XRDUG Seminar IV

Mathematical Profile Fitting of XRD Data

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XRDUG SESSION IV

Profile Fitting of XRD Data:

- Excellent method to create Peak Files (d-spacing and intensity files), with very reliable quantitative results such as integrated area, peak intensity, FWHM, 2θ position, with a more accurate $K\alpha_2$ stripping method compared to the Rachinger Method.

1. General requirements of profile fitting XRD data

- Fit a numerical function to x-ray diffraction data to determine important peak parameters such as the FWHM, peak position, peak intensity, integrated intensity (area), etc..

- Function must define the shape of the peak.

- Recognize that the shape (FWHM, asymmetries, shape of the tails, etc.) of a diffraction profile can be dramatically affected by various parameters including:

  ⇒ XRD scan effects: choice of step size, preset time (statistical quality of data), peak breadth and shape can change as a function of 2θ.

  ⇒ Diffractometer optics: wider slits can broaden peaks, asymmetries on the low angle side of low angle peaks (both Scintag units have an incident beam Soller slit which can reduce this problem), etc..

  ⇒ Sample aberrations: Surface roughness (powder or solid sample), edge effects (protruding or unfinished edges that are in the path of the beam, but not in the plane of the sample surface), chamfering of sample edges for polishing purposes (keep sample surfaces flat), etc..

  ⇒ Metallurgical effects: Deformation in the sample and/or sample surface, solid solutions, particle size effects including large distributions of particle sizes, variations in chemistry of alloys, micro-strain, different phases, crystallographic directions (i.e. stacking faults) etc..

- This requires various mathematical functions to properly describe all of the various peak shapes that maybe be encountered.

2. Mathematical profiles typically used to fit XRD data with equations utilize in the DMSNT software.

- Gaussian Profile (Figure 1 Gaussian Profile):

  $\Rightarrow$ General expression:

  $$I_{2\theta} = I_{2\theta \text{ at peak maximum}} \exp(-kx^2)$$

  $$k = \frac{0.6931}{(\frac{\beta}{2})^2} \longrightarrow \pm 1\,\sigma$$

  β = FWHM

  $\Rightarrow$ Gaussian expression can be approximated by the following equation:

  $$I_{2\theta} = \frac{I_{2\theta_o}}{(1+k^2x^2)^n}$$

  $$k = \frac{(2^{(\frac{1}{n})} - 1)^{\frac{1}{2}}}{\frac{\beta}{2}}$$

  $x = 2\theta_i - 2\theta_o$ = deviation from Bragg angle
  $2\theta_o$ (peak maximum)

  $n = \infty$

  $\Rightarrow$ As an approximation n=10 for Gaussian profiles: n<10 only has effects on the shape of the tails of the profile, emphasis of Cauchy profile.

⇒ Typically applies to broad peaks (e.g. strain broadening associated with cold worked materials).

- Lorentzian (Cauchy) Profiles (Figure 2 Lorentzian Profile)

  ⇒ General expression:

$$I_{2\theta} = \frac{I_{2\theta_o}}{(1+k^2x^2)}$$

$$k = \frac{(2-1)^{\frac{1}{2}}}{\frac{\beta}{2}}$$

$x = 2\theta_i - 2\theta_o$ = deviation from Bragg angle $2\theta_o$ (peak maximum)

  ⇒ Same as Gaussian expression except n = 1

  ⇒ Typically applies to crystallite size (particle size) broadening

- Principal difference between Gaussian and Lorentzian is the rate of decay of the tails, in general symmetric XRD peaks fall in between these two functions.

- Other functions used to profile fit symmetric XRD peaks:

  ⇒ General equation:

$$I_{2\theta} = \frac{I_{2\theta_o}}{(1+k^2x^2)^n}$$

$$k = \frac{(2^{(\frac{1}{n})} - 1)^{\frac{1}{2}}}{\frac{\beta}{2}}$$

$x = 2\theta_i - 2\theta_o$ = deviation from Bragg angle

$2\theta_o$ (peak maximum)

β = FWHM

$\Rightarrow$ Intermediate Lorentzian n = 1.5

$\Rightarrow$ Modified Lorentzian n = 2.0

$\Rightarrow$ Pseudo-Voight is the sum of Gaussian and Lorentzian profiles and the amount of each profile is a variable.

$\Rightarrow$ Pearson VII allows the value of n to vary.

- ♦ Typically, need to know which function best describes the XRD data; however, the Pearson VII function adapts to the XRD data provided the XRD data is symmetric
- ♦ Potential problem fitting to data with poor statistical quality, may fit to statistical deviations: a forced function may be better (ex. Gaussian, Lorentzian, Puesdo-Voight).

- For asymmetric XRD peaks use the Split Pearson function:

$$I_{2\theta} = \frac{I_{2\theta_o}}{(1 + k^2 x^2)^n} \longrightarrow \text{for x positive}$$

$$I_{2\theta} = \frac{I_{2\theta_o}}{(1 + k'^2 x^2)^{n'}} \longrightarrow \text{for } x \leq 0$$

$$k = \frac{(2^{(\frac{1}{n})} - 1)^{\frac{1}{2}}}{\frac{\beta}{2}}$$

$$k' = \frac{(2^{(\frac{1}{n'})} - 1)^{\frac{1}{2}}}{\frac{\beta}{2}}$$

$\Rightarrow$ Split Pearson allows the value of n and n' to vary independently.

$\Rightarrow$ The profiles to the left and right of the peak maximum are independent allowing the Split Pearson function to fit asymmetric XRD peaks.

$\Rightarrow$ Potential problem fitting to data with poor statistical quality, may fit to statistical deviations: a forced function may be better (ex. Gaussian, Lorentzian, Puesdo-Voight).

$\Rightarrow$ Make sure you expect an asymmetric peak shape, e.g. stacking faults, etc.

- Profiles are fit to the raw XRD data by minimization of the following equation:

$$R = 100\sqrt{\frac{\sum_i w_i^2 (I_{observed} - I_{calculated})^2}{\sum_i w_i^2 I_{observed}^2}}$$

w_i = weighting factor

R = the error in % between the observed and calculated profiles

⇒ Profile fit program varies the parameters for the chosen function and performs iterations until there is no further change in the error, uses a modified simplex method of convergence.

⇒ Requires that an initial profile be inserted that is a rough approximation of the XRD data.

⇒ Typically the user inputs the initial profile (although the DMSNT software can insert the initial profile) graphically by inputting the left FWHM, peak maximum and position, and right FWHM.

3. Comments on the Profile Fitting of XRD Data

- Profile fitting can be considered as a method of smoothing peaks without distortion.

- Allows for accurate integrated intensities (area) by direct numerical integration of the mathematical function representing the profile.

- Determines FWHM from the width at half maximum of the final profile and the peak position from the centriod of the profile.

- Excellent method to determine quantitative information from XRD peaks that overlap (unresolved peaks).

- Provides a method of accurate $K\alpha_2$ stripping by fitting a profile to the $K\alpha_2$ component of the peak (based on the fixed relationships between $K\alpha_1$ and $K\alpha_2$) and **reporting information only for the $K\alpha_1$ component**. See Figure 3 and 4.

- Typically the Pearson VII and Split Pearson functions provide the best fit.

- Determine which function provides the best fit to the raw XRD data by the profile that results in the lowest error value.

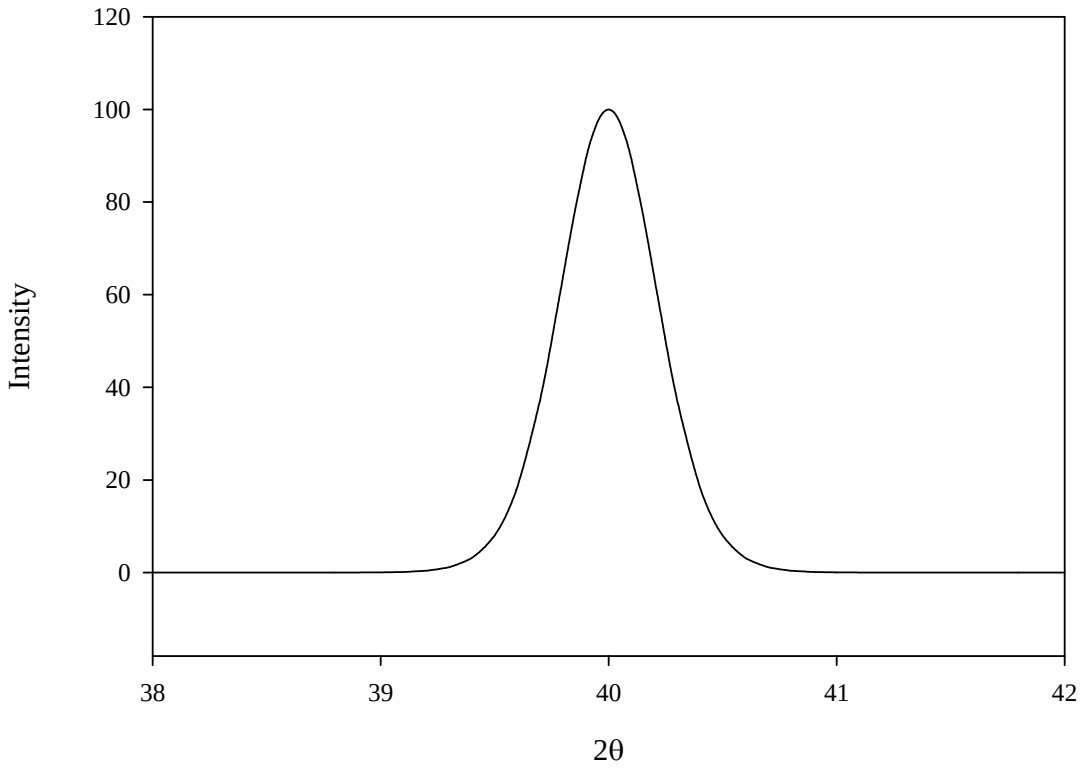

Figure 1 Gaussian Peak Profile

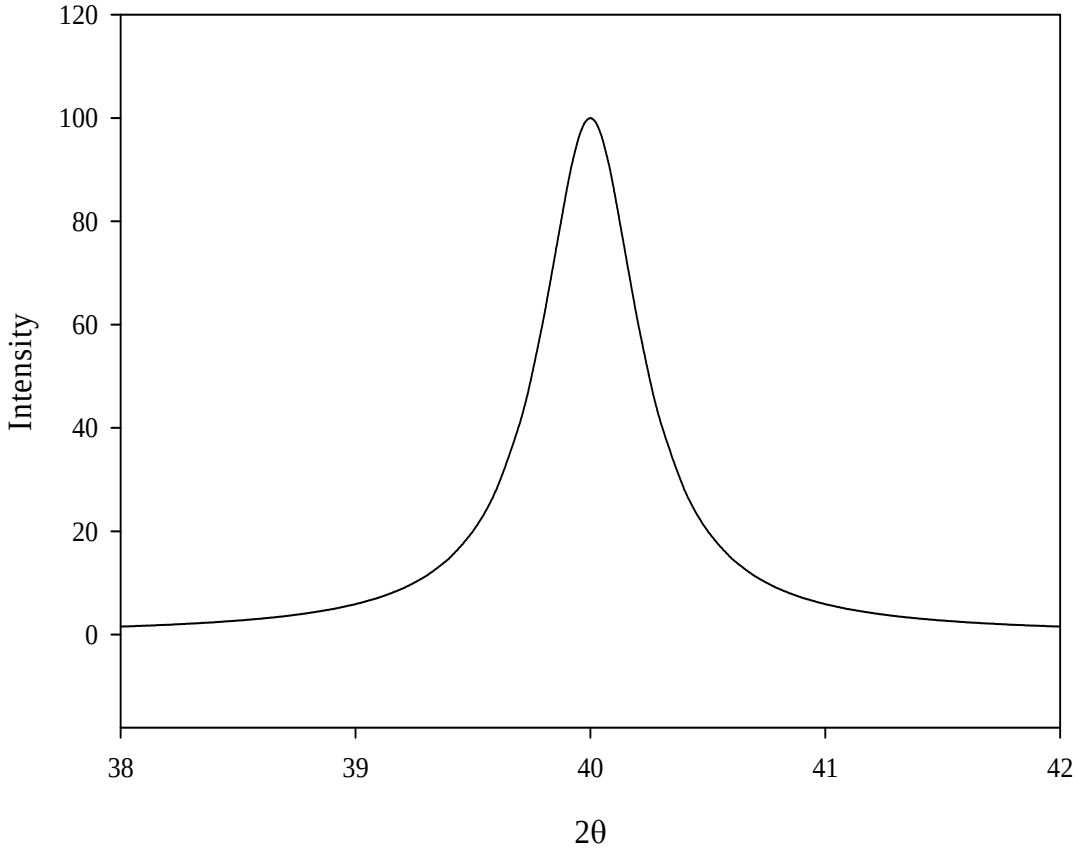

Figure 2 Lorentzian Profile

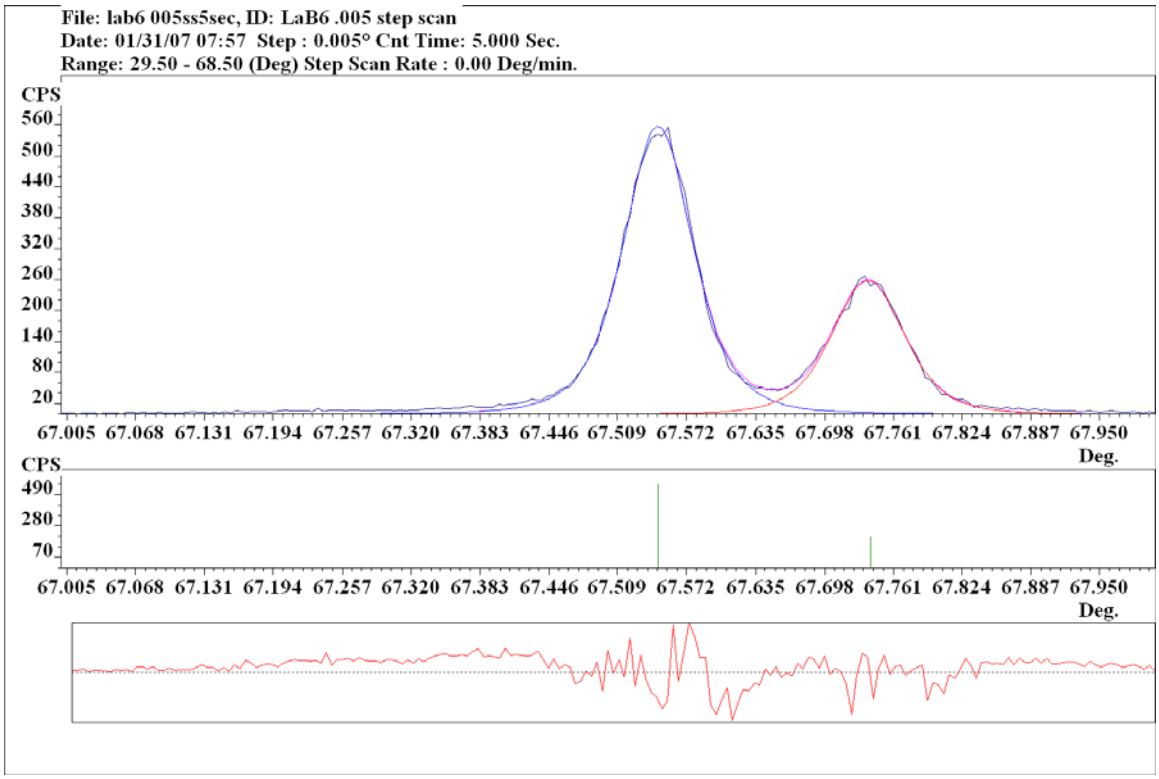

Figure 3 Profiles of Individual $K_{\alpha 1}$ and $K_{\alpha 2}$

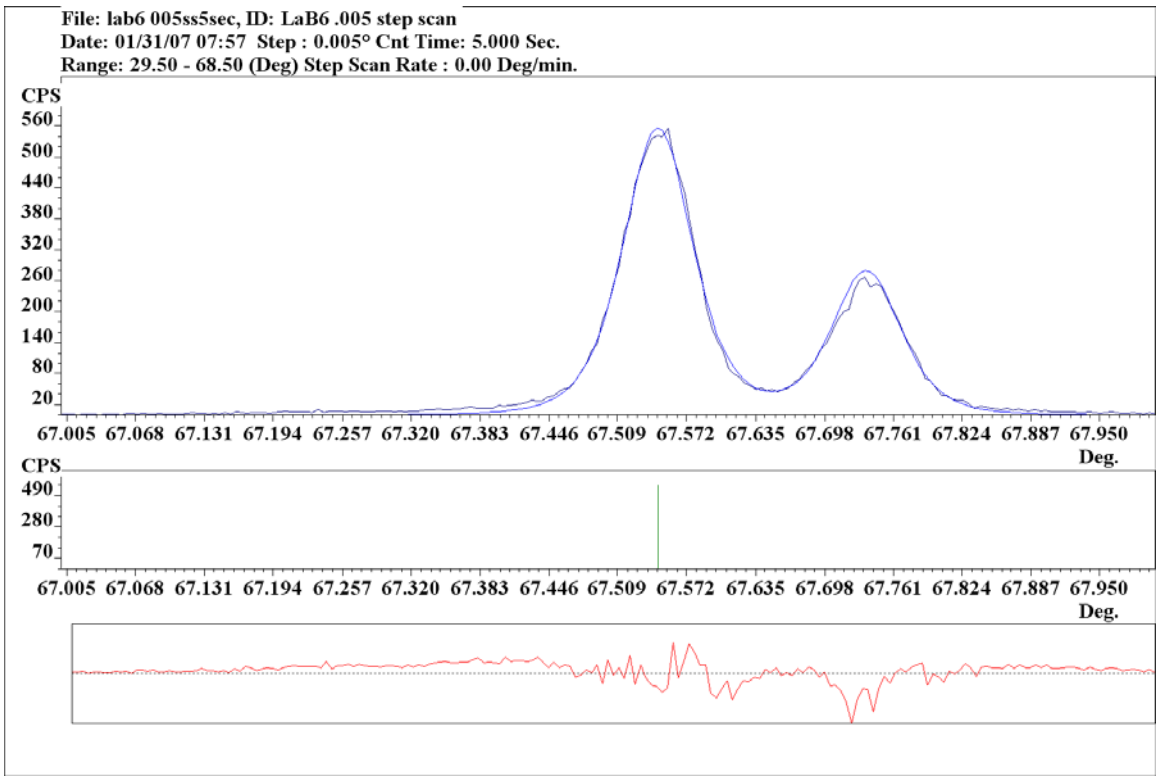

Figure 4 Profile Fit Using Automatic $K_{\alpha 2}$ Fit