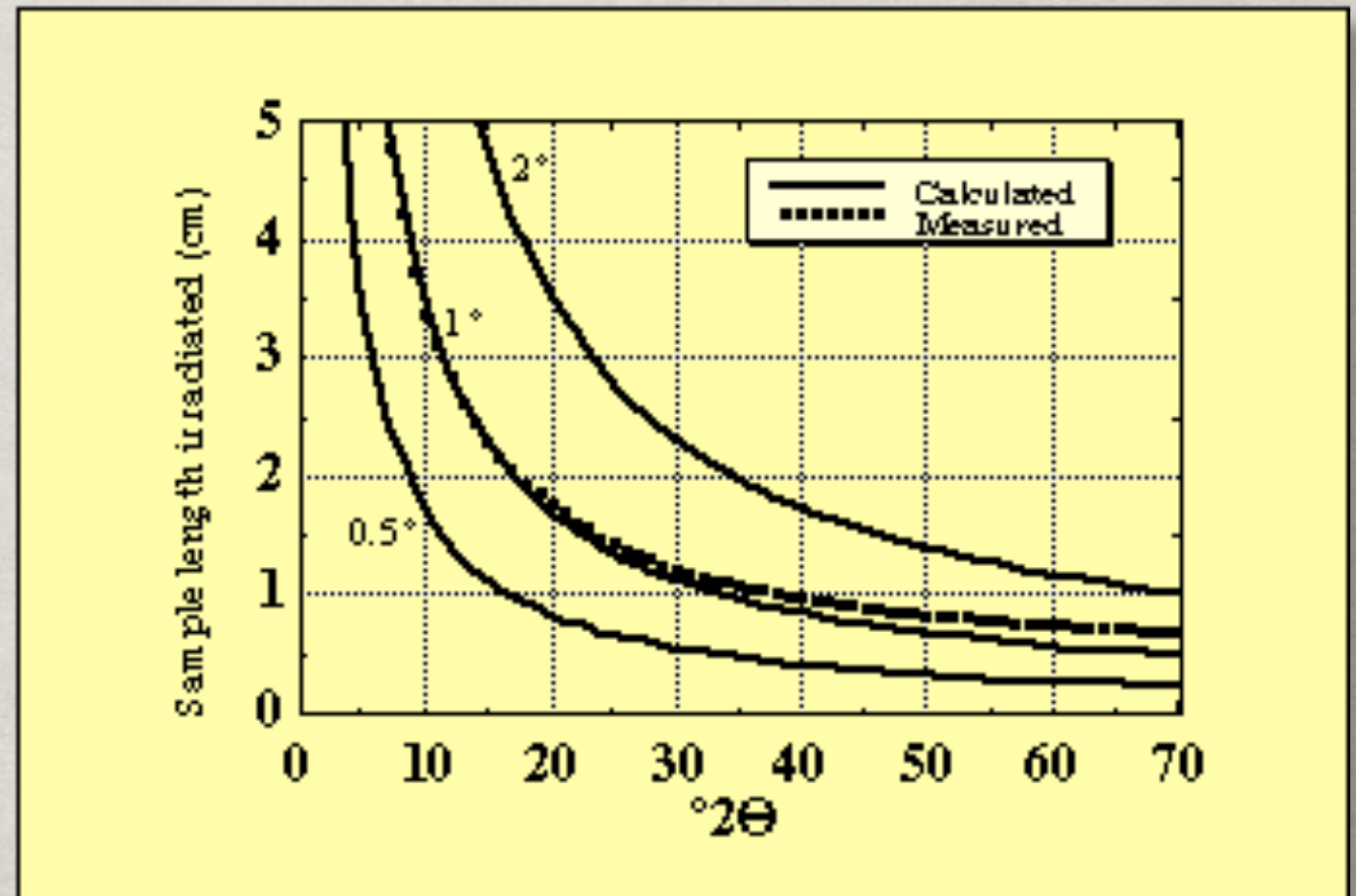
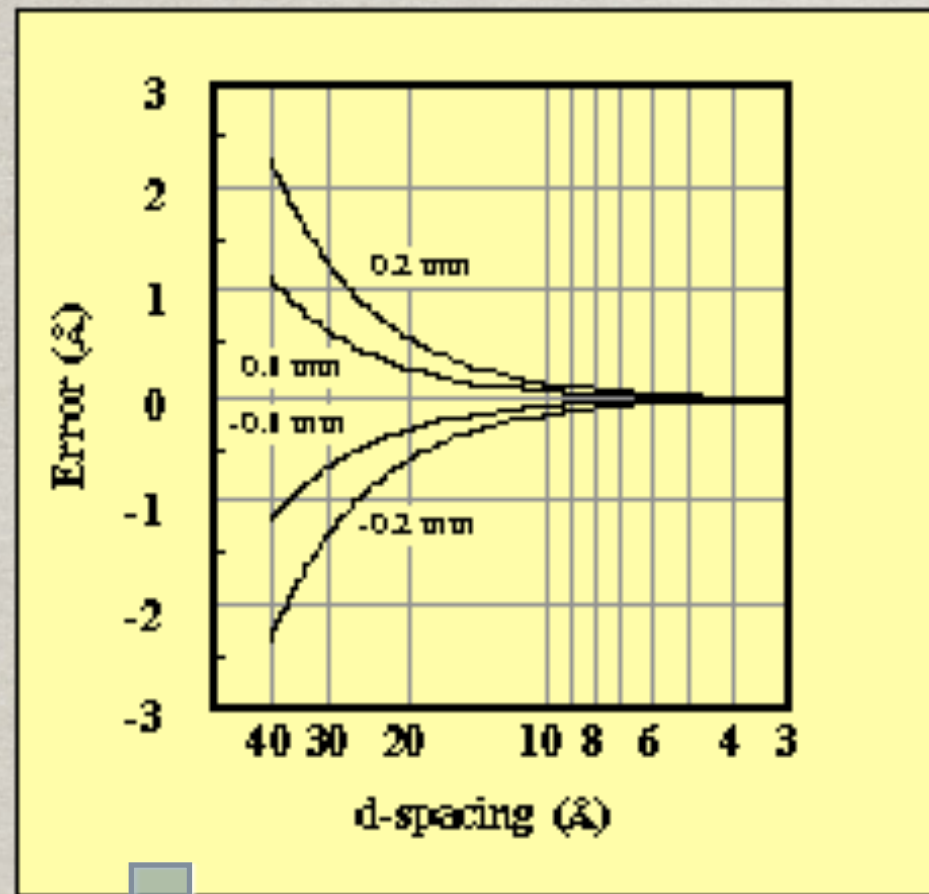
- ✱ The sample should be sufficiently large that the beam will be always entirely inside its volume/surface (for Bragg-Brentano check at low angle and sample thickness/transparency).

Zeolite sample, changing beam divergence, Krüger and Fischer, J. Appl. Cryst., 37, 472, 2004.



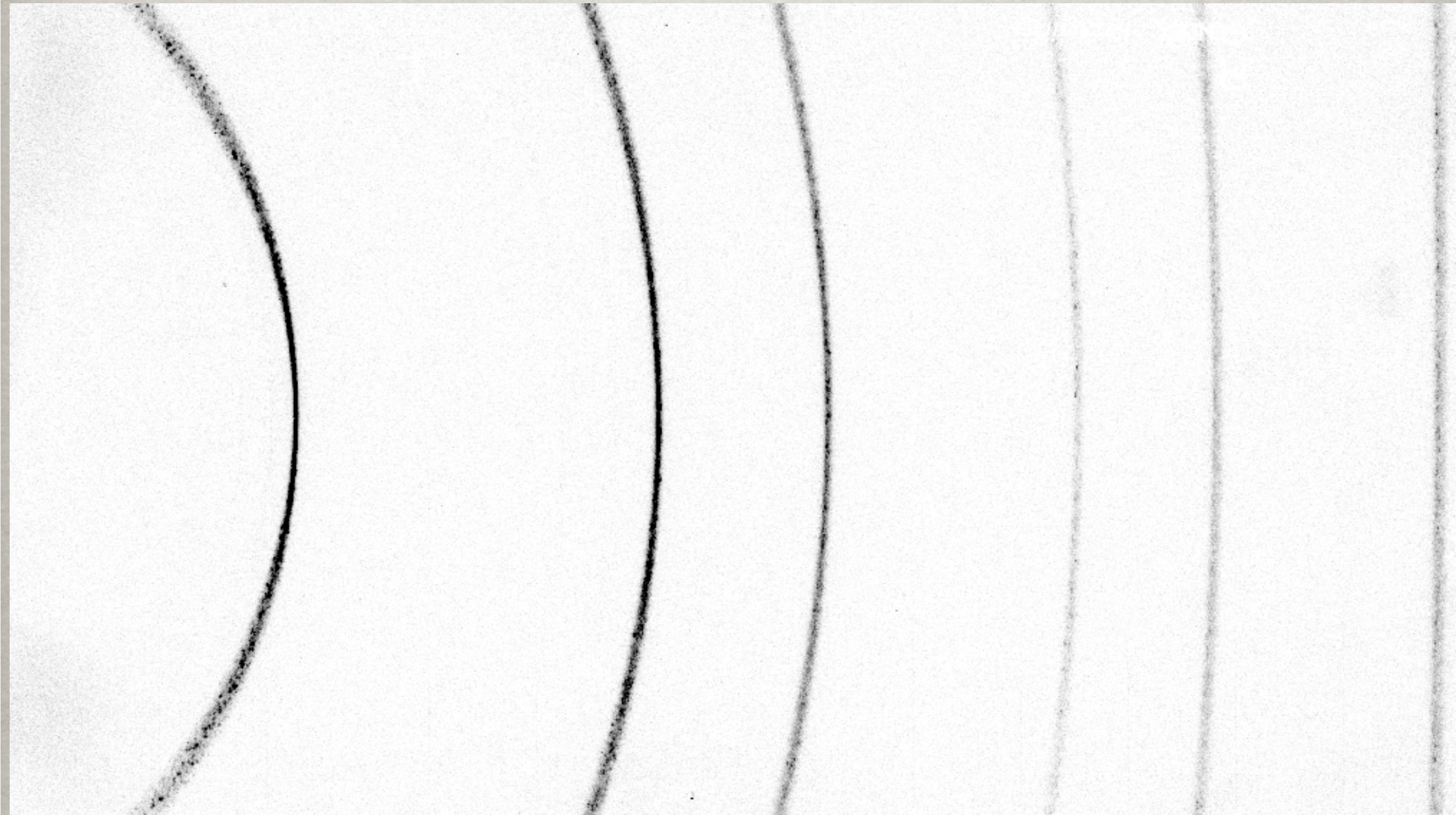
- ✱ On the right pattern, at low angle the beam goes out of the sample reducing relative peaks intensities and increasing air scattering/background

SAMPLE CHARACTERISTICS (2)

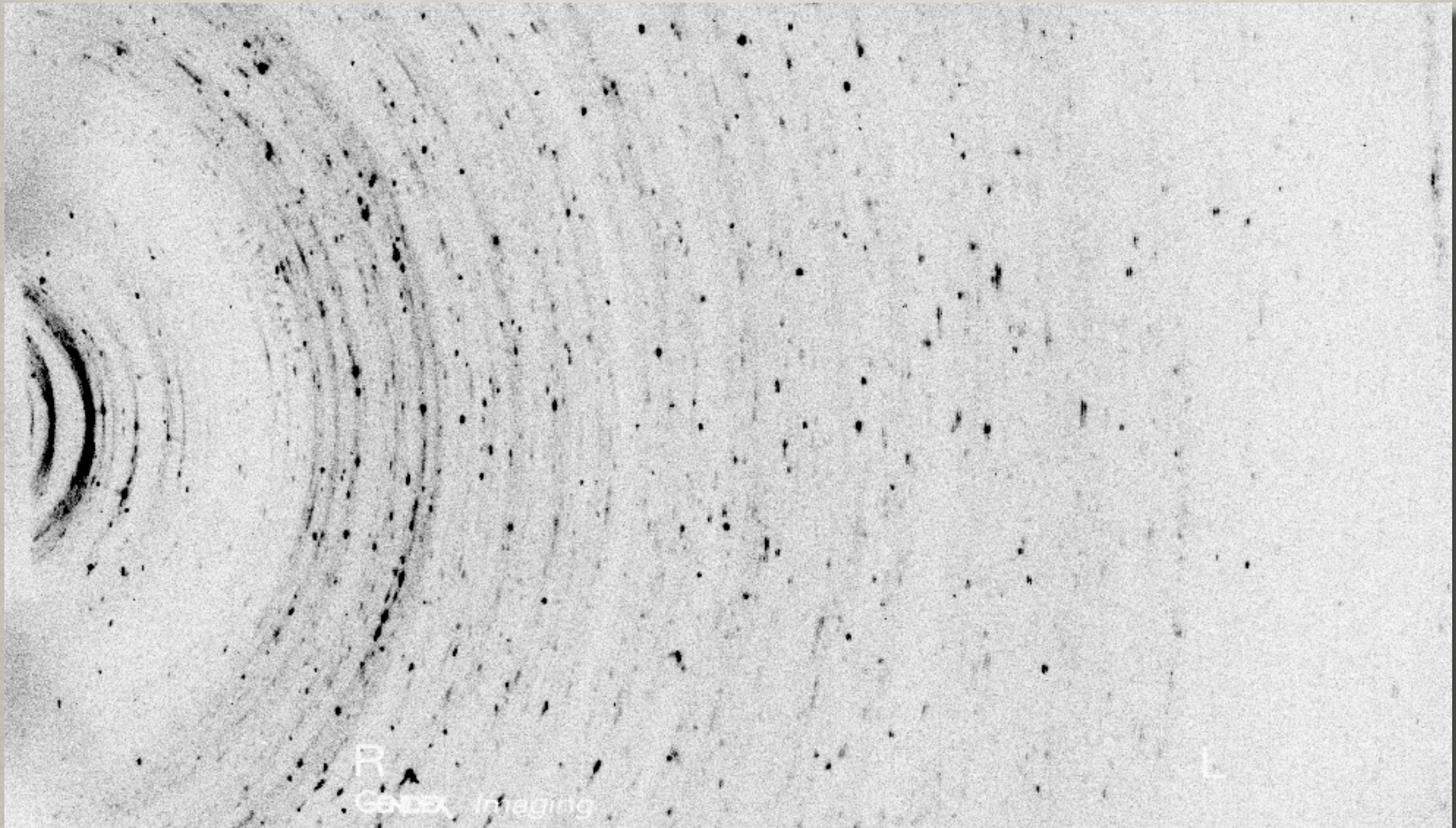


- ❁ Sample position is critical for good cell parameters (along with perfect alignment of the instrument).
- ❁ The number of diffracting grains at each position should be significant (> 1000 grains). Remember that only a fraction is in condition for the diffraction. Higher beam divergence or size increases this number. So the sample should have millions grains in the diffracting volume.

GRAIN STATISTICS (SUFFICIENT)



GRAIN STATISTICS (POOR)



SAMPLE CHARACTERISTICS

- ✱ The sample should be sufficiently large that the beam will be entirely inside its volume/surface (always)
- ✱ Sample position is critical for good cell parameters (along with perfect alignment of the instrument)
- ✱ The number of diffracting grains at each position should be significant (> 1000 grains). Remember that only a fraction is in condition for the diffraction. Higher beam divergence or size increases this number.
- ✱ Unless a texture analysis is the goal, no preferred orientations should be present. Change sample preparation if necessary.
- ✱ The sample should be homogeneous.
- ✱ Be aware of absorption contrast problems
- ✱ In Bragg-Brentano geometry the thickness should be infinite respect to the absorption.
- ✱ Quality of the surface matters.

AMBIENT CONDITIONS

- ✱ In some cases constant ambient condition are important:
 - ✱ temperature for cell parameter determination or phase transitions
 - ✱ humidity for some organic compounds or pharmaceuticals
 - ✱ can your sample be damaged or modify by irradiation (normally Copper or not too highly energetic radiations are not)
- ✱ There are special attachments to control the ambient for sensitive compounds

EXPERT TRICKS/SUGGESTION

- ✱ First get a good experiment/spectrum
- ✱ Know your sample as much as possible
- ✱ Do not refine too many parameters
- ✱ Always try first to manually fit the spectrum as much as possible
- ✱ Never stop at the first result
- ✱ Look carefully and constantly to the visual fit/plot and residuals during refinement process (no “blind” refinement)
- ✱ Zoom in the plot and look at the residuals. Try to understand what is causing a bad fit.
- ✱ Do not plot absolute intensities; plot at iso-statistical errors. Small peaks are important like big peaks.
- ✱ Use all the indices and check parameter errors.
- ✱ First get a good experiment/spectrum