The Analysis of X-ray Diffraction Profiles from Imperfect Solids by an Application of
Convolution Relations

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In this investigation an attempt has been made to correlate the experimentally observed X-ray diffraction
profile from imperfect solids with the one obtained theoretically from an approach of simultaneous convo-
lution of the true diffraction profile resulting from the imperfection content of the materials and the
instrumental profile, considering realistic distribution functions. The expressions for the intensity distrib-
utions are derived from the simultaneous convolution of Schoening's true profile (originating from the
Gaussian strain profile and the Cauchy crystallite-size profile) and the instrumental profile having either
Gaussian or Cauchy functional forms, and the theoretical forms are compared to those observed from
some silver- and copper-base cold-worked alloys and vapour-deposited thin silver films. The agreement is
fairly good for both first- and second-order reflections with small deviations in the tail region, which may
arise from uncertainty in the background-level estimation, consideration of functions purely symmetrical
in form and neglect of absorption and TDS effects. A further agreement of Schoening's true profile with
Stokes's corrected deconvoluted true profile implies the validity of Schoening's approximation.

Introduction

It is known from X-ray investigations on cold-worked
metals and alloys (Warren, 1959, 1969; Wagner, 1966;
Chatterjee, Halder & Sen Gupta, 1976) that the ob-
served X-ray diffraction profiles arise from a convolu-
tion of the true diffraction profiles and instrumental
profiles, and that a precise analysis of the observed
and deconvoluted true profiles yields a picture of
microstructural changes in the materials under study.
Since the method of integral breadth is frequently
employed in such studies because of its rapidity and
convenience (Ruland, 1968) and since the method com-
pares favourably with the widely used Fourier line-
shape method (Halder & Wagner, 1966), a series of in-
vestigations has recently been undertaken by us (Nandi
& Sen Gupta, 1975, 1976a, b, c) on the X-ray line-
breadth analysis, considering convolutions of true dif-
fraction profiles of Schoening's (1965) realistic form
with several functional forms representing the instru-
mental profile. From the close agreement between the
observed and the calculated integral breadths from
several f.c.c. cold-worked silver- and copper-base
alloys and also from vapour-deposited silver films it
has appeared that the Gaussian form of the instru-
mental profile when convoluted with the true profile
resulting from a Cauchy crystallite-size profile and a
Gaussian strain profile may approach very closely the
actual representation, yielding fairly accurate values
for the crystallite-size and strain parameters (Nandi &
Sen Gupta, 1976b). However, in deriving this conclu-
sion the agreement has been sought in terms of meas-
urements of the integral breadth only, which does not
reveal precisely the form of the intensity distribution.

In the present investigation, it is our aim to achieve
a direct correspondence between experimentally ob-
served diffraction profiles and those obtained theoret-
ically from realistic distribution functions as envisaged
in our earlier studies. This will naturally provide a
better confirmation of the functional forms assumed
for the respective profiles and hence the effective
crystallite-size and strain values. A consideration of
the intensity distribution for the deconvoluted true
profile has also been made from the expression derived
on the basis of the convolution of Cauchy and Gaussian
functions as well as from the Fourier method of de-
convolution by Stokes (1948), which is independent of
any assumption regarding the profile distribution.

Theoretical formulations

According to Nandi & Sen Gupta (1975), hereafter
referred to as I, the observed intensity profile I_{obs}(x)
in terms of strain profile I_{d}(x), crystallite-size profile I_{p}(x)
and instrumental profile I_{i}(x) can be written as

\[ I_{obs}(x) = T^{-1} \langle T[I_d(x)] T[I_p(x)] T[I_i(x)] \rangle. \quad (1) \]

We consider the true profile to be a convolution of a
Gaussian strain profile and a Cauchy crystallite-size
profile (Schoening, 1965, case b). For the instrumental
profile both Gaussian and Cauchy-type distribution
functions have been assumed.

The Gaussian strain function I_{d}(x) and the Cauchy
crystallite-size function I_{p}(x) with their respective
Fourier transforms \( T[I_{d}(x)] \) and \( T[I_{p}(x)] \) and integral
breadths \( B_{d} \) and \( B_{p} \) considered here are as follows
(equations 5, 6 of I):
\[ I_s(x) = C_s \exp \left( -K_s^2 x^2 \right); \]
\[ T[I_s(x)] = C_s K_s^{-1} \pi^{1/2} \exp \left( -\pi^2 u^2 / K_s^2 \right) \]
\[ B_s = e \tan \theta = \pi^{1/2} / K_s, \quad (1a) \]

\[ I_p(x) = C_p(1 + K_p^2 x^2); \]
\[ T[I_p(x)] = C_p K_p^{-1} \pi \exp \left( -2\pi|u| / K_p \right) \]
\[ B_p = \lambda / L \cos \theta = \pi / K_p, \quad (1b) \]

where \( C_s \) and \( K_s \) are the constants of the respective functions, \( x, u \) are the variables in real and Fourier space and \( L, \varepsilon \) denote the crystallite-size and strain respectively. The Gaussian and Cauchy instrumental profile functions may be obtained from equation (1a) and (1b) with proper replacement of the subscripts \( s \) and \( p \) with \( i \).

A. Intensity distribution of the observed profile

(i) Gaussian instrumental profile

The intensity expression is given by (equations 8–10 of 1)

\[ I_{obs}(x) = R_1 \int_{-\infty}^{+\infty} \exp \left[ -\left( \frac{\pi^2 u^2}{K_s^2} + \frac{\pi^2 u^2}{K_i^2} \right) \right. \]
\[ \left. + \frac{2\pi|u|}{K_p} + 2\pi i u \right] \] \( du, \quad (2) \]

where

\[ R_1 = \frac{C_s C_p C_i}{K_s K_p K_i} \pi^2. \quad (3) \]

After simplification, equation (2) becomes

\[ I_{obs}(x) = \frac{K_i R_1}{2\pi^{1/2}} \times \left[ \exp \left( Z_1^2 \right) \left( 1 - \text{erf} Z_1 \right) + \exp \left( Z_2^2 \right) \left( 1 - \text{erf} Z_2 \right) \right], \quad (4) \]

where

\[ K_1 = \frac{K_i K_p}{(K_i^2 + K_p^2)^{1/2}} \quad (4a) \]
\[ Z_1 = K_1 \left( \frac{1}{K_p} - i x \right) \quad (4b) \]
\[ Z_2 = K_1 \left( \frac{1}{K_p} + i x \right). \quad (4c) \]

According to Handbook of Mathematical Functions (1968), the error function with complex argument can be written as

\[ \text{erf}(C + i D) = \text{Re} + i \text{Im} \]

and

\[ \text{erf}(C - i D) = \text{Re} - i \text{Im} \quad (5) \]

where the real part \( \text{Re} \) is

\[ \text{Re} = \text{erf} C + \frac{\exp \left( -C^2 \right)}{2\pi C} (1 - \cos 2CD) \]
\[ + \frac{2}{\pi} \exp \left( -C^2 \right) \sum_{n=1}^{\infty} \frac{\exp \left( -\frac{1}{4} n^2 \right)}{n^2 + 4C^2} \]
\[ \times \left[ 2C - 2C \cos 2CD \cosh nD + n \sin 2CD \sinh nD \right] \quad (6a) \]

the imaginary part \( \text{Im} \) is

\[ \text{Im} = \frac{\exp \left( -C^2 \right)}{2\pi C} \sin 2CD + \frac{2}{\pi} \exp \left( -C^2 \right) \sum_{n=1}^{\infty} \frac{\exp \left( -\frac{1}{4} n^2 \right)}{n^2 + 4C^2} \]
\[ \times \left[ 2C \sin 2CD \cos nD + n \cos 2CD \sin nD \right] \quad (6b) \]

and

\[ \text{erf} C = \frac{2}{\pi^{1/2}} \int_0^C \exp \left( -t^2 \right) dt. \quad (6c) \]

Using these relations, we have the following expressions for the observed intensity profile:

\[ I_{obs}(x) = \frac{K_1 R_1}{\pi^{1/2}} \left[ \text{Re} \cos \left( \frac{2K_i^2 x}{K_p} \right) \right. \]
\[ + \left. \text{Im} \sin \left( \frac{2K_i^2 x}{K_p} \right) \right] \exp \left[ K_1 \left( \frac{1}{K_p^2} - x^2 \right) \right]. \quad (7) \]

(ii) Cauchy instrumental profile

In this case,

\[ I_{obs}(x) = R_2 \int_{-\infty}^{+\infty} \exp \left[ -\left( \frac{\pi^2 u^2}{K_s^2} + \frac{2\pi|u|}{K_s} \right) \right. \]
\[ + \left. \frac{2\pi|u|}{K_p} + 2\pi i u \right] \] \( du \quad (8) \]

where

\[ R_2 = \frac{C_s C_p C_i}{K_s K_p K_i} \pi^{5/2}. \quad (8a) \]

Proceeding as in (i), we get the following expression for the observed intensity profile:

\[ I_{obs}(x) = \frac{K_2 R_2}{\pi^{1/2}} \exp \left[ -K_2^2 - K_i^2 x^2 \right] \]
\[ \times \left[ \text{Re} \cos \left( 2K_2 K_i x \right) + \text{Im} \sin \left( 2K_2 K_i x \right) \right]. \quad (9) \]

where

\[ K_2 = K_s \left( \frac{1}{K_p} + \frac{1}{K_i} \right). \quad (9a) \]

B. Intensity distribution of the true profile

The true profile \( I_T(x) \), being a convolution of the strain profile \( I_s(x) \) and the crystallite-size profile \( I_p(x) \), is

\[ I_T(x) = \{ T^{-1} \langle T[I_s(x)] \cdot T[I_p(x)] \rangle \}. \quad (10) \]

We consider case (b) of Schoening's (1965) true profile distribution:

\[ I_T(x) = R \int_{-\infty}^{+\infty} \exp \left[ -\left( \frac{\pi^2 u^2}{K_s^2} + \frac{2\pi|u|}{K_s} + 2\pi i u \right) \right] \] \( du, \quad (11) \]

where

\[ R = \frac{C_p C_s}{K_s K_p} \pi^{3/2}. \quad (11a) \]
Proceeding as in A, we get the following expression for the intensity distribution of the true profile:

\[
I_T(x) = \frac{R K_p^2}{\pi^{1/2} x^2} \exp \left[ K_p^2 \left( \frac{1}{K_p^2} - x^2 \right) \right] \times \left[ \text{Re} \cos \left( \frac{2K_p^2 x}{K_p} \right) + \text{Im} \sin \left( \frac{2K_p^2 x}{K_p} \right) \right]. \tag{12}
\]

**Results and discussions**

Expressions (7) and (9) for the observed intensity distribution and expression (12) for the true profile distribution have been evaluated with an IBM 1130 computer, using the predetermined values of the strain (\(\epsilon\)) and crystallite-size (\(L\) in \(\text{Å}\)) parameters of some copper- and silver-base alloys and some silver films as tabulated in I. These values have later been found (Nandi & Sen Gupta, 1976b) to be very close to those determined from a direct approach considering convolutions of instrumental and true profiles. The values of the peak maxima (\(I_{\text{max}}\)) are obtained for the respective cases from expressions (7), (9), and (12) for \(x = 0\). The relative intensity \(I/I_{\text{max}}\) is then plotted for increasing positive and negative values of \(x\) away from the peak until it coincides with the background level. In a similar way, for the experimentally observed distribution, \(x = 0\) has been considered for that Bragg \(\theta\) where the peak maximum occurs and \(\Delta x\) corresponds to \(\Delta \theta\) or \(\Delta 2\theta\). The experimental and theoretically calculated relative intensities are then compared. Similarly, the relative intensities for the true profile obtained from expression (12) are compared with the ones obtained by applying Stokes's (1948) method. In Fig. 1 (a, b, c, d), the theoretical and observed relative intensities of the 111, 222, 200 and 400 profiles are plotted for a Cu-1.05 a/o Sb alloy. It is seen that for the low-order profiles the agreement is good near the peaks with slight deviations near the tail portions, where the background correction is to some extent uncertain. For the 400 profile, which is very diffuse, the experimental points are not so precise and hence the deviation is quite pronounced, although the general feature is well represented.

For the same alloy system with a higher percentage of Sb the respective profiles (Fig. 2a, b) are broadened in comparison with those of Fig. 1. Here also the agreement in the intensity distribution is quite good, as it is for an Ag-4.00 a/o Sb alloy (Fig. 2c) and for a silver film of thickness \(\sim 2125\) Å (Fig. 2d).

These results suggest that both Cauchy and Gaussian instrumental profiles, when convoluted with Schoening-type true profiles approach closely the experimental distributions, although in terms of percentage deviations in integral-breadth values (Nandi & Sen Gupta, 1975, 1976a, b), a better agreement was obtained with Gaussian than with the Cauchy instrumental profiles. Since the theoretical functions considered here are symmetrical, the observed asymmetry in the experimental profiles due to stacking faults (extrinsic or twin) (Warren, 1959; 1969; Wagner, 1966) and to the instrumental factor is not explained here. Further, the influences of thermal diffuse scattering (TDS: one- or multi-phonon scattering in general) and absorption including secondary extinction as estimated directly in certain cases by Bradaczek & Hosemann (1968) and later by Urban & Hosemann (1972) on the fundamental peak and the associated tails, have not here been accounted for since this involves considerable mathematical complexities arising from the consideration of proper functional forms for the respective cases and their successive convolutions. Nevertheless, our present observation in terms of crystallite-size, strain and overall instrumental parameters yields a
Fig. 3. Theoretical and observed relative intensities of the 111 profile (true profile) distribution of Cu-1.05 °/o Sb alloy.

Fig. 4. Theoretical and observed relative intensities of the 111 profile (true profile) of a silver film ~2125 Å thick.

good correspondence between theoretical and experimental profile distributions.

As regards the true profile distributions, the convolution of a Cauchy crystallite-size profile with the Gaussian strain profile (expression 12) compares favourably with the Stokes deconvoluted profile near the central region, as is seen in Figs. 3 and 4 for the 111 profile of Cu-1.05 °/o Sb and of the silver film ~2125 Å, respectively. The small difference in the tail portions appears to be due to an apparent increased background level of the Stokes profile resulting from the uncertainty in the background level estimation and the truncation point of the experimental profile, which may arise from the data processing (Young, Gerdes & Wilson, 1967), and also from the truncation effect in the summation of the Fourier coefficients. However, overall comparison in the two cases (Stokes and convoluted) for the true profile distribution implies, to some extent, predominance of Gaussian nature.

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References


