This then completes the development of $P(r,k_1,k_2)$, and the integrals in equation (12) have been reduced to functions of the parameters which describe the scattering system.

8. Summary

Mathematical expressions for the equatorial intensity have been presented which involve the Fourier transform of the fibril, interfibrillar interference function, and effects of lattice distortions in a quantitative manner. Also, allowances have been made for the effects of structural inhomogeneities by leaving the coherent size as a free parameter and allowing for the possibility of an additional scattering component due to associated electron-density fluctuations. One of the most important features of these equations is that the functional form of the Fourier transform of the fibril is known in the region $0<k<k_0$ and involves only a single parameter, R_e, which can be related to the radius of gyration of the fibril. It is emphasized that this expression for the fibril is not a model but a modification of the Guinier approximation and holds very well for $k<k_0$.

Mathematical expressions for the low-resolution Patterson function have also been derived, and their accuracy has been demonstrated to be within a few percent. Techniques for the use of these expressions, along with a different approach, are presented in the next paper of this series, where lattice distortions and higher-resolution data are also considered.

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Direct Evaluation of $K\alpha_1$ Fourier Coefficents in X-ray Profile Analysis

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Using a least-squares method of analyzing X-ray diffraction profiles, it is shown that one can calculate directly the Fourier coefficients of the $K\alpha_1$ component from the total $K\alpha$ doublet intensities. These Fourier coefficients can be calculated around any preferred points of the profile, *e.g.* the center of gravity or peak of the profile of $K\alpha_1$.

Introduction

Fourier analysis of X-ray diffraction lines normally requires that the intensity be given for the $K\alpha_1$ component alone. To this end a few methods of separating the $K\alpha$ doublet have been proposed. The works of Brill (1928), Jones (1938) and Finch (1949) all assume that the $K\alpha_1$ profile has a known functional form (*e.g.* Gaussian). This assumption is not valid in the case of line profiles taken from deformed materials (Warren, 1960) where Fourier analysis is extensively used. Also, the assumption of Papoulis (1955) that the profile is

symmetrical does not hold for materials that contain twin or double layer stacking faults (Warren, 1960). The well-known graphical method of Rachinger (1948) to separate the doublet is not accurate enough for the high-angle side of the profile (Warren, 1960). Keating (1959) has shown how to calculate the $K\alpha_1$ profile from the $K\alpha$ doublet and recently Gangulee (1970) has shown how to calculate the Fourier coefficients of $K\alpha_1$, after the coefficients of the $K\alpha$ doublet were determined.

Here we show how one can evaluate the coefficients of the $K\alpha_1$ profile directly from the experimental intensity profile eliminating the need of separating the $K\alpha_1$ profile from the $K\alpha_2$ profile or the need of calculating the coefficients of the doublet profile first. This method of evaluation also gives the Fourier coefficients of the $K\alpha_1$ profile analyzed around its center of gravity (or any other preferred point). This is important where two sets of Fourier coefficients *e.g.* of an 'annealed profile' and a 'broadened profile' are used in a Stokes correction to determine the coefficients of the true diffraction profile (Warren, 1960).

A recently developed least-squares-analysis method of computing the Fourier coefficients is employed; this method has been shown to have several important advantages over the normal Fourier transform method (Kidron & De Angelis, 1971).

Method of analysis

The Fourier-transform method

The intensity of an X-ray diffraction profile, normalized to give an integrated intensity of unity, is given by a Fourier series

$$I(h) \simeq \sum_{l=\infty}^{\infty} \{A_l \cos 2\pi lh + B_l \sin 2\pi lh\} \qquad (1)$$

where h is the reciprocal space variable and l is the harmonic number. Usually the variable h is changed into a dimensionless variable j, where $j=0$ coincides with the intensity maximum of the line (de Angelis, 1965) or with its center of gravity. By this change of variables equation (1) can be transformed into (de Angelis, 1965)

$$I(j) = A_0 + \sum_{l=1}^{\infty} \left\{2A_l \cos \frac{2\pi lj}{q} + 2B_l \sin \frac{2\pi lj}{q}\right\} \qquad (2)$$

where q is the number (even) of intervals along the profile, and

$$j0, = \pm 1, \pm 2, \text{------}, \pm [q/2)+1]$$

A Fourier transformation of (2) gives the coefficients A_l, B_l.

The least-squares method

In the least-squares analysis (LSA) (Kidron & de Angelis, 1971) the Fourier coefficients are computed from a set of linear equations of the form

$$I(n) = \sum_{k=1}^{p} F_k \cdot C_{n,k} \quad \begin{matrix} n=1,2,\text{----------},n \\ p=\text{odd.} \end{matrix} \qquad (3)$$

where $I(n)$ are the experimental intensities at different points along the line profile. F_k and $C_{n,k}$ are related to the coefficients in equation (2) by

$$\left.\begin{aligned} F_1 &= A_0 \\ F_k &= 2A_l \\ C_{j,k} &= \cos \frac{2\pi lj}{q} \end{aligned}\right\} \text{for } l=1,2,\text{------}, \frac{p-1}{2}$$

and $k=l+1$

$$\left.\begin{aligned} F_k &= 2B_l \\ C_{j,k} &= \sin \frac{2\pi lj}{q} \end{aligned}\right\} \text{for } l=1,2,\text{------}, \frac{p-1}{2}$$

and $k=l+\left(\frac{p+1}{2}\right)$

$B_0=0$, and is taken out of the equations (3).

In the LSA the terms $C_{n,k}$ are first calculated in the form of $C_{j,k}$ with $j=0, \pm 1, \text{----------}, \pm\left(\frac{q}{2}+1\right)$;

$j=0$ being the center of gravity (centroid) of the profile. Then $C_{j,k}$ are rearranged and written in the form $C_{n,k}$ with $n=1,2,\text{----------},m$ where $m=q+1$ and where $n=1$ corresponds to the first non-zero intensity point on the low-angle side of the profile, and $n=m$ is the last non-zero intensity point on the high-angle side of the profile.

The calculation of F_k in (3) by the LSA will give then the Fourier coefficients of the profile around its center of gravity.

Fourier coefficients of the $K\alpha_1$ component:

In evaluating the Fourier Coefficients of the $K\alpha_1$ profile the following assumptions are employed:

(*a*) The shapes of the $K\alpha_1$ profile (I_1) and of the $K\alpha_2$ profiile (I_2) are the same.

(*b*) The ratio R of the integrated intensity of I_1 to that of the doublet profile I is known.

(*c*) The separation between the centers of gravity of I_1 and I_2 is also known.

For filtered radiation R is usually $\frac{2}{3}$ and the angular separation between I_1 and I_2 is given by the relative change in wavelength. Nothing is assumed here concerning the shape of the line (symmetrical, Gaussian, *etc.*) and also the experimental data can be taken at arbitrary intervals, as long as these intervals are small enough to adequately depict the shape of the profile.

Because of assumption (*a*) the profiles I_1 and I_2 will have the same Fourier coefficients except for a normalization factor, when calculated around the centers of gravity of the respective lines. If s is the separation be-

tween the centers of gravity of $I_1(n)$ and $I_2(n)$ then their normalized profiles can be written as:

$$I_1(n)=I_2(n+s)=\sum_{k=1}^{p}F_k \,.\, C_{n,k} \quad n=1,2,\ \ldots\ ,(r-s) \quad (4)$$

where F_k are the Fourier coefficients of $I_1(n)$ above, and $n=1,2\ \ldots\ r$ giving the total span of the doublet. The total observed profile will be

$$I(n)=RI_1(n)+(1-R)I_2(n+s) \quad (5)$$

which according to (4) can be written as

$$\left.\begin{aligned} &I(n)=\sum_{k=1}^{p}F_k \,.\, C'_{n,k} \qquad n=1,2,\ \ldots \\ &\text{where} \\ &\qquad C'_{n,k}=RC_{n,k}+(1-R)C_{n-s,k} \\ &\text{and} \\ &\qquad C_{n,k}\neq 0 \text{ only for} \qquad r-s\geq n\geq 1\ . \end{aligned}\right\} \quad (6)$$

The set of equations (6) is similar to the set needed in the LSA and given in (3) except that in (6) F_k are the Fourier coefficients of the $K\alpha_1$ profile $I_1(n)$ alone. The actual calculation of F_k involves now the evaluation of $C_{n,k}$ and then a LSA of equations (6).

To check the whole procedure an 'experimental' doublet was generated. This consisted of two Gaussian ($\exp\{-k^2x^2\}$) profiles which were made deliberately asymmetric by taking $k=0{\cdot}15$ on the left side and $k=0{\cdot}10$ on the right. The ratio $R=I_1/I$ was taken as 0·67 and the doublet separation was $s=15$. The total profile was fed into a LSA computer program written to perform the computations as given be equations (4) to (6).

The resulting Fourier coefficients of the $K\alpha_1$ component are given in Table 1 together with the actual Fourier coefficients calculated directly from the $K\alpha_1$ profile (I_1) alone. Notice that both sets of results match perfectly up to the fourth decimal place except in four (out of 50) cases where there is a difference of 0·0001.

Table 1. *The Fourier coefficients of $K\alpha_1$ component I_1 calculated from the input of I_1 alone, and from the input of $I=I_1+I_2$*

Harmonic number	Calculated from I_1		Calculated from I	
l	A_l	B_l	A_l	B_l
0	1·0000	0·0000	1·0000	0·0000
1	0·9450	−0·0083	0·9450	−0·0083
2	0·7975	−0·0237	0·7975	−0·0237
3	0·6011	−0·0461	0·6011	−0·0461
4	0·4040	−0·0675	0·4040	−0·0675
5	0·2403	−0·0791	0·2403	−0·0791
6	0·1235	−0·0772	0·1235	−0·0772
7	0·0509	−0·0646	0·0509	−0·0646
8	0·0119	−0·0473	0·0119	−0·0473
9	−0·0056	−0·0308	−0·0056	−0·0308
10	−0·0112	−0·0180	−0·0112	−0·0180
11	−0·0112	−0·0095	−0·0112	−0·0095
12	−0·0093	−0·0045	−0·0093	−0·0044
13	−0·0072	−0·0017	−0·0072	−0·0017
14	−0·0054	−0·0003	−0·0054	−0·0003
15	−0·0041	0·0004	−0·0040	0·0004
16	−0·0031	0·0007	−0·0031	0·0007
17	−0·0023	0·0009	−0·0023	0·0008
18	−0·0018	0·0009	−0·0018	0·0009
19	−0·0014	0·0009	−0·0014	0·0009
20	−0·0011	0·0009	−0·0011	0·0009
21	−0·0008	0·0009	−0·0008	0·0008
22	−0·0006	0·0008	−0·0006	0·0008
23	−0·0004	0·0007	−0·0004	0·0007
24	−0·0003	0·0007	−0·0003	0·0007
25	−0·0002	0·0006	−0·0002	0·0006

The computed Fourier coefficients were also used to calculate back synthesized $I(n)$ and $I_1(n)$ profiles. This is given in Table 2 together with the input values for every second point. We see that the agreement is better than 0·001.

Table 2. *The input profiles and the profiles calculated back from the Fourier coefficients of $I_1(n)$*

n	The total profile $I(n)$		The total profile $I_1(n)$	
	Input	Back calculated	Input	Back calculated
2	0·0000	0·0000	0·0000	0·0001
4	0·0000	−0·0001	0·0000	−0·0001
6	0·0001	0·0002	0·0001	0·0002
8	0·0007	0·0006	0·0007	0·0006
10	0·0032	0·0032	0·0032	0·0033
12	0·0121	0·0121	0·0122	0·0121
14	0·0392	0·092	0·0392	0·0392
16	0·1054	0·1054	0·1054	0·1054
18	0·2369	0·2368	0·2369	0·2368
20	0·4449	0·4450	0·4449	0·4451
22	0·6978	0·6975	0·6977	0·6973
24	0·9147	0·9152	0·9139	0·9145
26	1·0003	1·0003	1·0000	1·0000
28	0·9719	0·9713	0·9608	0·9602
30	0·8850	0·8855	0·8521	0·8525
32	0·7785	0·7781	0·6977	0·6975
34	0·6933	0·6936	0·5273	0·5274
36	0·6528	0·6525	0·3679	0·3679
38	0·6453	0·6455	0·2369	0·2369
40	0·6297	0·6292	0·1409	0·1409
42	0·5723	0·5728	0·0773	0·0772
44	0·4961	0·4959	0·0392	0·0393
46	0·4077	0·4078	0·0183	0·0182
48	0·3142	0·3142	0·0079	0·0080
50	0·2256	0·2256	0·0031	0·0030
52	0·1503	0·1502	0·0012	0·0013
54	0·0927	0·0927	0·0004	0·0003
56	0·0528	0·0528	0·0001	0·0002
58	0·0278	0·0278	0·0000	0·0000
60	0·0135	0·0135	0·0000	0·0000
62	0·0061	0·0061	0·0000	0·0000
64	0·0025	0·0025	0·0000	0·0000
66	0·0010	0·0019	0·0000	0·0000
68	0·0003	0·0003	0·0000	0·0000
70	0·0001	0·0001	0·0000	0·0000

The same calculations were performed for a doublet made out of two symmetric Gaussian profiles ($k=0{\cdot}15$ both for left side and right side). The matching of the results was as above. This time the sine Fourier coefficients had to come out as zero, and in fact, in both cases, they were smaller than 10^{-4}. This also means that the Fourier coefficients of $I_1(n)$ were calculated around the center of gravity even when the input data was that of $I(n)$ where $I(n)=I_1(n)+I_2(n)$.

In the present work we assumed that $R=I_1/I$ was known. However, R can be easily calculated. It has been shown (Gangulee, 1970) that R can be determined by defining a 'residue' by

$$\text{Residue}=\sum_{n=1}^{n}|I_1'(n)|-I_n'(n)$$

where $I_1'(n)$ is the synthesized $I_1(n)$ profile assuming a given value of R. This 'residue' will be minimum for the correct value of R. The 'experimental' profile was calculated using $R=0{\cdot}67$. Then the profile $I_1(n)$ was calculated using different values of R and the corresponding 'residues' were determined. The plot of the 'residue' *versus* R had a minimum (residue $=0$) at $R=0{\cdot}67$ which is the true value of R.

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The Moments of a Powder Diffraction Profile in the Kinematic Tangent-Plane Approximation

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The nth moment of the diffraction line profile of a small or imperfect crystal is obtained in terms of the derivatives of $V(t)$, the volume common to the crystal and its 'ghost' displaced by a distance t parallel to the scattering vector, and of $J(t)-iK(t)$, the mean value of the product FF^* of the structure factors of unit cells separated by the same translation. The expression takes the form of a series that can be carried to any desired degree of approximation; previously only the first two or three terms had been obtained. For particle-size broadening by crystals of certain simple shapes the series terminates, giving an 'exact' expression.

Introduction

The intensities, positions, widths, asymmetries, ... of diffraction maxima in crystallography have been specified by such measures as peak height, peak position, width at half height, ratio of the intercepts of the chord at half height by the perpendicular through the peak, ... and other *ad hoc* constructs. In mathematics, and particularly statistics, however, the use of the moments of the distribution as measures of its properties is more common. Moments have in fact been used as measures of the effect of geometrical aberrations since the work of Spencer (1931), but their use as measures of the properties of diffraction profiles is comparatively recent, since the 'tails' of these profiles approach zero approximately as the inverse square of the distance from the centre of the profile, so that the zeroth moment (integrated intensity) is convergent, the first moment (centroid position) is convergent by reasonable convention, and all other moments diverge. Tournarie (1956 *a*, *b*), however, investigated the manner of divergence of the second moment (variance), and showed that the second moment of a deliberately truncated portion of the powder diffraction maximum was directly proportional to the length of the truncated portion, the proportionality factor being inversely proportional to the mean crystallite size of the specimen. To the degree

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