

An Improved Method for the Determination of Microstructural Parameters by Diffraction-Profile Fourier Analysis

BY MARCELLO ZOCCHI

*Istituto di Chimica Industriale del Politecnico, Sezione di Strutturistica, Piazza Leonardo da Vinci 32,
20133 Milano, Italy*

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Abstract

The analysis of the influence of the background and truncation errors on the Fourier transform of the diffraction profile is extended with respect to the work that has already been done by others and a critical evaluation of the established Fourier methods for the determination of the microstructural parameters – average dimensions of crystallites and paracrystalline microdomains, lattice-distortion parameters and cumulants of the strain distribution – is presented. It is shown that, contrary to the case of the cosine transform and of its logarithm whose functional behaviour is drastically changed by the truncation error, the first derivative of that transform is modified by this error only by an oscillatory factor which multiplies the first term of its series expansion. The suggestion follows of using this derivative function in the least-squares or curve-fitting determination of the microstructural parameters. It seemed proper to check these theoretical results by comparing them with experimental data, determining by a simple curve-fitting procedure based on this derivative function the microstructural parameters of a high-density polyethylene fibre in directions perpendicular to the fibre axis. The parameters so obtained are in good agreement with the structural data found in the literature for the same material. It is concluded that the use of this derivative function makes possible the reliable determination of important features of the microstructure of materials by a single-line Fourier technique even in the presence of a large truncation error.

1. Introduction

The main sources of error which may limit the accuracy of the methods for determining the microstructural parameters of polycrystalline materials by diffraction-profile Fourier analysis are the following:

- (i) poor knowledge of the functional relationships between these parameters and the Fourier coefficients;
- (ii) sampling and poor counting statistics;

(iii) wrong evaluation of the background intensity and unavoidable truncation of the measurement range of the diffraction profile (background and truncation errors).

Wilson (1942, 1962*a*) first gave a physical interpretation to the cosine Fourier coefficients in terms of particle-size* and strain contributions to the broadening of a diffraction profile; only recently, however, critical assessments of the reliability of the formulas expressing those contributions for both metallic (Mignot & Rondot, 1977) and polymeric (Vogel, Hasse & Hosemann, 1974) materials have been given, definitely reducing the seriousness of point (i) as a source of inaccuracy. In particular, Mignot & Rondot (1977) established for the second and fourth cumulants of the strain distribution in metals a hyperbolic dependence on the harmonic number, which has been an important controversial point in the past (see, for example, Gangulee, 1974). Sound criteria for solving the problem of the sampling error and of poor statistics have been given by Young, Gerdes & Wilson (1967) and by Wilson (1967), respectively.

Also, the errors mentioned in point (iii) have been the subject of consideration and concern by some workers in this field (for references see later), but, in this author's opinion, up to now no satisfactory criteria have been established for eliminating the consequences of these errors and for reliably determining the microstructural parameters of materials. For this reason, these errors, and especially the unavoidable truncation error, will be considered in this paper.

The results of the method of Fourier analysis proposed by Warren & Averbach (1950, 1952) are particularly bound to be affected by background and truncation errors (Eastbrook & Wilson, 1952) and therefore this method should not be used in its original form. Indeed, Wilson (1962*b*) proposed the variance analysis of the diffraction profile as a better alternative to the Warren–Averbach method also because the

* Here the word 'particle' means 'crystallite', while in the rest of the paper it has the more general meaning of 'coherence domain' and is applied to both 'crystallites' and 'paracrystalline microdomains'.

variance method is intrinsically independent of the truncation error and can be used in such a way as to take care also of the background error (Langford & Wilson, 1963).

As for the single-line Fourier methods (Smith, 1960; Pines & Sirenko, 1962; Mitra & Misra, 1967; Gangulee, 1974; Mignot & Rondot, 1977) developed for separating the particle-size and distortion components of the Fourier coefficients in the difficult cases in which, for various reasons, it is not possible to measure for every set of reflecting planes more than one intensity profile, background and truncation errors may be quite substantial. Indeed, the same reasons, *e.g.* the exceptionally broad and overlapping peaks in the diffraction patterns of cold-worked metals and polymeric materials, which make the use of a single-line method necessary, are sources of large errors of that kind. The variance analysis can also, in principle, be used as a single-line method but, in practice, this gives inaccurate results because, in order to implement this possibility, one has to rely not only on the slope of the variance range of the integration curve but also upon its intercept, which is known to be heavily affected by systematic errors (Langford, 1968*a*).

Thus, the background and truncation errors should be considered as important sources of serious inaccuracies in the determination of the microstructural parameters especially in cases in which the need of using a single-line technique is strong, *i.e.* for cold-worked metals and polymeric materials. In fact, this is strictly true only for the truncation error, since, as mentioned above, Langford & Wilson (1963) suggested a method based on the behaviour of the variance-range curve for correctly estimating the background level of any diffraction profile. Kulshreshtha, Dweltz & Radhakrishnan (1971) applied this method to the difficult case of polymeric materials.

In spite of the above considerations, relatively few authors (Pines & Sirenko, 1962; Young, Gerdes & Wilson, 1967; Langford, 1968*b*; Gilli & Borea, 1970; Mitra & Chaudhuri, 1974) seemed to be aware of the problem of these experimental errors and, in any case, nobody has suggested valid and general procedures for taking care of them in the important and difficult cases in which single-line Fourier techniques are required. In these cases, indeed, the microstructural parameters are usually refined by a least-squares method in the unrealistic hypothesis of the absence of systematic errors and, as a consequence, the refined values are far from being meaningful.

In the present paper, the analysis of the influence of the mentioned errors on the Fourier coefficients of the diffraction profiles will be extended with respect to work done by the cited authors and the first derivative of the cosine transform will be shown to be the proper function to be used in the least-squares determination of microstructural parameters.

2. Basic definitions

It is well known that the intensity distribution of a Bragg reflection can be represented by a Fourier series

$$I(h) = E(h) \sum_{n=-\infty}^{+\infty} [A(n) \cos(2\pi nh) + B(n) \sin(2\pi nh)],$$

where $h = (2d_o/\lambda) (\sin \theta - \sin \theta_B)$ is continuously variable in reciprocal space, θ is one half of the diffraction angle, θ_B is the Bragg angle, d_o is the interplanar spacing, λ is the radiation wavelength, $E(h)$ is a slowly-varying function of h , n is the harmonic number and $A(n)$ and $B(n)$ are the Fourier cosine and sine coefficients, respectively. In the following, the same symbols $A(n)$ and $B(n)$ will also be used for the corresponding coefficients normalized to $A(0) = 1$.

For the sake of simplicity, small particle size and distortions will be considered as the only contributors to the broadening of a diffraction profile and the following relationship will be taken as good:

$$A(n) = A_p(n) A_d(n),$$

where the suffixes p and d stand for 'particle sizes' and 'distortions', respectively.

Mignot & Rondot (1977) found for the normalized particle-size and microstrain Fourier components the expressions

$$A_p(t) = 1 - (\beta/d_o)t + (1/2\sqrt{2\pi\eta})(\beta/d_o)t^2 - \dots (1a)$$

and

$$A_d(t) = \exp[-(\alpha/d_o)t + \gamma t^3 + \dots], \quad (1b)$$

with the following meaning for the various symbols: $t = nd_o$ is a distance in real space normal to the given set of reflecting planes, $\beta = 1/M$, where M is the average number of lattice cells in the crystallites of the sample along the normal to the reflecting planes, η is the standard deviation of the particle-size distribution, $\alpha = 2\pi^2[C_2(t)t/d_o]h_B^2$ and $\gamma = (\frac{3}{2})\pi^4[C_4(t)t/d_o^4]h_B^4$, where $C_2(t)$ and $C_4(t)$ are the second and fourth cumulants of the strain distribution and $h_B = (2d_o/\lambda) \sin \theta_B$. The products $C_2(t)t$ and $C_4(t)t$ are constant, since the two cumulants have a hyperbolic dependence on t .

In fact, Eastabrook & Wilson (1952) found that a relation of type (1*b*) is valid only for large values of t . However, this limitation should not affect our reasoning in the following sections since Mignot & Rondot also verified the fact that the expression

$$A(t) = (1 - \beta t/d_o) \exp(-\alpha t/d_o), \quad (2)$$

previously used by others (*e.g.* Warren, 1959; Smith, 1960), is in general a reasonable approximation to

$$A(t) = A_p(t)A_d(t)$$

in many practical cases.

As mentioned in the *Introduction*, Vogel, Haase & Hosemann (1974) extended the Warren & Averbach method to paracrystalline materials characterized by lattice distortions of the second kind (Hosemann & Bagchi, 1962), for which the $A_d(t)$ component in (1b) can be approximated by

$$A_d(t) = \exp(-2\pi^2 g^2 h_B^2 t/d_0),$$

where $g = (\bar{d}_0^2 - \bar{d}_0^2)^{1/2}/\bar{d}_0$ is the relative standard deviation of the spacing distribution of the given set of reflecting planes with mean interplanar spacing \bar{d}_0 within one paracrystalline microdomain.

Therefore, α in (1b) can be redefined in a more general form as

$$\alpha = 2\pi^2 G^2 h_B^2,$$

where the constant G^2 can have one of the two following meanings:

$$G^2 \begin{cases} = C_2(t)t/d_0, & \text{for microstrains} \\ = g^2, & \text{for paracrystalline distortions.} \end{cases}$$

For convenience in the following sections, the adimensional continuous variable $m = t/d_0$ is substituted for t ; in the case of no truncation, m , for integral values, is the same as the harmonic number n , while, when the profile has been measured in the interval R of h , it can be substituted for $n\delta/d_0 = n/R$ (δ is the Fourier period).

3. Truncation and background errors

When both errors are present, if R is the interval of h (symmetrically chosen with respect to the centroid of the intensity distribution), within which the diffraction profile has been measured, one has approximately*

$$A_o(n) = K \int_{-R/2}^{+R/2} [I(h) + C + Dh] \cos(2\pi nh/R) dh,$$

where K is a constant and the background error is supposed to be a linear function of h with slope D and level C . More conveniently, one can write

$$A_o(m) = K \int_{-R/2}^{+R/2} [I(h) + C + Dh] \cos(2\pi mh) dh, \quad (3)$$

where the above defined variable m has been substituted for the ratio n/R . Since

$$\int_{-R/2}^{+R/2} h \cos(2\pi mh) dh = 0,$$

one has the result that, in the determination of the cosine transform of a symmetrically truncated profile, the slope of the background can be ignored and only

* Here and in what follows, the symbols with the suffix o refer to observed quantities affected by the considered errors.

the wrong evaluation of its average level is a possible source of error. Therefore, (3) reduces to

$$\begin{aligned} A_o(m) &= K \int_{-R/2}^{+R/2} [I(h) + C] \cos(2\pi mh) dh \\ &= K \int_{-R/2}^{+R/2} I(h) \cos(2\pi mh) dh + KC \sin(\pi Rm)/\pi m. \end{aligned} \quad (4)$$

Since, for not too small values of M , the expression $1 - \beta m$ in (2) is reasonably approximated by $\exp(-\beta m)$, $I(h)$, the Fourier transform of $A(m)$, can be taken as approximately proportional to (see also Kulshreshtha, Dweltz & Radhakrishnan, 1971) $(\alpha + \beta)/[(\alpha + \beta)^2 + 4\pi^2 h^2]$ and the corresponding normalized Fourier cosine coefficients can be approximated by the series expansion

$$A(m) = 1 - (\alpha + \beta)m + \frac{1}{2}(\alpha + \beta)^2 m^2 - \dots \quad (5)$$

Thus, within the limits of these approximations, the integral in (4) can be written

$$\int_{-R/2}^{+R/2} \frac{\alpha + \beta}{(\alpha + \beta)^2 + 4\pi^2 h^2} \cos(2\pi mh) dh.$$

By means of the substitutions $y = 2\pi h/(\alpha + \beta)$ and $X = \pi R/(\alpha + \beta)$, one obtains

$$\begin{aligned} A_o(m) &= \frac{K}{2\pi} \int_{-X}^{+X} \cos[(\alpha + \beta)ym]/(1 + y^2) dy \\ &\quad + KC \sin(\pi Rm)/\pi m. \end{aligned}$$

Expansion of $\cos[(\alpha + \beta)ym]$ in a Maclaurin series, repetitive integration of the form $\int y^n/(1 + y^2) dy$ (see, for example, Spiegel, 1968) and normalization to $A_o(0) = 1$ give

$$\begin{aligned} A_o(m) &= Z_o \left[1 + \sum_{i=1}^{\infty} [(\alpha + \beta)^{2i}/(2i)!] F_i m^{2i} \right] \\ &\quad + C_o \sin(\pi Rm)/m, \end{aligned}$$

where

$$Z_o = \arctan X / [\arctan X + C\pi R],$$

$$C_o = C / [\arctan X + C\pi R],$$

and

$$F_i = 1 + \sum_{j=1}^i (-1)^j X^{(2j-1)}/(2j-1) \arctan X;$$

$\arctan X + C\pi R$ is proportional (with constant π/K) to the integrated intensity of the reflection under consideration.

Since, in most experiments, R is several times larger than $(\alpha + \beta)/\pi$, the width at half maximum of the con-

sidered Cauchy intensity distribution, one has usually $X > 3$ and therefore, for $i \geq 2$,

$$\left| \frac{X^{(2i-1)}}{(2j-1) \arctan X} \right| \gg \left| 1 + \sum_{j=1}^{i-1} (-1)^j \frac{X^{(2j-1)}}{(2j-1) \arctan X} \right|.$$

Thus, as a first approximation, one can write

$$F_i = (-1)^i X^{(2i-1)} / (2i-1) \arctan X$$

and

$$A_o(m) = Z_o \left[1 - (\alpha + \beta) m(2/\pi) \sum_{i=1}^{\infty} (-1)^{(i+1)} / 2i \times (\pi Rm)^{(2i-1)} / (2i-1)(2i-1)! + \frac{1}{2}(\alpha + \beta)^2 m^2 \right] + C_o \sin(\pi Rm) / m, \quad (6)$$

where $1/\arctan X$ has been approximated by $2/\pi$. If the background correction has been reliably carried out according to Langford & Wilson (1963), $C \simeq 0$ and (6) can be simplified to

$$A_o(m) = 1 - (\alpha + \beta) m(2/\pi) \sum_{i=1}^{\infty} (-1)^{(i+1)} / 2i \times (\pi Rm)^{(2i-1)} / (2i-1)(2i-1)! + \frac{1}{2}(\alpha + \beta)^2 m^2, \quad (7)$$

i.e. to a form convenient for an easy comparison with the series expansion (5). It is immediately seen that, within the limits of the approximations introduced in the above treatment, the truncation error modifies only the term in m of this expansion and that the modification is given by the summation in (7).

It can be easily shown by computation that this summation is an oscillating and rapidly increasing function of m . This means that $A_o(m)$ is modified by the truncation error, not only by the introduction of an oscillatory effect but, more importantly, by a change in its 'average' functional behaviour. In other words, $A_o(m)$ does not oscillate about the theoretical function $A(m)$, but about a different function of m ; for this reason any least-squares or regression procedure based on the approximate equation (5) or on (1) or (2) and using the experimentally determined values of $A_o(m)$, is bound to give erroneous microstructural parameters.

Moreover, consideration of (7) definitely shows that the common assumption that the effect on $A_o(m)$ by the truncation error is limited to relatively small values of m is unsound and also that the so-called 'log method', proposed by several authors in the past (*e.g.* Pines & Sirenko, 1962; Rothman & Cohen, 1969) and based on a mythical parallelism between the curves of $\ln A(m)$ and $\ln A_o(m)$, can give only inaccurate results.

It should be noted that no absolute novelty is contained in the above results and that the discussed features of (7) constitute nothing but a quantitative formulation of the well-known 'hook' effect (Warren, 1959; Young, Gerdes & Wilson, 1967; Gilli & Borea,

1970). However, the lack of a more quantitative approach has brought many workers in the past to follow inaccurate analytical procedures, mainly based on the above wrong assumption that the truncation effect is limited only to small values of m and therefore to small values of the harmonic number n .

4. The derivative of the cosine transform

Within the validity of (2), the first derivative of the cosine transform is given by

$$A'(m) = -(\alpha + \beta - \alpha \beta m) \exp(-\alpha m) \quad (8)$$

or, considering only the first two terms of its series expansion, by

$$A'(m) = -(\alpha + \beta) + (\alpha^2 + 2\alpha\beta)m. \quad (9)$$

It will be shown in this section that this derivative function, in view of the properties of the corresponding 'observed' function $A'_o(m)$, can be usefully considered for accurately determining the microstructural parameters by a single-line method, even in the presence of a large truncation error.

From (6), one easily obtains

$$A'_o(m) = -Z_o \left[(\alpha + \beta)(2/\pi) \sum_{i=1}^{\infty} (-1)^{(i+1)} \times (\pi Rm)^{(2i-1)} / (2i-1)(2i-1)! - (\alpha + \beta)^2 m \right] + C_o [\pi Rm \cos(\pi Rm) - \sin(\pi Rm)] / m^2, \quad (10)$$

where the summation has been transformed by the derivation operation to a well-known series expansion of the sine integral $\int_0^{\pi Rm} \sin u/u \, du$, whose functional behaviour is characterized by damped oscillations about the constant $\pi/2$.

It may be interesting to note that, since

$$\lim_{m \rightarrow 0} [\pi Rm \cos(\pi Rm) - \sin(\pi Rm)] / m^2 = 0, \quad A'_o(0) = 0,$$

which is a consequence of the 'hook' effect at small values of m .

After minimization of the background error by the variance method, (10) reduces to

$$A'_o(m) = -(\alpha + \beta)(2/\pi) \int_0^{\pi Rm} \sin u/u \, du + (\alpha + \beta)^2 m, \quad (11)$$

where $(2/\pi) \int_0^{\pi Rm} \sin u/u \, du$, with its damped oscillations about the value 1, represents the effect of the truncation error on the derivative of the series expansion (5). Thus, the first term of this derivative is modified by the truncation error, while the second term is left unchanged. If, within the limits of validity of (2), one considers (9) as a better approximation to $A'(m)$,

an improved expression for $A'_o(m)$ can be obtained by substituting $\alpha^2 + 2\alpha\beta$ for $(\alpha + \beta)^2$ in (11) as follows:

$$A'_o(m) = -(\alpha + \beta)(2/\pi) \int_0^{\pi R m} \sin u/u \, du + (\alpha^2 + 2\alpha\beta) m. \quad (12)$$

This equation states that, because of the truncation error, the experimentally determined function $A'_o(m)$ 'oscillates' about the theoretical curve $A'(m)$ according to the behaviour of the sine integral, which is determined only by the known value of R . The oscillation period of $A'_o(m)$ is $2/R$ with the first maximum at $m = 0$ [where $A'_o(0) = 0$] and the first minimum at $m = 1/R$.

It is evident from the above considerations that the possibility exists of determining meaningful microstructural parameters by least-squares or curve-fitting procedures, based on the function $A'(m)$ and on its approximate expression (9), even in the presence of severe truncation effects. In view of the importance of this possibility, in the following section the validity of (12) will be verified both by computing and by comparison with the results obtained from the experimental data of a polymeric material.

5. Computing details and experimental

The following procedure was followed:

(i) the intensity profiles of two equatorial reflections, 110 and 200, of a fibre of high-density polyethylene were measured by an X-ray diffractometer and, after background correction according to Langford & Wilson (1963), Fourier transformed by a computer program which also calculated the values of $A'_o(m)$;

(ii) the microstructural parameters G (in this case $G = g$, see § 2) and M were determined by curve fitting, using the values of $A'_o(m)$ (the first 30 values for 110 and the first 20 values for 200) and assuming that for these values a linear regression based on (9) constituted a valid procedure;

(iii) equation (12) was used, with the parameters determined in (ii), for computing curves which are plotted in Fig. 1 together with the $A'_o(m)$ values derived in (i) from the experimental data.

The reason for choosing the 110 and 200 reflections in this testing procedure is that the microstructure of this material in the directions of the 110 and 200 Bragg vectors has been the subject of several investigations by Hosemann and co-workers using a multiple-order method and that therefore reliable values of g and M are available in their published works for a comparison (for references see Table 2).

Polyethylene fibres were hot-drawn from a sample of high-density Marlex 6002 (density, $\rho = 0.9585 \text{ Mg m}^{-3}$). The X-ray intensities were measured by a General Electric XRD6 diffractometer equipped for fibre work. The profiles of the 110 ($R = 0.1183$) and

200 ($R = 0.1621$) reflections were determined by step-scanning in steps of 0.02° (2θ), with Ni-filtered Cu $K\alpha$ radiation analysed through a PHA circuit.

The α_1 - α_2 doublet separation was performed according to Gangulee (1970) but no correction was made for the instrumental broadening in view of the fact that this effect should be much smaller than the intrinsic broadening of this polymeric material. For both reflections, the background correction was performed following the cited procedure by Langford & Wilson (1963) and using the computer program written by Edwards & Toman (1969).

A Fortran program was written for Fourier transforming the diffraction profiles and calculating the $A'_o(m)$ values according to point (i) above.

The first $A'_o(m)$ values for the two measured reflections (30 values for 110 and 20 for 200) are reported in Table 1. For both reflections the $B'_o(m)$ values of the sine transforms were found to be negligibly small.

The primary intensity data are available on request from the author.

6. Results and discussion

The results presented in Fig. 1 (a and b) clearly show the validity of a method of structural analysis based on

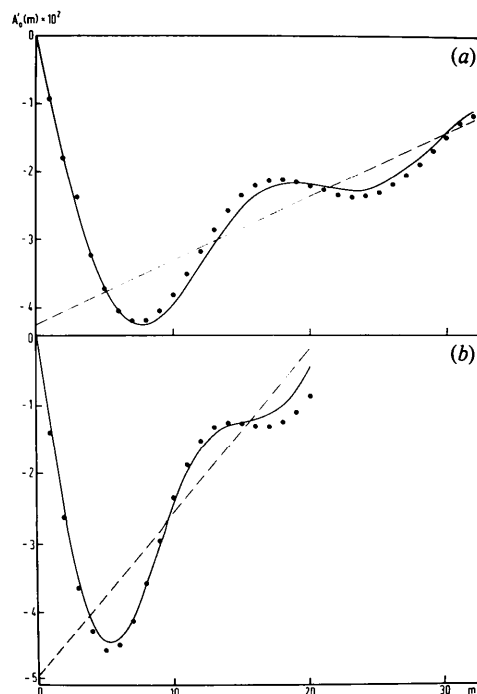


Fig. 1. Experimentally determined $A'_o(m)$ values (dots) and $A'_o(m)$ curves calculated from (12) on the basis of the parameters obtained by a linear-regression procedure (see text for details) for both the 110 (a) and the 200 (b) reflections. The straight (dashed) lines have been calculated from (9) on the basis of the same parameters.

Table 1. Normalized $A_o(m)$ values obtained by Fourier transformation of the 110 and 200 diffraction profiles of a polyethylene fibre

The standard deviations (σ), estimated on the basis of the formula given by Delhez & Mittemeijer (1975), are indicated in parentheses.

m	$A_o(m)$	
	110	200
1	0.995(8)	0.986 (10)
2	0.982(8)	0.945 (10)
3	0.960(8)	0.881 (11)
4	0.930(8)	0.801 (11)
5	0.896(8)	0.712 (12)
6	0.857(8)	0.621 (13)
7	0.815 (9)	0.534 (14)
8	0.773 (9)	0.457 (15)
9	0.732 (9)	0.392 (16)
10	0.692 (9)	0.339 (17)
11	0.656 (9)	0.297 (18)
12	0.622 (10)	0.263 (19)
13	0.592 (10)	0.235 (21)
14	0.565 (10)	0.209 (22)
15	0.540 (10)	0.184 (23)
16	0.518 (11)	0.158 (25)
17	0.496 (11)	0.132 (28)
18	0.475 (11)	0.107 (31)
19	0.454 (11)	0.083 (35)
20	0.432 (12)	0.064 (40)
21	0.409 (12)	
22	0.386 (12)	
23	0.362 (13)	
24	0.339 (13)	
25	0.316 (14)	
26	0.293 (14)	
27	0.272 (15)	
28	0.252 (15)	
29	0.235 (16)	
30	0.219 (16)	

the fitting of the values of $A'_o(m)$ on the theoretical line $A'(m)$, given by (9), and therefore on the validity of (12). The standard deviations for the experimental values have been estimated by simply doubling the ones obtained for the $A_o(m)$ values according to Delhez & Mittemeijer (1975) (see Table 1). No single dot is further than 2σ from the corresponding point on the calculated curve. The fact that the oscillations of this curve are slightly smaller than the ones of the curve passing through the experimental dots can be mainly attributed to some inaccuracies in the operation of background correction. It is important to note that for both reflections the dashed lines in Fig. 1 are practically coincident with the straight lines (not shown in the figure for clarity) obtained by the regression procedure.

The results of the structural analysis are given in Table 2 where the values of M and g are reported together with the values of the product $\alpha^* = g\sqrt{M}$. Hosemann (1975) found that α^* is a quantity whose value depends only on the nature and strength of the chemical bonding along a direction parallel to the considered Bragg vector. Therefore, for a given para-

Table 2. Microstructural parameters of a polyethylene fibre along directions perpendicular to the reflecting planes (100) and (110)

For the meaning of the symbols see text.

Reflecting planes	d_o (Å)	M	g	α^*	α_H^*	References
(100)	7.40	14	0.019	0.07	0.10	Hosemann & Wilke, 1968
(110)	4.09	34	0.026	0.15	0.14 _s	Hosemann, 1975

† The data reported in this column are average values computed from the microstructural parameters given in the cited references.

crystalline material, α^* is largely independent of any physical treatment undergone by the material and of particular values of the microstructural parameters. This means that in this kind of material $M^{1/2}$ has a hyperbolic dependence on g . Hosemann obtained for α^* , in a variety of different structures, values in the range 0.05–0.30 and found for the reflecting planes (100) and (110) of polyethylene the α^* values (α_H^*) presented in Table 2 (see references therein). The good agreement with the corresponding α^* values obtained

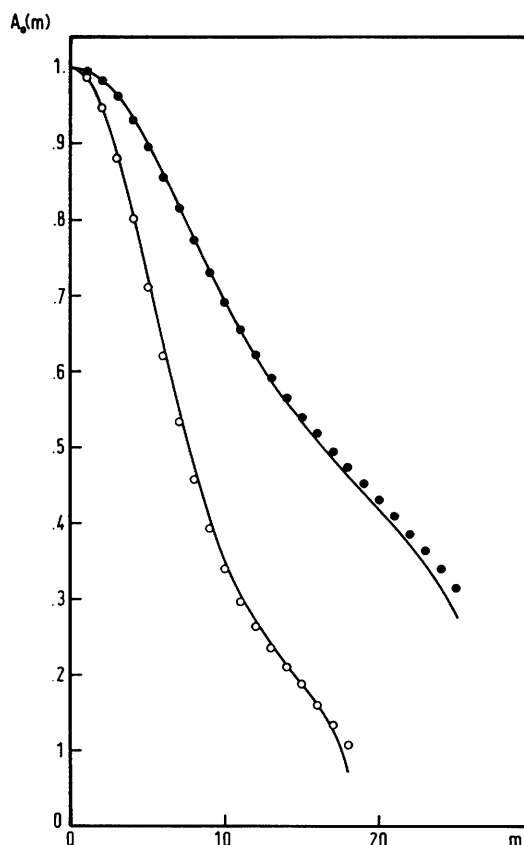


Fig. 2. Experimental $A_o(m)$ values from Table 1 (dots for the 110 reflection and circles for the 200 reflection) and $A_o(m)$ curves (full lines) calculated by (7) on the basis of the parameters obtained by the procedure outlined in point (ii) of § 5 and illustrated by Fig. 1 for both reflections. The summation in (7) has been truncated to its ninth term.

by the procedure described in § 5 corroborates the above conclusions on the validity of (12) and of the proposed single-line method.

Of course, a least-squares procedure based on (7) is a possible alternative to using (9) and (12) as suggested above. For substantiating this alternative, the found parameters were used for computing, by means of (7), the $A_o(m)$ curves presented in Fig. 2.*

Taking into account all the approximations introduced in the derivation of (7), the effect of truncating the summation in it, and the standard deviations in Table I, the agreement between the experimental $A_o(m)$ values and the curves computed by means of (7) must be considered very good. However, in the author's opinion the method based on the derivative function is to be preferred since it has the advantage of allowing the determination of the parameters by a simple linear regression procedure or even by a graphical straight-line fitting of the data obtained from the experiment.

7. Conclusions

The results discussed in the previous section indicate the possibility of using (9) for determining the microstructure of materials by single-line Fourier analysis also in difficult cases of large truncation errors.

The possibility of applying a single-line method to the microstructural analysis of paracrystalline materials is also very relevant to the solution of the practical problem of making easier the description of order in polymers in terms more meaningful than the misleading 'degree of crystallinity' (Bonart, Hosemann & McCullough, 1963).

While it is possible, in principle, to extend the applicability of the proposed method by deriving expressions for $A'(m)$ from more general equations, like (1), thus determining other microstructural parameters, like η and γ , a limitation to these developments is imposed by the precision attainable in the intensity measurements. Further studies are necessary in order to ascertain the practical feasibility of these possibilities.

The importance of the above conclusions can be evaluated considering not only the possibilities offered by the general applications of a single-line method to problems of polymer science but also the fact that this method allows one to apply the Fourier analysis to the notoriously difficult cases of ferrous materials with both ferritic and austenitic structures. Application work is in progress also in this field.

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References

- BONART, R., HOSEMAN, R. & MCCULLOUGH, R. L. (1963). *Polymer*, **4**, 199–211.
- DELHEZ, R. & MITTEMEIJER, E. J. (1975). *J. Appl. Cryst.* **8**, 612–614.
- EASTABROOK, J. N. & WILSON, A. J. C. (1952). *Proc. Phys. Soc. London. Sect. B*, **65**, 67–75.
- EDWARDS, H. J. & TOMAN, K. (1969). *J. Appl. Cryst.* **2**, 240.
- GANGULEE, A. (1970). *J. Appl. Cryst.* **3**, 272–277.
- GANGULEE, A. (1974). *J. Appl. Cryst.* **7**, 434–439.
- GILLI, G. & BOREA, P. A. (1970). *J. Appl. Cryst.* **3**, 205–211.
- HOSEMAN, R. (1975). *Makromol. Chem. Suppl.* **1**, 559–577.
- HOSEMAN, R. & BAGCHI, S. N. (1962). *Direct Analysis of Diffraction by Matter*, pp. 239–246. Amsterdam: North Holland.
- HOSEMAN, R. & WILKE, W. (1968). *Makromol. Chem.* **118**, 230–249.
- KULSHRESHTHA, A. K., DWELTZ, N. E. & RADHAKRISHNAN, T. (1971). *J. Appl. Cryst.* **4**, 116–125.
- LANGFORD, J. I. (1968a). *J. Appl. Cryst.* **1**, 131–138.
- LANGFORD, J. I. (1968b). *J. Appl. Cryst.* **1**, 48–59.
- LANGFORD, J. I. & WILSON, A. J. C. (1963). In *Crystallography and Crystal Perfection*, edited by G. N. RAMACHANDRAN, pp. 207–222. London: Academic Press.
- MIGNOT, J. & RONDOT, D. (1977). *Acta Cryst.* **A33**, 327–333.
- MITRA, G. B. & CHAUDHURI, A. K. (1974). *J. Appl. Cryst.* **7**, 350–355.
- MITRA, G. B. & MISRA, N. K. (1967). *Acta Cryst.* **22**, 454–456.
- PINES, B. YA. & SIRENKO, A. F. (1962). *Sov. Phys. Crystallogr.* **7**, 15–20.
- ROTHMAN, R. L. & COHEN, J. B. (1969). *Adv. X-ray Anal.* **12**, 208–235.
- SMITH, R. S. (1960). *IBM J. Res. Dev.* **4**, 205–207.
- SPIEGEL, M. R. (1968). *Mathematical Handbook*. New York: McGraw-Hill.
- VOGEL, W., HAASE, J. & HOSEMAN, R. (1974). *Z. Naturforsch. Teil A*, **29**, 1152–1158.
- WARREN, B. E. (1959). *Prog. Met. Phys.* **8**, 147–202.
- WARREN, B. E. & AVERBACH, B. L. (1950). *J. Appl. Phys.* **21**, 595–598.
- WARREN, B. E. & AVERBACH, B. L. (1952). *J. Appl. Phys.* **23**, 1059.
- WILSON, A. J. C. (1942). *Proc. R. Soc. London Ser. A*, **180**, 277–285.
- WILSON, A. J. C. (1962a). *X-ray Optics*. New York: John Wiley.
- WILSON, A. J. C. (1962b). *Proc. Phys. Soc. London*, **80**, 286–294.
- WILSON, A. J. C. (1967). *Acta Cryst.* **23**, 888–898.
- YOUNG, R. A., GERDES, R. J. & WILSON, A. J. C. (1967). *Acta Cryst.* **22**, 155–162.

* In fact, before performing this calculation, following the same reasoning which led to (12), in the third term of (7) $\alpha^2 + 2\alpha\beta$ was substituted for $(\alpha + \beta)^2$.