Introduction to diffraction and the Rietveld method

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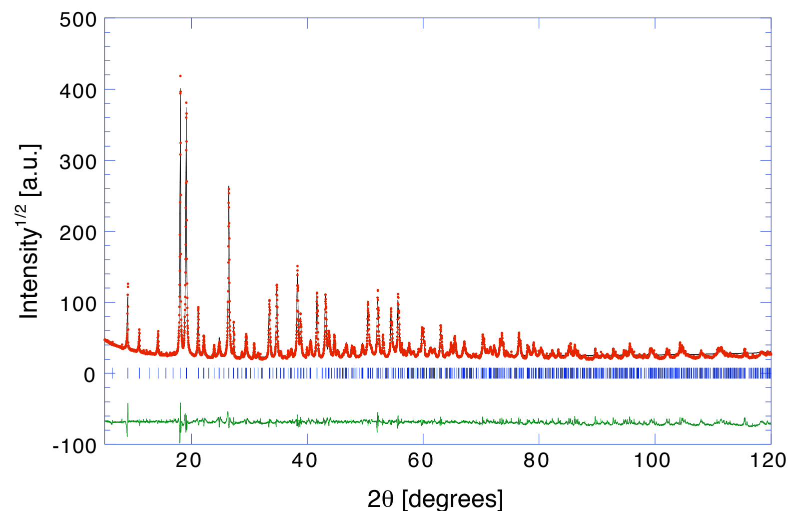
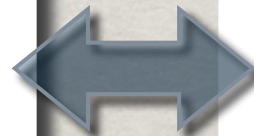
Goal of the Rietveld method

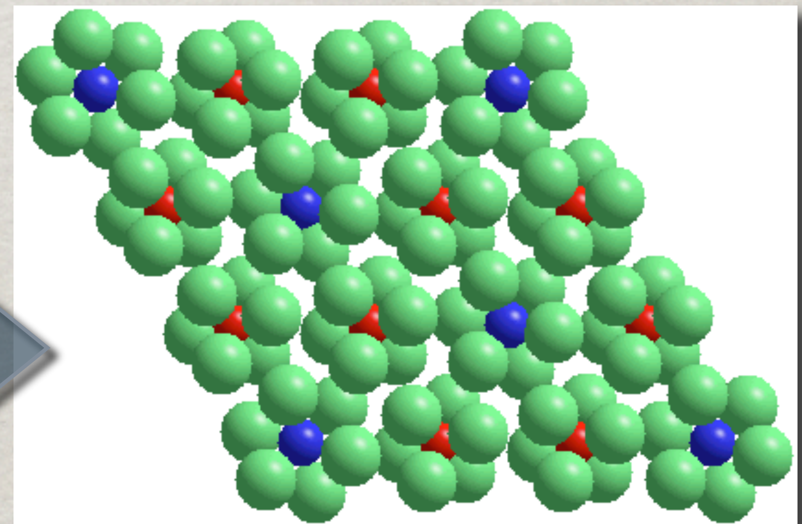
- To minimize the residual function using a non-linear least squares algorithm

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

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

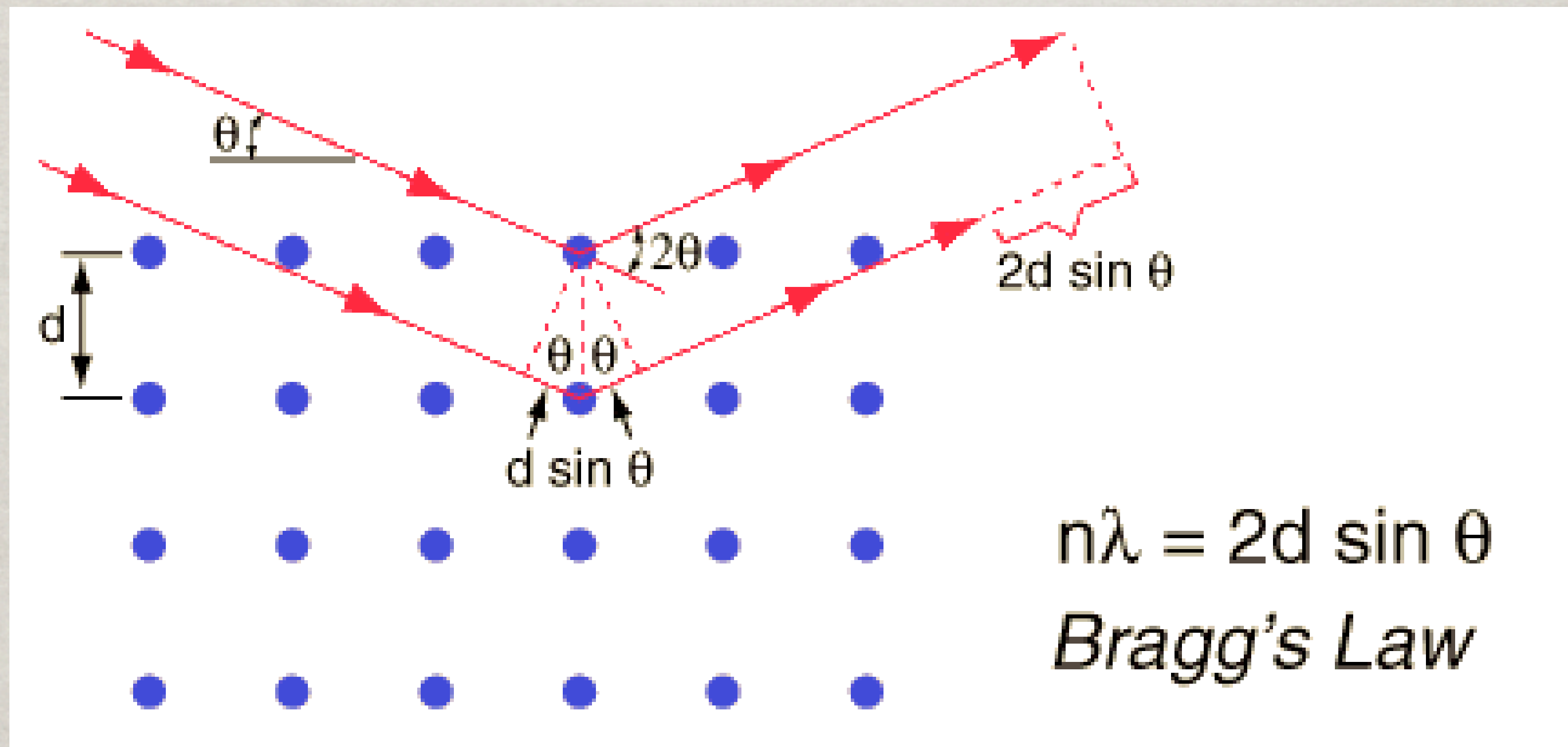






Bragg law

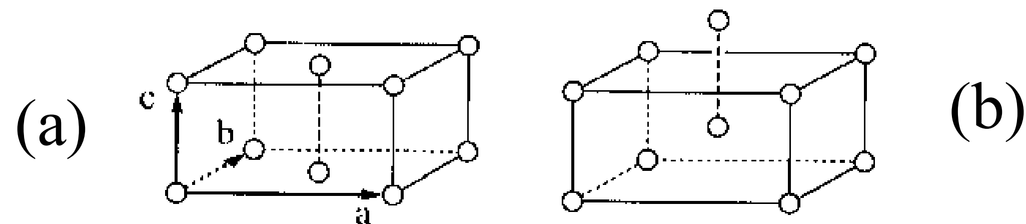
- Constructive interference and interplanar spacing:



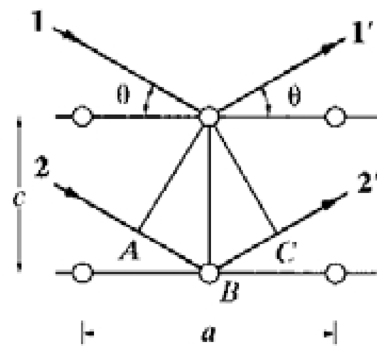
Bragg law and intensities

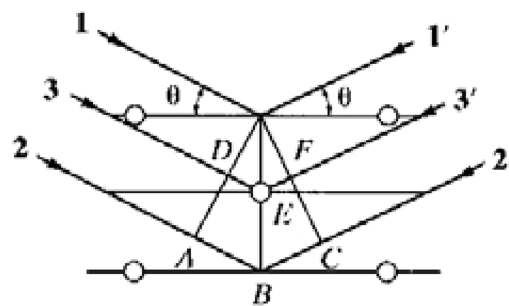
- Considering the diffraction from the (001) plane

(a)



(b)

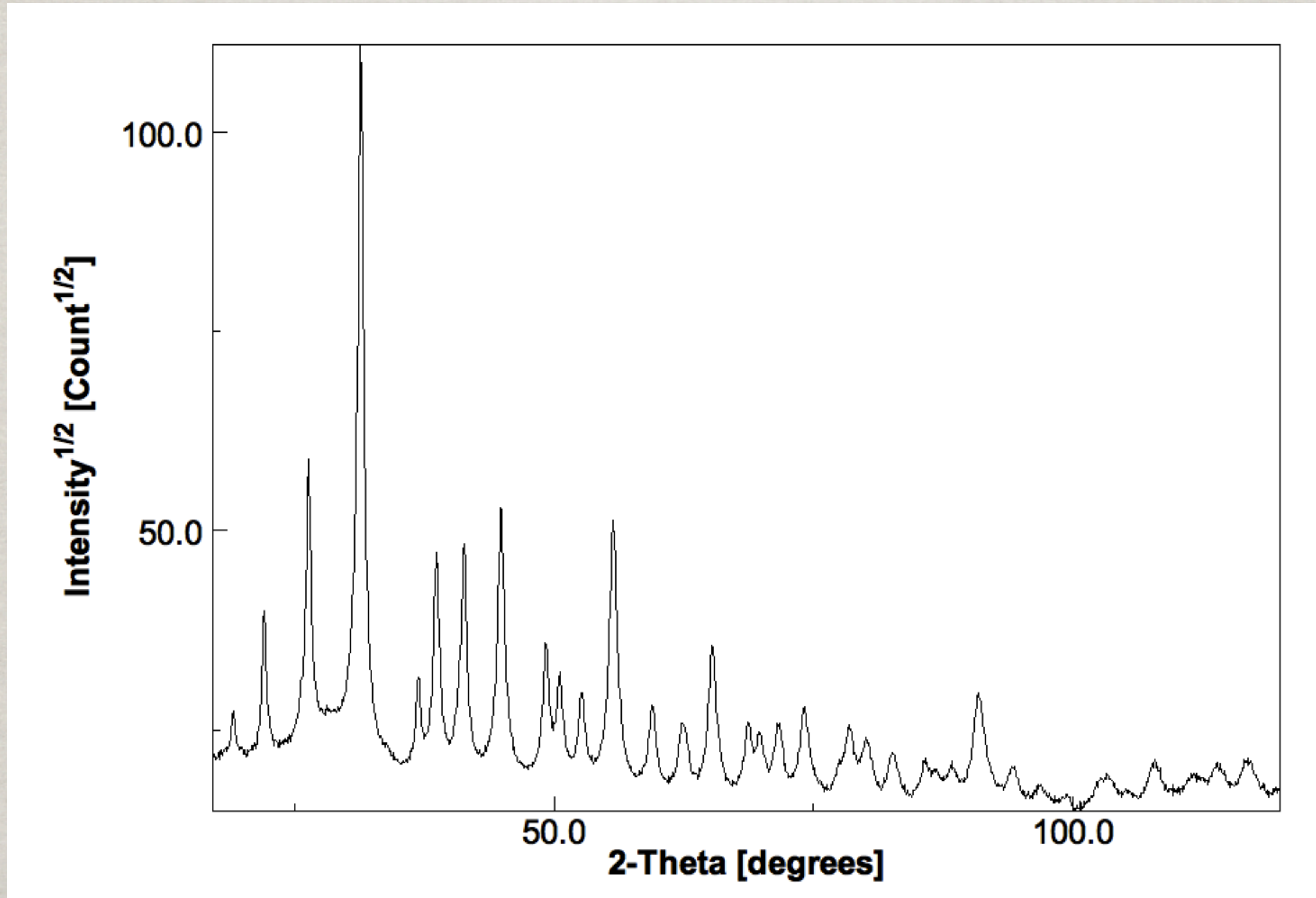




(a) (b)

If the path length between rays 1 and 2 differs by λ, the path length between rays 1 and 3 will differ by $\lambda/2$ and destructive interference in (b) will lead to no diffracted intensity

A typical diffraction pattern



Diffraction intensities

- The intensity in a powder diffractometer

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

- The structure factor:

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

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:

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

- where:

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

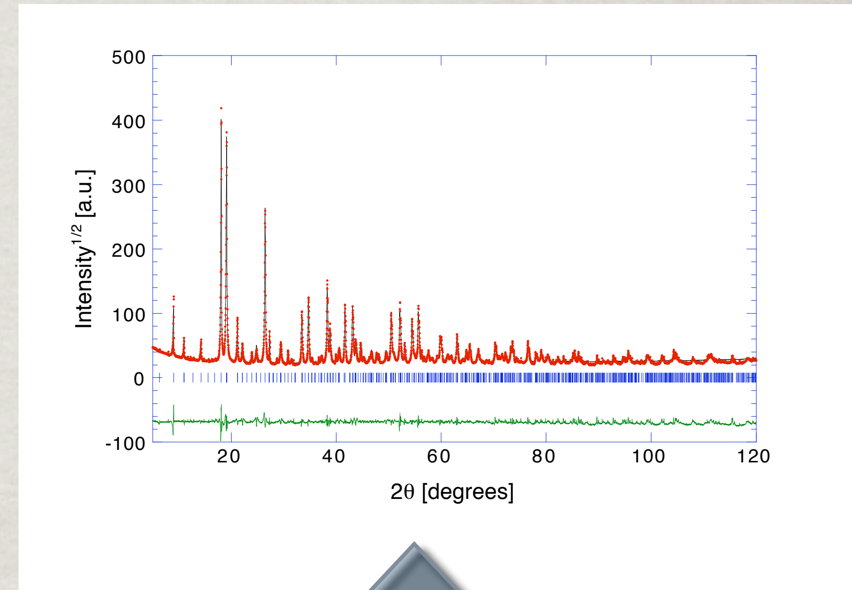
P_k = preferred orientation function

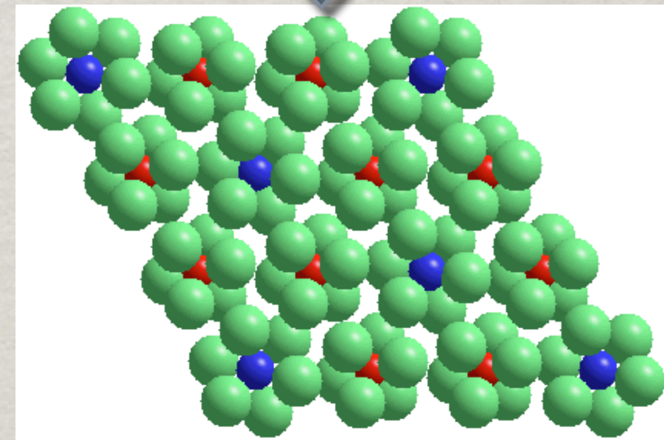
$S(2\theta_i - 2\theta_k)$ = profile shape function

(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):

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

- the spectrum is calculated by the classical intensity equation:

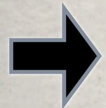
$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left| F_{k,j} \right|^2 S_j \left(2\theta_i - 2\theta_{k,j} \right) P_{k,j} A_j + bkg_i$$

- 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).

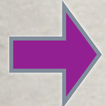
The classical Rietveld method

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

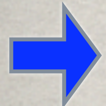
- The spectrum (at a 2θ point i) is determined by:



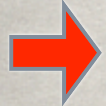
  - a background value



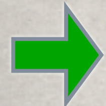
  – some reflection peaks that can be described by different terms:



  - 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

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

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

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

  - 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

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

- 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

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

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

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

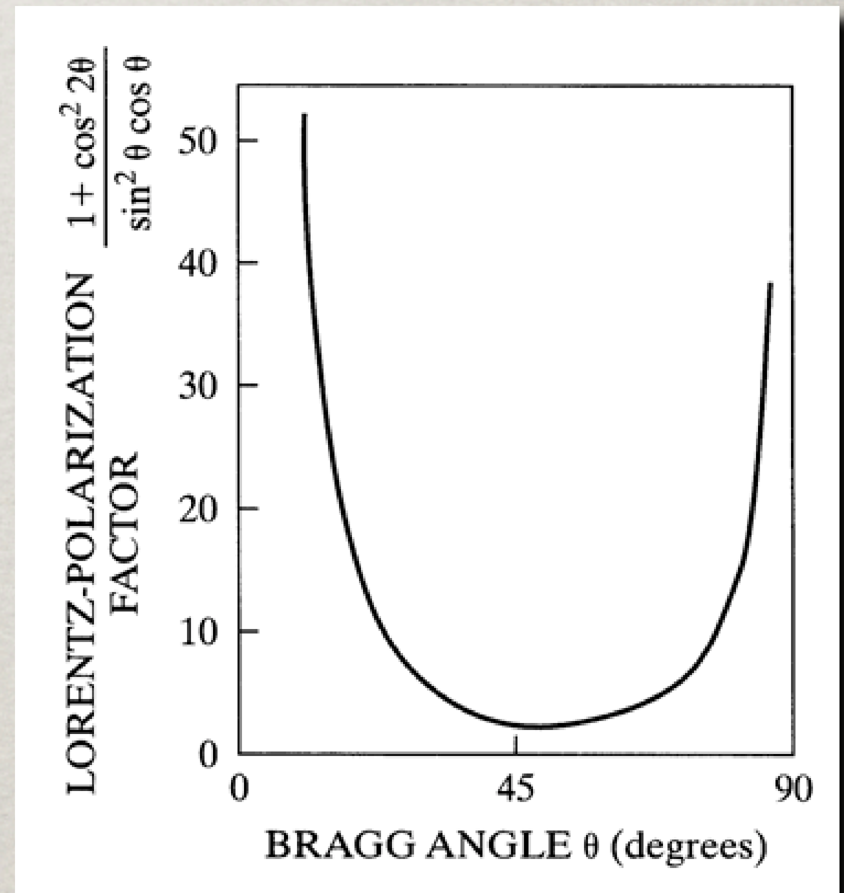
  - S_j = phase scale factor (the overall Rietveld generic scale factor)
  - S_F = beam intensity (it depends on the measurement)
  - f_j = phase volume fraction
  - V_j = phase cell volume (in some programs it goes in the F factor)
- In Maud the last three terms are kept separated.

The classical Rietveld method

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

- 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:

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



The classical Rietveld method

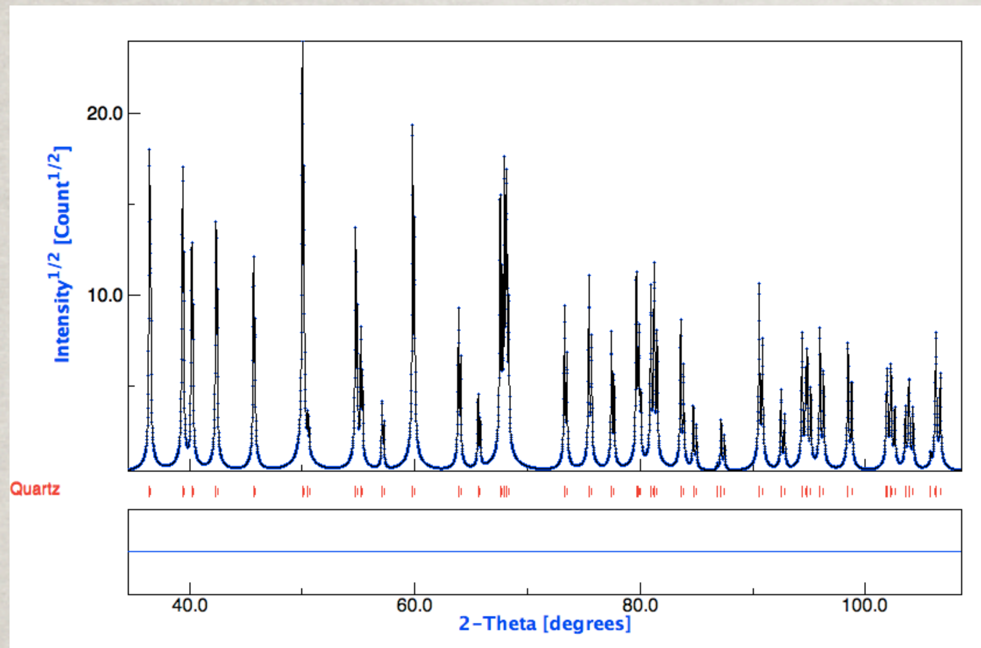
$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

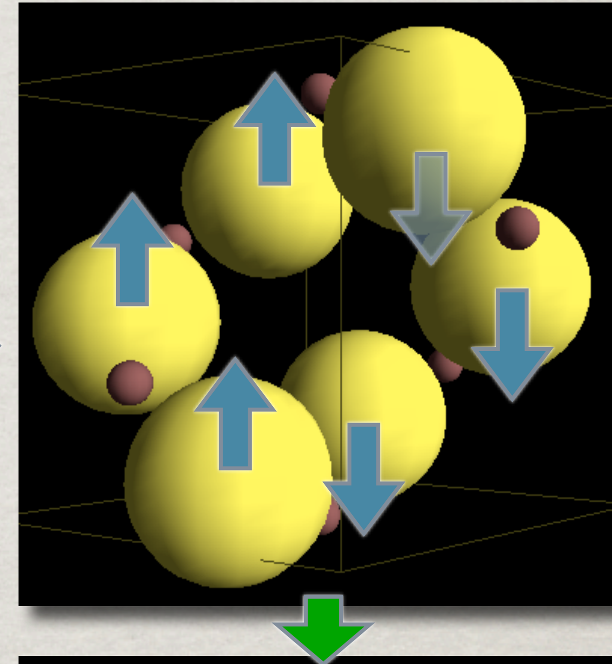
- Under a generalized structure factor we include:
  - The multiplicity of the k reflection (with h, k, l Miller indices): m_k
  - The structure factor
  - The temperature factor: B_n

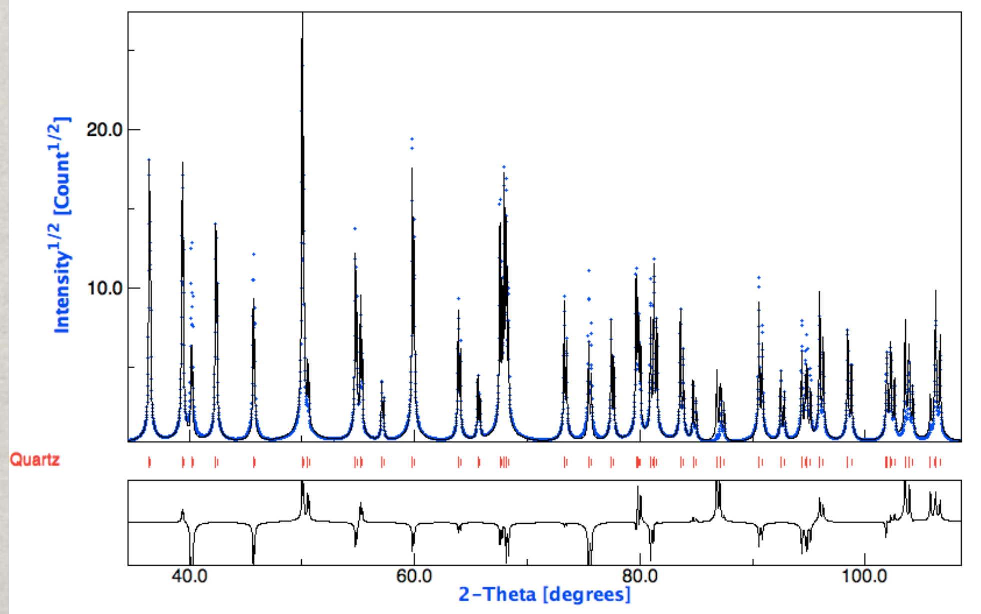
$$\left|F_{k,j}\right|^2 = m_k \left| \sum_{n=1}^{N} f_n e^{-B_n \frac{\sin^2\theta}{\lambda^2}} \left(e^{2\pi i\left(hx_n + ky_n + lz_n\right)}\right) \right|^2$$

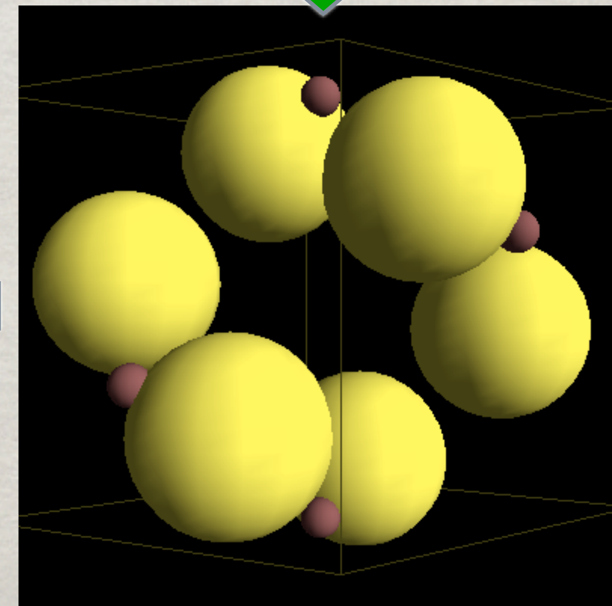
    - N = number of atoms
    - x_n, y_n, z_n coordinates of the nth atom
    - f_n, atomic scattering factor

Atom positions and Structure Factors



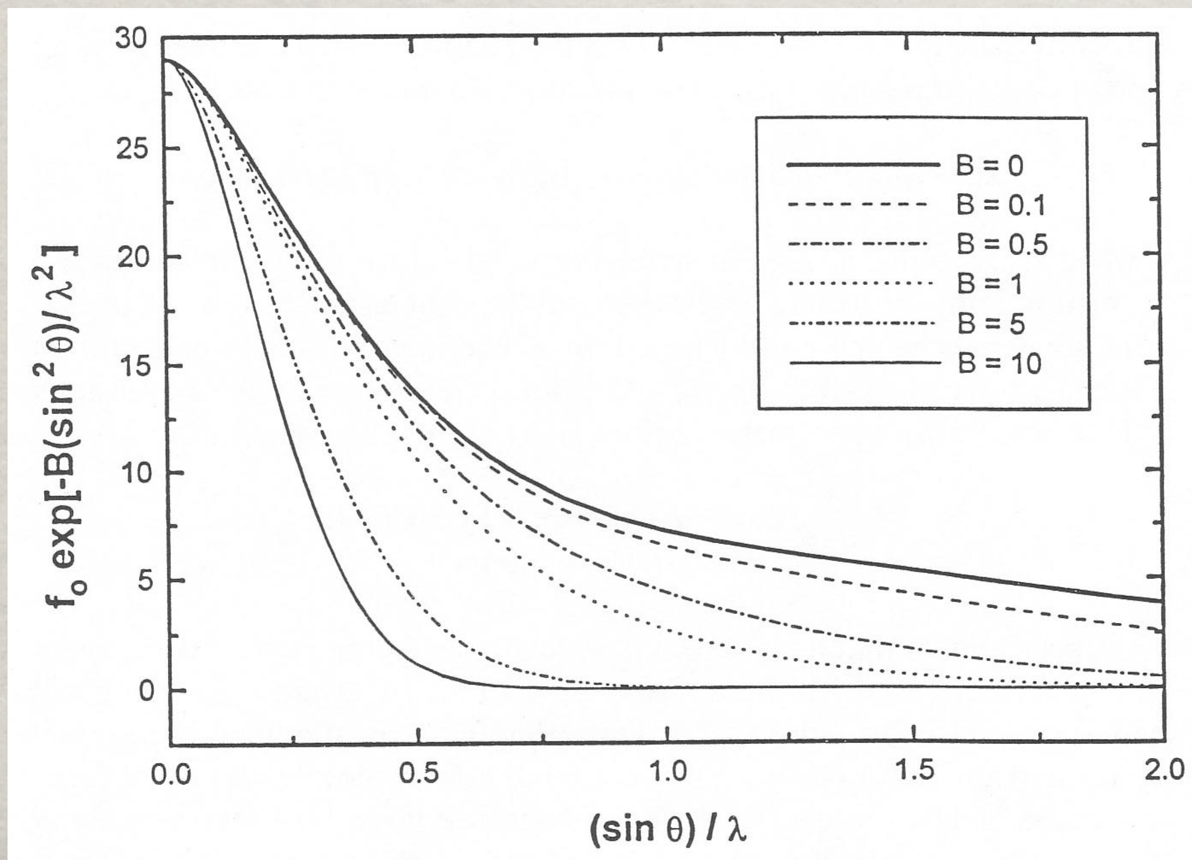


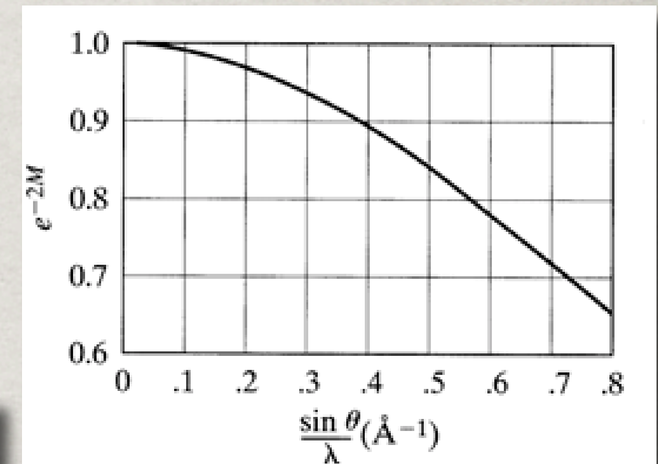


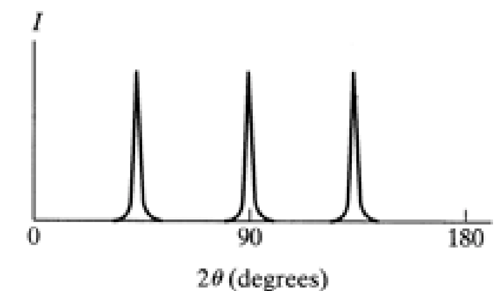


Atomic scattering factor and Debye-Waller

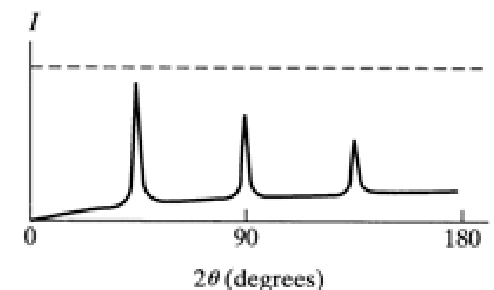
- The atomic scattering factor for X-ray decreases with the diffraction angle and is proportional to the number of electrons.
- The temperature factor (Debye-Waller, B) accelerates the decrease.







(a) No thermal vibration



(b) Thermal vibration

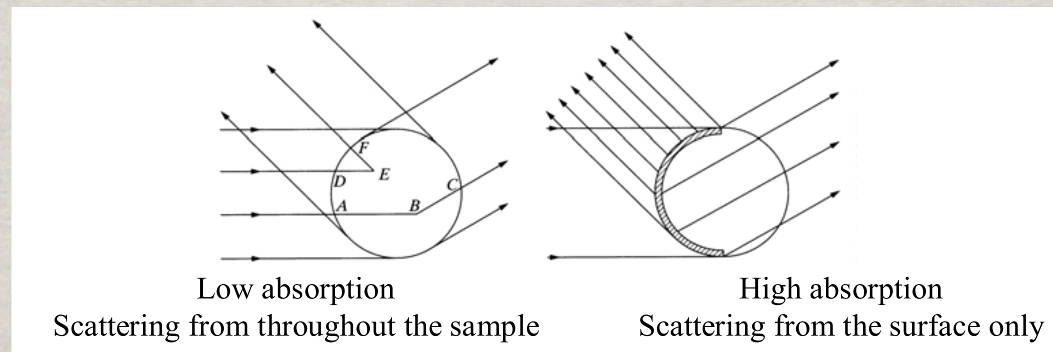
The classical Rietveld method

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

- 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



Low absorption
Scattering from throughout the sample

High absorption
Scattering from the surface only

  - There could be problems for microabsorption (absorption contrast)

The classical Rietveld method

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

- 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

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

- 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:

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

    - the shape parameters are:

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

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

The classical Rietveld method

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

- 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:

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

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

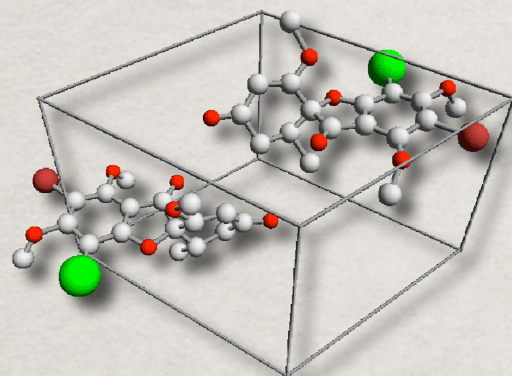
$$R_{wp} = \sqrt{\frac{\sum_{i=1}^{N}\left[w_i\left(I_i^{\exp} - I_i^{calc}\right)\right]^2}{\sum_{i=1}^{N}\left[w_i I_i^{\exp}\right]^2}}, \qquad w_i = \frac{1}{\sqrt{I_i^{\exp}}}$$

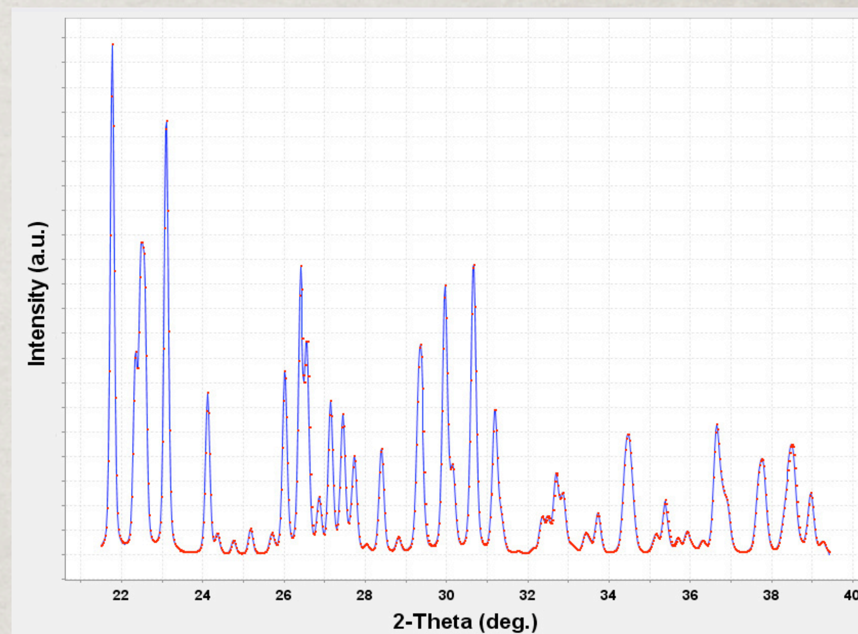
$$R_{\exp} = \sqrt{\frac{(N-P)}{\sum_{i=1}^{N}\left[w_i I_i^{\exp}\right]^2}}, \qquad w_i = \frac{1}{\sqrt{I_i^{\exp}}}$$

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

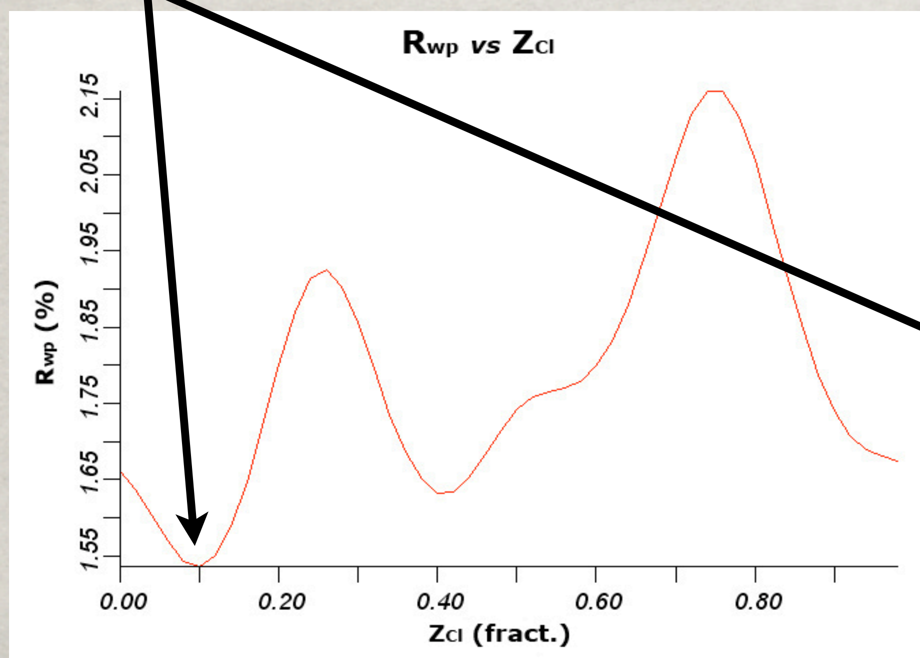
Local minima: bromo-griseofulvin

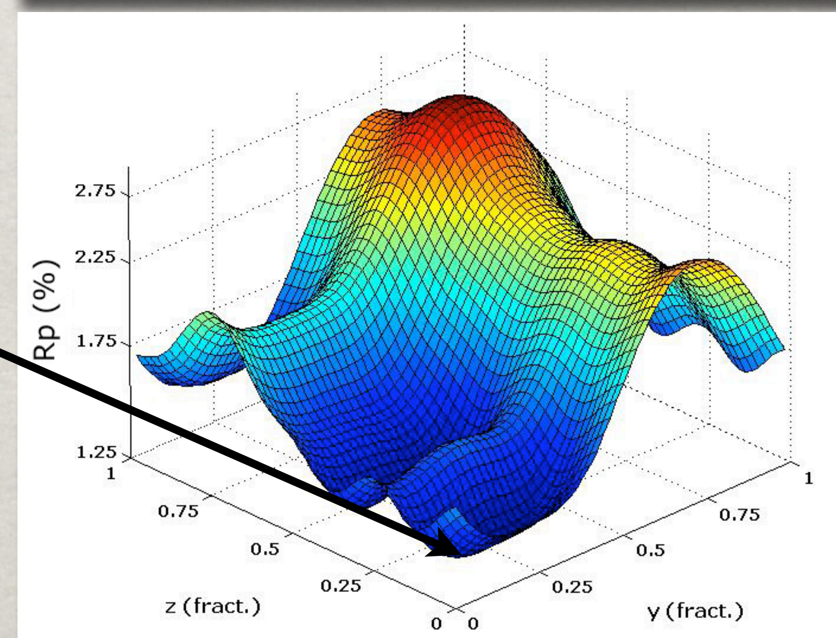
M. Bortolotti, PhD thesis, Trento, 2007





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 then 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

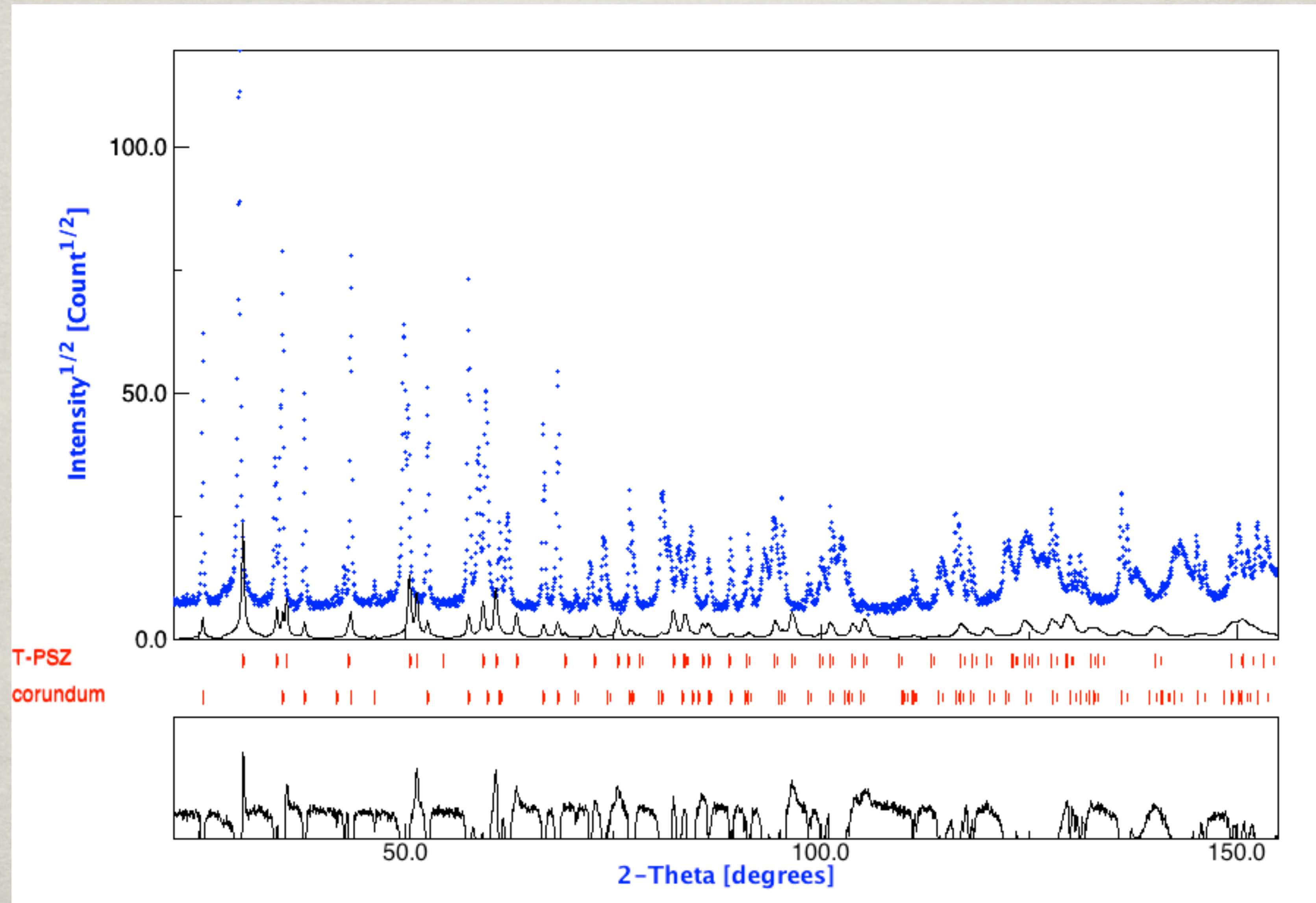
- Experiment:
  - choose the correct instrument/s
  - select the experiment conditions
  - prepare the sample and collect the pattern/s
- Analysis:
  - verify the data quality and perform the qualitative analysis
  - Rietveld refinement:
    - load or input the phases in the sample
    - adjust manually some parameters (cell, intensities, background)
    - refine overall intensities and background
    - refine peaks positions
    - refine peaks shapes
    - refine structures
- Assess the results

Rietveld refinement procedure

- First select the appropriate Rietveld program; depending on what you need to analyze there could be a best solution.
- Several choices at ccp14.ac.uk (free programs):
  - GSAS: most used; very good for crystal structure refinement and TOF neutron; not easy to use but there is a lot of knowledge around. A friendly graphical interface available with Expgui.
  - FullProf: best for magnetic materials; good for crystal structure refinements; no graphical interface (in preparation).
  - Maud: for material scientists; good for quantitative phase analysis, size-strain and texture. Best in the case of texture/strain problems. Come with a graphical user interface.
  - Rietan, Arit, Brass, DBWS, XRS-82, Topas-academic, XND etc.
- Some commercial ones:
  - BGMN, Topas etc.

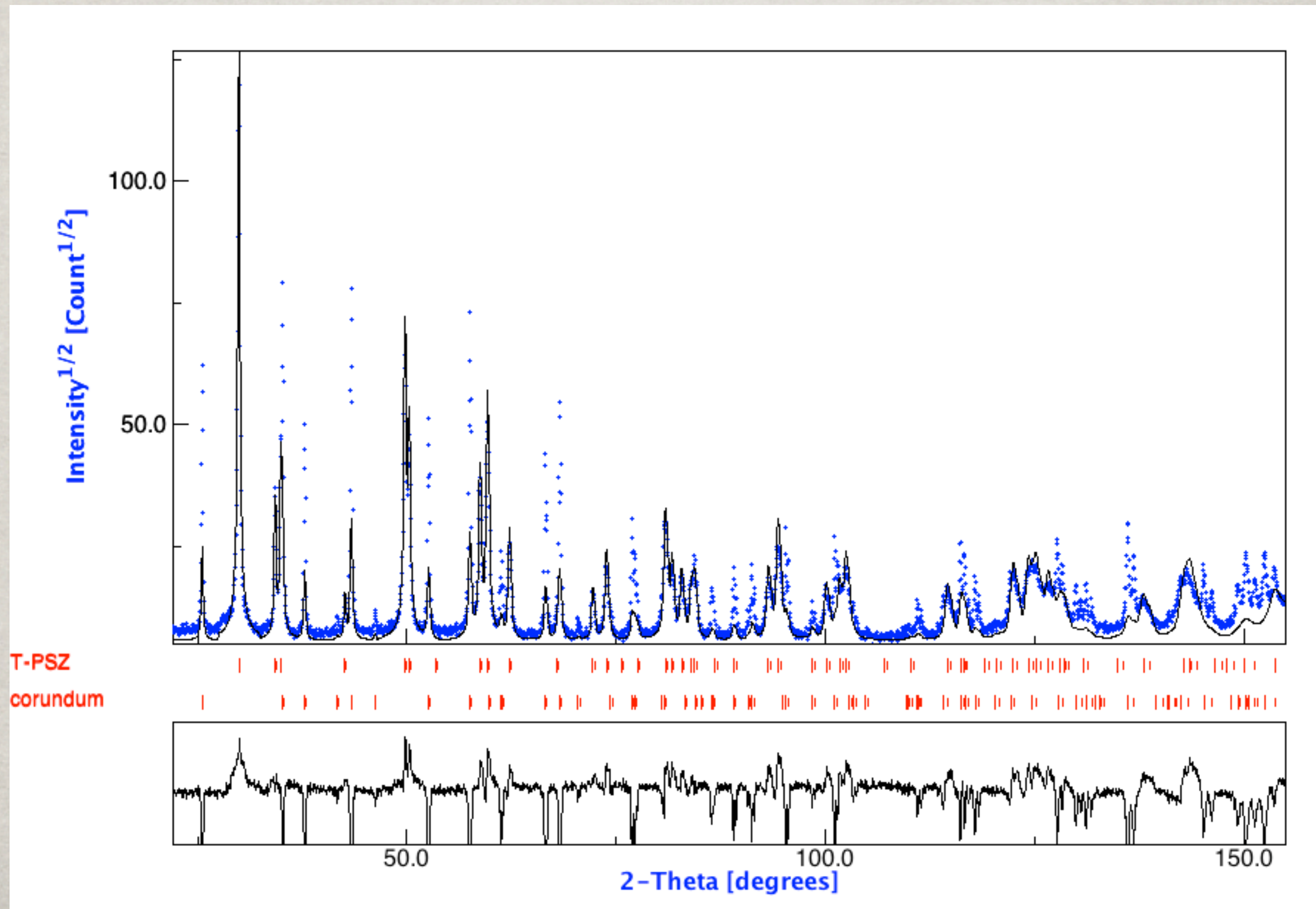
Starting point: defining the phases

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



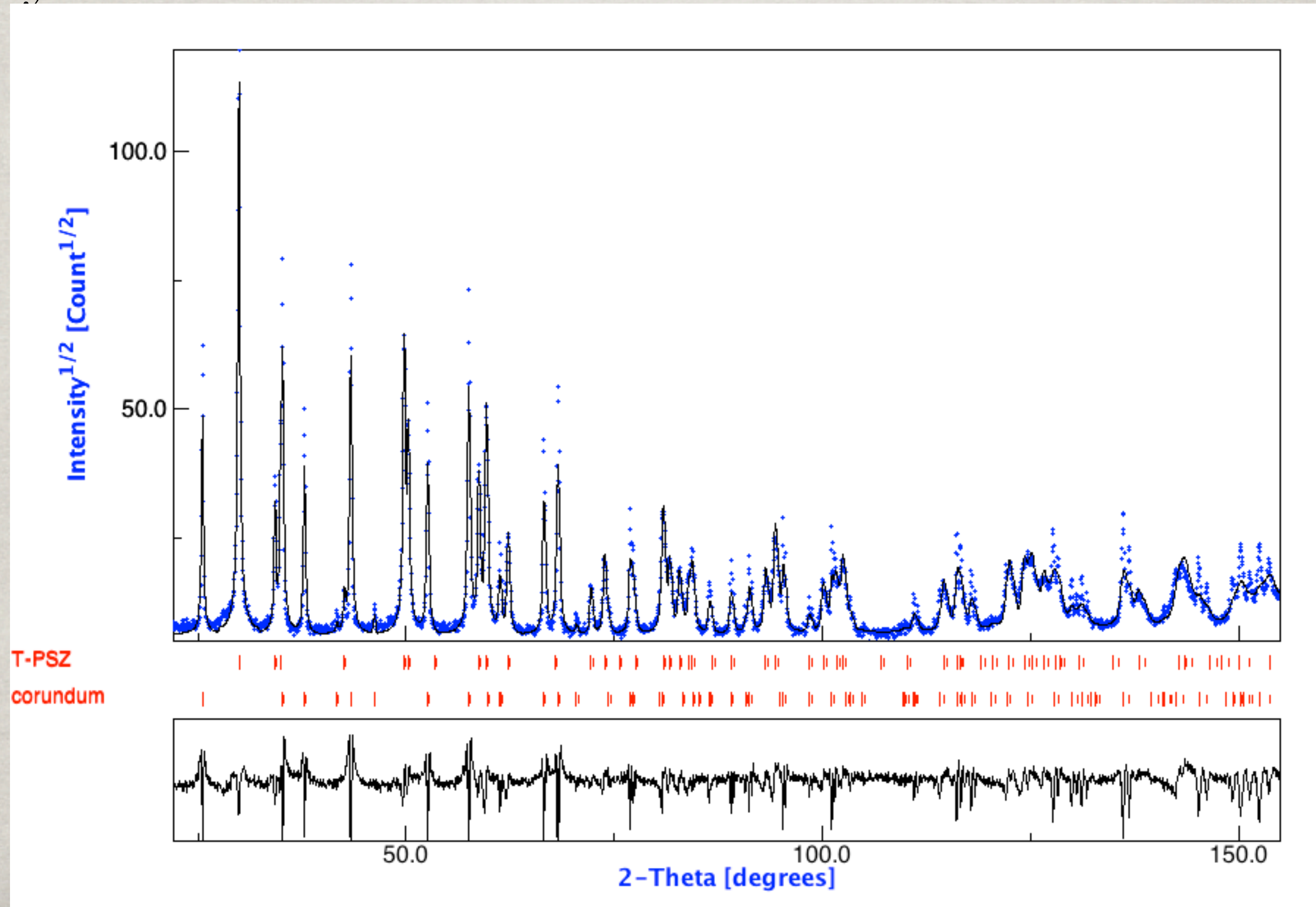
Adjusting manually: cell parameters, intensities

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



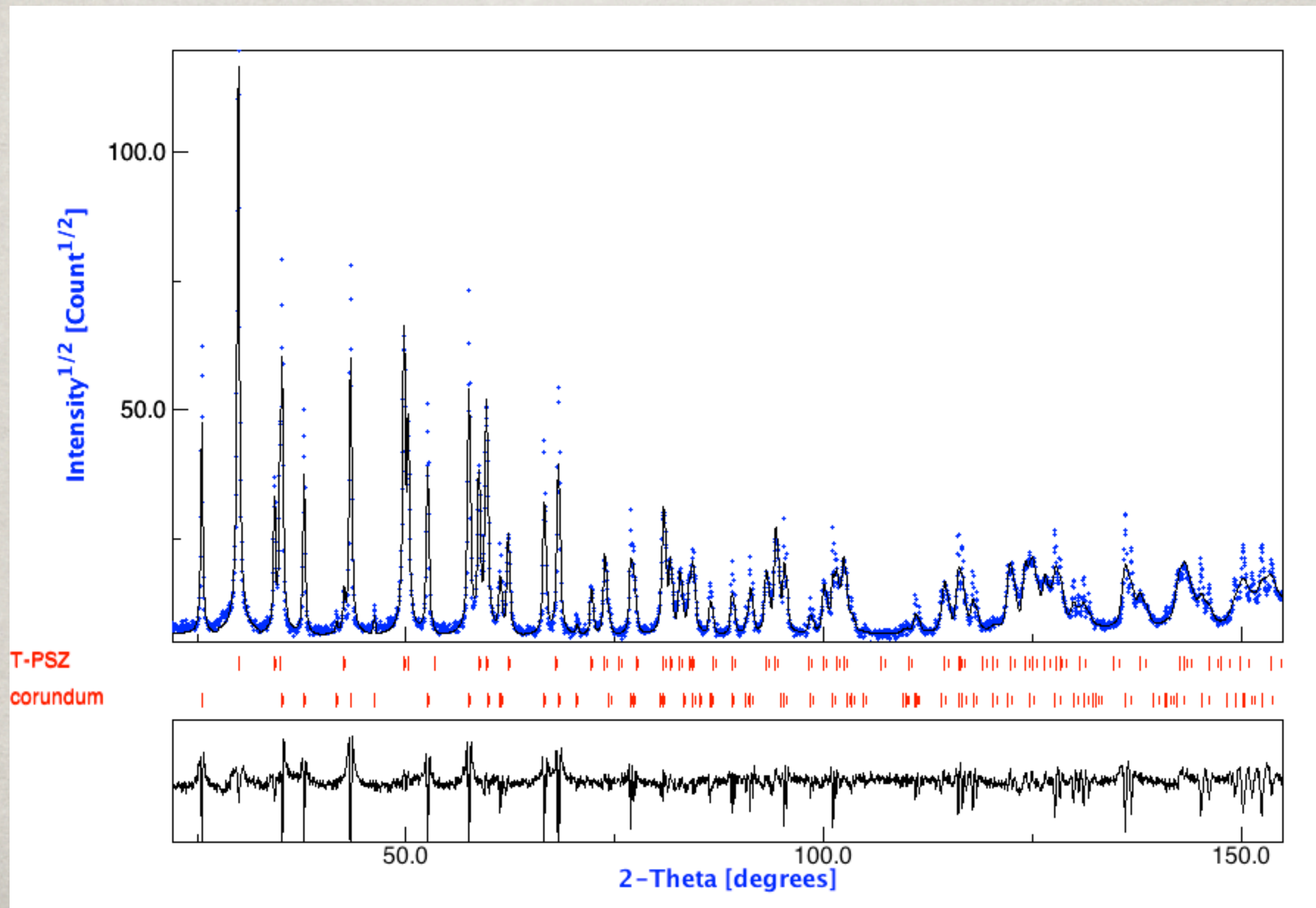
Step 1: Refining scale factors and background

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



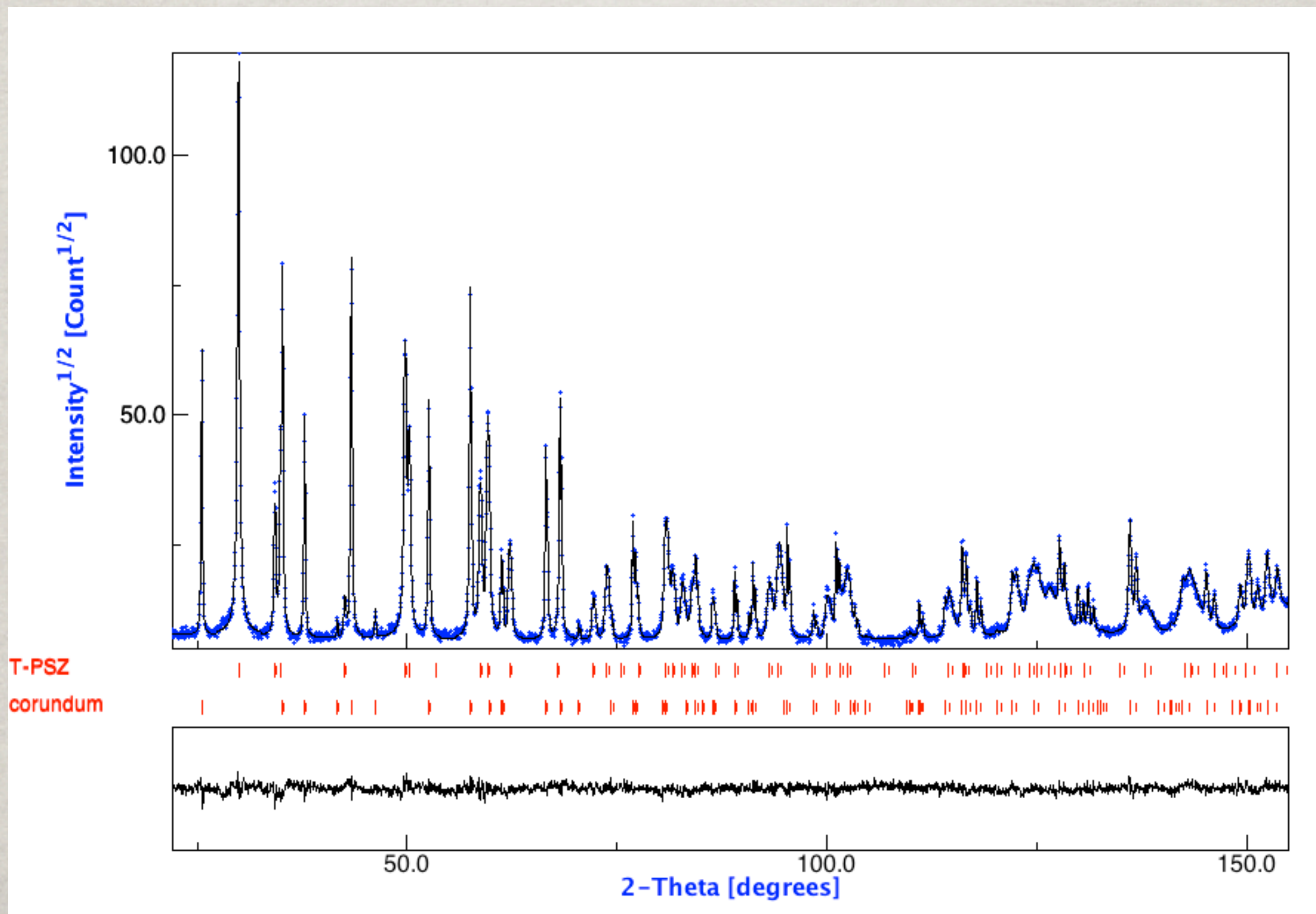
STEP 2: PEAKS POSITIONS

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



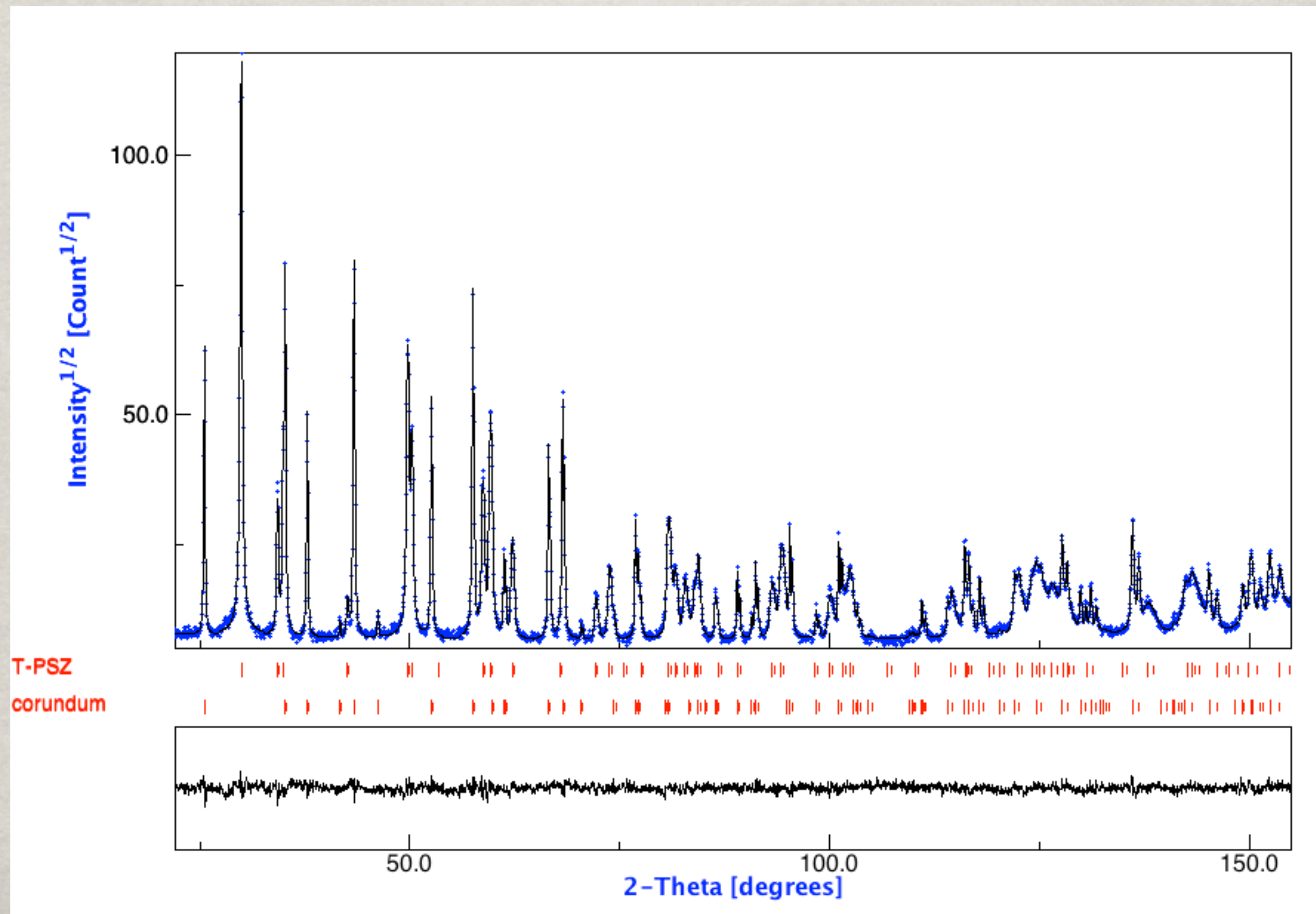
Step 3: peaks shapes

- 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%



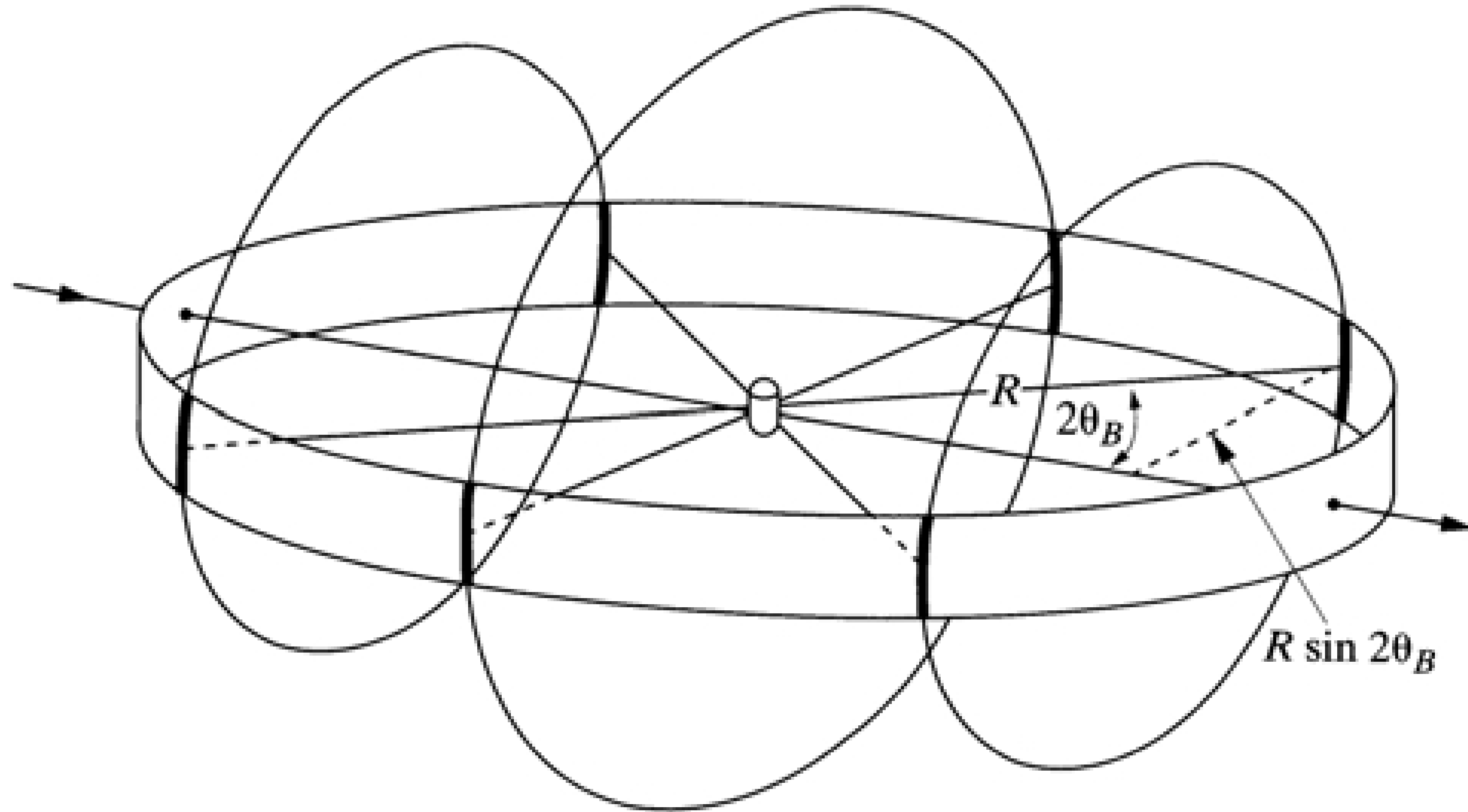
Quality of the experiment

- 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

- Rietveld analyses do not require at all the most powerful instrument but the one suitable for the analysis:
  - quantitative analyses of samples with big grain sizes (metal?, high crystal symmetries) require a diffracting volume of statistical significance => large sampling volume, large beam, with not too low divergence => a medium to low resolution diffractometer
  - structural refinements of low symmetries compounds (monoclinic, triclinic) require often a high resolution diffractometer
- A low and linear background is the first requirement
- No additional lines (beta lines) are also in general preferred
- Large collectable ranges are important
- High diffraction intensities should be achieved
- Smaller peak broadening help the analysis reducing overlaps
- Simple geometries are better for subsequent Rietveld fitting
- There is not the perfect instrument to get everything

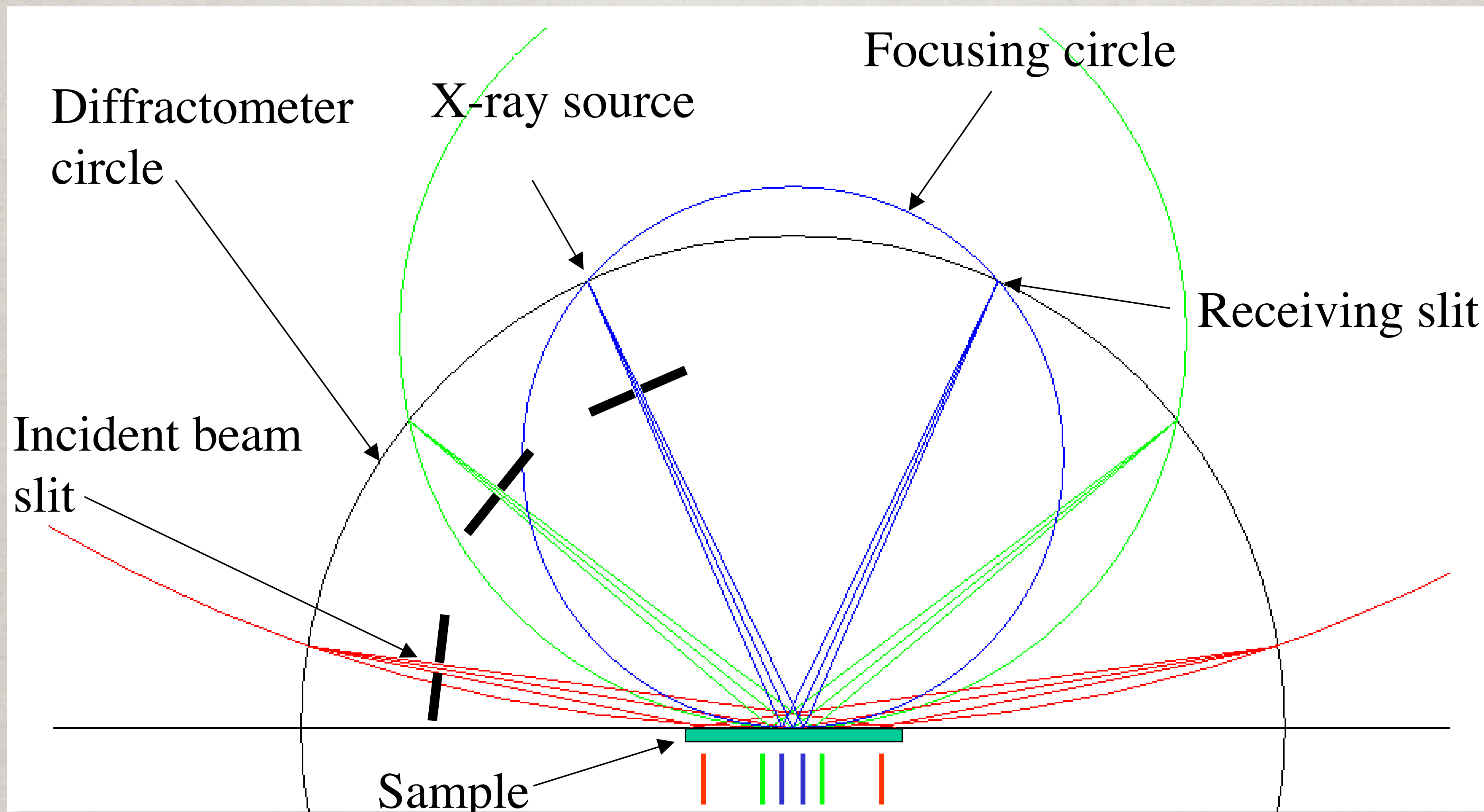
Powder diffraction and Debye-Scherrer camera



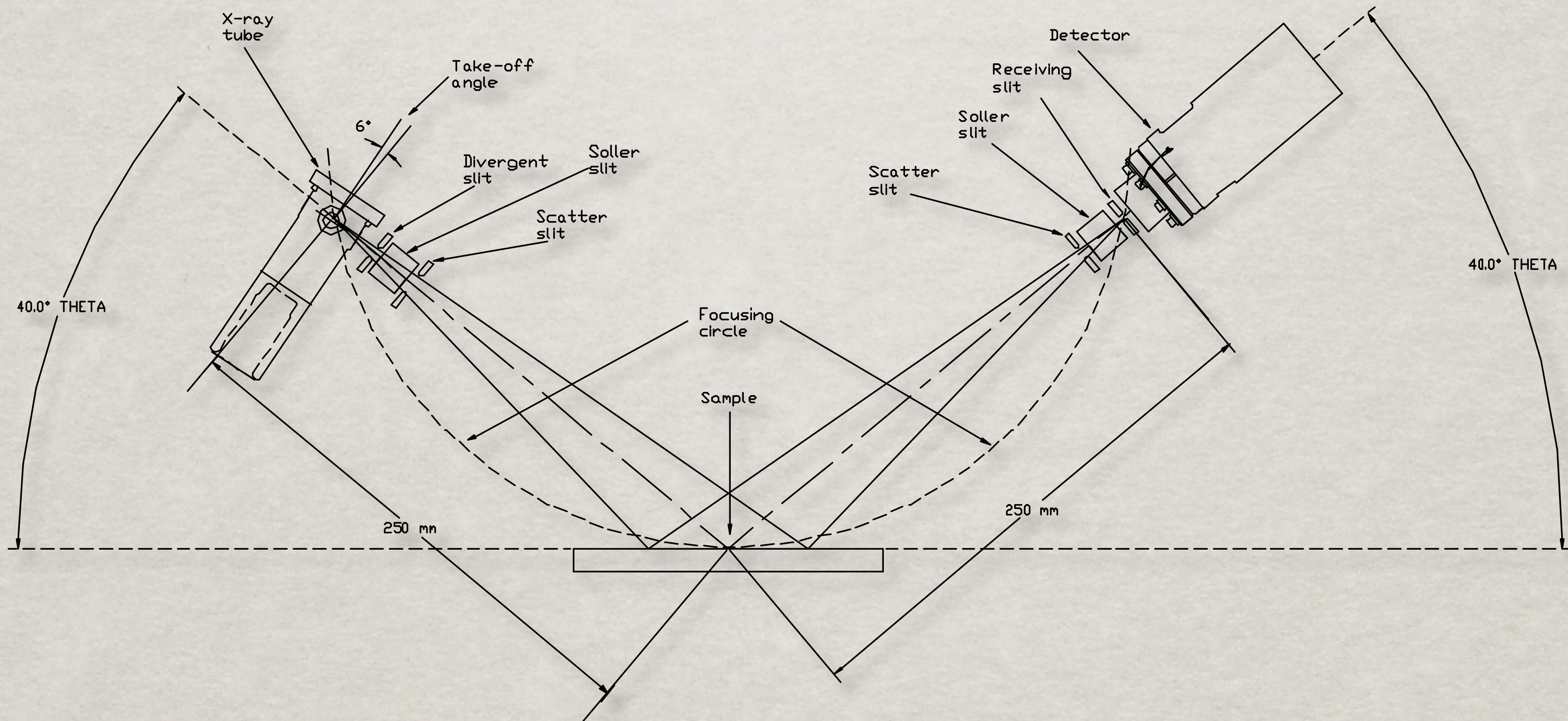
A modern diffractomer

Bragg Brentano 2-THETA:THETA Setup

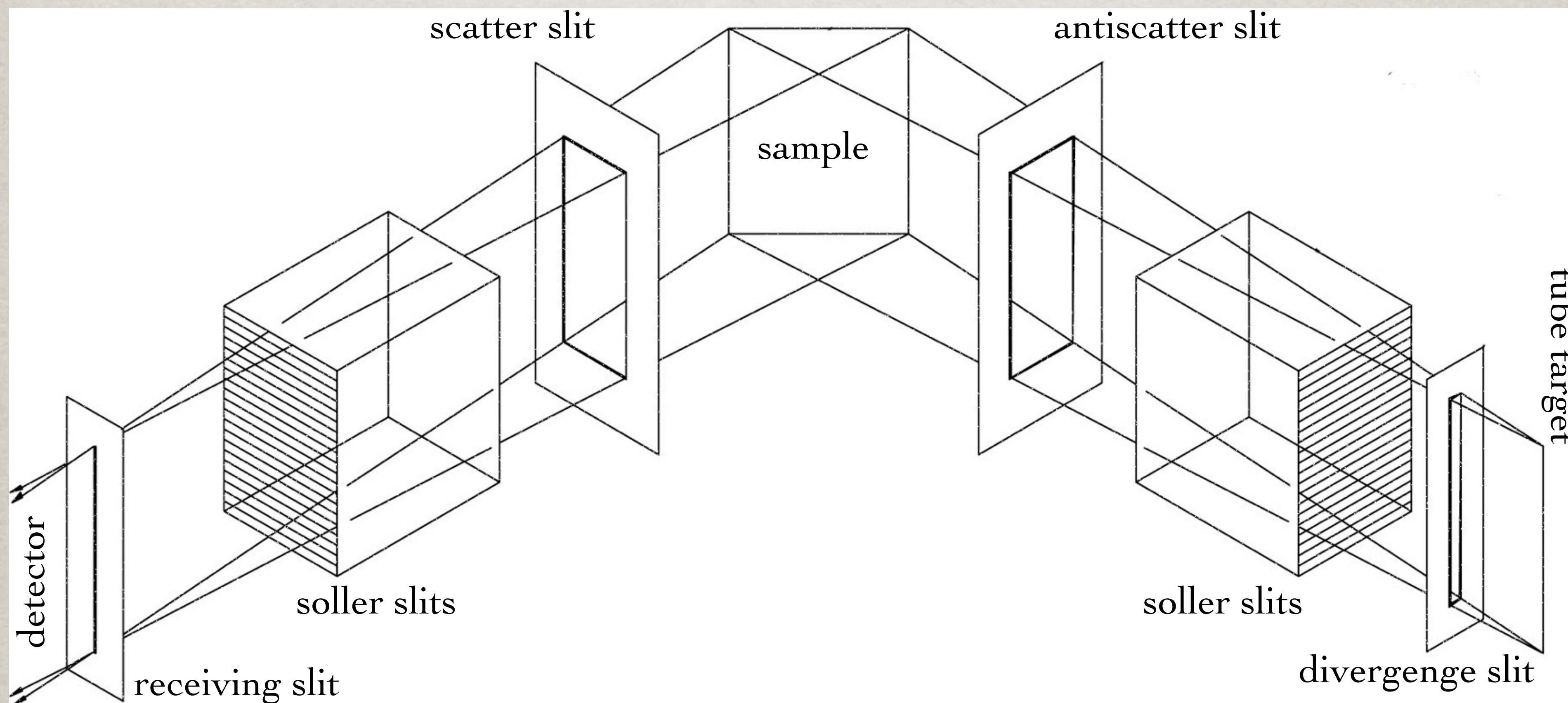
Parafocusing circle (Bragg-Brentano)



Theta-theta diffractometer



Slits system in Bragg-Brentano



High resolution instruments

- These instruments put the emphasis on the smaller line width obtainable:
  - Pro:
    - less overlapped peaks (more details for structural refinements)
    - higher accuracy for microstructural analyses
    - better separation for multiple phases
    - smaller sampling volumes
    - higher cell determination accuracy
  - Cons:
    - smaller sampling volumes
    - low divergence (less grain statistic) => less accuracy in intensity
    - smaller intensities => higher collection times
    - more difficult to fit
    - more sensible to models
- Good for structural refinements when high precision is requested

Low resolution instruments

- Pro:
  - higher intensities
  - better statistics (higher sampling volumes, more grains diffracting)
  - faster collection times
  - easier to fit
- Cons:
  - less details for complicated structures or samples
  - less precision (not always less accuracy)
  - not suitable for low symmetries compounds or determination of size-strain for highly crystallized samples
- These instruments are good for normal quantitative and qualitative analyses or when good statistic of grains is required (texture etc.).

A good overall instrument

- For quantitative analysis:
  - medium resolution
  - monochromator on the diffracted beam
  - Cu radiation ?
- Structural refinements or structure determination
  - high resolution (and high intensities => very long collection times)
  - monochromator
  - no $K\alpha_2$ (structure determination)
- Microstructural analyses
  - high resolution
- Texture and residual stress analyses
  - medium to low resolution
  - fast collection times
  - extremely good statistic

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

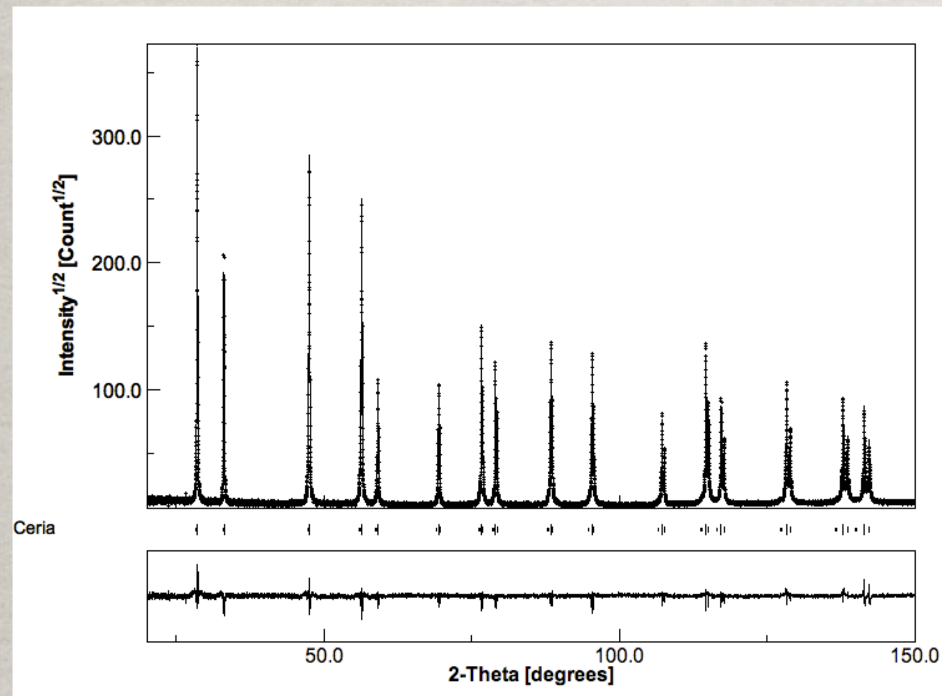
- The background should be linear, no strange bumps, no additional lines and as low as possible

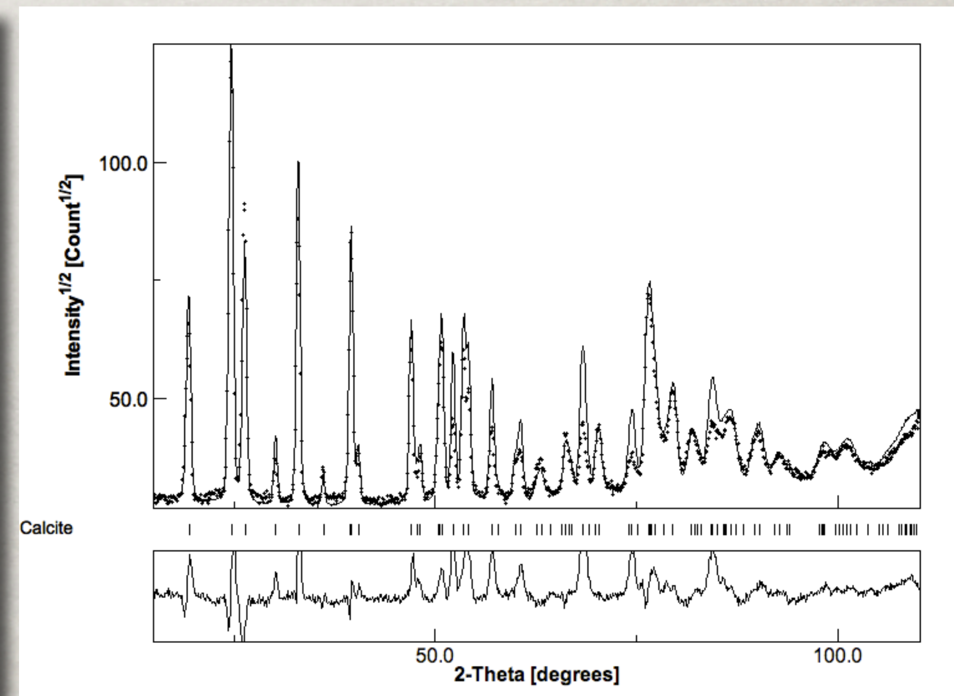
- Check the omega zero

- 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 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° 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)

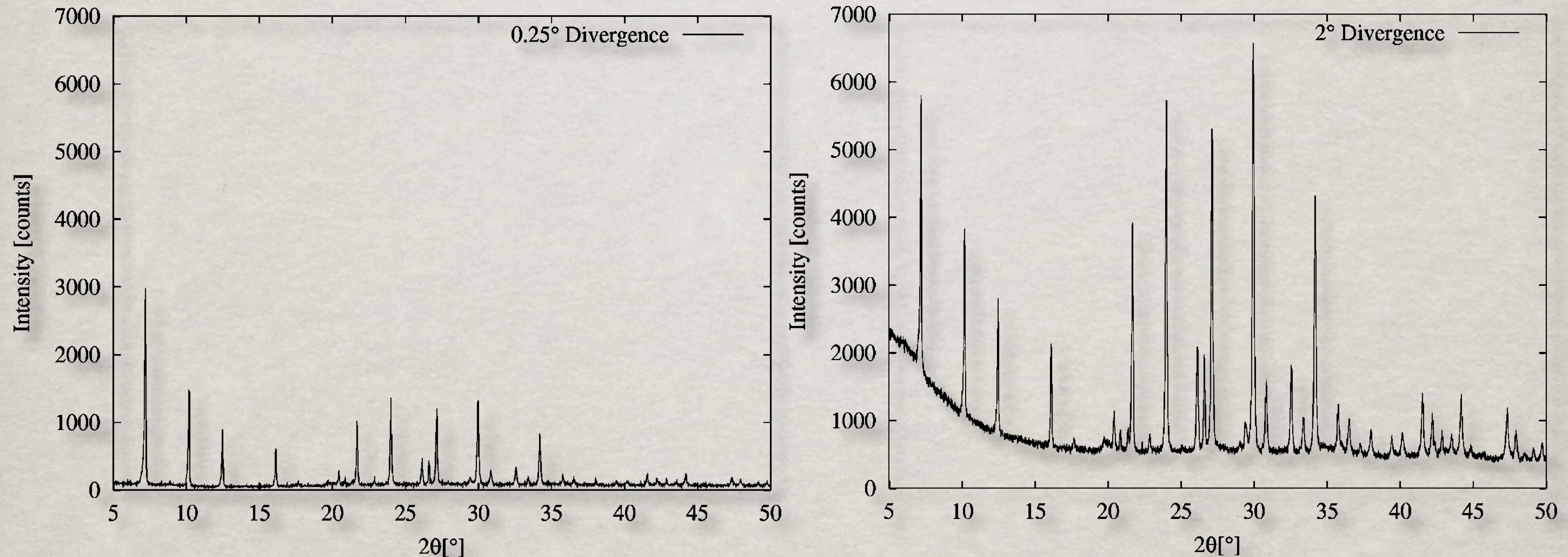
Total collection time

- 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!

Sample characteristics (1)

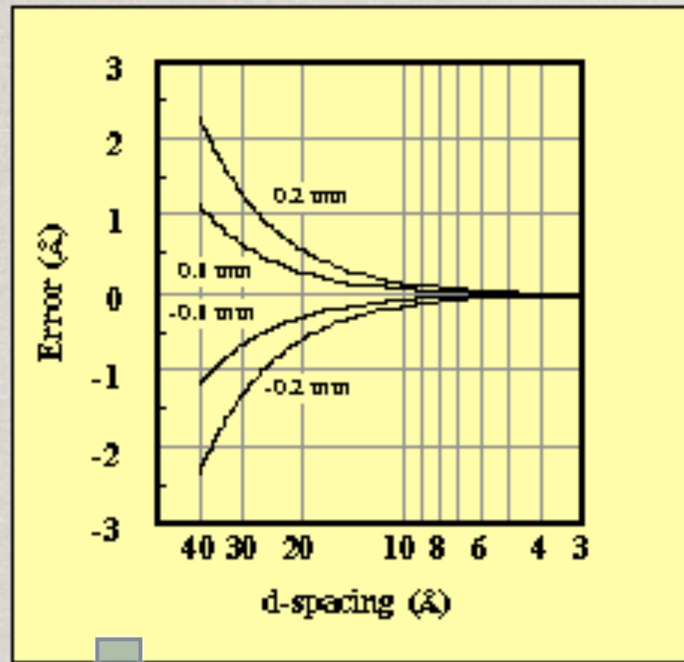
- The sample should be sufficiently large that the beam will be always entirely inside its volume/surface (for Bragg-Brentano check at low angle and sample thickness/transparency).

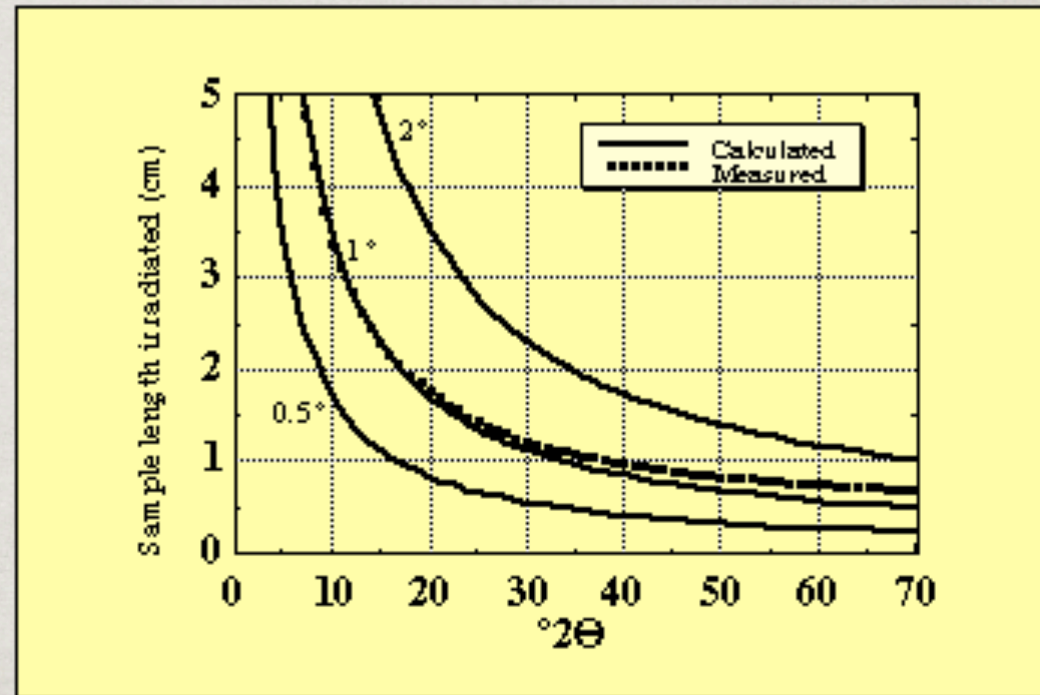
Zeolite sample, changing beam divergence, Krüger and Fischer, J. Appl. Cryst., *37*, *472*, *2004*.



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

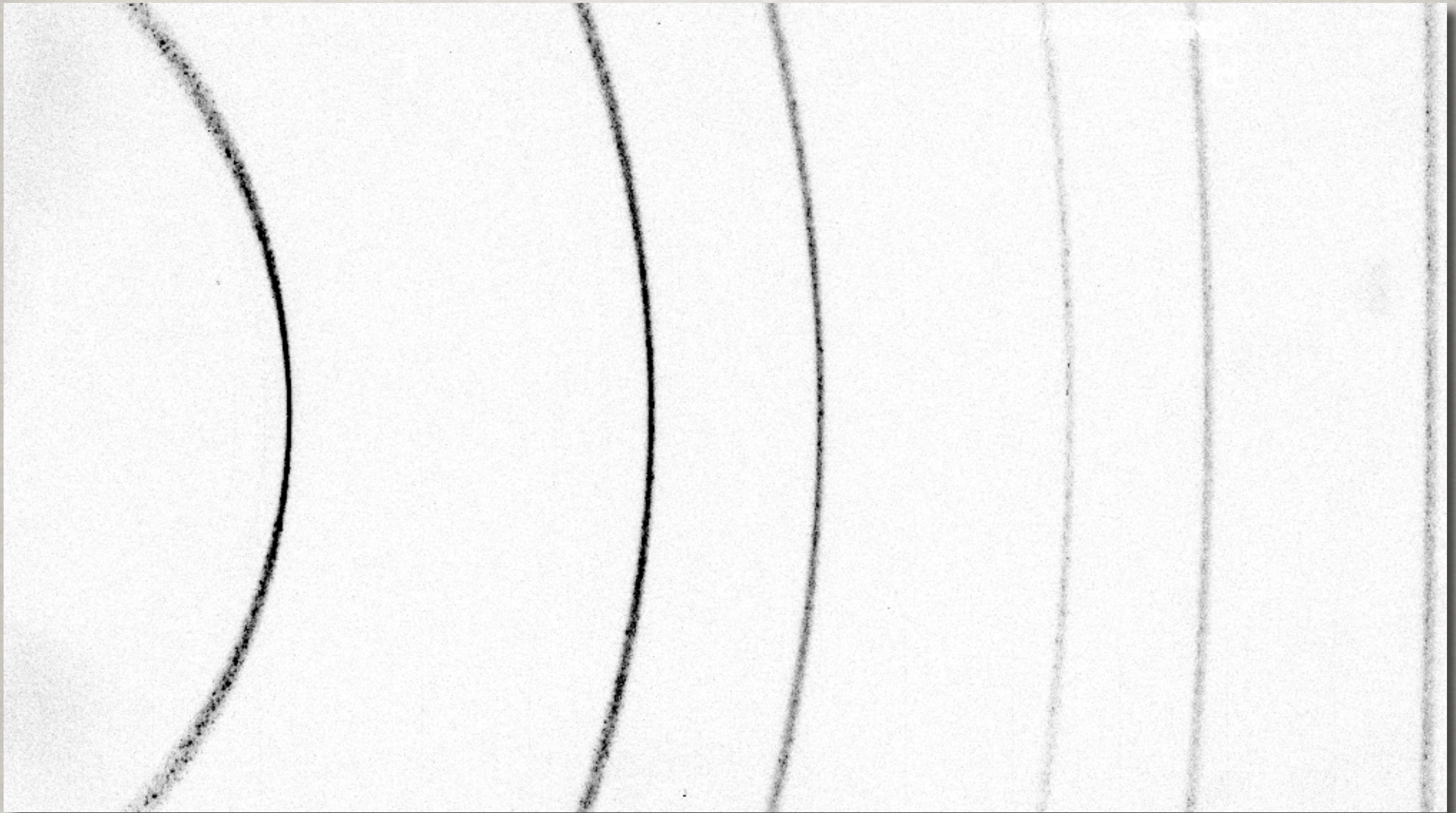
Sample characteristics (2)



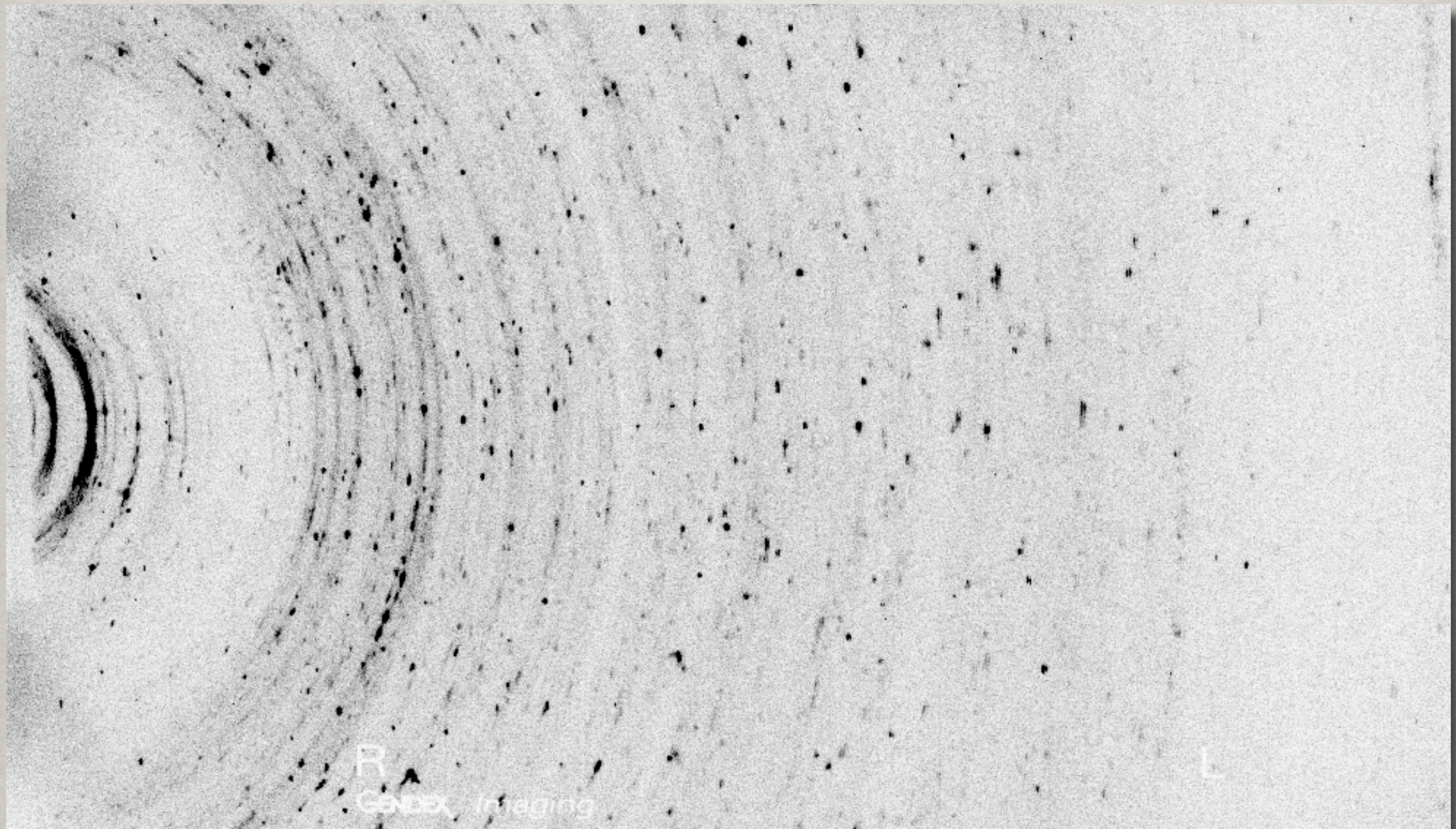


- Sample position is critical for good cell parameters (along with perfect alignment of the instrument).
- The number of diffracting grains at each position should be significant (> 1000 grains). Remember that only a fraction is in condition for the diffraction. Higher beam divergence or size increases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

Non classical Rietveld applications

- Along with the refinement of crystal structures the concept of the Rietveld method has been extended to other diffraction analyses. Most of them more useful for people working on material science. These are:

  - Quantitative phase analyses
  - Amorphous quantification
  - Microstructural analyses
  - Texture and Residual stresses

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