Introduction to Rietveld refinements

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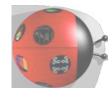
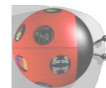


The Rietveld method

- 1964-1966 - Need to refine crystal structures from powder. Peaks too much overlapped:
  - Groups of overlapping peaks introduced. Not sufficient.
  - Peak separation by least squares fitting (gaussian profiles). Not for severe overlapping.
- 1967 - First refinement program by H. M. Rietveld, single reflections + overlapped, no other parameters than the atomic parameters. Rietveld, Acta Cryst. 22, 151, 1967.
- 1969 - First complete program with structures and profile parameters. Distributed 27 copies (ALGOL).
- 1972 - Fortran version. Distributed worldwide.
- 1977 Wide acceptance. Extended to X-ray data.
- Today: the Rietveld method is widely used for different kind of analyses, not only structural refinements.

- "If the fit of the assumed model is not adequate, the precision and accuracy of the parameters cannot be validly assessed by statistical methods". Prince.



Principles 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:

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

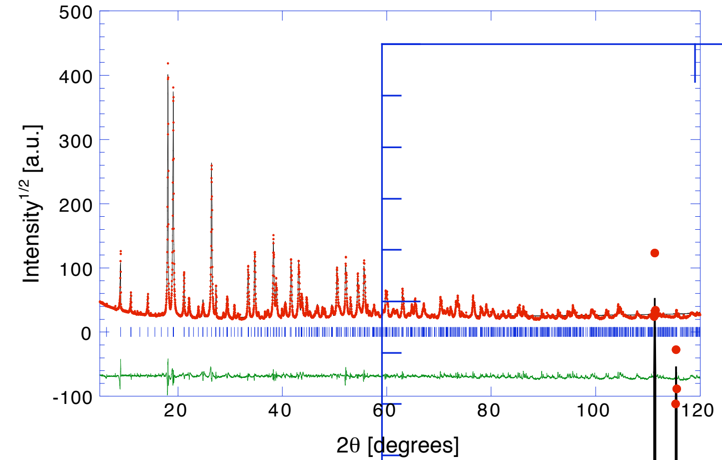
P_k = preferred orientation function

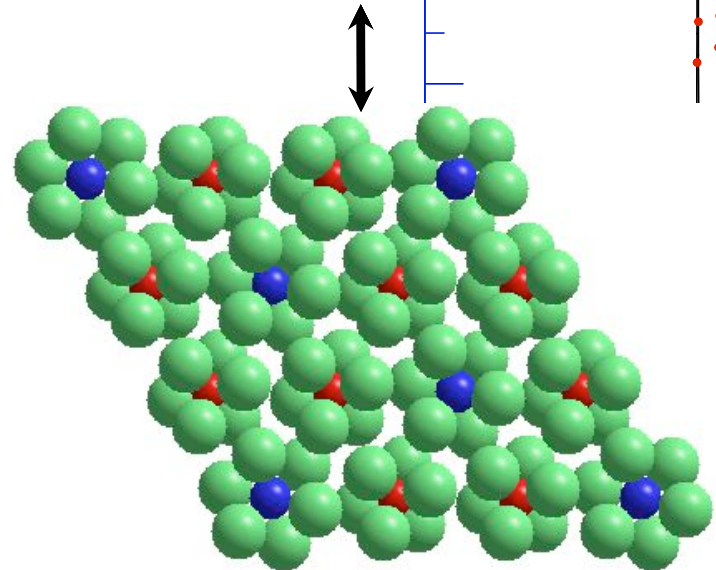
$S(2\theta_i - 2\theta_k)$ = profile shape function

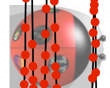
(PV : η,HWHM)

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

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







Non classical Rietveld applications

- Quantitative analysis of crystalline phases (Hill & Howard, J. Appl. Cryst. 20, 467, 1987)

$$I_i^{calc} = \sum_{n=1}^{Nphases} S_n \sum_k L_k \left|F_{k;n}\right|^2 S\left(2\theta_i - 2\theta_{k;n}\right) P_{k;n} A + bkg_i$$

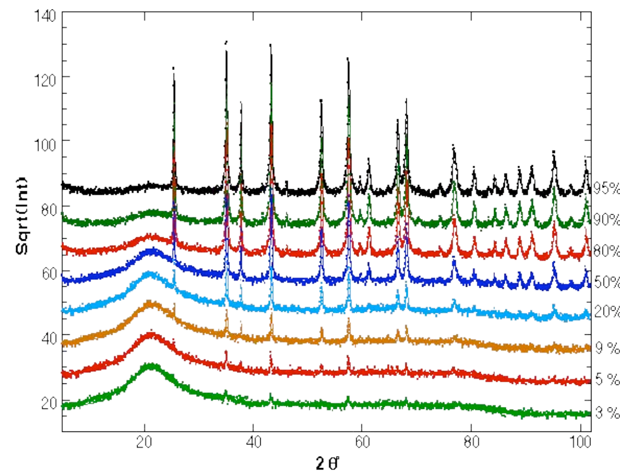
$$W_p = \frac{S_p (ZMV)_p}{\sum_{n=1}^{Nphases} S_n (ZMV)_n}$$

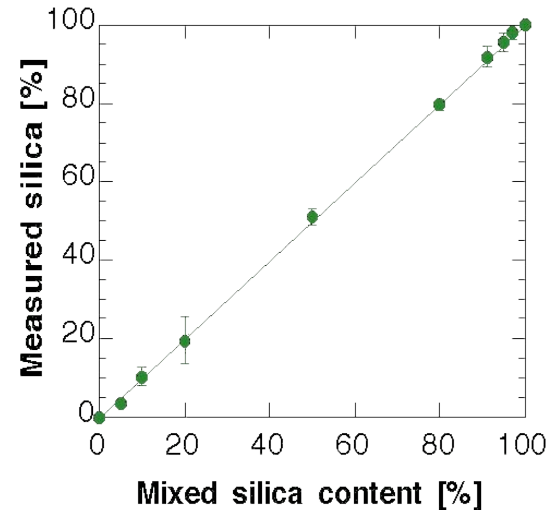
Z = number of formula units

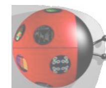
M = mass of the formula unit

V = cell volume

- Non crystalline phases (Lutterotti et al, 1997)
  - Using Le Bail model for amorphous (need a pseudo crystal structure)

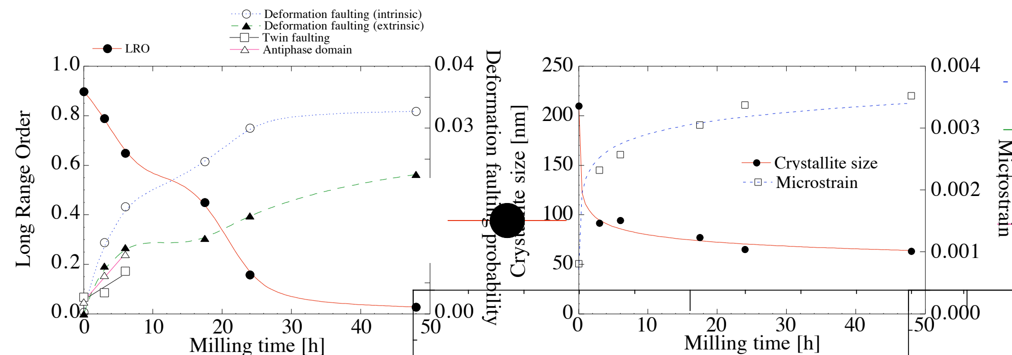


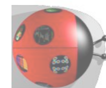




Non classical Rietveld applications

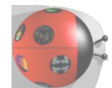
- Microstructure:
  - Le Bail, 1985. Profile shape parameters computed from the crystallite size and microstrain values (<M> and <ϵ2>1/2)
    - More stable than Caglioti formula
    - Instrumental function needed
  - Popa, 1998 (J. Appl. Cryst. 31, 176). General treatment for anisotropic crystallite and microstrain broadening using harmonic expansion.
  - Lutterotti & Gialanella, 1998 (Acta Mater. 46(1), 101). Stacking, deformation and twin faults (Warren model) introduced.





Rietveld Stress and Texture Analysis (RiTA)

- Characteristics of Texture Analysis:
  - Powder Diffraction
  - Quantitative Texture Analysis needs single peaks for pole figure meas.
  - Less symmetries -> too much overlapped peaks
  - Solutions: Groups of peaks (WIMV, done), peak separation (done)
- What else we can do? -> Rietveld like analysis?
  - 1992. Popa -> harmonic method to correct preferred orientation in one spectrum.
  - 1994. Ferrari & Lutterotti -> harmonic method to analyze texture and residual stresses. Multispectra measurement and refinement.
  - 1994. Wenk, Matthies & Lutterotti -> Rietveld+WIMV for Rietveld Texture analysis.
  - 1997. GSAS got the harmonic method (wide acceptance?).

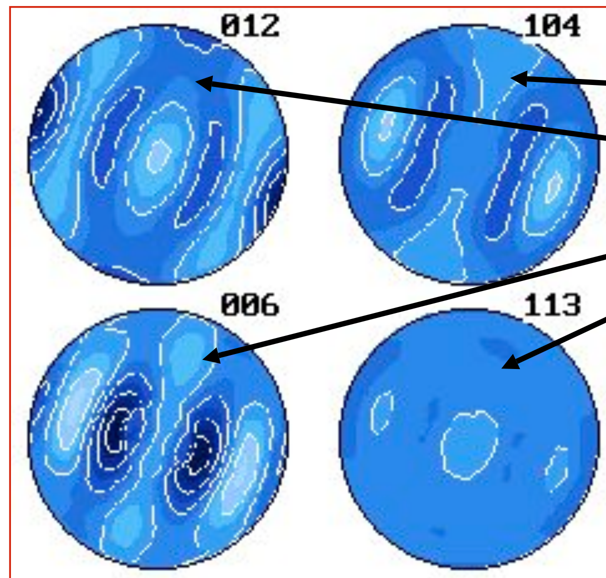


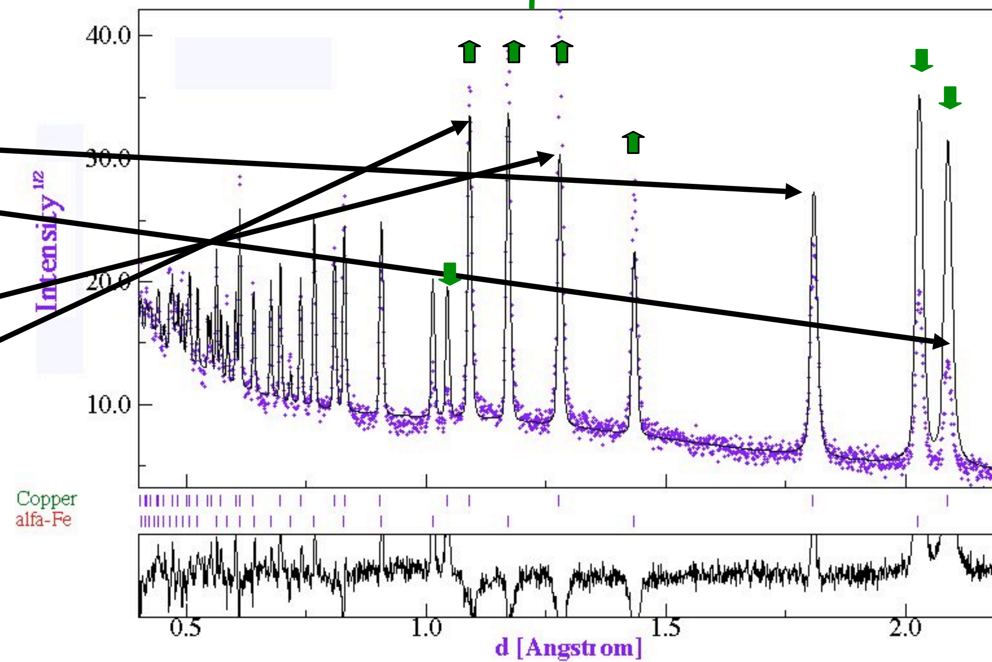
Non classical applications: Texture

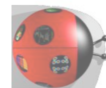
Orientation Distribution Function (ODF)

From pole figures

From spectra







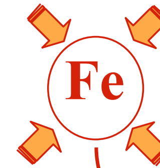
Non classical applications: strains & stresses

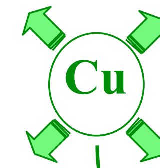
- **Macro elastic strain tensor (I kind)**
- **Crystal anisotropic strains (II kind)**

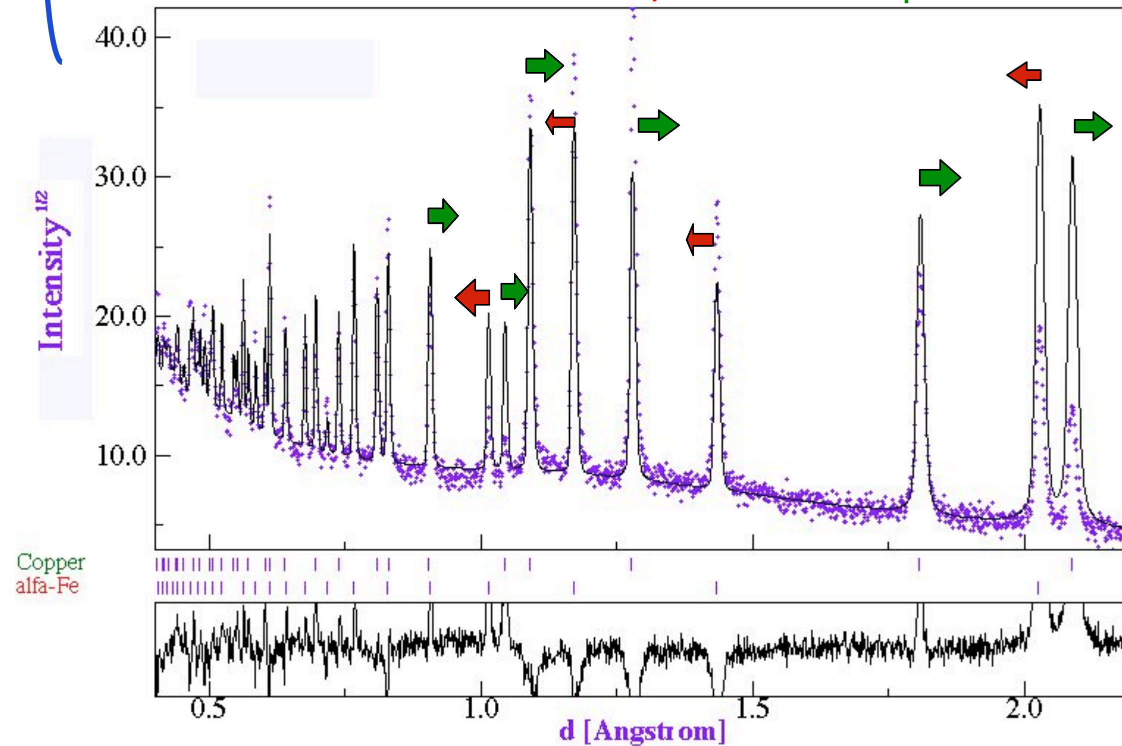
C

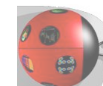
Macro and micro stresses

Applied macro stresses









The classical Rietveld method

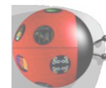
- The function to minimize by a least squares method (non linear):

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

- 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

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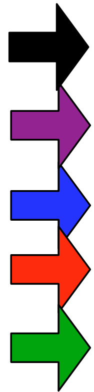
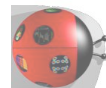
- The spectrum (at a 2θ point i) is determined by:



  - 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



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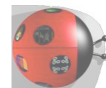
- The more used background in Rietveld refinements is a polynomial function in 2θ :

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

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



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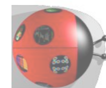
- Starting with the “Diffraction Intensities”, the factors are:
  - A scale factor for each phase
  - A Lorentz-Polarization factor
  - The multiplicity
  - The structure factor
  - The temperature factor
  - The absorption
  - The texture
  - Problems: extinctions, absorption contrast, graininess, sample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



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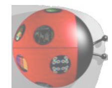
- The scale factor (for each phase) is written in classical Rietveld programs as:

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

  - 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.



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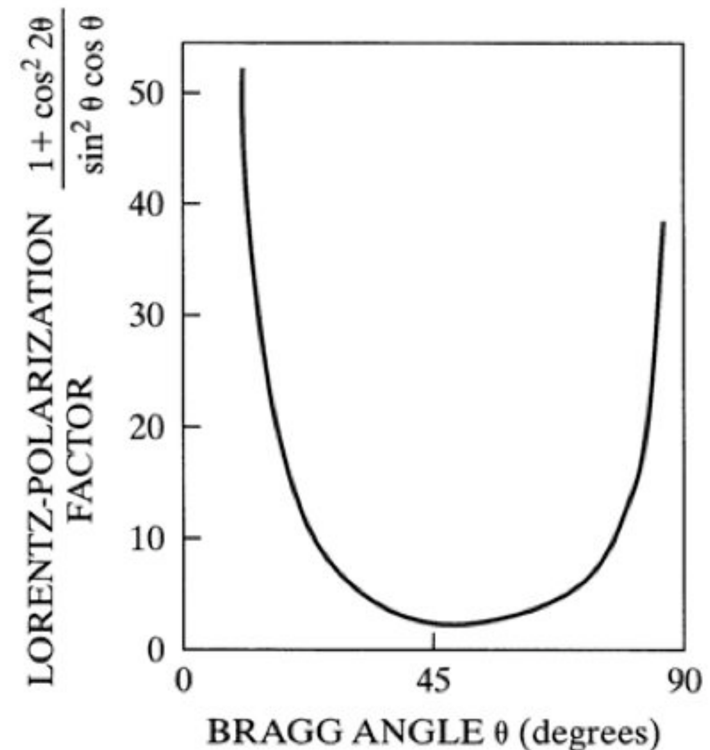
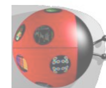
$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

- 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:

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





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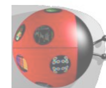
- Under a generalized structure factor we include:
  - The multiplicity of the k reflection (with h, k, l Miller indices): m_k
  - The structure factor
  - The temperature factor: B_n

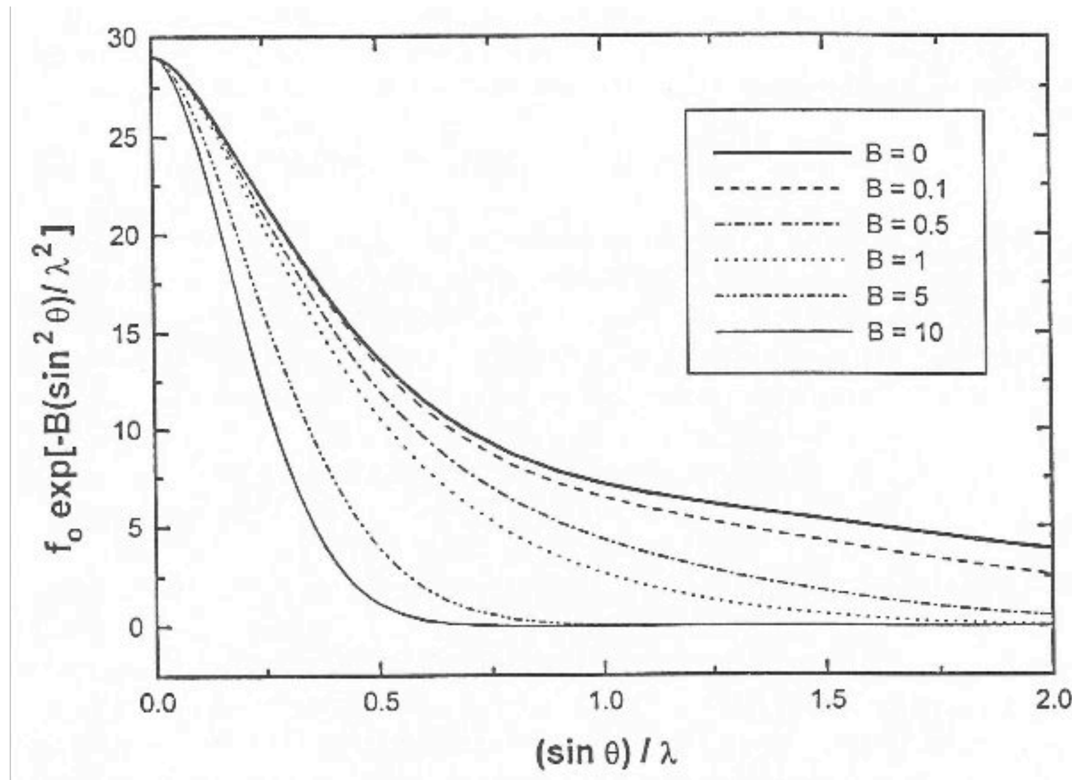
$$\left|F_{k,j}\right|^2 = m_k \left| \sum_{n=1}^{N} f_n e^{-B_n \frac{\sin^2\theta}{\lambda^2}} \left(e^{2\pi i\left(hx_n + ky_n + lz_n\right)}\right) \right|^2$$

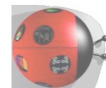
- N = number of atoms
- x_n, y_n, z_n coordinates of the nth atom
- f_n, atomic scattering factor



Atomic scattering factor and Debye-Waller

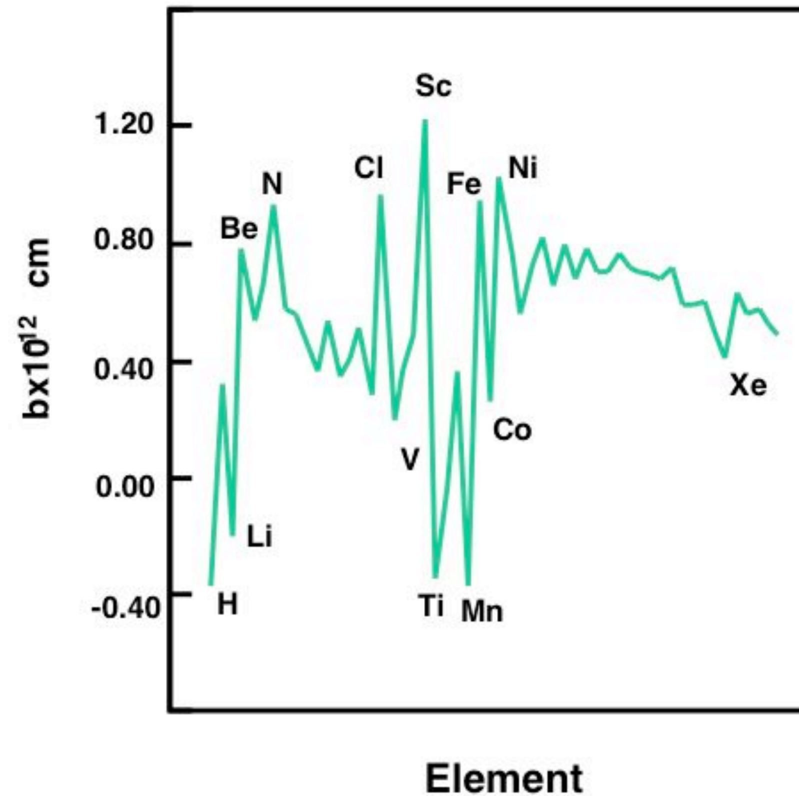
- The atomic scattering factor for X-ray decreases with the diffraction angle and is proportional to the number of electrons. For neutron is not correlated to the atomic number.
- The temperature factor (Debye-Waller) accelerate the decreases.

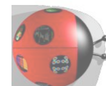




Neutron scattering factors

- For light atoms neutron scattering has some advantages
- For atoms very close in the periodic table, neutron scattering may help distinguish them.





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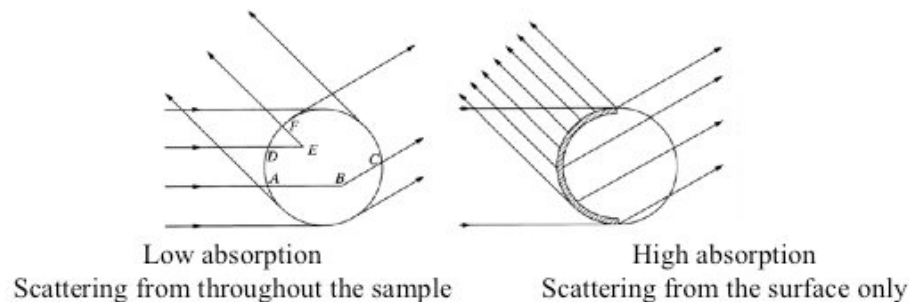
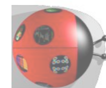
- The absorption factor:
    - in the Bragg-Brentano case (thick sample):

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

    - 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)



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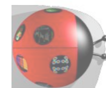
- The texture (or preferred orientations):
  - The March-Dollase formula is used:

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

    - 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)



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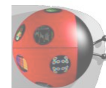
- The profile shape function:
  - different profile shape function are available:
    - Gaussian (the original Rietveld function for neutrons)
    - Cauchy
    - Voigt and Pseudo-Voigt (PV)
    - Pearson VII, etc.
  - For example the PV:

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

- the shape parameters are:

$$\text{Caglioti formula}: \quad \omega^2 = W + V\tan\theta + U\tan^2\theta$$

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



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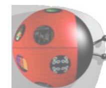
- The number of peaks is determined by the symmetry and space group of the phase.
- One peak is composed by all equivalent reflections m_k
- The position is computed from the d-spacing of the hkl reflection (using the reciprocal lattice matrix):

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

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



Quality of the refinement

- Weighted Sum of Squares:

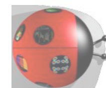
$$WSS = \sum_{i=1}^{N} \left[w_i \left(I_i^{\exp} - I_i^{calc} \right) \right]^2, \qquad w_i = \frac{1}{\sqrt{I_i^{\exp}}}$$

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

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

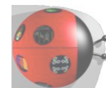
$$R_{\exp} = \sqrt{\frac{(N - P)}{\sum_{i=1}^{N} \left[w_i I_i^{\exp} \right]^2}}, \qquad w_i = \frac{1}{\sqrt{I_i^{\exp}}}$$

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



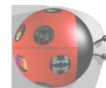
The R indices

- 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.



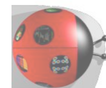
WSS and GofF (or sigma)

- 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



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