

TEACHING AND EDUCATION IN CRYSTALLOGRAPHY

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Peak Decomposition using Pearson Type VII Function

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Abstract

An X-ray diffraction peak-decomposition procedure using a Pearson type VII function is described and implemented in a Microsoft Excel spreadsheet to aid a beginning student of X-ray diffraction.

1. Introduction

In analyzing an X-ray diffraction peak, it is often desirable to separate the $K\alpha_1$ component from $K\alpha_2$ (Gupta & Cullity, 1980). A variety of analytical functions describing the peak-profile shape (Young, 1993) and algorithms for profile analysis (Yoshioka & Ohya, 1993) have been developed. These algorithms are usually implemented in a higher-level programming language on a computer. This paper outlines a peak-decomposition procedure using Pearson type VII functions, which is implemented in a Microsoft Excel spreadsheet (Gottfried, 1996) to aid a beginning student of X-ray diffraction. The procedure and the implementation can be modified easily to use an analytical function other than Pearson type VII.

2. Theory

In Fig. 1, the intensity I_{corr} (corrected for Lorentz-polarization and absorption factors) is plotted as a function of the scattering angle 2θ for the 113 peak from an α -alumina 0.3 μm powder specimen using Cu $K\alpha$ radiation and a curved graphite crystal monochromator. To improve the numerical precision of computations, for each data point i , the angle $2\theta_i$ is scaled by $2\theta_{\text{ref}}$ such that

$$x_i = 2\theta_i - 2\theta_{\text{ref}} \quad (1)$$

and the corrected intensity $I_{\text{corr},i}$ is scaled by I_{max}

$$y_i = I_{\text{corr},i}/I_{\text{max}} \quad (2)$$

where $(2\theta_{\text{ref}}, I_{\text{max}})$ are the coordinates of the maximum as shown in Fig. 1. Another advantage of scaling the data

points is that it provides suitable starting values for the coordinates of the peak maximum during curve fitting, which are independent of the peak selected, *i.e.* $x \simeq 0$ and $y \simeq 1$.

If the $K\alpha_1$ component of the peak can be described by a function $f(x)$, then the $K\alpha_2$ component, separated from $K\alpha_1$ by angle δ , can be expressed as $kf(x - \delta)$ where k is the intensity ratio commonly chosen to be $\frac{1}{2}$ (Yoshioka & Ohya, 1993). The separation angle δ obtained from differentiating the Bragg's law is given by

$$\delta = 2(\Delta\lambda/\lambda) \tan \theta \quad (3)$$

where $\Delta\lambda$ is the difference between wavelengths of $K\alpha_1$ and $K\alpha_2$ radiation, and λ can be the weighted average of the two wavelengths. Another description of δ [equation 1 in Gupta & Cullity (1980)] may be used instead, but it is more expensive computationally.

When a simple linear background contribution $g(x) = px + q$ to intensity is assumed, the complete profile becomes

$$y(x) = f(x) + 0.5f(x - \delta) + g(x). \quad (4)$$

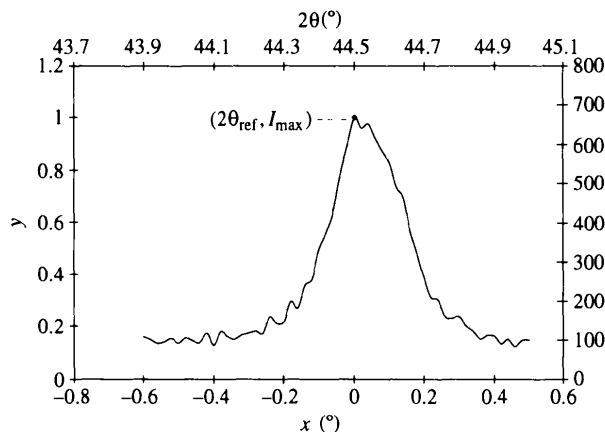


Fig. 1. Incompletely resolved $K\alpha$ doublet.

The Pearson type VII function has been found to describe the $K\alpha$ peak shape to a good approximation (Hall *et al.*, 1977). Its form is

$$f(x) = a \left[1 + \frac{(x-d)^2}{b^2} \right]^{-m} \quad (5)$$

where (d, a) are the coordinates of the peak maximum, exponent m is a shape factor that determines the rate at which the tails fall, and b is proportional to the full width at half-maximum (FWHM) $[= 2b(2^{1/m} - 1)^{1/2}]$. When the exponent $m = 1$, the shape becomes Cauchy; $m = 2$, modified Lorentzian; and $m = \infty$, Gaussian.

Assuming that m and b are identical for $K\alpha_1$ and $K\alpha_2$ peaks, and substituting (5) in (4) yields

$$y(x) = a \left[1 + \frac{(x-d)^2}{b^2} \right]^{-m} + \frac{a}{2} \left[1 + \frac{(x-d-\delta)^2}{b^2} \right]^{-m} + (px + q). \quad (6)$$

The six profile parameters a, b, m, d, p and q can be obtained by a nonlinear least-squares curve-fitting procedure which minimizes the sum of the squares of deviation of the curve from the data ordinates

$$S(a, b, m, d, p, q) = \sum_i [y(x_i) - y_i]^2. \quad (7)$$

3. Implementation

The Solver utility of Microsoft Excel 7.0a is employed to obtain the six profile parameters. Fig. 2 shows the spreadsheet.

3.1. Input data

The input data $(2\theta_i, I_{corr,i})$ are in the cell range A6:B61. Please note that rows 8–59 are hidden in Fig. 2.

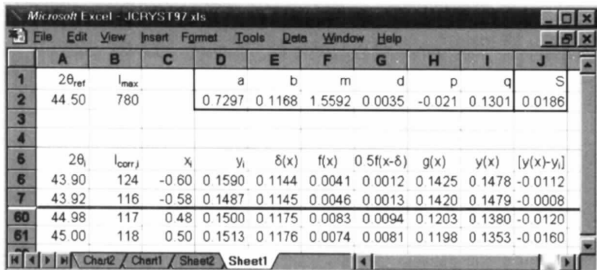


Fig. 2. Excel spreadsheet set-up.

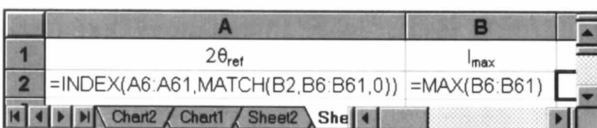


Fig. 3. Scaling formulae.

3.2. Scaling

I_{max} in cell B2 is obtained by finding the largest value using the MAX function in the range B6:B61. The formula to find the corresponding scattering angle $2\theta_{ref}$ is shown in Fig. 3. The MATCH function in the formula locates the position of I_{max} among the $I_{corr,i}$ values, and the INDEX function finds the corresponding value among the $2\theta_i$ values. Equations (1) and (2) are used to obtain scaled values (x_i, y_i) in the cell range C6:D61 as shown in Fig. 2.

3.3. Separation angle

Equation (3) is used to compute the corresponding separation angle $\delta(x_i)$ in the cell range E6:E61. The formula is shown in Fig. 4. The DEGREES function converts the resulting value to degrees.

3.4. Parameters

The curve-fitting parameters a, b, m, d, p and q are in named cells D2:I2 with appropriate names listed in the row above the values as shown in Fig. 2. Reasonable starting values are assigned to the parameters, e.g. $a = 1, b = 0.5^\circ, m = 2, d = 0^\circ, p = 0$ and $q = 0$.

3.5. Scaled intensities

Formulae for scaled intensities $f(x), f(x - \delta)/2$ and $g(x)$ representing the $K\alpha_1, K\alpha_2$ and the background contributions, respectively, appear in cells F6:H61 as

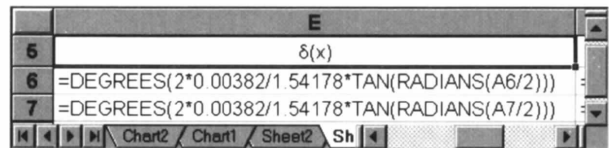


Fig. 4. Formula for doublet separation angle.

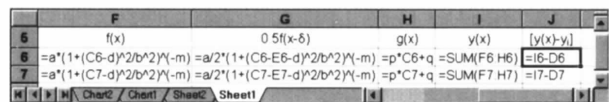


Fig. 5. Formulae for intensity contributions and deviation.

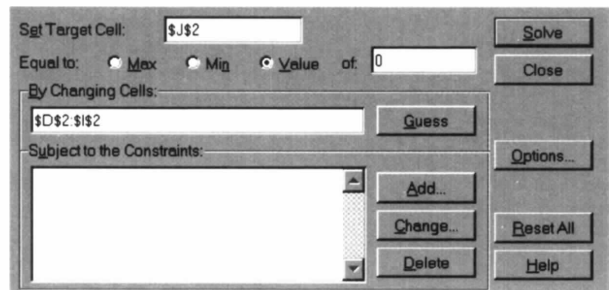


Fig. 6. Solver utility dialog box.

shown in Fig. 5. The three contributions are summed in cells I6:I61 and the deviation from the data (y_i) is computed in J6:J61. The sum of the squares of deviation $S = \text{SUMSQ}(J6:J61)$ is computed in cell J2 (see Fig. 2). A user needs to enter only one row (C6:J6) of formulae. The copy or fill tool can then be used to copy these formulae to rows 7–61.

3.6. Solver utility

The Solver utility is selected from the Tools menu. The sum-square deviation S in cell J2 is set to be minimized with respect to the six parameters in cells D2:I2 as shown in Fig. 6.

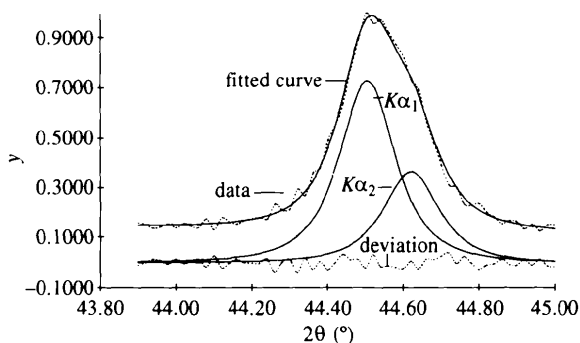


Fig. 7. Curve fitting and deviation.

The Solver Options dialog box permits a user to alter the default settings of parameters such as the maximum number of iterations, precision and tolerance. When the Solver produces the best scenario with respect to the options chosen, the individual components, deviation and the sum curve can be plotted to evaluate the quality of the curve-fitting procedure as shown in Fig. 7. The results (see Fig. 2) show that the $K\alpha_1$ peak is located at $44.5035^\circ (= d + 2\theta_{ref})$ with relative intensity of $a = 0.73$, and has $b = 0.12^\circ$ ($\text{FWHM} \approx 0.175^\circ$). The peak shape is a composite of Cauchy and modified Lorentzian types ($1 < m < 2$).

This Microsoft Excel file (Windows 95) is available on the WWW at www.rit.edu/~skgame/xray/pearson.xls.

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