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Correction and Interpretation of Fourier Coefficients of X-ray Diffraction Patterns from Very Small, Distorted Crystals

BY D. H. KOBE*

Hanford Laboratories, Richland, Washington, U.S.A.

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This paper presents a method for correcting the Fourier coefficients of (00*l*) X-ray diffraction patterns from powders of very small, distorted crystals to take into consideration a function of the diffraction angle that should multiply the Fourier series. The function, which is usually assumed constant, is the product of the crystal structure factor, the polarization factor, and the Lorentz factor, and can vary greatly over the diffraction peak in some cases. The corrected coefficients must then be separated into the particle size coefficients and the distortion coefficients. A method for obtaining the discrete particle size distribution function directly from the particle size coefficients is presented. The distortion coefficients are used to determine the moments of the distortion, from which the probability density functions for the distortion can be obtained by means of a Gram–Charlier series.

Introduction

An equation has been derived (Warren & Averbach, 1950) which expresses the power diffracted in an (00*l*) diffraction pattern from a powder of very small, distorted crystals as a function of diffraction angle. The function is in the form of a Fourier series

$$p(x)=q(x)\sum_{n=-\infty}^{\infty} C_n \exp(-2\pi inx)\,, \tag{1}$$

where

$$x=2a\sin\theta/\lambda$$

and

$$q(x)=K|F|^2(1+\cos^2 2\theta)/2\sin^2\theta\,. \tag{2}$$

The angle θ is the diffraction angle, a is the interplanar spacing in the (00*l*) direction, λ is the wavelength of the X-rays, F is the crystal structure factor, and K is a constant. The factor $(1+\cos^2 2\theta)/2$ in equation (2) is the polarization factor and $1/\sin^2\theta$ is the Lorentz factor. Because of the Lorentz factor, $q(x)$ is a very rapidly varying function at small angles.

The coefficient C_n can be written as

$$C_n=A_nB_n(l)\,, \tag{3}$$

where

$$A_n=(1/J)\sum_{j=|n|+1}^{\infty}(j-|n|)m_j \tag{4}$$

and

$$B_n(l)=\langle\exp(-2\pi ilZ_n)\rangle\,. \tag{5}$$

The term J is the average number of cells per column, m_j is the fraction of columns with j cells, and $a(n+Z_n)$ is the distance between two points n cells apart, all in the (00*l*) direction. The angular brackets denote an average with respect to Z_n over the sample. From equations (3), (4), and (5) it can be seen that $C_0=1$.

* Present address: Department of Physics, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.

Correction of the coefficients for the multiplying function

If the value of $q(x)$ at the middle of the interval is used, equation (1) becomes

$$p(x)=q(l)\sum_{m=-\infty}^{\infty} D_m \exp(-2\pi imx)\,. \tag{6}$$

The coefficients D_m are obtained from the observed diffraction peak and the instrumental broadening function by the method of Stokes (1948). The variation of $q(x)$ over the diffraction peak will cause the coefficients D_m to differ from C_m, with the amount of difference dependent on the slope of the function $q(x)$.

Equating equation (1) and (6), and dividing through by $q(x)$ gives

$$\sum_{n=-\infty}^{\infty} C_n \exp(-2\pi inx) = [q(l)/q(x)]\sum_{m=-\infty}^{\infty} D_m \exp(-2\pi imx)\,. \tag{7}$$

Now the function $q(l)/q(x)$ may be expanded in a Fourier series

$$q(l)/q(x)=\sum_{k=-\infty}^{\infty} Q_k \exp(-2\pi ikx)\,. \tag{8}$$

If equation (8) is substituted into equation (7) the result is

$$\sum_{n=-\infty}^{\infty} C_n \exp(-2\pi inx) = \sum_{k=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} Q_kD_m \exp[-2\pi i(k+m)x]\,. \tag{9}$$

Now let $n=k+m$, so that $k=n-m$. Then equation (9) becomes

$$\sum_{n=-\infty}^{\infty} C_n \exp(-2\pi inx) = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} Q_{n-m} D_m \exp(-2\pi inx) . \quad (10)$$

Since a Fourier series is unique, the corresponding coefficients in equation (10) can be equated

$$C_n = \sum_{m=-\infty}^{\infty} Q_{n-m} D_m . \quad (11)$$

Therefore, to obtain the corrected coefficient C_n, equation (11) shows that an infinite sum must be performed. In practice, it is only necessary to sum until the desired degree of convergence is obtained.

Since all the terms in equation (11) are complex, it may be broken into its real and imaginary parts. If the real and imaginary parts of the coefficients are denoted by the superscripts r and i respectively, we have

$$C_n^r = \sum_{m=-\infty}^{\infty} (Q_{n-m}^r D_m^r - Q_{n-m}^i D_m^i) \quad (12)$$

$$C_n^i = \sum_{m=-\infty}^{\infty} (Q_{n-m}^i D_m^r + Q_{n-m}^r D_m^i) . \quad (13)$$

Now from the definition of the Fourier coefficient for a real function, $D_{-m} = D_m^*$. Therefore, equations (12) and (13) may be rewritten to give

$$C_n^r = Q_n^r D_0^r + \sum_{m=1}^{\infty} (Q_{n-m}^r + Q_{n+m}^r) D_m^r - Q_n^i D_0^i + \sum_{m=1}^{\infty} (-Q_{n-m}^i + Q_{n+m}^i) D_m^i . \quad (14)$$

$$C_n^i = Q_n^i D_0^r + \sum_{m=1}^{\infty} (Q_{n-m}^i + Q_{n+m}^i) D_m^r + Q_n^r D_0^i + \sum_{m=1}^{\infty} (Q_{n-m}^r - Q_{n+m}^r) D_m^i . \quad (15)$$

In practice, these equations can be simplified since $D_0 = 1$ and D_m^i are generally small. It is now only necessary to determine the coefficients Q_k to enable the corrected coefficients to be calculated from equations (14) and (15).

The coefficient Q_k in equation (8) is

$$Q_k = \int_{l-\frac{1}{2}}^{l+\frac{1}{2}} [q(l)/q(x)] \exp(2\pi ikx) dx . \quad (16)$$

Now the function $q(l)/q(x)$ may be approximated by a polynomial

$$q(l)/q(x) = \alpha x^2 + \beta x + \gamma . \quad (17)$$

Substituting equation (17) into equation (16) and performing the integration gives

$$Q_k = \begin{cases} [\alpha(-1)^k/2\pi^2 k^2] + i[s(-1)^k/k], & k \neq 0 \\ 1 + (\alpha/12), & k = 0 \end{cases}$$

where

$$s = -[\alpha l + (\beta/2)]/\pi .$$

A higher order polynomial may be used to obtain a better approximation.

It may be asked why the observed diffraction peak $f(x)$ cannot be divided directly by $q(x)$ and then corrected for the instrumental broadening function $g(x)$. This procedure may be satisfactory when the instrumental broadening is very small, or $q(x)$ is a very slowly varying function. However, in general, this procedure is not mathematically justifiable because of the form of the convolution integral for instrumental broadening (Jones, 1938)

$$f(x) = \int_{-\infty}^{\infty} p(y) g(x-y) dy . \quad (18)$$

If equation (1) is substituted into equation (18), the function $q(y)$ cannot be taken outside of the integral unless it is a constant. If $g(x-y)$ is a delta function, the integral reduces to $p(x)$. Equations (14) and (15) should be used in cases where $q(x)$ changes appreciably over the pattern or the instrumental broadening is important.

Interpretation of particle size coefficients

Once the coefficients $C_n(l)$ have been obtained, each of them can be separated into the corresponding A_n and $B_n(l)$ if more than one order of reflection has been measured (Warren & Averbach, 1952). It will be assumed in the rest of this paper that the separation can be made, or that A_n or B_n is unity for all n.

Previous workers (Bertaut, 1949; Warren & Averbach, 1950) have introduced a continuous particle size probability density function, and replaced the summation in equation (4) with an integration. If n is assumed to be a continuous variable, the particle size probability density function is proportional to the second derivative of A_n. A more direct and mathematically simpler method has been found by using equation (4) directly, which yields the physically more meaningful discrete particle size distribution function.

Equation (4) may be rewritten in the form

$$A_n = (1/J) \sum_{j=1}^{\infty} (j - |n|) m_j - (1/J) \sum_{j=1}^{|n|} (j - |n|) m_j . \quad (19)$$

Now by definition of m_j we have

$$\sum_{j=1}^{\infty} m_j = 1$$

and

$$\sum_{j=1}^{\infty} j m_j = J .$$

Therefore equation (19) becomes

$$A_n = 1 - (|n|/J) + (1/J) \sum_{j=1}^{|n|} (|n| - j) m_j . \quad (20)$$

Without making any assumptions J may be calculated by setting $n = 1$ in equation (20)

$$A_1 = 1 - (1/J) \quad (21)$$

since the coefficient A_1 is known. However, unless very accurate data are used, this equation may not be applicable because of the error in the coefficients for small n caused by inaccurate measurement of the tails of the diffraction peak (Eastabrook & Wilson, 1952).

The terms m_j may be calculated from equation (20). Let

$$\alpha_{n-1} = J(A_n - 1) + |n| \,, \tag{22}$$

which can be calculated from the coefficients. Substituting equation (20) into equation (22) gives

$$\alpha_{n-1} = \sum_{j=1}^{|n|} (|n| - j) m_j \,. \tag{23}$$

The set of equations represented in equation (23) may be written out

$$\begin{aligned} \alpha_1 &= m_1 \\ \alpha_2 &= 2m_1 + m_2 \\ \alpha_3 &= 3m_1 + 2m_2 + m_3 \\ &\cdots\cdots \end{aligned} \tag{24}$$

Equation (24) may easily be solved consecutively for the unknowns m_j. The distribution function for the particle size is

$$F(y) = \sum_{k=1}^{[y]} m_k \,, \tag{25}$$

where $[y]$ denotes the largest integer less than y. If $F(y)$ is plotted against y, a discrete distribution function will result. If equation (25) does not correlate the data in a physically meaningful way, either the data are not sufficiently accurate or equation (1) is not applicable to the problem.

Interpretation of distortion coefficients

From the distortion coefficients in equation (5), the moments of the distortion indices Z_n may be obtained. The probability density function for Z_n, $P_n(Z_n)$, can be determined from the moments by means of a Gram–Charlier series. This method provides a means for obtaining an approximate probability density function, even if only one or two orders are measured. The other method (Warren & Averbach, 1950) for obtaining the distortion probability density functions requires that l be assumed to be a continuous variable and that enough orders are measured to determine $B_n(l)$ as a function of l between zero and infinity. It is generally difficult to obtain this many orders.

The coefficient B_n in equation (5) can be written as follows

$$B_n(l) = \langle \cos (2\pi l Z_n) \rangle - i \langle \sin (2\pi l Z_n) \rangle \,. \tag{26}$$

Equating the real and imaginary parts of equation (26) and expanding the trigonometric functions in a Maclaurin series gives

$$Re\, B_n(l) = 1 - \frac{(2\pi l)^2}{2!} \langle Z_n^2 \rangle + \frac{(2\pi l)^4}{4!} \langle Z_n^4 \rangle - \dots \tag{27}$$

$$Im\, B_n(l) = -2\pi l \langle Z_n \rangle + \frac{(2\pi l)^3}{3!} \langle Z_n^3 \rangle - \dots \tag{28}$$

If m orders are measured in the $(00l)$ direction, equation (27) and (28) may each be solved for m moments. Therefore, the moments through $\langle Z_n^{2m} \rangle$ can be calculated.

These moments may now be used in a Gram–Charlier series (Rietz, 1927) to give the probability density function for the distortion indices. The density function for the nth distortion index is

$$P_n(Z_n) = \frac{1}{(2\pi)^{\frac{1}{2}} \sigma_n} \left[1 + \sum_{k=3}^{\infty} \frac{1}{k!} \left\langle H_k \left(\frac{Z_n - \langle Z_n \rangle}{\sigma_n} \right) \right\rangle \times H_k \left(\frac{Z_n - \langle Z_n \rangle}{\sigma_n} \right) \right] \exp \left[- \frac{(Z_n - \langle Z_n \rangle)^2}{2\sigma_n^2} \right] , \tag{29}$$

where

$$\sigma_n = [\langle Z_n^2 \rangle - \langle Z_n \rangle^2]^{\frac{1}{2}}$$

and

$$\left\langle H_k \left(\frac{Z_n - \langle Z_n \rangle}{\sigma_n} \right) \right\rangle = \int_{-\infty}^{\infty} H_k \left(\frac{Z - \langle Z_n \rangle}{\sigma_n} \right) P_n(Z) dZ \,.$$

The function $H_k(y)$ is the Hermite polynomial, which is defined as

$$H_k(y) = y^k - \frac{k(k-1)}{2} y^{k-2} + \frac{k(k-1)(k-2)(k-3)}{2 \times 4} y^{k-4} - \dots .$$

The angular brackets again denote the expected value. Equation (29) reduces to the Gaussian density function if only the first and second moments are used. In practice, probably no more than four or five orders can be measured, so that the maximum value of k in equation (29) will be eight or ten.

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