**SHORT COMMUNICATIONS**


**The elimination of an approximation in the Warren–Averbach analysis.** By R. DELHEZ and E. J. MITTEMEIJER,

Laboratory of Metallurgy, Delft University of Technology, Rotterdamseweg 137, Delft, The Netherlands

(Received 17 December 1975; accepted 9 February 1976)

The Warren–Averbach analysis for the separation of particle size and strain involves a cosine and a logarithmic power series expansion. It is shown that the neglect of higher-order terms in the logarithmic series expansion introduces larger errors at small values of the strain than the cosine series while at larger values the dominance is less pronounced. Furthermore it is shown that the power series expansion for the logarithm is superfluous and as a result the Warren–Averbach analysis can be improved. In common practice the differences between the improved method and the original one can easily be 10% for particle-size Fourier coefficients and 30% for mean square strain values.

The separation of cold-work distortion and particle-size broadening in X-ray diffraction line profiles is usually obtained by applying the well known Warren–Averbach analysis (Warren, 1969). The method is based on a Fourier analysis of the pure line profile.

Each Fourier coefficient \( A(n, l) \) – usually obtained after some deconvolution technique or \( \alpha_2 \)-elimination procedure – can be written as the product of a ‘size’ Fourier coefficient \( A^S(n) \) and a ‘distortion’ Fourier coefficient \( A^D(n, l) \) according to the convolution theorem. If the diffracting domains are thought to consist of columns of unit cells perpendicular to the diffracting planes, described as \( (00l) \) planes, then

\[
A^S(n) = \frac{N(n)}{N_3} \tag{1}
\]

\[
A^D(n, l) = \langle \cos 2\pi lZ(n) \rangle \tag{2}
\]

where \( N(n) \) is the average number per column of pairs of unit cells a distance \( n \) cells apart, \( N_3 \) is the average domain size in unit cells perpendicular to \( (00l) \) and \( Z(n) \) is the difference between the displacements of two unit cells \( n \) cells apart. If \( e(n) \) is defined by \( e(n) = Z(n)/n \):

\[
A(n, l) = \frac{N(n)}{N_3} \cdot \langle \cos 2\pi l e(n) \rangle \tag{3}
\]

Since \( A^S(n) \) is dependent on \( l \) and \( A^D(n) \) is not, size and strain effects can be separated by taking the logarithm of (3):

\[
\ln A(n, l) = \ln \frac{N(n)}{N_3} + \ln \langle \cos 2\pi l e(n) \rangle \tag{4}
\]

Two power series expansions are applied:

\[
\langle \cos 2\pi l e(n) \rangle = 1 - \frac{\langle (2\pi l e(n))^2 \rangle}{2!} + R^\cos_4 \tag{5}
\]

\[
\approx 1 - \pi l^2 n^2 \langle e^2(n) \rangle ,
\]

\[
\ln \left[1 - \pi l^2 n^2 \langle e^2(n) \rangle \right] = - \pi l^2 n^2 \langle e^2(n) \rangle + R^\ln_4 \tag{6}
\]

where \( R^\cos_4 \) and \( R^\ln_4 \) are the remainders of the two series expansions. In practice terms in higher orders of \( l^2 \) are neglected. From (4), (5) and (6) it follows that

\[
\ln A(n, l) \approx \ln \frac{N(n)}{N_3} - \pi l^2 n^2 \langle e^2(n) \rangle \tag{7}
\]

If at least two orders of a reflexion are available then values for \( N(n)/N_3 \) and \( \langle e^2(n) \rangle \) can be obtained, numerically or graphically, from the slope and intercept of a plot of \( \ln A(n, l) \) versus \( l^2 \).

Recently Mitra & Chaudhuri (1974) considered the errors originating from the series expansion for the cosine. They calculated the ratio of the third to the second term of this power series for some practical values of \( l \) and \( e(n) \) (cf. their Table 1*). Here we will compare the errors arising from both series expansions.

It can be shown (cf. Appendix 1):

\[
\left| R_{\ln}^{\text{max}} \right| = 3 \left| R_{\cos}^{\text{max}} \right| . \tag{8}
\]

Since the cosine is underestimated with \( |R_{\cos}^{\text{max}}| \) and the logarithm is overestimated with \( |R_{\ln}^{\text{max}}| \) it follows from (8) that the logarithmic series expansion introduces an error in the final result at least twice that of the cosine series expansion.

Let us also consider the ratio \( R \) of the relative errors caused by truncation of the series after the terms with \( l^2 \). Defining \( q = \pi l^2 n^2 \langle e^2(n) \rangle \), it follows from (5) and (6) with the additional assumption \( e(n) = \sqrt{\langle e^2(n) \rangle} \) that:

* This table contains two cases where the logarithmic series expansion is impossible, because of negative values of the argument.

![Fig. 1. The relative error in the series expansion for the cosine: \( R_{\cos}^{\text{max}}/2q \); the relative error in the series expansion for the logarithm: \( R_{\ln}^{\text{max}}/\ln(1-q) \) and their ratio \( R \) as a function of \( q = \pi l^2 n^2 \langle e^2(n) \rangle \).](image-url)
expansions and their ratio \( R \), as defined by (9), are plotted in
portance than in the cosine series; at larger values of
order terms in the logarithmic series is of much more im-
importance. Differences in \( \epsilon^2(n) \) at small values of \( n \)
were found. The differences in \( \epsilon^2(n) \) at small values of \( n \)
are discussed above. However to our knowledge it has not
been noticed that these errors can be reduced to nil because
the series expansion for the logarithm can be simply avoided
in the following way.

The direct substitution of the power series expansion
for \( \langle \cos 2\ln e(n) \rangle \) according to (5) in (3) yields:
\[
A(n, l) \sim \frac{N(n)}{N_3} - \frac{N(n)}{N_3} 2\pi^2 n^2 \langle \epsilon^2(n) \rangle.
\]

Now the influences of size and strain are not separated as in (4).
However if two orders of a reflexion are available the values
of \( N(n)/N_3 \) and \( \langle \epsilon^2(n) \rangle \) are readily obtained numerically,
or graphically from a plot of \( A(n, l) \) versus \( l^2 \).

Results of the usual Warren–Averbach method [equation
(7)] were compared with the results based on (10) for
experimental line profiles. For all \( n \), values of \( A^4(n) \) and values
of \( \langle \epsilon^2(n) \rangle \) obtained with (10) were smaller than the values
deducted from (7), as is shown in Appendix 2. In a case where
\( \langle \epsilon^2(n) \rangle \approx 10^{-6} \) the differences between the values of \( A^4(n) \)
obtained from both methods were less than 2\% for small
values of \( n \); for larger values of \( n \) differences of 10\% and more
were found. The differences in \( \langle \epsilon^2(n) \rangle \) at small values of \( n \)
were 15\% and less; at larger values of \( n \) the differences increased: 30\% and more.

In practice the second order of a reflexion is usually
measured less accurately than the first order. Therefore
spurious variations may be present on the Fourier coefficients
of the second order. This will produce spurious ripples
on the \( A^4(n) \)-curve. These ripples will be enhanced in the
\( A^5(n) \)-curve obtained from (7) as compared to the \( A^4(n) \)-curve
obtained from (10), as is shown in Appendix 2. Also
\( \langle \epsilon^2(n) \rangle \) obtained from (7) is more sensitive to spurious
variations in the Fourier coefficients of the second order as
compared to \( \langle \epsilon^2(n) \rangle \) obtained from (10) (cf. Appendix 2).

A more refined multiple-order technique is possible by
considering one more term in the series for \( \langle \cos 2\ln e(n) \rangle \).
If terms in \( \epsilon^6 \) and higher orders are neglected, the Fourier
coefficient of the total line profile can be expressed as:
\[
A(n, l) \approx C_1 - C_2 l^2 + C_3 l^4
\]

where
\[
C_1 = \frac{N(n)}{N_3}, \quad C_2 = 2\pi^2 n^2 \langle \epsilon^2(n) \rangle, \quad C_3 = 2\pi^2 n^4 \langle \epsilon^4(n) \rangle / 3.
\]

In fact (11) is an improved formulation of the multiple-order
technique proposed by Mitra & Chaudhuri (1974). As in
(10), again the influences of size and strain are not separated,
but the three coefficients \( C_1, C_2 \) and \( C_3 \) are readily obtained
if three orders of a reflexion are available. After substitution
of \( C_1 \) [ \( = \frac{N(n)}{N_3} \) ] in \( C_2 \) and \( C_3 \) values for \( \langle \epsilon^2(n) \rangle \) and
\( \langle \epsilon^4(n) \rangle \) are found.

Obviously the number of orders of a reflexion necessary
for the evaluation of (10) and (11) can be reduced by one if

\( A^4(n) \) is approximated by \( 1 - n/N_3 \), as was done by Mitra &
Misra (1967) who for the rest used the logarithmic series
expansion.

We are indebted to Professor B. Okkerse and Dr F. W.
Schapink for critically reading the manuscript.

Financial support of the Stichting voor Fundamenteel
Onderzoek der Materie (F.O.M.) is gratefully acknowledged.

APPENDIX 1

Applying the formulation of Lagrange for the remainder
(e.g. Jeffreys & Swirles, 1962) we arrive at the following
expressions for \( R_{4x}^n \) and \( R_{4s}^n \):
\[
R_{4x}^n = \frac{\ell^4}{4!} \langle \epsilon^4 \cos \theta_i \ell^4 \rangle, \quad 0 < \theta_i < 1,
\]
\[
R_{4s}^n = -\frac{3\ell^4}{4!} \langle \epsilon^2 \rangle^2 \langle \epsilon^2 \rangle^2 \theta_i^4 / 4 + 3 \langle \epsilon^2 \theta_i^2 \rangle^2 + 1,
\]
\[\frac{1}{(1 - \langle \epsilon^2 \theta_i^2 \rangle^2/\ell^4)} \]
where \( \epsilon = 2\pi n(n) \).

A maximal estimate for the remainder \( |R_{4s}^n| \) is obtained
if \( \theta_i = 1 \) and a minimal estimate for \( |R_{4x}^n| \) follows if \( \theta_i = 0 \).
If \( \langle \epsilon^2 \rangle^2 \) may be approximated by \( \langle \epsilon^4 \rangle \) equation (8) is
obtained.

APPENDIX 2

Two orders of a reflexion are characterized by \( l_1 \) and \( l_2 \)
(\( l_1 > l_2 \)).
The suffixes 7 and 10 are used to distinguish between
results derived from (7) and (10) respectively.

For the usual Warren–Averbach method [equation
(7)] it follows that
\[
A^{(7)}(n) = \{A(n, l_1)\}_1 - \{A(n, l_2)\}_1,
\]
\[
\langle \epsilon^2(n) \rangle_7 = -\frac{1}{2\pi^2 n^2} \{2\pi n A(n, l_2) - 2\pi n A(n, l_1)\}/(l_1^2 - l_2^2)
\]
and for the method based on (10):
\[
A^{(10)}(n) = \{A(n, l_1)\}_2 - \{A(n, l_2)\}_2,
\]
\[
\langle \epsilon^2(n) \rangle_{10} = -\frac{1}{2\pi^2 n^2} \{2\pi n A(n, l_2) - 2\pi n A(n, l_1)\}/(l_1^2 - l_2^2).
\]

Since \( l_1 > l_2 > 0 \) and since \( A(n, l_1)/A(n, l_2) > 1 \) for \( n \neq 0 \) if the
line profiles contain both particle size and strain broadening,
it follows that
\[
A^{(7)}(n)/A^{(10)}(n)_{10} > 1 \quad \text{and} \quad \langle \epsilon^2(n) \rangle_7/\langle \epsilon^2(n) \rangle_{10} > 1.
\]

If it is assumed that the errors \( \Delta A^{(7)}(n) \) and \( \Delta \langle \epsilon^2(n) \rangle \)
are determined entirely by the error in \( A(n, l_2) \), it can be shown that
\[
\Delta A^{(7)}(n)/\Delta A^{(10)}(n)_{10} > 1 \quad \text{and} \quad \Delta \langle \epsilon^2(n) \rangle_7/\Delta \langle \epsilon^2(n) \rangle_{10} > 1.
\]

Because \( A(n, l_1)/A(n, l_2) \) usually increases with \( n \) the ratios
mentioned increase with \( n \).

References

JEFFREYS, H. & SWIRLES, B. (1962). Methods of Mathematical
Physics, p. 51. Cambridge Univ. Press.
Reading, Mass.: Addison-Wesley.