Second FullProf School 2023:

Diffraction data analysis of energy materials

NEUTRONS
FOR SOCIETY

Diffraction equations, single crystals and powders, indexing.

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Outline

1. Summary of diffraction equations. Single Crystals and Powders. Indexing powder patterns. Le Bail fit of powder patterns

2. Live presentation of indexing and Le Bail fits

3. Mathematical modeling of powder diffraction patterns

4. The Voigt approach to peak shapes

5. Live: Coming back to peak fitting in WinPLOTR-2006

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Diffraction Equations for crystals

In a crystal the atoms positions can be decomposed as the vector position of the origin of a unit cell plus the vector position with respect to the unit cell

$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j$$

$$A_N(\mathbf{s}) = \sum_{lj} b_j \exp(2\pi i \mathbf{s}\cdot\mathbf{R}_{lj}) = \sum_{l} \exp(2\pi i \mathbf{s}\cdot\mathbf{R}_l) \sum_{j=1,n} b_j \exp(2\pi i \mathbf{s}\cdot\mathbf{r}_j)$$

$$\sum_l \exp(2\pi i \mathbf{s}\cdot\mathbf{R}_l) = 0 \quad \textit{for general}\ \mathbf{s}$$

$$\sum_l \exp(2\pi i \mathbf{s}\cdot\mathbf{R}_l) = N \quad \textit{for}\ \ \mathbf{s} = \mathbf{H} \ \rightarrow \mathbf{H}\mathbf{R}_l = L_H \quad \text{integer}$$

$\boxed{\mathbf{s} = \mathbf{H}}$ Laue conditions: the scattering vector is a reciprocal lattice vector of the crystal

$$I_N(\mathbf{H}) \sim \left| \sum_{j=1,n} b_j \exp(2\pi i \mathbf{H}\cdot\mathbf{r}_j) \right|^2 = \left| F(\mathbf{H}) \right|^2$$

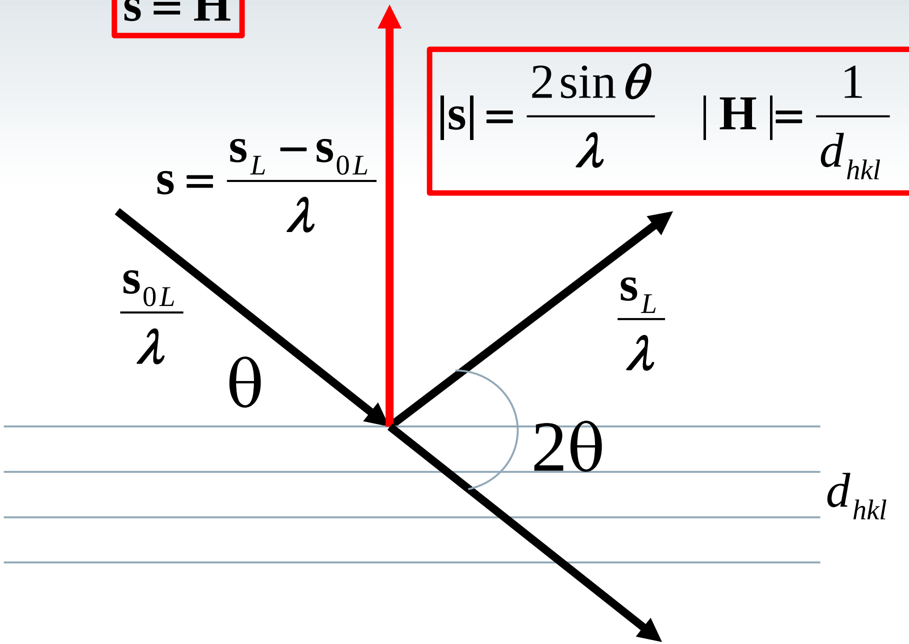
Diffraction Equations for crystals

The Laue conditions have as a consequence the Bragg Law

Laue conditions: the scattering vector is a reciprocal lattice vector of the crystal

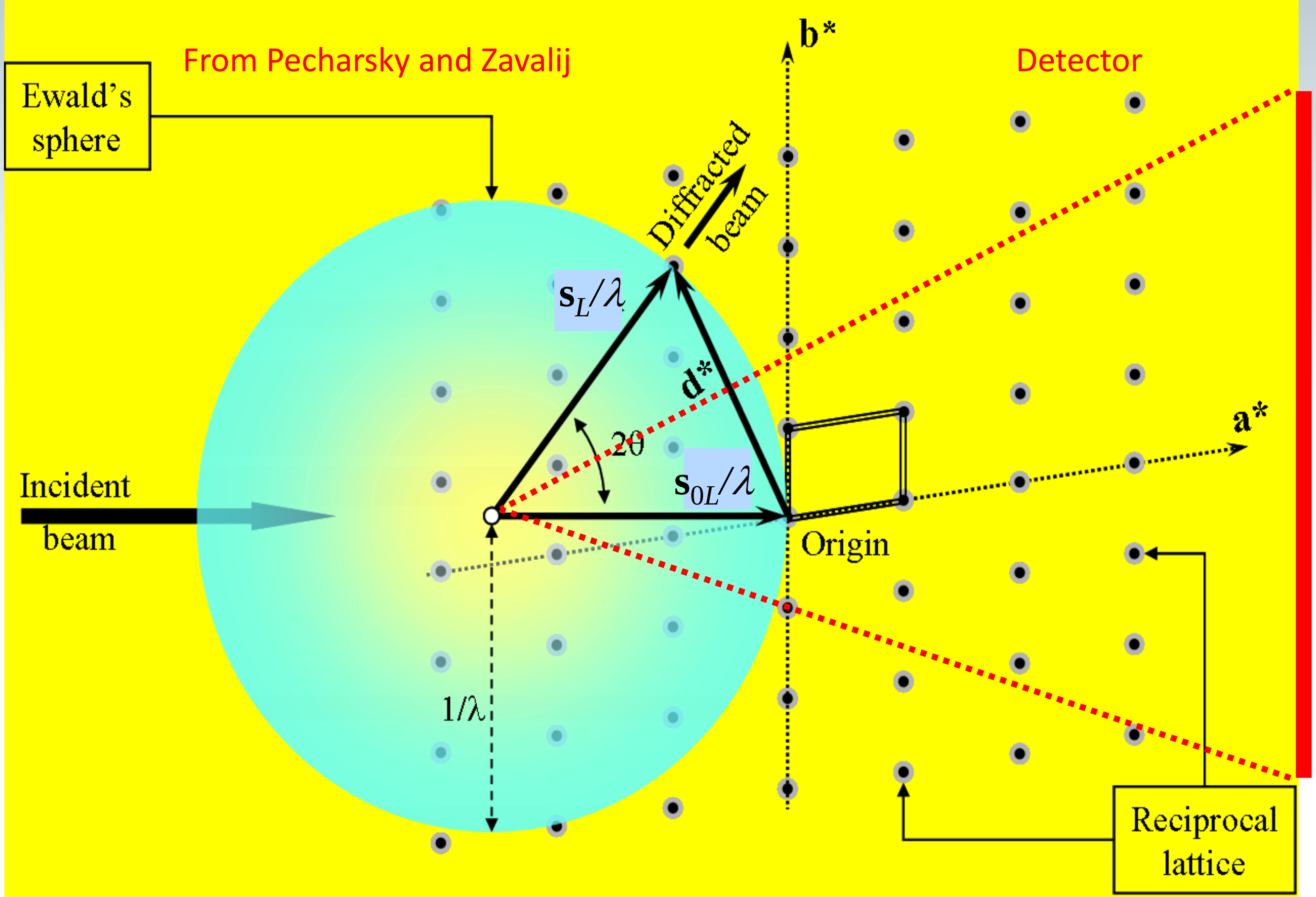
$$\boxed{\mathbf{s} = \mathbf{H}}$$

$$\boxed{|\mathbf{s}| = \frac{2\sin\theta}{\lambda} \qquad |\mathbf{H}| = \frac{1}{d_{hkl}} \qquad \Rightarrow \qquad 2d_{hkl}\sin\theta = \lambda}$$

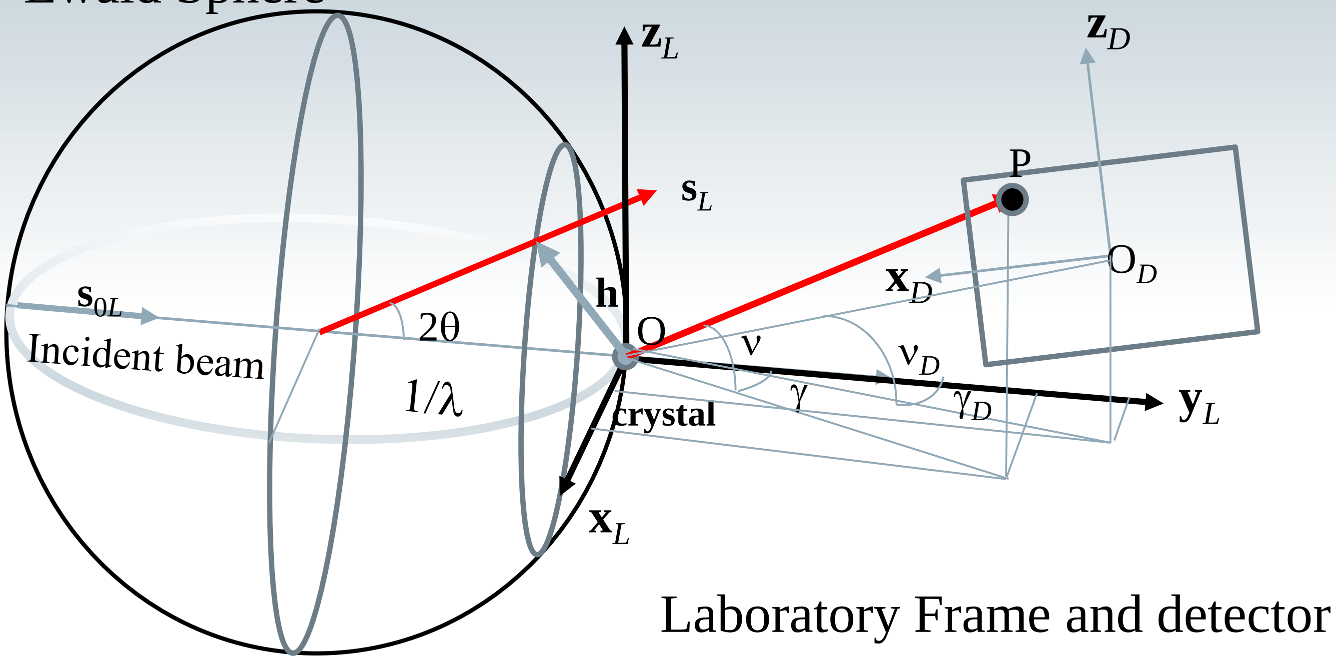


$$\mathbf{s} = \frac{\mathbf{s}_L - \mathbf{s}_{0L}}{\lambda}$$

Ewald construction



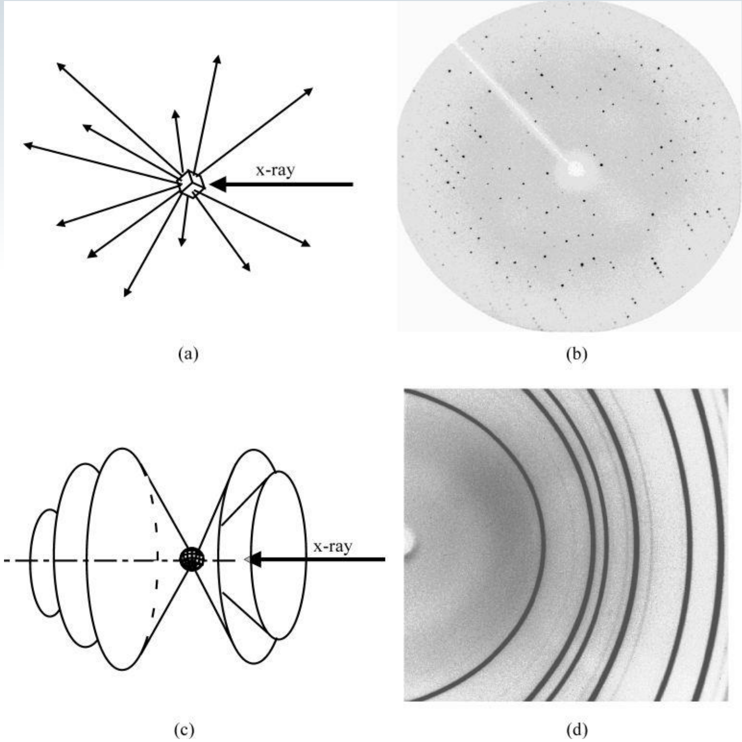
Ewald construction



Diffraction patterns

Single Xtal - 2D image + scan –> 3D Int vs 2θ

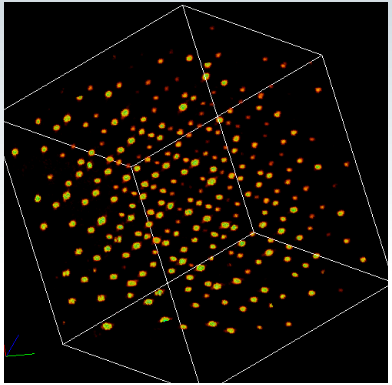
Powder - 2D image –> 1D Int vs 2θ



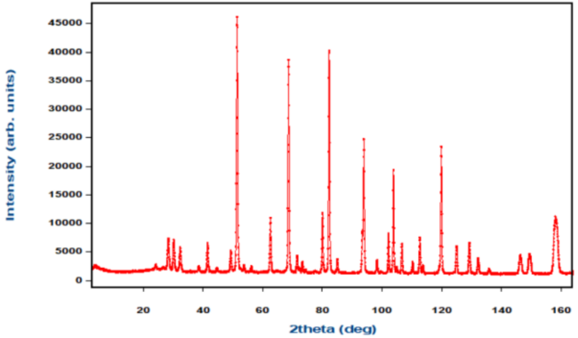
(a) (b)

(c) (d)

Courtesy of Jim Britten



Single Crystal



Powder or polycrystalline solid

The indexing problem

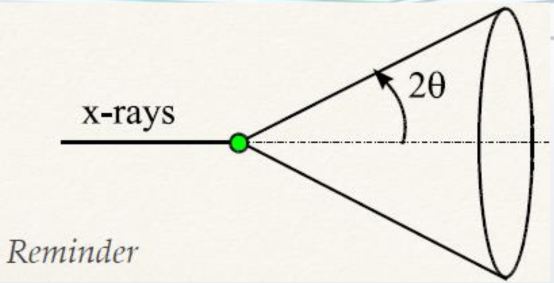
- **Single Crystal:**
  - Unit cell and symmetry unambiguous
  - Each reflection: correct Miller indices *hkl*
  - Diffracted intensity (structure amplitude $|F|_{hkl}$) accurate
- **Powder:**
  - **nothing** of all this is known …

Information in a powder pattern:

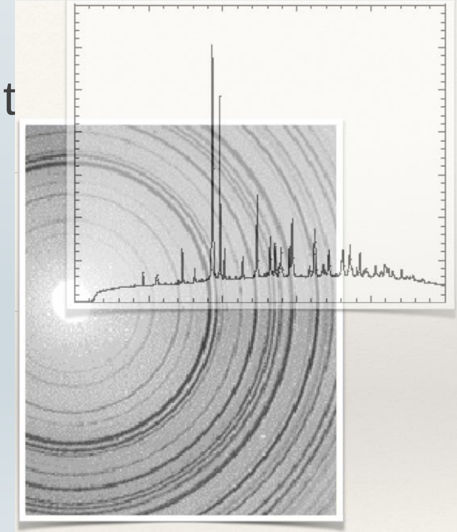
1:Peak positions determine the unit cell dimensions

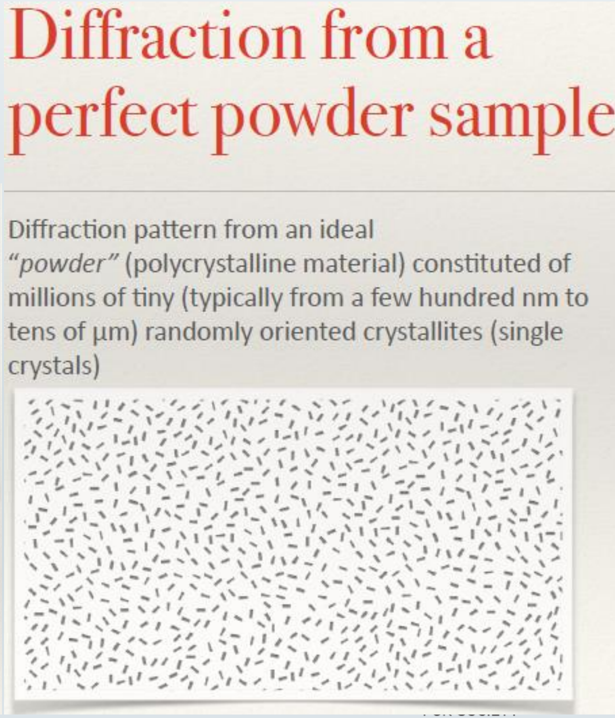
2: Peak shapes

3: Integrated intensities



Reminder



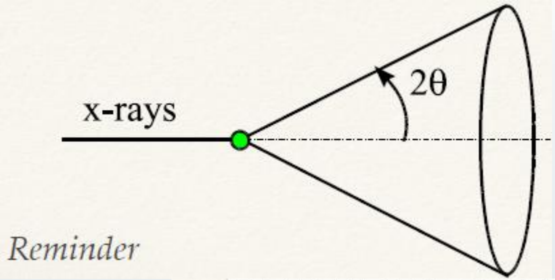


Diffraction from a perfect powder sample

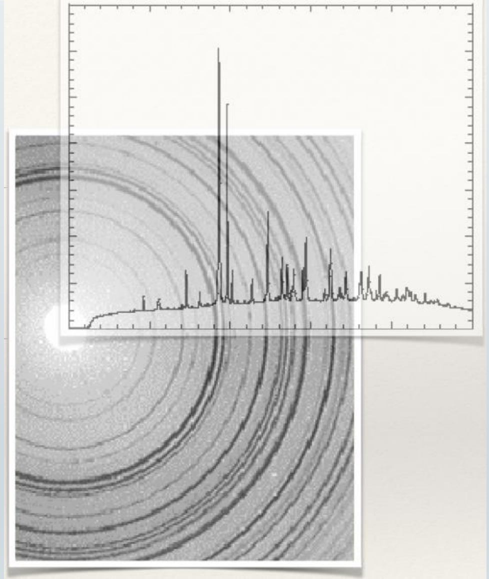
Diffraction pattern from an ideal *"powder"* (polycrystalline material) constituted of millions of tiny (typically from a few hundred nm to tens of μm) randomly oriented crystallites (single crystals)

The indexing problem

Prerequisites



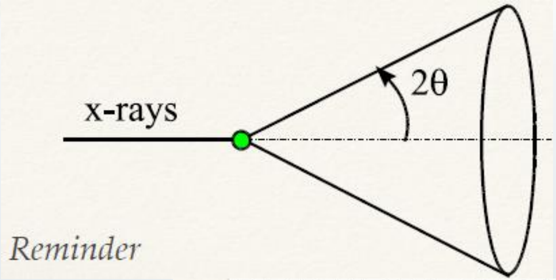
1. Good sample — preferably single-phase
2. Best quality powder pattern
   - Best technique
   - Well-known 2Θ zero shift
   - zero point error worse than statistical errors of same magnitude
   - $\sigma(2\Theta) < 0.02$ degrees
3. At least 20 accurate low-angle peak positions
   - High resolution, e.g. synchrotron XRD and parallel geometry optics: high resolution monochromator
   - Include weak lines
   - Likely space groups from peaks present and those systematically absent

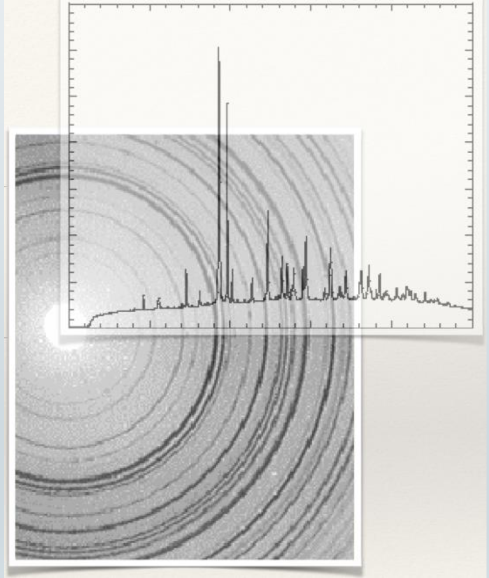


The indexing problem

“Powder indexing is not like structure analysis, which works well on good data, and will usually get by on poor data given a little more time and attention. Powder indexing works beautifully on good data, but with poor data it will usually not work at all”

Shirley, R: “Data accuracy for powder indexing,” *Natl. Bur. Stand. (US) Spec. Publ.* **567** (1980) 361-382





For a given wavelength the peak positions are determined by the Bragg’s law and the unit cell dimensions

$$Q = (1/d)^2 = (2\sin\theta/\lambda)^2 = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2kl\,b^*c^*\cos\alpha^* + 2hl\,a^*c^*\cos\beta^* + 2hk\,a^*b^*\cos\gamma^*$$

$$Q = h^2A + k^2B + l^2C + kl\,D + hl\,E + hk\,F$$

Indexing = finding the six constants *A*, *B*, … *F*

Indexing programs

ITO

J.W. Visser, *J. Appl. Cryst.* **2** (1969) 89.

Good for unit cells of compounds in low symmetry

TREOR

P.E. Werner, *Z. Krist.* **120** (1964) 375.

Trial- and error method, separately for cubic, hexagonal, tetragonal, orthorhombic, monoclinic and triclinic systems

DICVOL

D. Louër, *J. Appl. Cryst.* **18** (1972) 271. A. Boultif, D. Louër, *J. Appl. Cryst.* **37** (2004) 724.

Successive dichotomy method, originally not for monoclinic and triclinic lattices.

Other programs: McMaille, TOPAS, Xcell, …

Criteria for a good indexing

P.M. de Wolff, J. Appl. Cryst. 1 (1968) 108

Typical based upon the first 20 lines:

$$M_{20} = \frac{Q_{20}}{2N_{20}\left|\langle \Delta Q \rangle\right|}$$

M_{20} combines two concepts, forming the denominator if the above formula:

- data accuracy, reflected by the agreement between Q_{obs} and Q_{calc} (in $<\Delta Q>$)
- the idea of small cell volume V through N_{20} = number of theoretical lines up to the 20th observed line ($N_{calc} \sim 4\pi V_{tricl}/3d^3$ for a triclinic lattice)

$$F_N = \frac{N}{\langle \Delta 2\theta \rangle N_{poss}}$$

N_{poss} is the number of theoretically possible until the *N*th observed reflexion

Smith G.S. and Snyder R.L., J. Appl. Cryst. 12 (1979), 60-65

Implementation in FullProf suite

- determination of peak positions (using WinPLOTR):
  - profile fitting procedure
  - automatic peak search
  - by hand

LIVE demo: Y_2O_3, $PbSO_4$
Indexing → Le Bail fit → Check group

- save peaks for indexing programs:
  - create input file for DICVOL, TREOR, ITO
- if successful, run the indexing program:
  - create input `.PCR` file for FullProf (Le Bail fit).
  - The agreement of the observed versus calculated pattern is the best criteria for a good indexing
- CHECK_group:
- search for a convenient space group from the extracted intensities

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The calculated profile of powder diffraction patterns

$$\boxed{y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i}$$

$$I_{\mathbf{h}} = I_{\mathbf{h}}\left(\boldsymbol{\beta}_{\mathbf{I}}\right)$$

Contains structural information:
atom positions, magnetic moments, etc

$$\Omega = \Omega(x_{\mathbf{h}i}, \boldsymbol{\beta}_{\mathbf{P}})$$

Contains micro-structural information:
instr. resolution, defects, crystallite size…

$$b_i = b_i\left(\boldsymbol{\beta}_{\mathbf{B}}\right)$$

Background: noise, incoherent scattering
diffuse scattering, ...

The model to calculate a powder diffraction pattern is:

$$y_{ci} = \sum_{\mathbf{h}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$$\int_{-\infty}^{+\infty} \Omega(x) dx = 1$$

Profile function characterized by its full width at half maximum **(FWHM=*H*)** and *shape* parameters **(η, m, ...)**

$$\Omega(x) = g(x) \otimes f(x) = instrumental \otimes intrinsic\, profile$$

$$h(x) = g(x) \otimes f(x)$$ usual notation in literature

The calculated profile of powder diffraction patterns

$$y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

The symbol {h} means that the sum is extended only to those reflections contributing to the channel “*i*” .

This should be taken into account (resolution function of the diffractometer and sample broadening) before doing the actual calculation of the profile intensity.

This is the reason why some Rietveld programs are run in two steps

Several phases ($\phi = 1, n_\phi$) contributing to the diffraction pattern

$$y_{ci} = \sum_{\phi} s_\phi \sum_{\{\phi\mathbf{h}\}} I_{\phi,\mathbf{h}}\ \Omega(T_i - T_{\phi,\mathbf{h}}) + b_i$$

Several phases (ϕ = 1,… n_ϕ) contributing to several (p=1,… n_p) diffraction patterns

$$y_{ci}^{p} = \sum_{\phi} s_\phi^{p} \sum_{\{\phi\mathbf{h}\}} I_{\phi,\mathbf{h}}^{p}\ \Omega^{p}(T_i - T_{\phi,\mathbf{h}}) + b_i^{p}$$

$$\boxed{y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i}$$

$$I_{\mathbf{h}} = S\left\{L p O A C F^2\right\}_{\mathbf{h}}$$

Integrated intensities are proportional to the square of the structure factor *F*. The factors are:
Scale Factor (S), Lorentz-polarization (*Lp*), preferred orientation (*O*), absorption (*A*), other “corrections” (*C*)

Crystallographic R-factors used in Rietveld Refinement

$$'I_{obs,k}' = I_{calc,k} \sum_i \left\{ \frac{\Omega(T_i - T_k)(y_{obs,i} - B_i)}{(y_{calc,i} - B_i)} \right\}$$

Provides ‘observed’ integrates intensities for calculating Bragg R-factor

$$'F_{obs,k}' = \sqrt{\frac{'I_{obs,k}'}{jLp}}$$

In some programs the crystallographic R_F-factor is calculated using just the square root of ‘$I_{obs,k}$’

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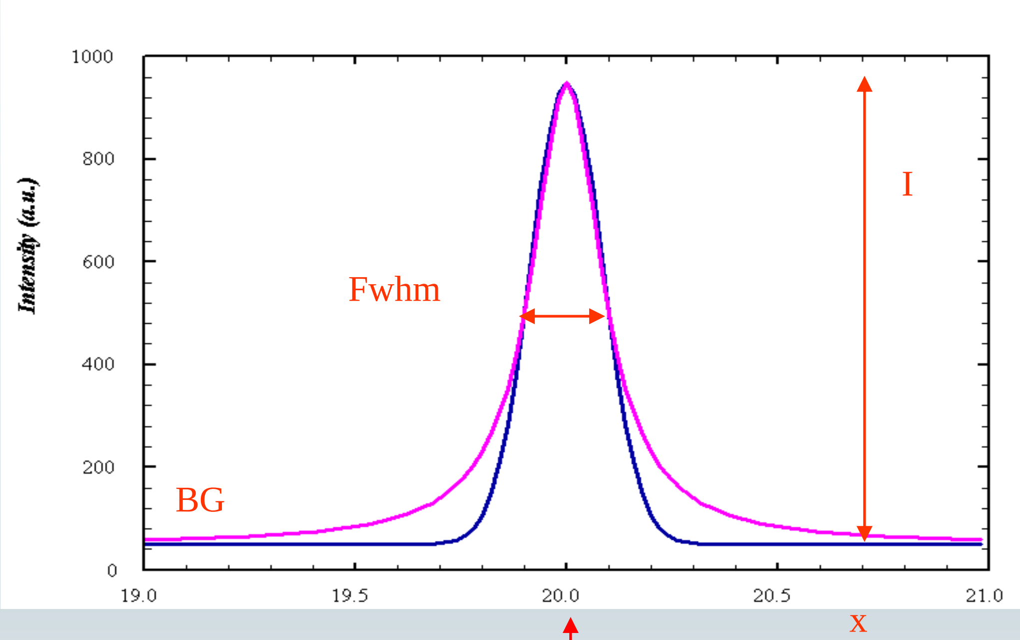
Comparison of **Gaussian** and **Lorentzian** peak shapes of the same peak height “I” and same width “Fwhm”



Convolution properties of Gaussian and Lorentzian functions

$$L(x, H_1) \otimes L(x, H_2) = L(x, H_1 + H_2)$$

$$G(x, H_1) \otimes G(x, H_2) = G(x, \sqrt{H_1^2 + H_2^2})$$

$$L(x, H_L) \otimes G(x, H_G) = V(x, H_L, H_G)$$

The Voigt function

$$V(x) = L(x) \otimes G(x) = \int_{-\infty}^{+\infty} L(x-u)G(u)du$$

$$V(x) = V(x, H_L, H_G) = V(x, \beta_L, \beta_G)$$

The pseudo-Voigt function

$$pV(x) = \eta L'(x) + (1-\eta)G'(x)$$

$$pV(x) = pV(x, \eta, H)$$

Properties of the Voigt function

$$V(x) = V_1(x) \otimes V_2(x)$$

The Voigt function has proven to be a very good experimental approximation in many cases

$$\beta_L = \beta_{1L} + \beta_{2L}$$

Lorentzian breadths simply have to be summed

$$\beta_G^2 = \beta_{1G}^2 + \beta_{2G}^2$$

Gaussian breadths have to be summed quadratically

$$\beta_{fL} = \beta_{hL} - \beta_{gL}$$

$$\beta_{fG}^2 = \beta_{hG}^2 - \beta_{gG}^2$$

Correction for instrumental broadening

Instrument and sample contribution to broadening

$$H_{hG}^{2} = U_f \tan^2\theta + \frac{I_{fG}}{\cos^2\theta} + H_{gG}^{2}$$

$$H_{hL} = X_f \tan\theta + \frac{Y_f}{\cos\theta} + H_{gL}$$

The Gaussian and Lorentzian contributions of the instrument must be determined experimentally with a size/strain-free sample

Sample

Instrument

Modeling the Gaussian and Lorentzian components for the general anisotropic case in FullProf

Instrument resolution function characterized by: $(U, V, W, X, Y)_g$

$$H_{hG}^2 = (\boxed{U_g} + U_f + (1-\xi_f)^2 D_{fST}^2(\boldsymbol{\alpha}_D))\tan^2\theta + \boxed{V_g}\tan\theta + \boxed{W_g} + \frac{I_{fG}}{\cos^2\theta}$$

$$H_{hL} = (\boxed{X_g} + X_f + \xi_f D_{fST}(\boldsymbol{\alpha}_D))\tan\theta + \frac{[\boxed{Y_g} + Y_f + F_f(\boldsymbol{\alpha}_S)]}{\cos\theta}$$

$$D_{fST}^2(\boldsymbol{\alpha}_D) = 10^{-8}\; 8\mathrm{Ln}2 \left(\frac{180}{\pi}\right)^2 \frac{\sigma^2(M_{hkl})}{M_{hkl}^2}$$

Example: General 2θ dependence of the instrumental broadening (determined by a standard sample)

$$H_{hG}^2 = (U_f + (1-\xi_f)^2 D_{fST}^2(\boldsymbol{\alpha}_D))\tan^2\theta + \frac{I_{fG}}{\cos^2\theta} + \boxed{H_{gG}^2}$$

$$H_{hL} = (X_f + \xi_f D_{fST}(\boldsymbol{\alpha}_D))\tan\theta + \frac{[Y_f + F_f(\boldsymbol{\alpha}_S)]}{\cos\theta} + \boxed{H_{gL}}$$

The Gaussian and Lorentzian components of the instrumental Voigt function are interpolated between empirically determined values.
If needed, axial divergence is convoluted numerically with the resulting profile.

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