Powder diffraction and the Rietveld method

- Principles
- Example

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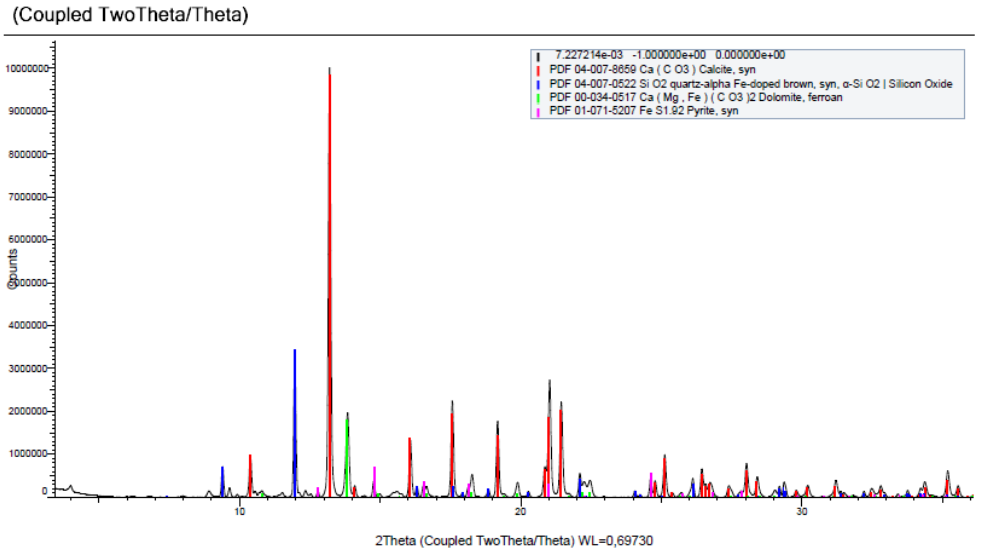
Analysis of powder diffraction data

The fingerprint method

- The position and relative intensities of Bragg peaks are unique for a crystalline phase → a «fingerprint».
- «Automatic» identification of known phases from databases (powder X-ray diffraction!)



Analysis of powder diffraction data

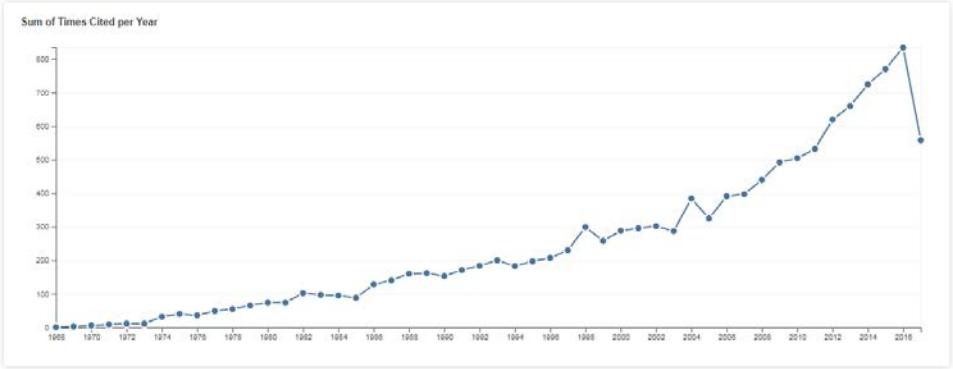
Crystal structure determination

Indexing	Find the size and shape of the unit cell
Space group determination	Find the space group or possible space groups
Structure solution	Find the approximate atomic arrangement within the unit cell
Structure refinement	Make the structure model as accurate as possible

Analysis of powder diffraction data.

The Rietveld method

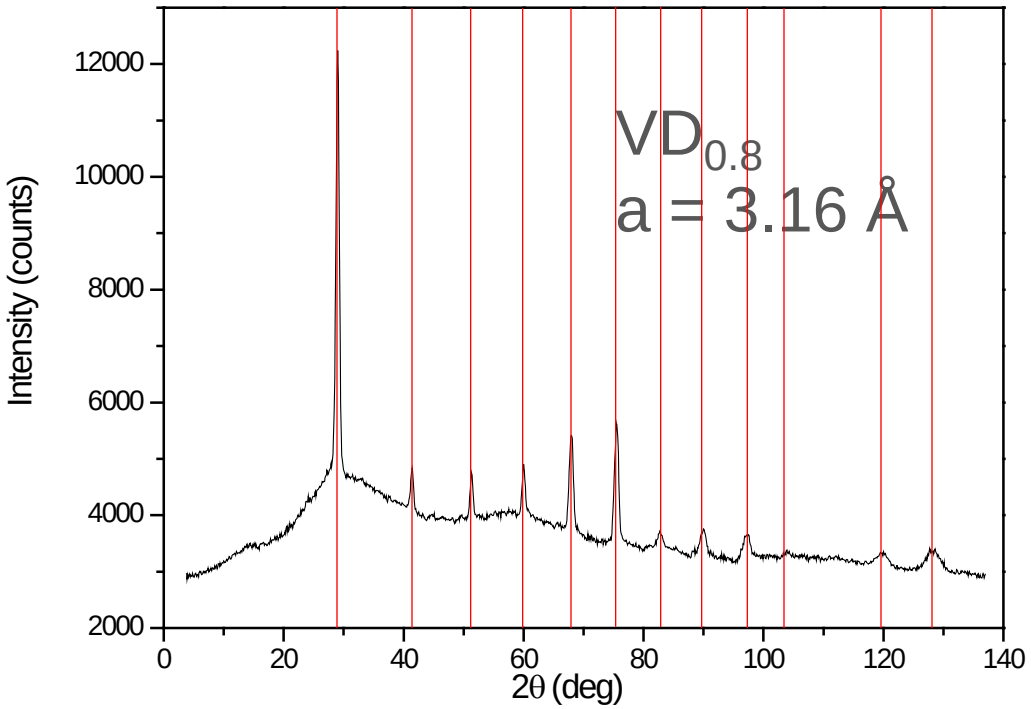
- Introduced by Hugo Rietveld in 1967
  H. M. Rietveld, Acta Cryst. 22 (1967) 151
  H. M. Rietveld, J. App. Cryst. 2 (1969) 65
- Revolutionized analysis of powder diffraction data. Cited 12324 times.



- Developed as a technique for *structure refinement*.

The Rietveld method

- Developed as a technique for *structure refinement*.

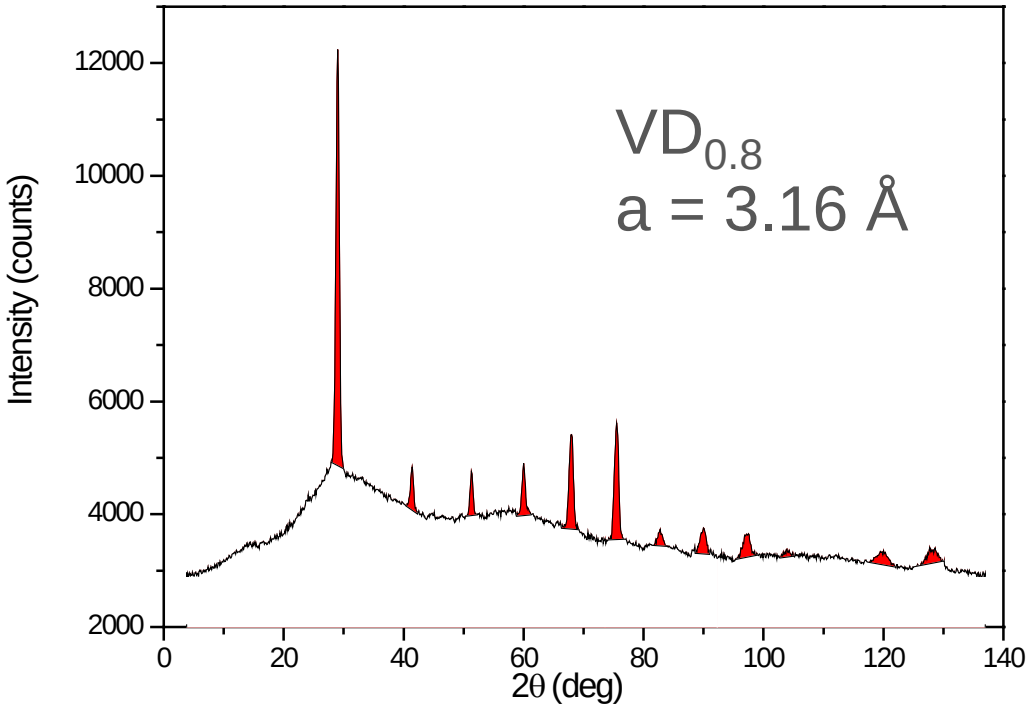


The pre-Rietveld way

hkl	Intensity
110	
200	
211	
220	
310	
....	

The Rietveld method

- Developed as a technique for *structure refinement*.



The pre-Rietveld way

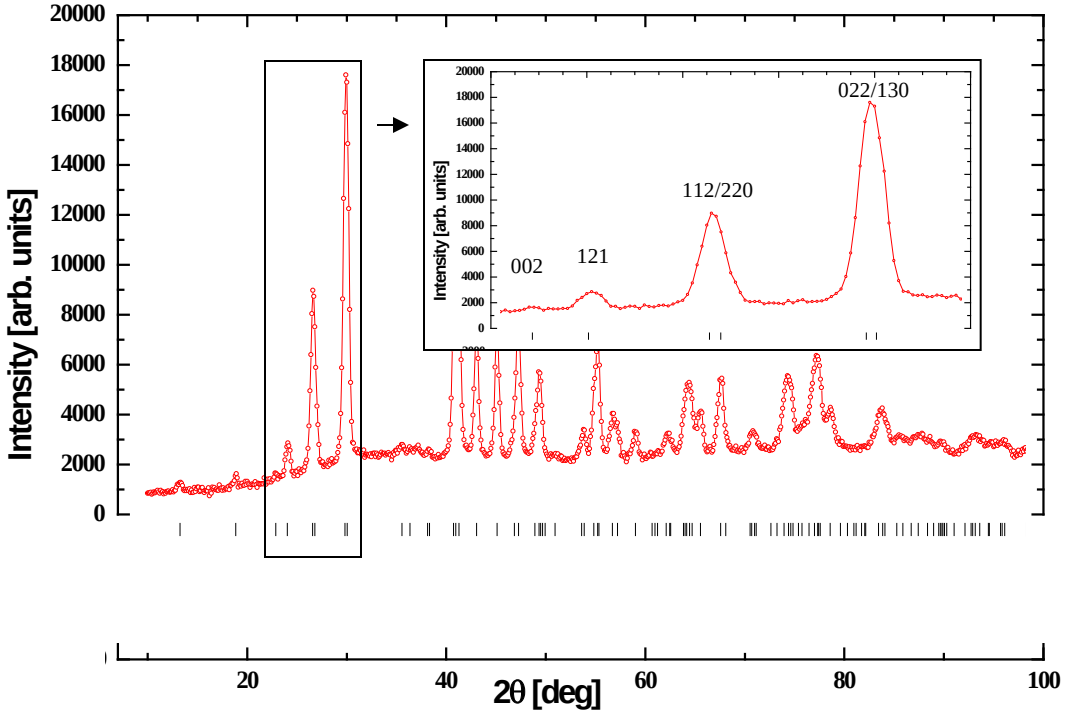
hkl	Intensity
110	1000

$$I_{hkl} \propto \left| \sum_j b_j \cdot e^{2\pi i (hx_j + ky_j + lz_j)} \right|^2$$

310	285
....	....

The Rietveld method

- Developed as a technique for *structure refinement*.



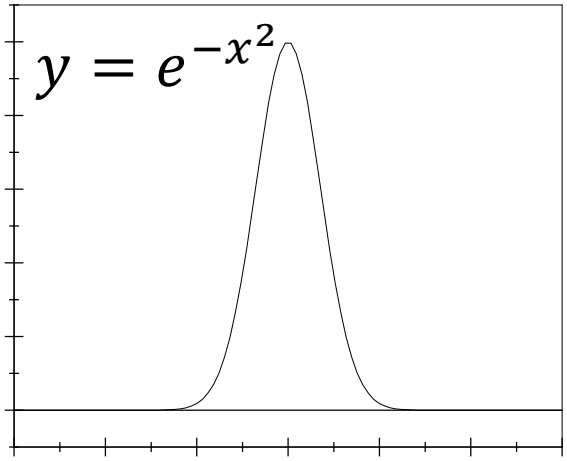
The pre-Rietveld way

hkl	Intensity
101	23
110	34
002	10
121	120
112+220	450
022+130	1000

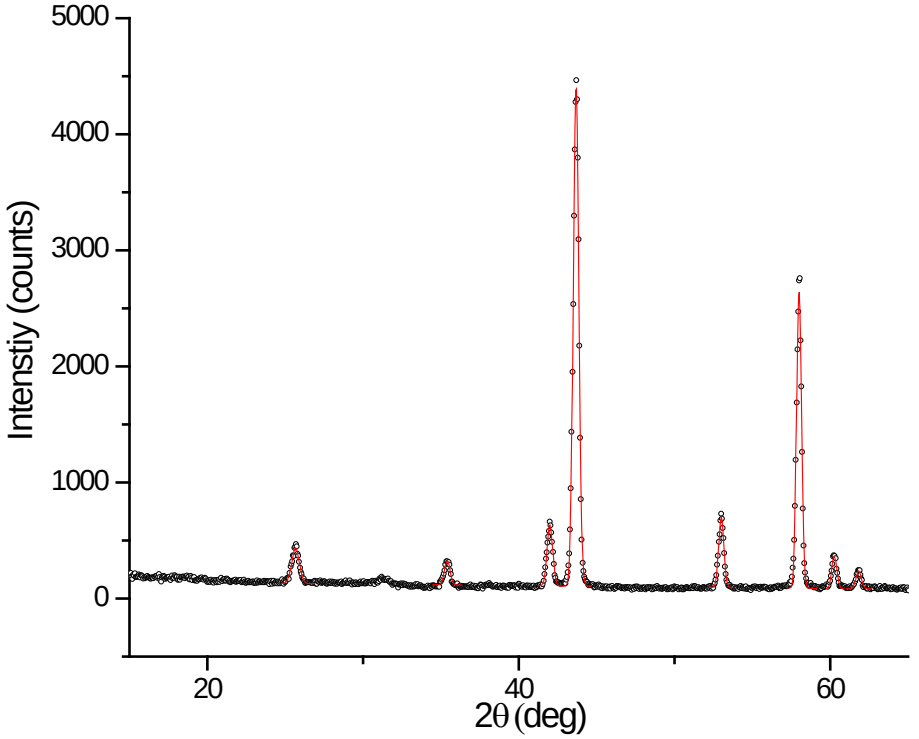
The Rietveld method

Rietveld's observations:

Well-resolved Bragg- peaks in his PND data had the shape of Gaussian curves.



The Gaussian curve



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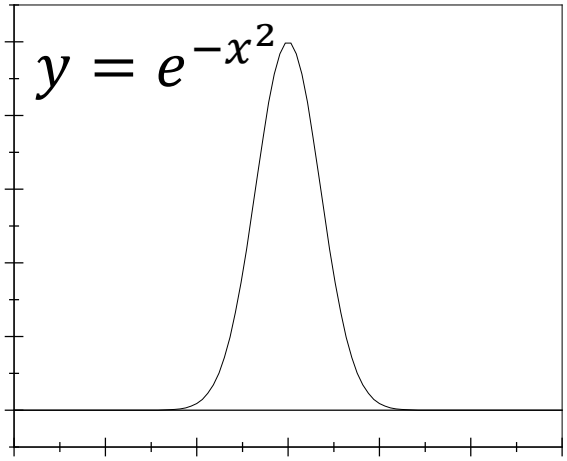

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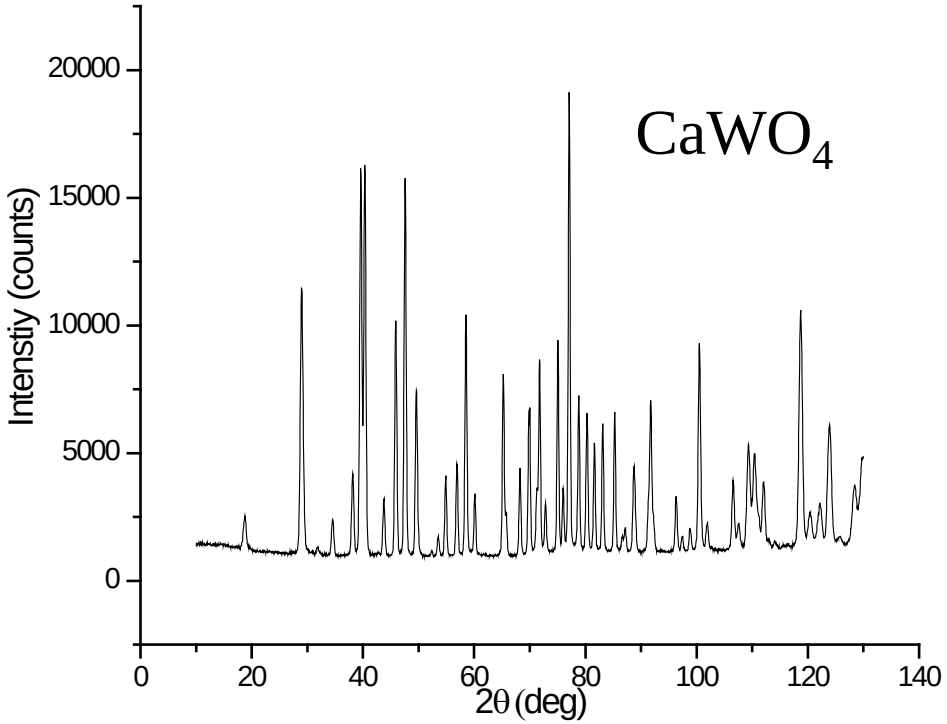

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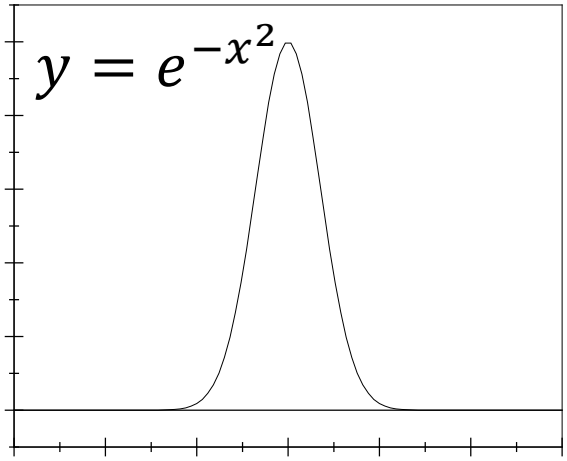

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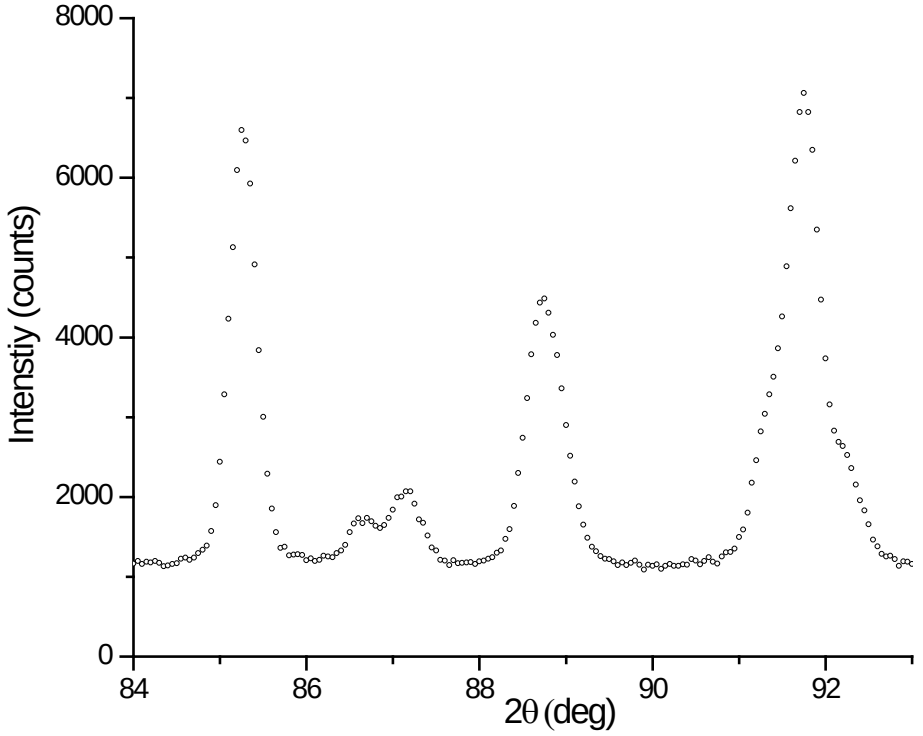

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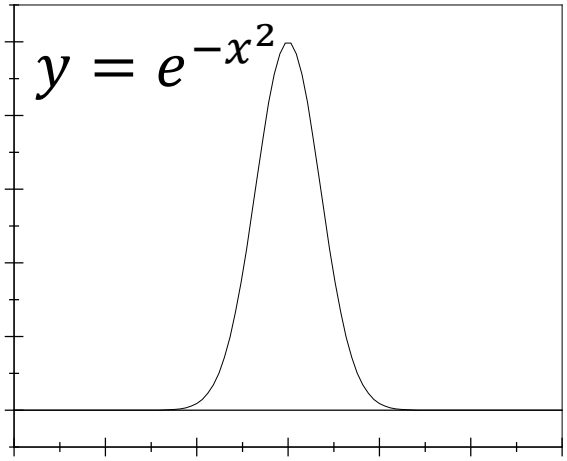

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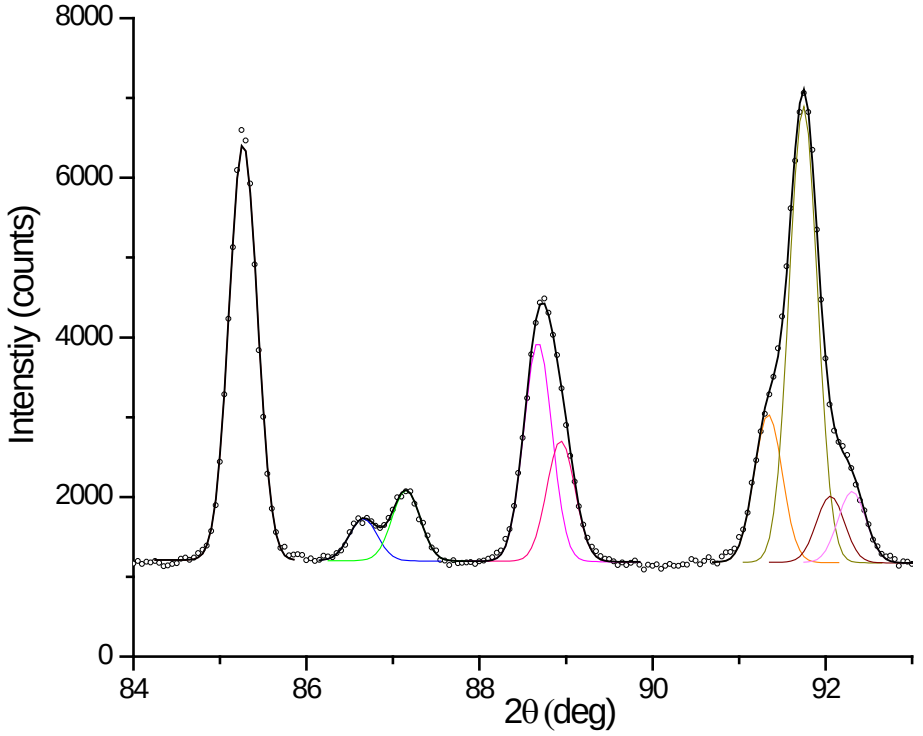
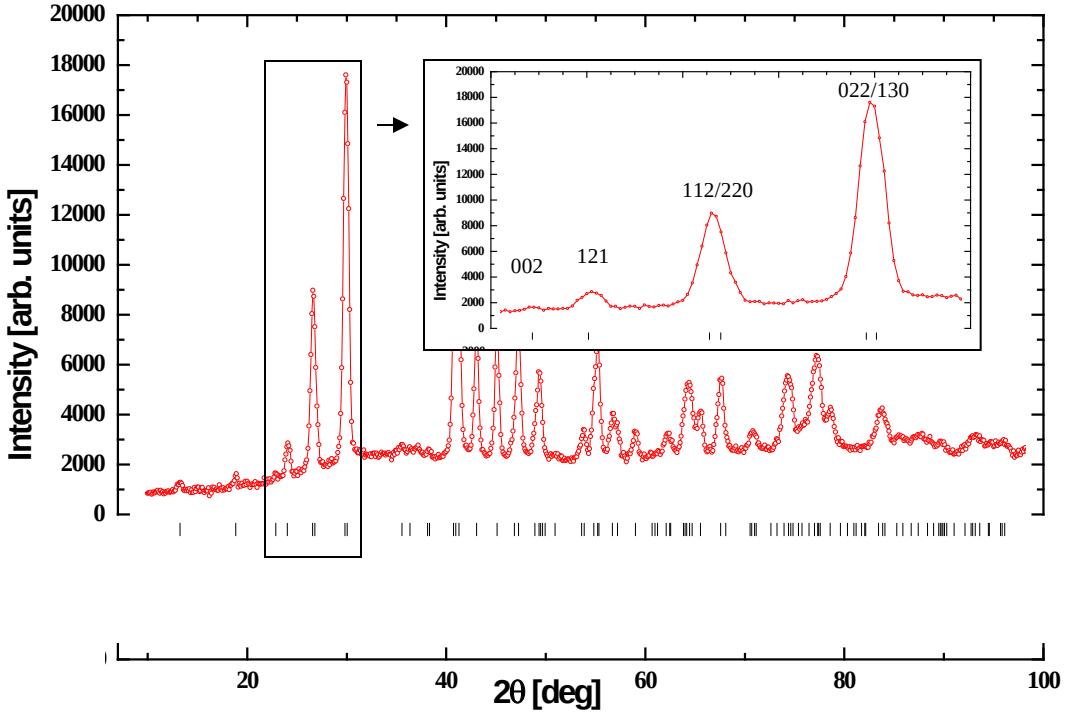


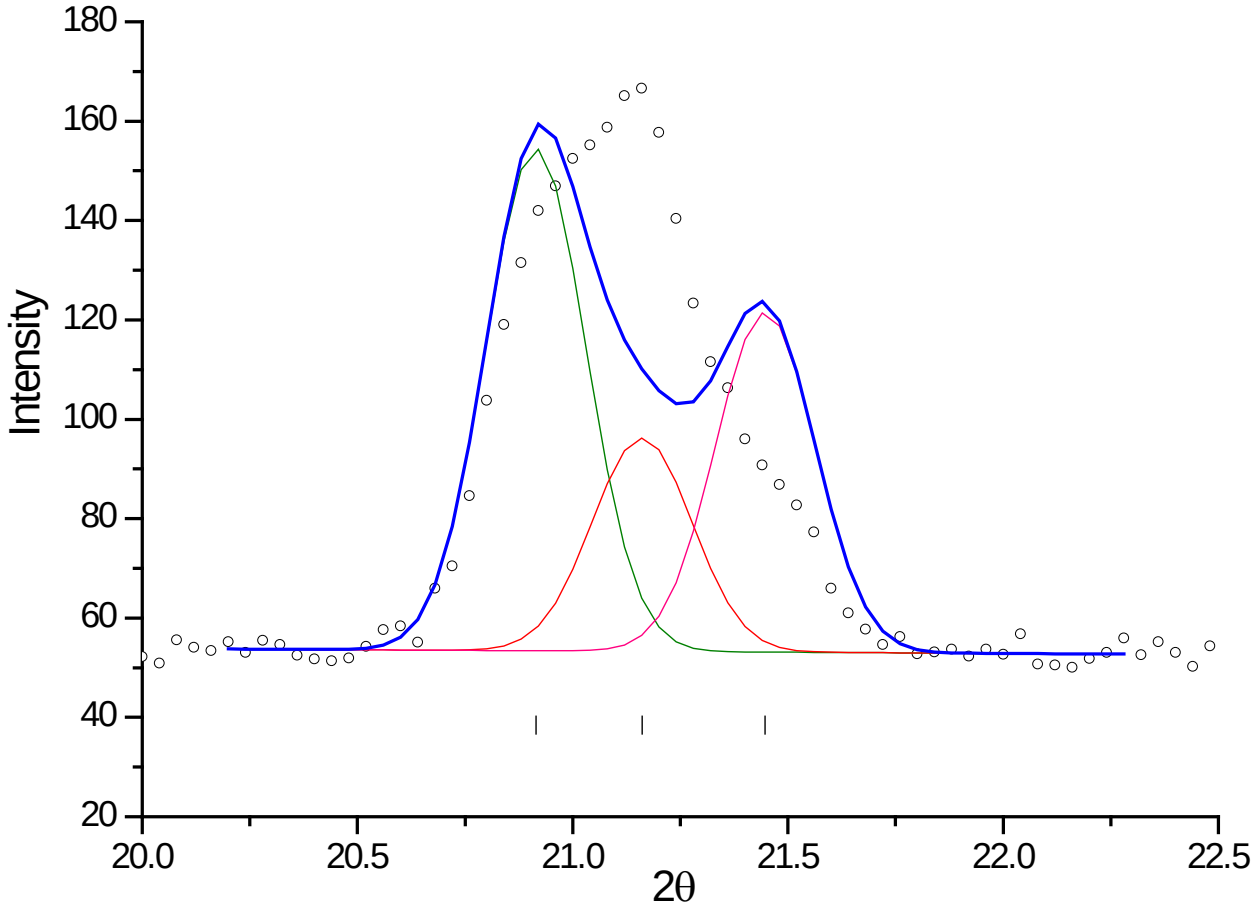
The Rietveld method

- Developed as a technique for *structure refinement*.

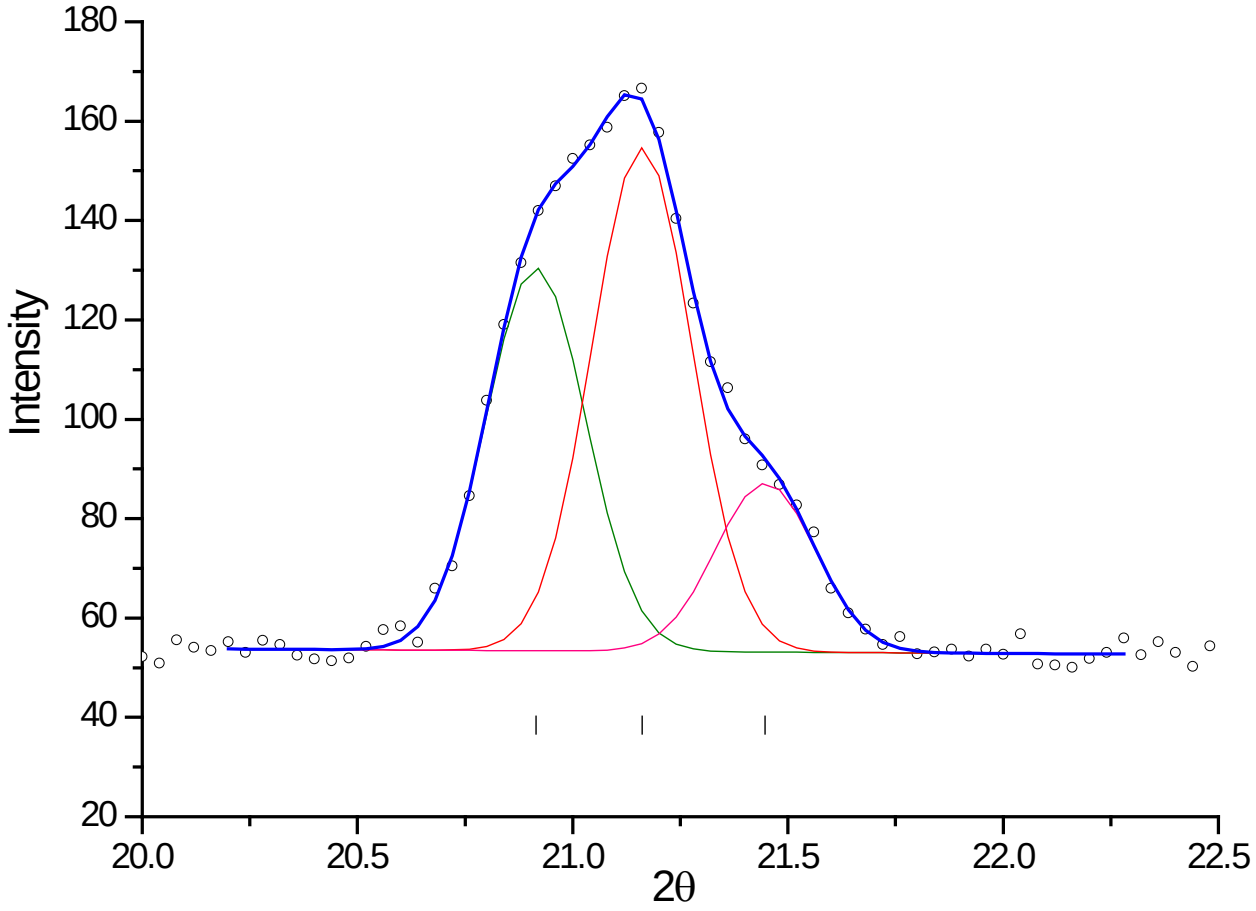


Rietveld's idea: Why not fit the entire calculated profile from the model to the data, instead of just the integrated intensities?

The Rietveld method

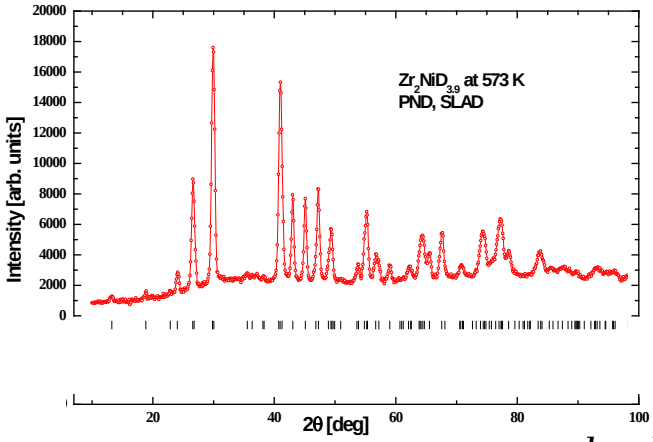


The Rietveld method



The Rietveld method

The calculated profile



$$y_i^{calc} = s\sum_K L_K \left|F_K\right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background}$$

calculated intensity in point *i*

The Rietveld method

The calculated profile

scale factor

$$y_i^{calc} = s \sum_K L_K \left| F_K \right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background}$$

calculated intensity in point *i*

The Rietveld method

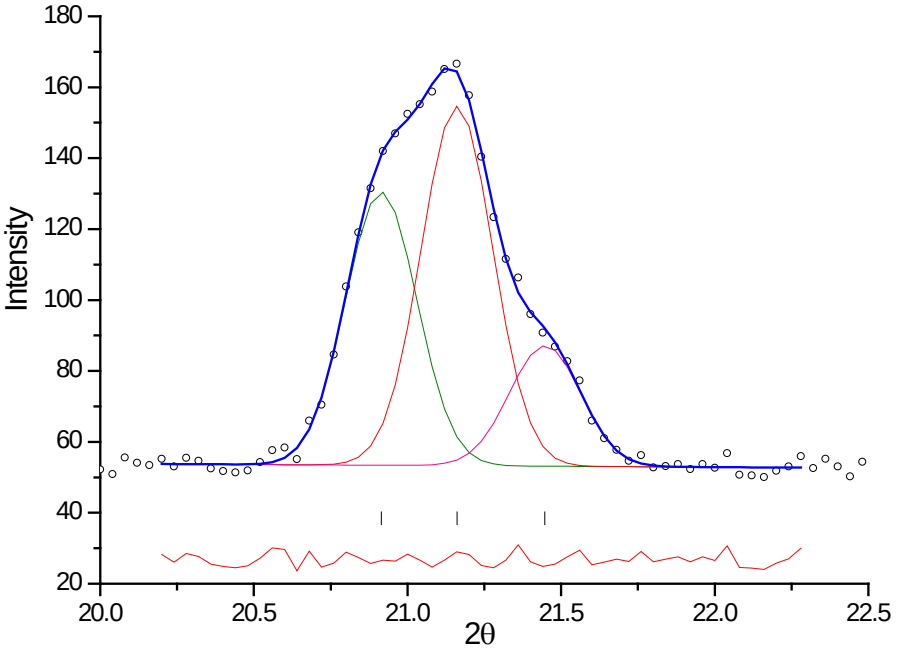
The calculated profile

scale factor

$$y_i^{calc} = s \sum_K L_K \left| F_K \right|^2 \phi(2$$

calculated intensity in point *i*

Sum over all Bragg peaks, K, that contribute with intensity to point *i*

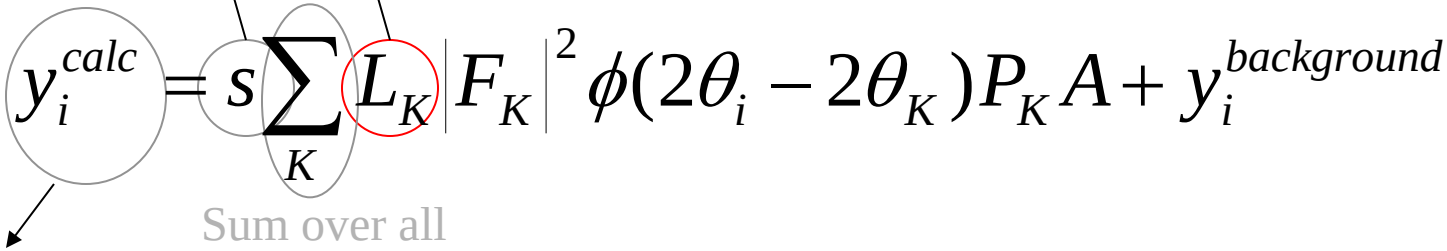


The Rietveld method

The calculated profile

Lorentz factor and multiplicity = $1/(\sin\theta \sin 2\theta)$ for powders

scale factor



calculated intensity in point *i*

Sum over all Bragg peaks, K, that contribute with intensity to point *i*

The Rietveld method

The calculated profile

scale factor

Lorentz factor and multiplicity

$$y_i^{calc} = s\sum_K L_K \left|F_K\right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background}$$

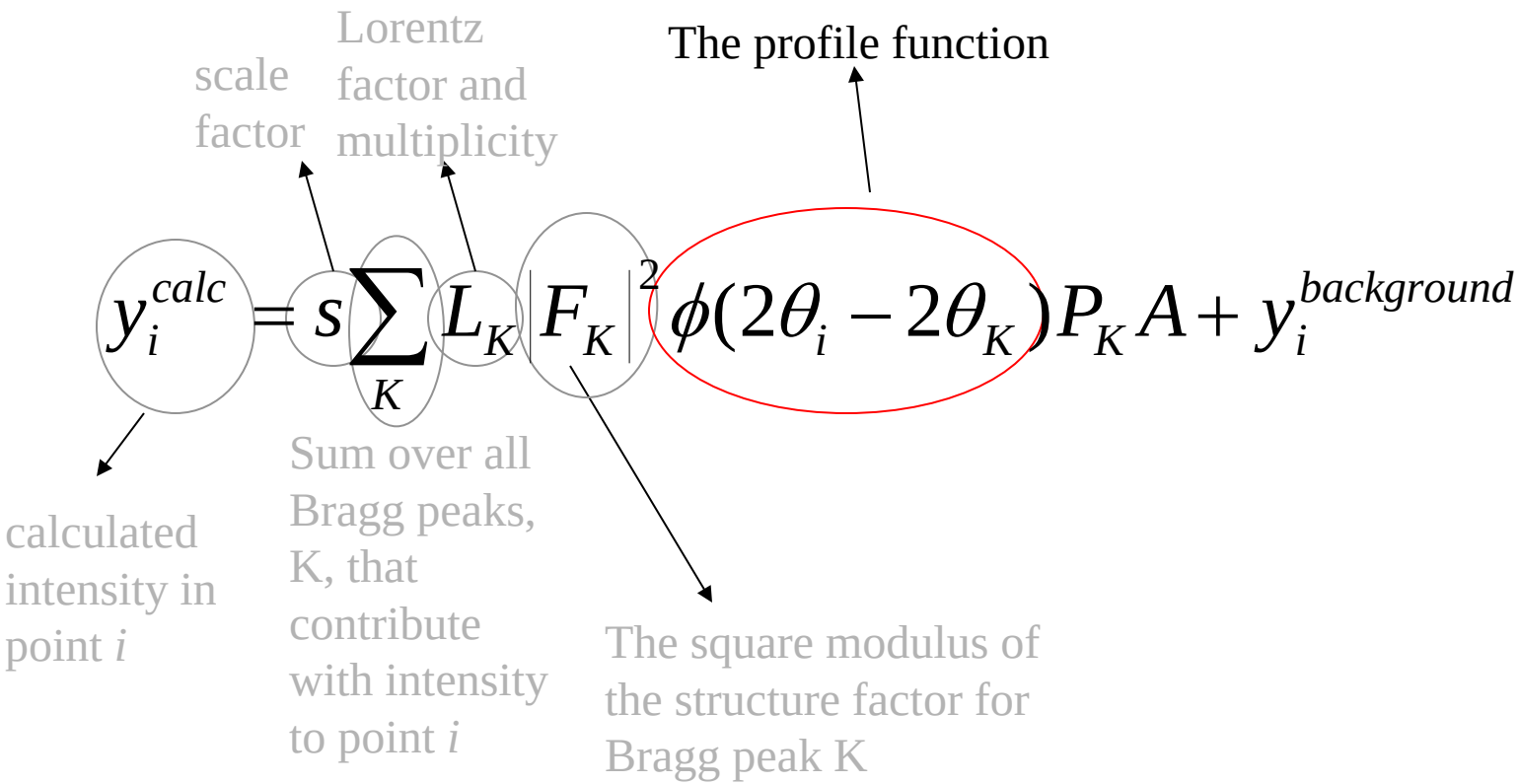
calculated intensity in point *i*

Sum over all Bragg peaks, K, that contribute with intensity to point *i*

The square modulus of the structure factor for Bragg peak K

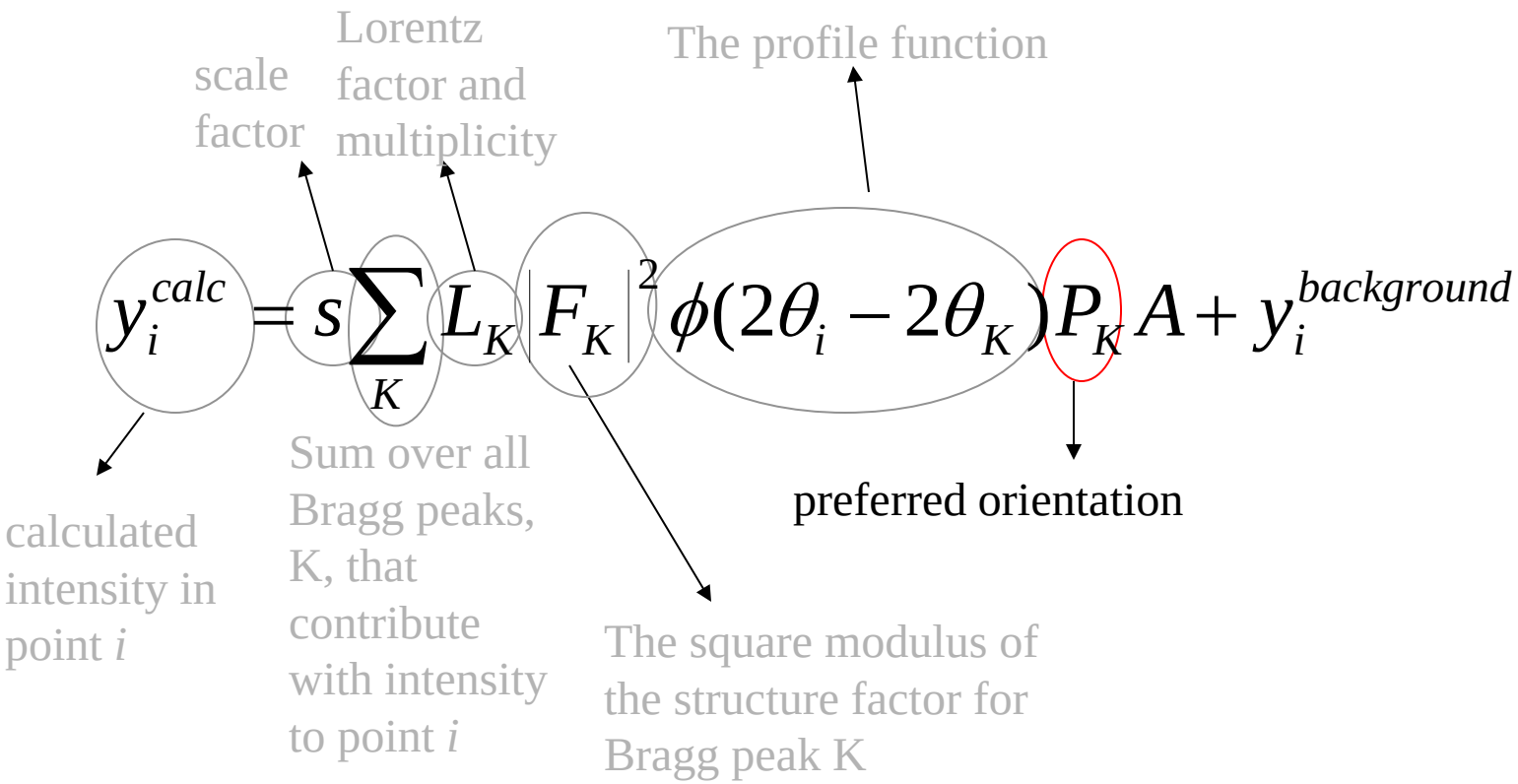
The Rietveld method

The calculated profile



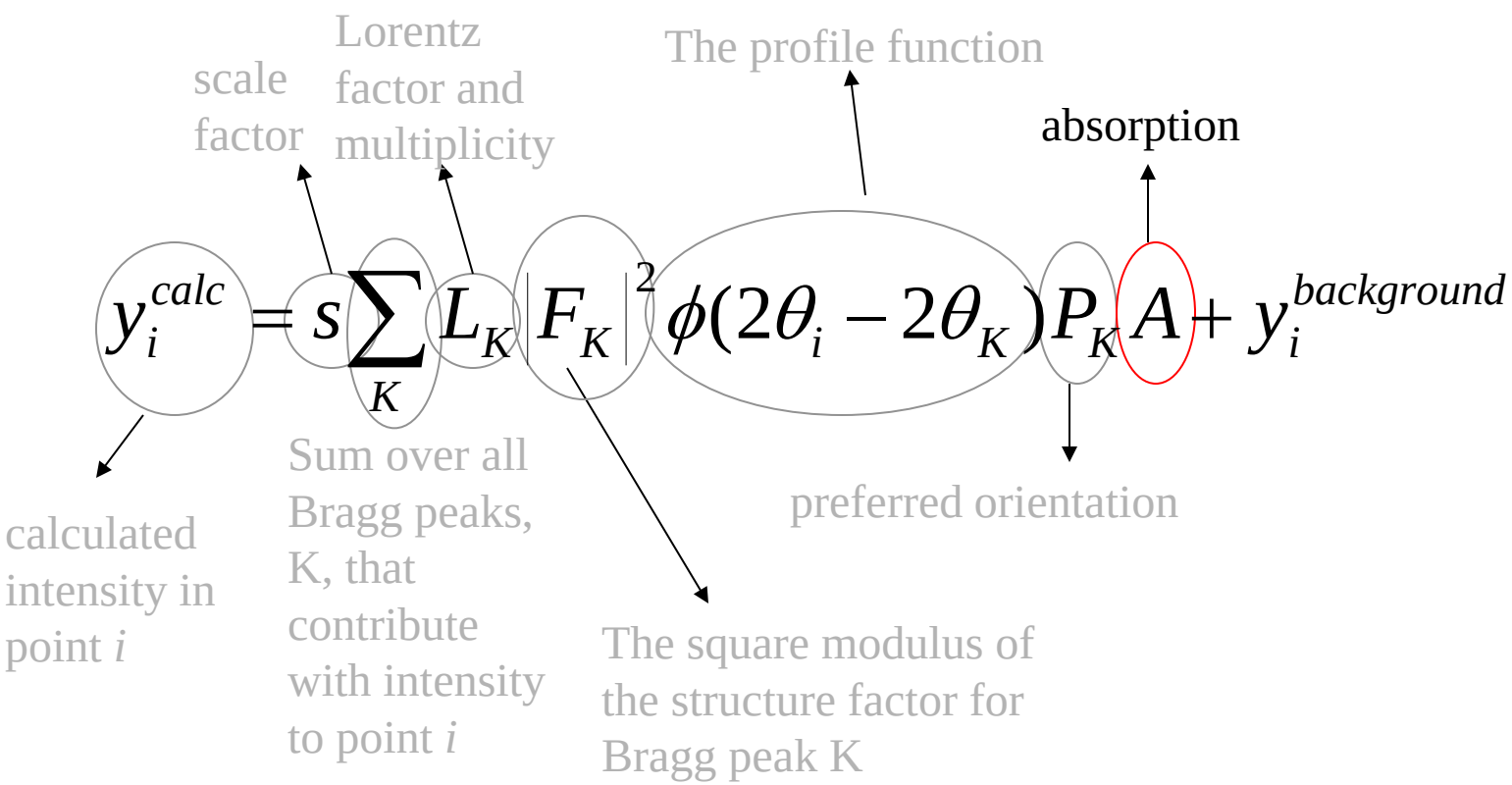
The Rietveld method

The calculated profile



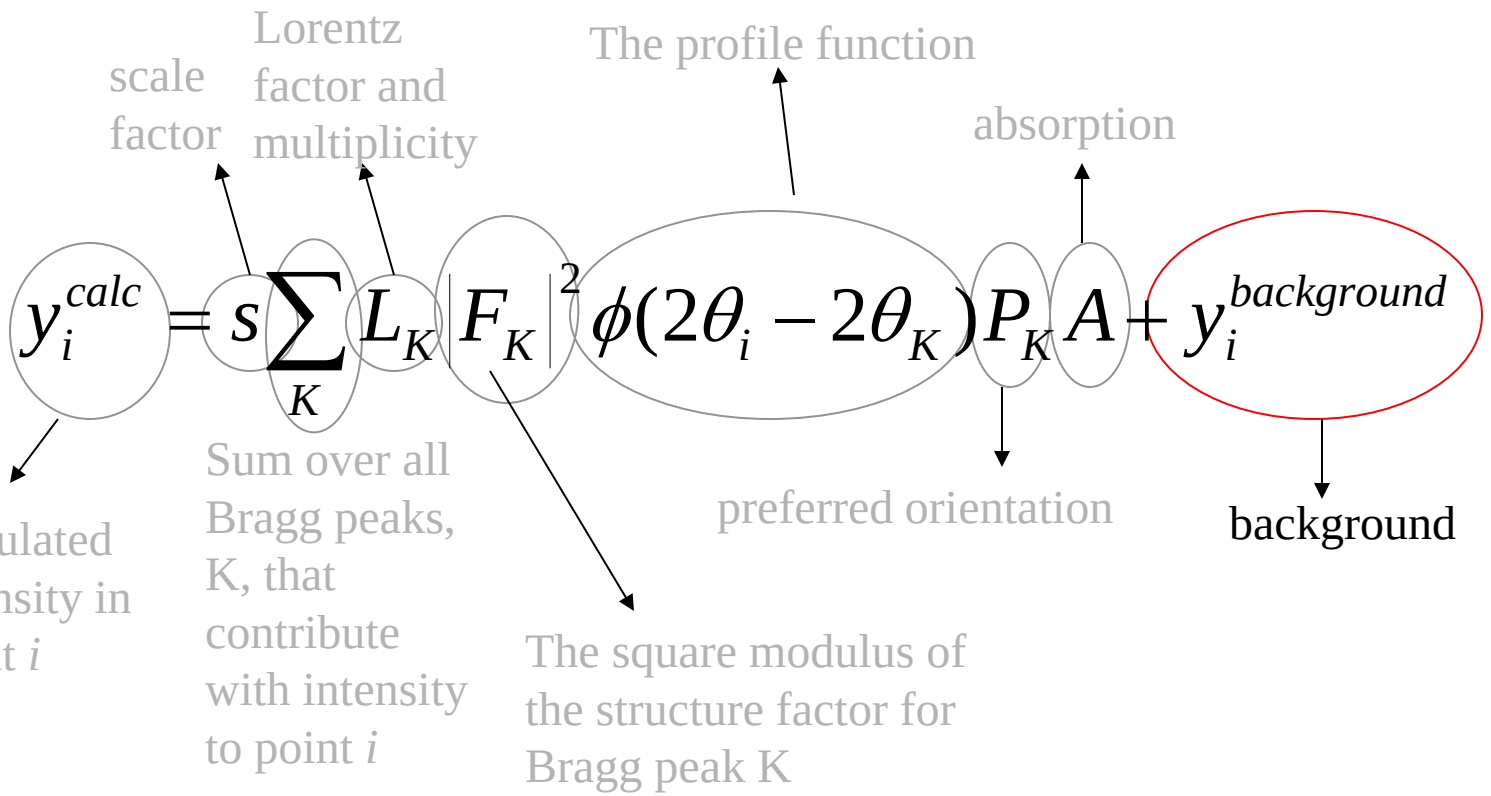
The Rietveld method

The calculated profile



The Rietveld method

The calculated profile



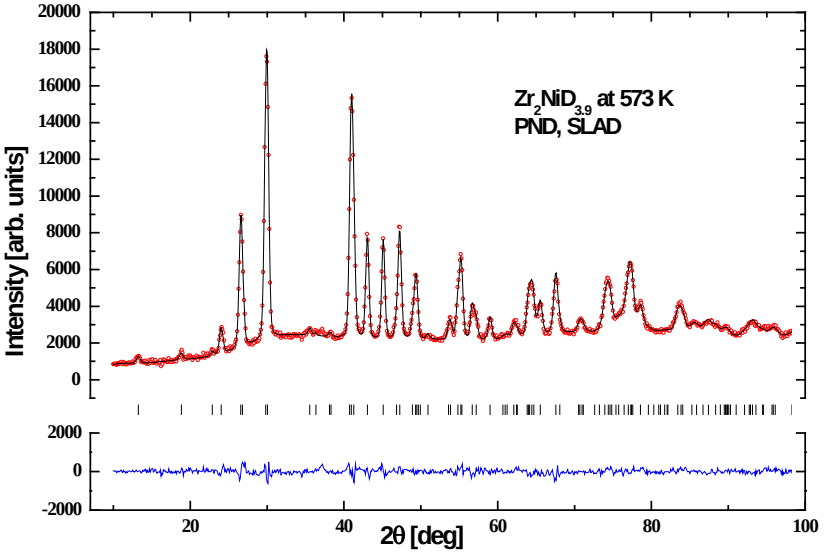
The Rietveld method

Fitting the profile

$$y_i^{calc} = s\sum_K L_K \left|F_K\right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background}$$

The parameters in y_i^{calc} undergo a *least-square refinement* to minimize R_{wp}

$$R_{wp} = \sqrt{\frac{\sum_i w_i \left(y_i^{obs} - y_i^{calc}\right)^2}{\sum_i w_i \left(y_i^{obs}\right)^2}}$$



The Rietveld method

The structure factor

$$y_i^{calc} = s\sum_K L_K \left|F_K\right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background}$$

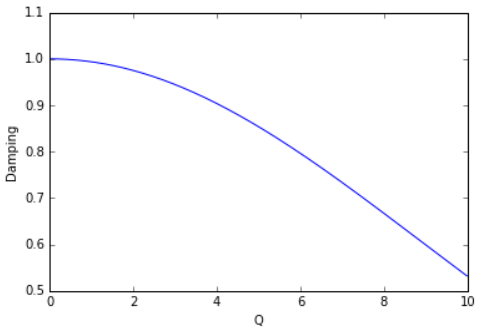
$$\left|F_K\right|^2 = \left|\sum_i b_i \cdot e^{2\pi i(\vec{r}_i \cdot \vec{K})}\right|^2 = \left|\sum_i b_i \cdot e^{2\pi i(hx_i + ky_i + lz_i)}\right|^2$$

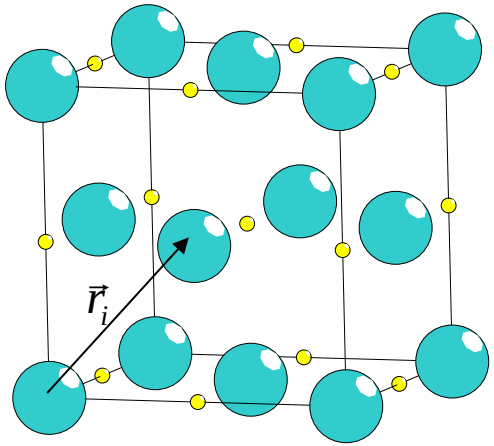
$$b(\theta) = b \cdot e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$$

The displacement factor

$$B = 8\pi^2 U$$

The square mean shift of the atom from its equilibrium position.



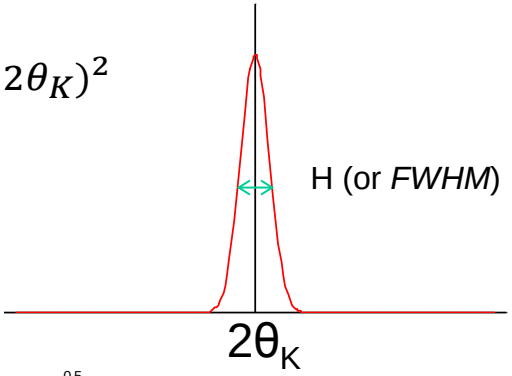


The Rietveld method

The profile function

$$y_i^{calc} = s\sum_K L_K \left|F_K\right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background}$$

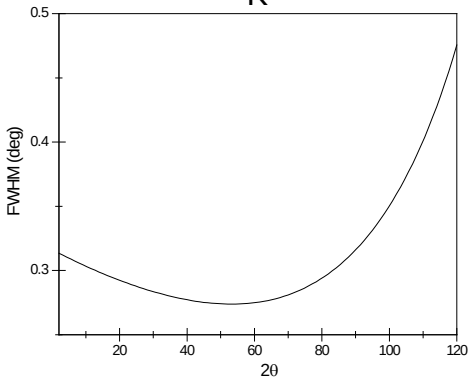
Gaussian: $\phi(2\theta_i - 2\theta_K)_{gauss} = \frac{2\sqrt{ln2}}{H\sqrt{\pi}} e^{\frac{-4\ln 2}{H^2}(2\theta_i - 2\theta_K)^2}$



H varies with 2θ!

Caglioti equiation: $H = \sqrt{(U\tan^2\theta + V\tan\theta + W)}$

Refineable parameters

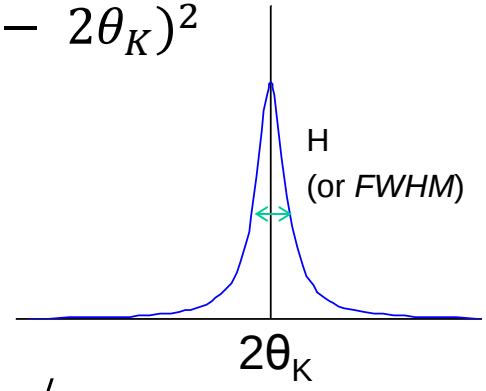


The Rietveld method

The profile function

$$y_i^{calc} = s\sum_K L_K \left|F_K\right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{background}$$

Lorentzian: $\phi(2\theta_i - 2\theta_K)_{lortenz} = \frac{2\sqrt{ln2}}{H\pi} \frac{1}{1 + \frac{4}{H^2}(2\theta_i - 2\theta_K)^2}$



pseudo-Voigt: $\phi(2\theta_i - 2\theta_K)_{pseudo-Voigt} = \eta \cdot \phi_{lorentz} + (1-\eta) \cdot \phi_{gauss}$

$H = \sqrt{(U \tan^2\theta + V \tan\theta + W)}$

Refineable parameter

Fullprof: Npr = 5

GSAS: N.A.

The Rietveld method

Sample contributions to the profile function

Broadening due to particle size: $\beta_{size} = \frac{\lambda K}{D \cos\theta} \propto \frac{1}{\cos\theta}$ Scherrer equation

~1

«Particle size» (volume-weighted average size of coherent domains)

Mostly lorentzian

Broadening due to strain: $\beta_{strain} = B\varepsilon \tan\theta \propto \tan\theta$

strain

Mostly gaussian

$$H = \sqrt{(U \tan^2\theta + V \tan\theta + W)}$$

$$\phi(2\theta_i - 2\theta_K)_{pseudo-Voigt} = \eta \cdot \phi_{lorentz} + (1-\eta) \cdot \phi_{gauss}$$

The Rietveld method

The Thompson-Cox-Hastings pseudo-Voigt

Sample independent!

$$H_{gauss} = \sqrt{(U \tan^2\theta + V \tan\theta + W + \frac{Z}{\cos^2\theta})}$$

$$H_{lorentz} = X \tan\theta + \frac{Y}{\cos\theta}$$

Size-dependent

Strain-dependent

$$\beta_{size} \propto \frac{1}{\cos\theta}$$

Mostly lorentzian

$$\beta_{strain} \propto \tan\theta$$

Mostly gaussian

Fullprof: Npr = 7

GSAS: type 2

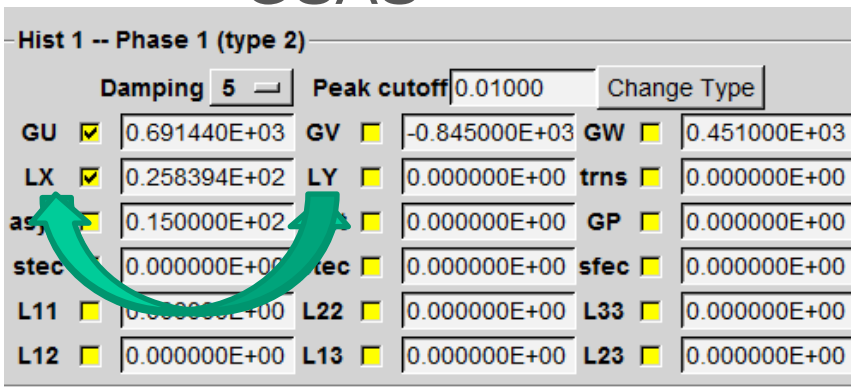
The (Thompson-Cox-Hastings) pseudo-Voigt

Fullprof

```
!-------> Profile Parameters for Pattern #  1
!  Scale          Shape1       Bov        Str1       Str2       Str3    Strain-Model
 0.38120        0.00000    0.00000    0.00000    0.00000    0.00000        0
    11.00000        0.000      0.000      0.000      0.000      0.000
!      U          V          W          X          Y        GauSiz   LorSiz Size-Model
   0.361019  -0.551548   0.335122   0.000000   0.000000   0.000000  0.000000     0
       0.000      0.000      0.000      0.000      0.000      0.000     0.000
!      a          b          c        alpha       beta       gamma     #Cell Info
   7.633083   7.633083   6.520463  90.000000  90.000000  90.000000
   81.00000   81.00000  101.00000    0.00000    0.00000    0.00000
```

*10000/(2.35^2)

GSAS



Z

Sample independent!

$$H_{gauss} = \sqrt{(U\tan^2\theta + V\tan\theta + W + \frac{Z}{\cos^2\theta})}$$

$$H_{lorentz} = X\tan\theta + \frac{Y}{\cos\theta}$$

Size-dependent

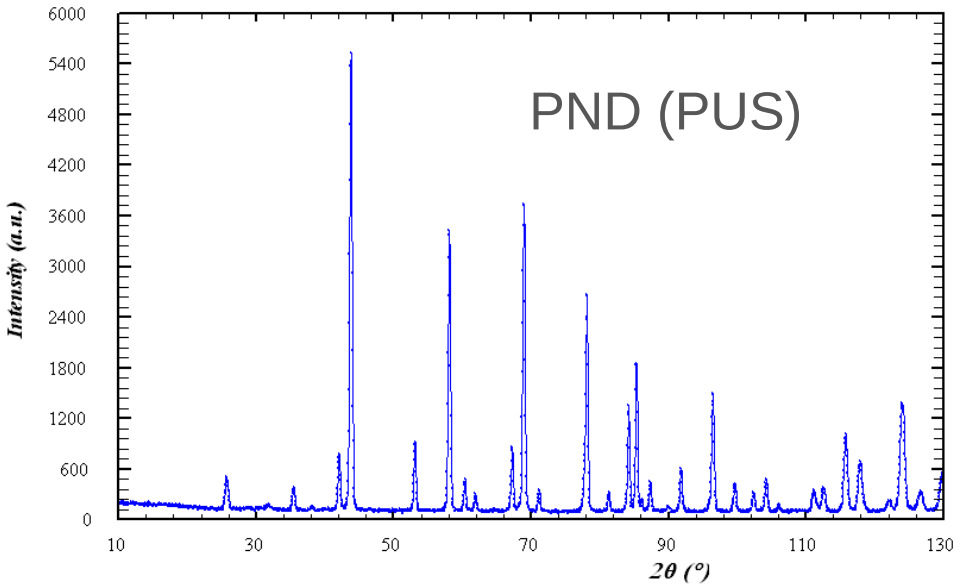
Strain-dependent

The Rietveld method

Joint exercise

Approximate model of Al_2O_3:

- Trigonal, space group R –3 c
- a ~ 4.75 Å, c ~ 12.99 Å
- Al in 0 0 ~0.35
  O in ~0.29 0 ¼



We want a more accurate structure model!

Le Bail refinements

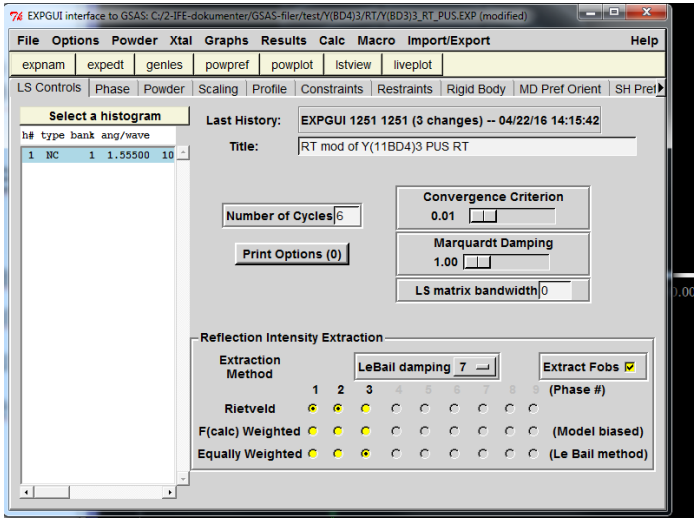
«structureless Rietveld»

- Bragg peak posititions are caluclated from unit cell and space group, but all intensities can vary freely.
- Good for checking the unit cell
- … or to refine the profile parameter if the structure model is bad.

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:    10.63
!-------------------------------------------------------------------------------
Th2Al1D4
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   3   0   0 1.0 0.0 5.0   2   0   0   0   0      1996.359   0   7   1
!
```

Jbt = 0 : Rietveld

Jbt = 2 : Le Bail («profile matching)



Evaluating the fit

$$R_F = \sqrt{\frac{\sum_K \left| (I_K^{"obs"})^{1/2} - (I_K^{calc})^{1/2} \right|}{\sum_i \left(I_K^{"obs"} \right)^{1/2}}}$$

Single crystal-like. But we don't observe independent intensities for overlapping reflections!

$$R_{wp} = \sqrt{\frac{\sum_i w_i \left(y_i^{obs} - y_i^{calc} \right)^2}{\sum_i w_i \left(y_i^{obs} \right)^2}}$$

Most often used. But can be highly influenced by factors that do not imply a poor structure model.

$$\chi^2 = \frac{R_{wp}}{R_{\exp}} \qquad R_{\exp} = \sqrt{\frac{N}{\sum_i w_i \left(y_i^{obs} \right)}}$$

Should be close to 1 when there are no systematic errors in the model, but in many cases that's not possible.

Evaluating the fit

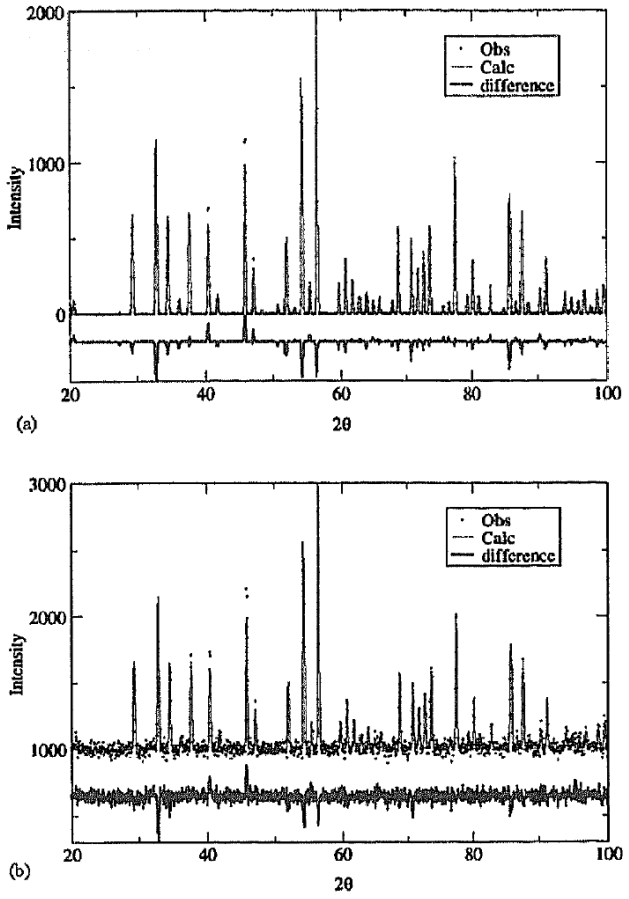


Figure 1. A demonstration of the effect of background on a Rietveld fit. Two simulated fits are shown, where the models have the same discrepancies from the simulated data and where the Bragg intensities and counting times are equivalent. However, in case (a) no background is present, R_{wp}=23% and χ^2=2.54, while in case (b), significant background is present, R_{wp} =3.5% and χ^2=1.31.

$$R_{wp} = \sqrt{\frac{\sum_i w_i \left(y_i^{obs} - y_i^{calc}\right)^2}{\sum_i w_i \left(y_i^{obs}\right)^2}}$$

Most often used. But can be highly influenced by factors that do not imply a poor structure model.

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Should be close to 1 when there are no systematic errors in the model, but in many cases that's not possible.

Evaluating the fit

_R_ factors in Rietveld analysis: How good is good enough?

Brian H. Toby
BESSRC/XOR, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois

Powder Diffraction **21** (1), March 2006

In my experience, the most important way to determine the quality of a Rietveld fit is by viewing the observed and calculated patterns graphically and to ensure that the model is chemically plausible.

Conclusion

- Rietveld refinement is an effective technique to refine crystal structure models against powder diffraction data.
- It can also be used for quantitative phase analysis and to extract microstructural information.
- Except for simple cases, it requires active participation from the user. It’s not a black-box technique!