Rietveld Quantitative Phase Analysis (least-squares refinement procedure)

- **The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured profile.**

Peak shape

- The shape of a powder diffraction reflection depends on the characteristics of the beam, the experimental arrangement, and the sample size and shape.

  Their convolution produces almost exactly a Gaussian peak shape (Fig. 1).

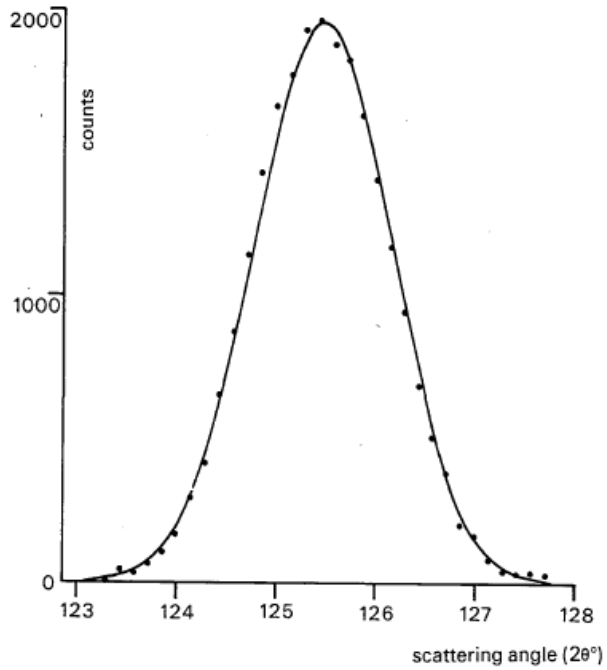

Fig. 1 Comparison of a measured diffracted peak (dot curve) with a calculate Gaussian peak profile (solid curve)

- Assuming this Gaussian peak shape for each Bragg peak, its distribution to the measured profile y_i at position $2\theta_i$ is:

$$y_i = I_k \exp[\frac{-4\ln(2)}{H_k^2}(2\theta_i - 2\theta_k)^2]$$

  where H_k is full-width at half-maximum, $2\theta_i$ is the calculated position of the Bragg peak, and I_k is the calculated intensity of the reflex (determined from the structure factor, the Lorentz factor, and multiplicity of the reflection)

- At very low diffraction angles, the peaks begin to show a pronounced asymmetry. This is mainly because of the use of finite slit heights together with finite sample heights.

  →This vertical divergence effect causes the maximum of the peak to shift to lower angles, but does not affect the integrated peak area. Rietveld used a semi-empirical correction factor, A_s to account for this asymmetry

$$y_i = I_k \exp\left[\frac{-4\ln(2)}{H_k^2}(2\theta_i - 2\theta_k)^2\right] \times \{1 - P(2\theta_i - 2\theta_k)^2 . s/\tan\theta_k\}$$

  Where P is the asymmetry parameter and s=+1, 0, -1 depending on the difference $2\theta_i - 2\theta_k$ being positive, zero, or negative respectively.

- As can be seen from Fig. 2 this correction has two main effects: **the peak is shifted to lower angles and the Gaussian peak shape is made slitly asymmetric.**
- At a given position more than one diffraction peak may contribute to the profile. The intensity is simply the sum of all reflections contributing at the point $2\theta_i$

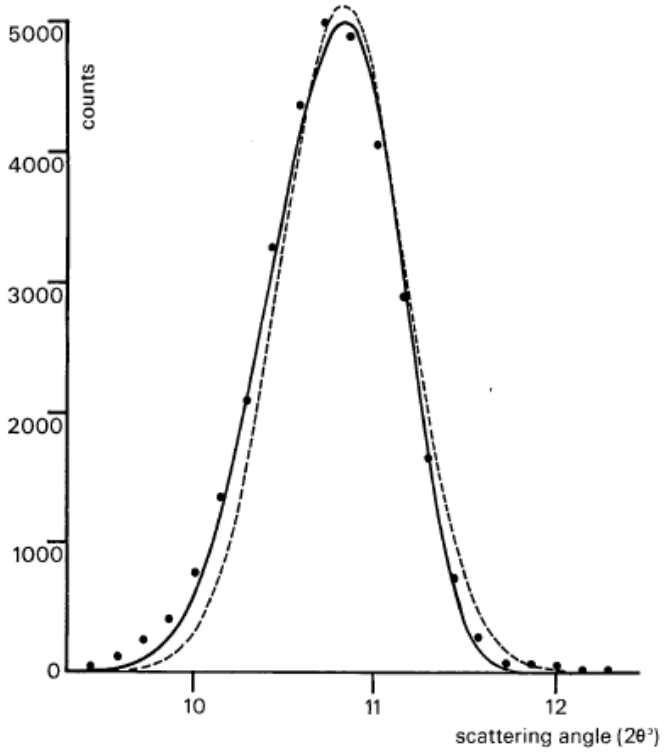

Fig. 2 Comparison of an asymmetric measured diffracted peak (dot curve) with a symmetric (dashed-line curve) and an asymmetry-corrected (solid curve) calculated profile

Peak width

- The formula given by Caglioti, Paoletti (1958) to express the angular dependence of the halfwidths of the diffraction peaks can be simplified to :

$$H_k^2 = Utan^2\theta_k + Vtan\,\theta_k + W$$

where U, V and W are the halfwidth parameters and may be refined during the fit.

- Width of the diffraction peaks are found to broaden at higher Bragg angles (Fig. 3).
- This simple formula also takes account of the peak broadening resulting from the particle-size effect**.**

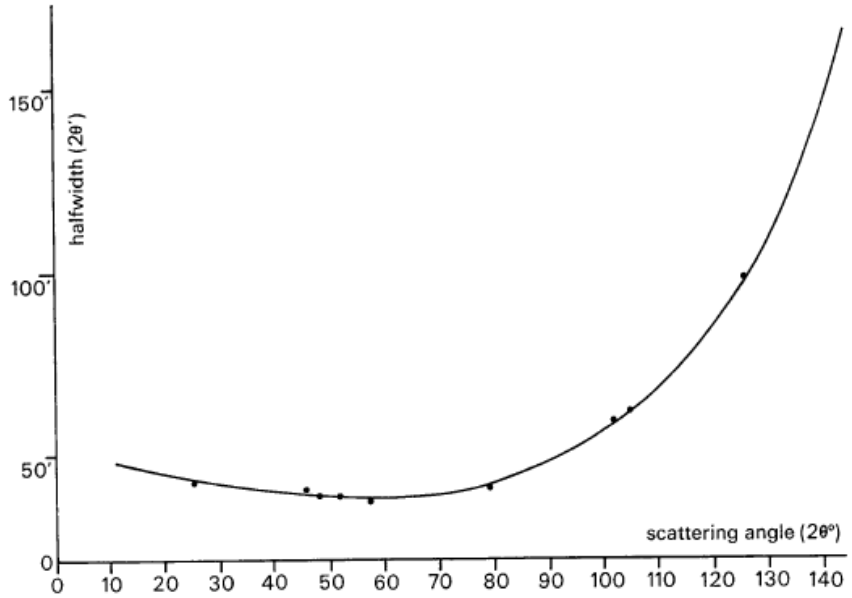

Fig. 3 Variation of peak width with Bragg angle; measured halfwidths (dots), calculated curve (solid cline).

Preferred orientation correction

- In powder samples there is a tendency for plate- or rod-like crystallites to align themselves along the axis of a cylindrical sample holder.
- **In solid polycrystalline samples the production of the material may result in greater volume fraction of certain crystal orientations (commonly referred to as texture).**

  → In such cases the reflex intensities will vary from that predicted for a **completely random distribution.**

- Rietveld allowed for moderate cases of the former by introducing a correction factor:

$$I_{corr} = I_{obs}\exp(-G \propto^2)$$

where I_{obs} is the intensity expected for a random sample, G is the preferred orientation parameter and is a measure for the half-width of the assumed Gaussian distribution of the normal about the preferred orientation direction. α is the acute angle between the scattering vector and the normal of the crystallites.

Least-squares Refinement

The principle of the profile refinement method (Rietveld Method) is best demonstrated by the form of the function M which has to be minimized with respect to the parameters.

$$\boldsymbol{M = \sum_{i} W_i \{ y_t(obs) - \frac{1}{c} y_t(calc)\}^2}$$

- The counter measures at position $2\theta_i$ a number of counts Y_i.
- Background correction B_i for each intensity Y_i.
- To the corrected intensity $y_i=Y_i-B_i$ is assigned a statistical weight W_i.

Approximated values for all parameters are required for the first refinement cycle. These are refined in subsequent refinement cycle until a certain convergence criterion has been reached.