

X-RAY LINE BROADENING AND PURE DIFFRACTION CONTOURS

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Summary

In analysing the data from experiments designed to distinguish between particle size and distortion broadening from polycrystalline materials, it is customary either to employ correction formulae to obtain the true broadening β , or to derive the pure diffraction contour in terms of a Fourier series whose coefficients may be evaluated from the experimental line profiles. The first method leads to values of β that are critically dependent upon the particular functions chosen to represent the diffraction line profiles and the second method, whilst removing this ambiguity, only yields the pure diffraction contour numerically and not analytically.

By applying Fourier methods, it is shown that the pure diffraction contours associated with particular causes of broadening can in fact be identified with certain types of analytic functions. In particular, the Cauchy and Gaussian distributions, which have often been arbitrarily employed in the past to represent the pure diffraction contour and experimental line profiles, are only strictly applicable to particular types of particle size and lattice distortion effects respectively. The case of combined size and distortion broadening is also considered, and for pure particle size broadening correction curves are derived corresponding to different types of particle size distributions.

I. INTRODUCTION

It is well known that radial broadening of X-ray diffraction lines from polycrystalline materials is associated with small particle size or variations in lattice spacing (e.g. due to faults in the crystal or heterogeneous lattice strains) over the volume of the material irradiated by the X-ray beam. In some cases it is clear which of these factors is predominant, but in others either effect, or a combination of them, may equally well be the cause of the broadening, and several methods have been suggested for differentiating between the various possibilities.

The problem is complicated by the necessity for correcting the broadening actually observed for instrumental effects before the true broadening due to the inherent condition of the material can be obtained. To carry out this correction it is customary either to employ correction formulae relating the true (required) integral line breadth β to the total observed breadth B and the instrumental breadth b (Scherrer 1920 ; Jones 1938 ; Warren and Biscoe 1938 ; Taylor 1941 ; Schoening, van Niekerk, and Haul 1952), or to analyse the experimentally determined line profiles by somewhat laborious mathematical procedures (Stokes 1948 ; Paterson 1950).

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In the first class, the values obtained for β , for given values of b/B , depend markedly, for the range covered by most experimental data, upon the particular correction formula adopted. Shull (1946) has shown that the true line profile after correcting for instrumental broadening (hereafter termed the "pure diffraction contour"), and hence the most appropriate correction formula, may be derived if the experimental line shapes are assumed or known to conform to particular types of analytic functions. Unfortunately, however, unless extremely accurate experimental techniques are employed, this criterion is of limited use, because the various types of functions which may be chosen to fit the observed profiles only differ appreciably in shape in regions close to their "tails" where possible percentage errors in measurement of line intensity are greatest. This uncertainty as to the proper relationship between β , B , and b is of particular consequence in attempting to distinguish between particle size and distortion broadening from deformed metals by investigating the variation of β with diffraction angle and X-ray wavelength, and has contributed to the conflicting nature of the results obtained in this field in the past (Brindley 1940; Smith and Stickley 1943; Stokes, Pascoe, and Lipson 1943; Megaw and Stokes 1945; Wood and Rachinger 1949).

Uncertainties of this type may be avoided by the use of the second class of method mentioned above and the more recent work on cold-worked metals has tended to adopt this type of procedure (Patterson 1950; Warren and Averbach 1950, 1952*a*, 1952*b*; Auld and Garrod 1952; McKeehan and Warren 1953; Smith 1953; Williamson and Hall 1953). In this case the pure diffraction contour is obtained numerically but not analytically.

Line breadth, however, is only one of the parameters associated with the broadened X-ray diffraction lines. Recently, it has been shown that much additional information may be obtained from a study of the shape of the pure diffraction contour. The latter is represented by a Fourier series obtained numerically from the experimental X-ray data by Stokes's method (1948), and the dependence of the Fourier coefficients on frequency can be used to investigate particle size broadening (Bertaut 1950, 1952; Warren and Averbach 1950), distortion broadening (Warren and Averbach 1950, 1952*a*) or a combination of the two effects (Eastabrook and Wilson 1952; Paterson 1952; Warren and Averbach 1952*b*).

It is important to note that in all of this work mentioned above, either analytic functions have been employed as direct or tacit assumptions for representing the X-ray line profiles or, alternatively, the pure diffraction contours have been obtained *numerically* from experimental data by computation. The question therefore arises whether in fact pure diffraction contours, due to particular causes of broadening, can be identified with particular types of analytic functions and, if so, the range of validity associated with the use of such functions.

In the present paper an attempt is made to investigate some aspects of this problem by the use of the Fourier methods referred to previously.

II. VALIDITY OF ANALYTIC FUNCTIONS FOR THE PURE DIFFRACTION CONTOUR

The following analysis for a randomly oriented polycrystalline material applies to any reflection which can be of the form $00l$ with respect to an appropriate system of orthogonal axes. As shown previously (Eastabrook and Wilson 1952; Paterson 1952), the pure diffraction contour for a material exhibiting line broadening may be represented quite generally by

$$I(X) = R \int_{-\infty}^{\infty} A(m, l) \exp(2\pi i m X) dm, \dots\dots\dots (1)$$

where $X = (2\theta - 2\theta_0)\lambda^{-1} a_3 \cos \theta_0$,

a_3 = length of unit cell axis in $[00l]$ direction,

θ_0 = Bragg angle for peak intensity,

m = (variable) difference in coordinates in $[00l]$ direction between any pair of cells in the crystal,

R = constant for a particular experimental arrangement.

$A(m, l)$ is a Fourier transform of $I(X)$ and may be expressed as the product of two other quantities (Eastabrook and Wilson 1952),

$$A(m, l) = N(m)J(m, l), \dots\dots\dots (2)$$

where $N(m)$ depends only upon the size and shape of the crystallites in the sample and $J(m, l)$ depends upon the lattice distortion.

If the analysis is restricted to diffraction contours that are symmetrical about the peak value, it follows that for any given $00l$ reflection, $A(m, l)$ may be written as

$$A(m) = P \int_{-\infty}^{\infty} I(x) \cos(2\pi m x / T) dx, \dots\dots\dots (3)$$

where $x = 2(\theta - \theta_0)$,

$T = \lambda / (a_3 \cos \theta_0)$,

P = constant.

Eastabrook and Wilson (1952) have shown that, if $A(m)$ is plotted against m , the initial slope is a measure of the reciprocal of the mean particle size \bar{M} (in units of a_3) in the $[00l]$ direction and the initial curvature gives a lower limit to the mean square strain \bar{e}^2 ; that is,

$$-\left(\frac{d\hat{A}}{d|m|}\right)_{|m|=0} = (\bar{M})^{-1}, \dots\dots\dots (4)$$

$$\left(\frac{d^2\hat{A}}{d|m|^2}\right)_{|m|=0} \simeq -4\pi^2 \bar{e}^2, \dots\dots\dots (5)$$

where $\hat{A}(m) = A(m)/A(0)$.

(a) *The Functions* $(1+a^2x^2)^{-1}$, $\exp(-k^2x^2)$, and $(1+c^2x^2)^{-2}$

The pure diffraction contour $I(x)$ is related to the intensity distribution $g(x)$ due to instrumental factors and the total distribution $h(x)$ from a material exhibiting line broadening by the equation (Jones 1938)

$$h(x) = \frac{\int_{-\infty}^{\infty} g(u)I(x-u)du}{\int_{-\infty}^{\infty} I(x)dx}, \quad \dots\dots\dots (6)$$

where u is the parameter of integration.

$h(x)$ and $g(x)$ are the experimentally observed line profiles, and various authors have from time to time suggested different analytic functions to represent the experimental data. Among these are the functions $(1+a^2x^2)^{-1}$, $\exp(-k^2x^2)$, and $(1+c^2x^2)^{-2}$.

It can easily be shown (Shull 1946) that, if $h(x)$ and $g(x)$ are of the form $(1+a^2x^2)^{-1}$, then $I(x)$ also conforms to this type of function, and similarly for the function $\exp(-k^2x^2)$. It is therefore of interest to inquire whether these analytic forms for $I(x)$ can be identified with particle size or distortion broadening or a combination of the two effects. If $h(x)$ and $g(x)$ are, however, of the form $(1+c^2x^2)^{-2}$, $I(x)$ is not of this form and cannot be readily evaluated analytically from (6). Nevertheless, for reasons to be discussed later, this form for $I(x)$ is also investigated below.

Case 1

Let $I(x) = (1+a^2x^2)^{-1}$, then from (3)

$$A(m) = P(\pi/a) \exp(-2\pi |m|/aT).$$

Hence

$$\left(\frac{dA}{d|m|} \right)_{|m|=0} = -\frac{2\pi}{aT}, \quad \dots\dots\dots (7)$$

$$\left(\frac{d^2A}{d|m|^2} \right)_{|m|=0} = \frac{4\pi^2}{a^2T^2}, \quad \dots\dots\dots (8)$$

$A(m)$ has a finite initial slope and therefore the function $(1+a^2x^2)^{-1}$ can represent particle size broadening. If distortion broadening were also present, from (5) and (8), e^2 would have to be negative. Since this is physically impossible, this particular intensity distribution for $I(x)$ can only correspond with pure particle size broadening, and $A(m)$ may be replaced by $\text{const.} \times N(m)$. In such cases, Bertaut (1950) has shown that it is possible to derive useful information about the particle size and size distribution in the sample. The following results follow directly from the relationships he has established.

(i) The mean particle size \bar{M} in the $[00l]$ direction is given by

$$\bar{M} = \frac{aT}{2\pi}, \quad \dots\dots\dots (9)$$

This follows from Bertaut's analysis, which shows that

$$\bar{M} = t(0),$$

where

$$t(m) \equiv -N(m) \left/ \left(\frac{dN}{d|m|} \right) \right|_{|m|=0} = \int_{|m|}^{\infty} (M - |m|) p(M) dM, \dots (10)$$

and $p(|m|)$ is the size distribution function.

(ii) The "apparent particle size" L as defined by Jones (1938) is given by

$$L = \int_{-\infty}^{\infty} N(m) dm / N(0) = aT/\pi, \dots (11)$$

where \bar{M} and L are in units of a_3 .

It may be noted here that, since the integral line breadth

$$\beta = \int_{-\infty}^{\infty} I(x) dx / I(0) = \pi/a,$$

it follows from (11) that

$$(\beta \cos \theta_0) / \lambda = (a_3 L)^{-1},$$

which is the familiar relationship for particle size broadening.

(iii) The mean square particle size

$$\bar{M}^2 = \int_{-\infty}^{\infty} t(m) dm = a^2 T^2 / 2\pi^2 = 2(\bar{M})^2. \dots (12)$$

(iv) The mean square deviation in particle size

$$\bar{\varepsilon}^2 = (aT/2\pi)^2. \dots (13)$$

(v) The size distribution function

$$p(|m|) = d^2 t / d|m|^2 = (2\pi/aT) \exp(-2\pi|m|/aT). \dots (14)$$

(vi) The fraction of particles having dimensions M in the range $|m| \leq M < \infty$ out of the total number of particles contributing to the diffraction is given by

$$\int_{|m|}^{\infty} p(M) dM = -dt/d|m| = \exp(-2\pi|m|/aT). \dots (15)$$

Case 2

Let $I(x) = \exp(-k^2 x^2)$, then

$$A(m) = P(\pi^{1/2}/k) \exp(-\pi^2 m^2 / k^2 T^2). \dots (16)$$

It follows from (4) and (16) that $\bar{M} = \infty$ if k is finite.

Hence this type of function cannot represent particle size broadening. To investigate the possibility of distortion broadening we can replace (Am) by $\text{const.} \times J(m)$.

From (5) the root mean square strain in the $[00l]$ direction is given approximately by

$$(\bar{e}^2)^{\frac{1}{2}} = (2k^2 l^2 T^2)^{-\frac{1}{2}}. \quad \dots\dots\dots (17)$$

Since $\lambda = 2d \sin \theta_0$, $d = a_3/l$, $\beta = \pi^{\frac{1}{2}}/k$, it follows by substitution in (17) that the "apparent tensile strain" η is given by

$$\eta = \beta \cot \theta_0 = 2(\pi \bar{e}^2)^{\frac{1}{2}}. \quad \dots\dots\dots (18)$$

This is the result found by Stokes and Wilson (1944) by other methods, for distortion broadening due to a Gaussian distribution of lattice strains.

Case 3

Let $I(x) = (1 + c^2 x^2)^{-2}$, then

$$A(m) = P(\pi/2c)(1 + 2\pi |m|/cT) \exp(-2\pi |m|/cT), \quad \dots (19)$$

and

$$(d\hat{A}/d|m|)_{|m|=0} = 0.$$

Thus this function cannot represent particle size broadening. However (19) is of the correct form to represent distortion broadening. It follows that

$$(\bar{e}^2)^{\frac{1}{2}} = (clT)^{-1}, \quad \dots\dots\dots (20)$$

and

$$\eta = \pi(\bar{e}^2)^{\frac{1}{2}}. \quad \dots\dots\dots (21)$$

(b) Other Types of Particle Size Broadening

It is of interest to consider the pure diffraction contours associated with types of particle size distributions other than the somewhat unlikely case in practice given by the Cauchy contour $(1 + a^2 x^2)^{-1}$. This may be investigated by reversing the previous procedure; that is, the particle size distribution is assumed and the corresponding diffraction contour is then obtained.

By replacing $N(m)$ in (1) by the expression for $N(m)$ in terms of the size distribution function $p(|m|)$ given by (10), it follows that for a contour symmetrical about the peak value

$$I(x) = K \int_0^\infty p(M) (\pi x/T)^{-2} \sin^2(\pi M x/T) dM, \quad \dots\dots (22)$$

where, by definition,

$$\int_0^\infty p(M) dM = 1$$

and K is a constant.

This is a general expression which enables the intensity distribution for the $00l$ reflection to be determined if the size distribution function is known. In general, as Jones (1938) has pointed out, $p(M)$ is not known and is likely to vary for each material, but three possible examples are given below.

(i) Consider first the simple case in which the crystals are all of the same size and the same external shape, which is here taken to be cubic.

In this case $M = \overline{M} = L$. Hence

$$I(x) = KL^2(\pi Lx/T)^{-2} \sin^2(\pi Lx/T), \quad \dots\dots\dots (23)$$

that is, the intensity distribution is of the familiar form $D(nx)^{-2} \sin^2 nx$ where D and n are constants. The same result has been obtained by other methods by Stokes and Wilson (1942) as part of a more generalized treatment of the diffraction from polycrystalline aggregates of uniform particle size.

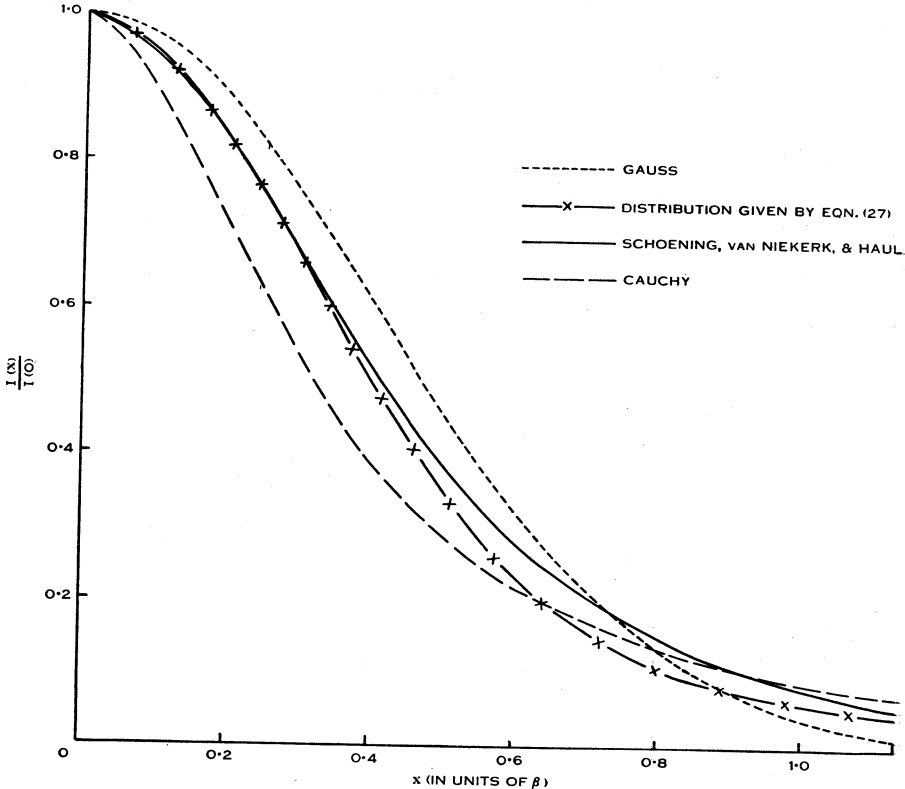


Fig. 1.—Types of distribution functions representing $I(x)$.

(ii) Let

$$p(M) = (2/\pi)^{\frac{1}{2}} \sigma^{-1} \exp(-M^2/2\sigma^2), \quad \dots\dots\dots (24)$$

where σ is the root mean square value of M .

By integration of (22) it follows that

$$I(x) = 2K(2\pi x/T)^{-2} [1 - \exp\{-\frac{1}{2}\sigma^2(2\pi x/T)^2\}]. \quad \dots\dots (25)$$

(iii) One objection to (24) is that $p(M)$ is a maximum for $M=0$. To obtain a skew distribution about a non-zero value of M let

$$p(M) = (2/\pi)^{\frac{1}{2}} S^{-3} M^2 \exp(-M^2/2S^2), \quad \dots\dots\dots (26)$$

where S is a constant. Then

$$I(x) = 2K(2\pi x/T)^{-2} [1 - (1 - 4\pi^2 S^2 x^2/T^2) \exp\{-\frac{1}{2}S^2(2\pi x/T)^2\}]. \quad \dots\dots\dots (27)$$

TABLE 1
PURE DIFFRACTION CONTOURS ASSOCIATED WITH DIFFERENT CAUSES OF LINE BROADENING

Pure Diffraction Contour $I(x)$	Type of Broadening	Size Distribution Function $p(M)$	" Apparent Particle Size " L	Mean Particle Size* \bar{M}
$(1+a^2x^2)^{-1}$	Particle size	$\frac{2\pi}{aT} \exp\left(-\frac{2\pi M}{aT}\right)$	$\frac{aT}{\pi}$	$\frac{aT}{2\pi}$
$(nx)^{-2} \sin^2 nx$	"	Dirac delta function : $\delta\left(M - \frac{nT}{\pi}\right)$	$\frac{nT}{\pi}$	$\frac{nT}{\pi}$
$\frac{T^2}{2\pi^2\sigma^2x^2} \left(1 - \exp\left(-\frac{2\pi^2\sigma^2x^2}{T^2}\right)\right)$	"	$\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{1}{\sigma} \cdot \exp\left(-\frac{M^2}{2\sigma^2}\right)$	$\left(\frac{\pi}{2}\right)^{\frac{1}{2}} \sigma$	$\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \sigma$
$\frac{T^2}{6\pi^2S^2x^2} \left\{1 - (1 - 4\pi^2S^2x^2) \exp\left(-\frac{2\pi^2S^2x^2}{T^2}\right)\right\}$	"	$\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{1}{S^3} \cdot M^2 \exp\left(-\frac{M^2}{2S^2}\right)$	$3\left(\frac{\pi}{8}\right)^{\frac{1}{2}} S$	$\left(\frac{8}{\pi}\right)^{\frac{1}{2}} S$
$\exp(-k^2x^2)$	Distortion	" Apparent Tensile Strain " η		
$(1+c^2x^2)^{-2}$	"	$\frac{2(2\pi e^2)^{\frac{1}{2}}}{\pi(e^2)^{\frac{1}{2}}}$		

* Particle sizes are expressed in units of axial length a_3 .

The results of the preceding analysis are summarized in Table 1 and in Figures 1 and 2. In these figures, the constants for each function have been adjusted for convenience so as to make the areas under the curves all equal.

(c) *Combined Particle Size and Distortion Broadening*

In the examples considered so far, either particle size or distortion broadening has alone been operative. Both effects may however be present in the same sample and Warren and Averbach (1952*b*) have shown how the experimental

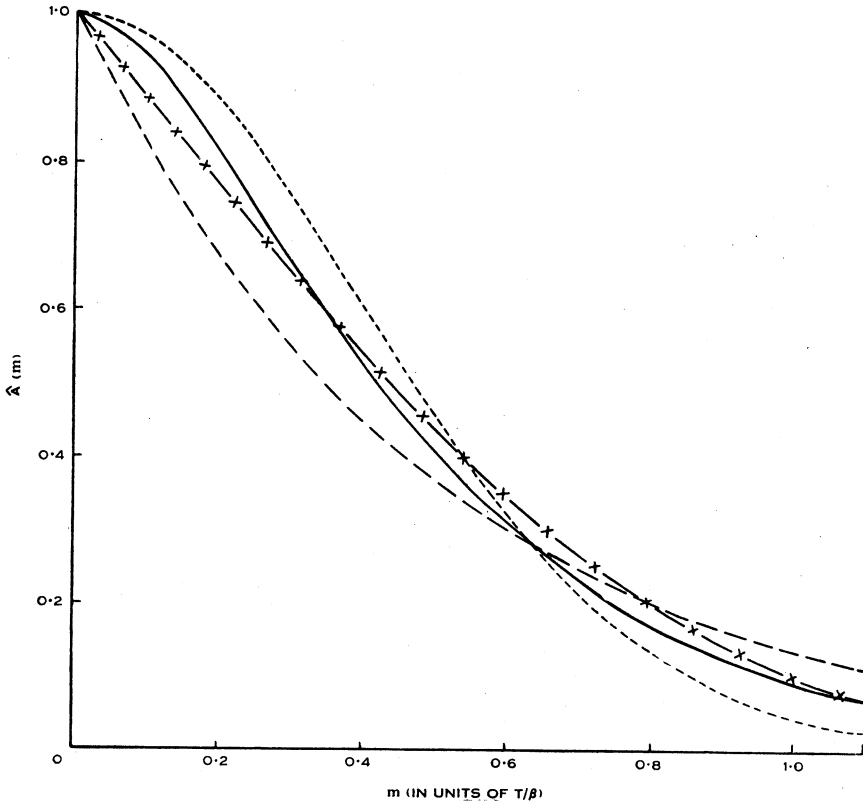


Fig. 2.—Transforms of functions in Figure 1.

data may, in favourable cases, be analysed numerically to determine the relative influence of the two factors. It is, however, of interest to reverse this procedure and examine analytically how particular models of size and distortion combinations may be expected to modify the shape of the function $A(m, l)$ for any given reflection.

The problem is of particular importance in connexion with the effect of cold-work on polycrystalline metals. On the assumption that both particle size and distortion broadening are contributory factors, a number of models may be assumed. Two extreme cases are as follows :

(1) First, as a result of plastic deformation, each grain in the aggregate may become dissociated into a number of units. Some of these units are strain free but of such dimensions that particle size broadening occurs ; in other units

the size is still sufficiently large for no appreciable size broadening, but distortion broadening occurs due to heterogeneous lattice strains. Under these circumstances the intensity distribution in a reflection is the sum of the contributions due to the particle size and distortion factors treated independently. This would correspond with the assumption made by Hall (1949) in taking the total line breadth β as the simple sum of the breadths due to each factor separately.

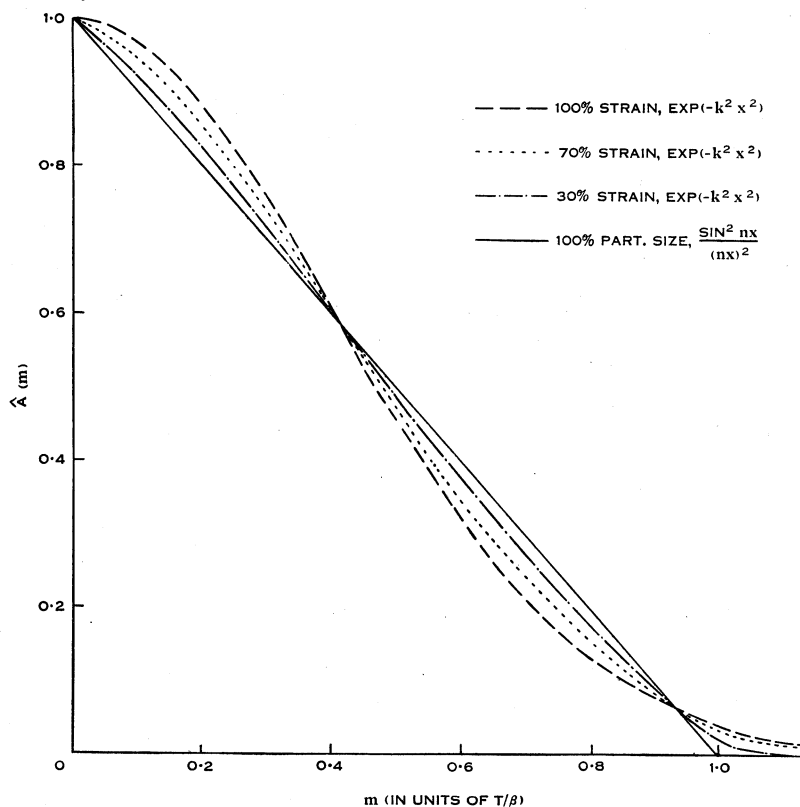


Fig. 3.—Transforms for combined particle size and distortion broadening given by equation (29).

(2) Secondly and more probably, after plastic deformation each grain may become dissociated into a number of small, heterogeneously distorted units. The intensity distribution for any reflection is then the resultant coherent scattering in a given direction of the incident beam produced by these domains, and is given by equation (1) for crystals of the cubic class.

As an illustration of the method of treatment, a particular example corresponding to each of these cases is considered below.

Case 1

On the first hypothesis, suppose for simplicity that the crystallites conform to one or the other of only two possible types :

(i) A given proportion of the total number contains crystallites sufficiently large for no size broadening to occur and in which the strain distribution function

is assumed to be Gaussian. The intensity distribution in the reflected beam due to these crystallites is thus of the form $\exp(-k^2x^2)$.

(ii) The remainder are strain free and of a small uniform size. For these, the diffraction contour is represented by the function $(nx)^{-2} \sin^2 nx$.

The resultant pure diffraction contour is then given by

$$I(x) = C \exp(-k^2x^2) + D(nx)^{-2} \sin^2 nx. \quad \dots\dots (28)$$

Hence

$$A(m) = K_1(\pi^{1/2}/k) \exp(-\pi^2m^2/k^2T^2) + K_2(\pi/n)(1 - \pi |m|/nT)^*, \dots (29)$$

where K_1 and K_2 are parameters whose relative magnitudes determine the contributions due to distortion and particle size effects respectively. For 100 per cent. strain broadening $K_1=1$, $K_2=0$ and for 100 per cent. size broadening $K_1=0$, $K_2=1$.

Figure 3 shows the form of $\hat{A}(m)$ for values of $(K_1, K_2) = (1, 0)$, $(0.7, 0.3)$, $(0.3, 0.7)$, and $(0, 1)$.

Case 2

In this example, it is assumed that the sample consists of small distorted crystals of uniform size and with a Gaussian distribution of lattice strains. Hence

$$A(m) = N(m)J(m) = P(1 - \pi |m|/nT) \exp(-\pi^2m^2/k^2T^2)^*, \dots (30)$$

where P is a constant and n and k have the same significance as in the previous example. By assigning various values to n and k varying relative contributions of particle size and distortion broadening respectively can be represented. For pure size broadening, $k=\infty$ and for pure strain broadening $n=\infty$. The true diffraction line breadth is given by

$$\beta^{-1} = \pi^{-1/2}kT \operatorname{erf}(n/k) - (k^2T/\pi n)\{1 - \exp(-n^2/k^2)\}. \dots (31)$$

In Figure 4 $\hat{A}(m)$ is plotted for values of n/k of 0, 2, 5, ∞ . The curves all represent the same value for β .

(d) Correction Curves for Particle Size Broadening

To obtain the true integral breadth β from the measured values B and b it is convenient and customary to obtain, if possible, correction curves in which β/B may be plotted as functions of b/B . The principal correction formulae which have been suggested are summarized in Table 2. As pointed out in Section I, these formulae are based upon the subjective choice of various types of analytic functions to represent the experimental X-ray line profiles, and in general are without reference to the particular cause of broadening involved. The preceding analysis, however, indicates how given types of analytic functions

* The particle size factor in (29) and (30) is zero outside the range $0 \leq |m| \leq nT/\pi$.

may be assigned to particular forms of particle size distributions. It is therefore of interest to investigate the dependence of the appropriate correction curve upon the particular type of particle size broadening considered.

The appropriate relationship between B , b , and β can, however, only be obtained if two of the three functions in equation (6) above are known. Assuming

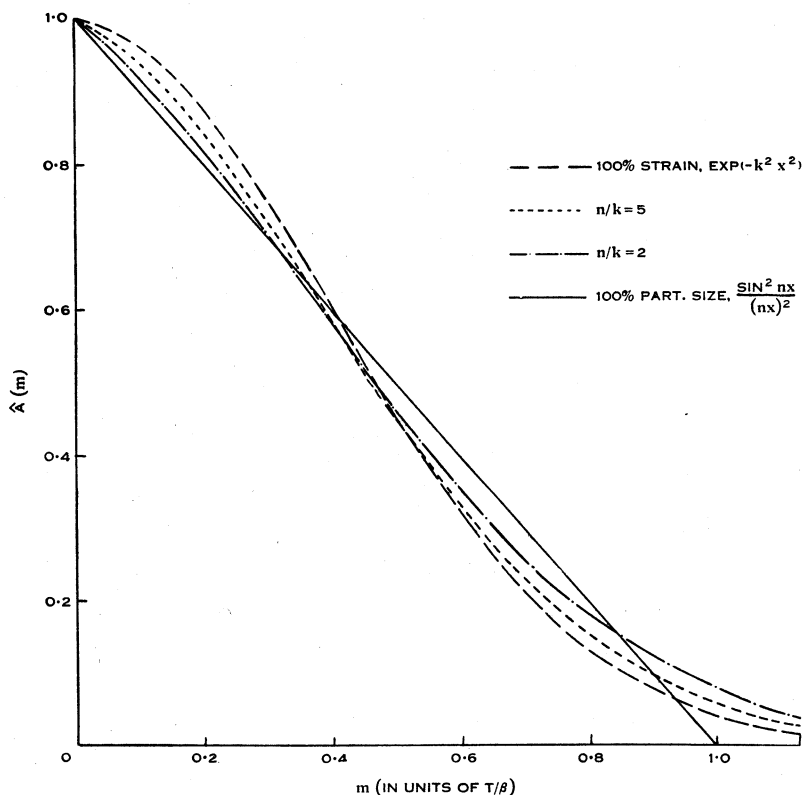


Fig. 4.—Transforms for combined particle size and distortion broadening given by equation (30).

that $I(x)$ and $g(x)$ are known, the integral breadth B may be obtained by either of the following two methods.

(i) From (6) it follows that if transforms of $h(x)$ and $g(x)$ are given by

$$H(m) = \int_{-\infty}^{\infty} h(x) \exp(2\pi i m x) dx,$$

$$G(m) = \int_{-\infty}^{\infty} g(x) \exp(2\pi i m x) dx$$

respectively, then

$$\begin{aligned} H(m) &= \hat{A}(Tm)G(m), \\ H(0) &= G(0). \end{aligned}$$

TABLE 2
RELATIONSHIP BETWEEN B , b , AND β FOR VARIOUS LINE PROFILES

Authors	Correction Formula	Type of Function Representing Experimental Profiles $g(x)$ and $h(x)$ for Correction Formula to be Valid
(I) Scherrer (1920)	$\beta = B - b$	$(1 + a^2 x^2)^{-1}$
(II) Warren and Biscoe (1938) ..	$\beta = (B^2 - b^2)^{\frac{1}{2}}$	$\exp(-k^2 x^2)$
(III) Jones (1938)	Correction curves relating β/B to b/B	Shape of $g(x)$ determined experimentally, $I(x)$ assumed to be of type $(1 + a^2 x^2)^{-1}$ or $\exp(-k^2 x^2)$
(IV) Taylor (1941)	$\beta = [(B - b)(B^2 - b^2)^{\frac{1}{2}}]^{\frac{1}{2}}$	No assumptions as to $g(x)$ and $h(x)$ but β taken arbitrarily as geometric mean of (I) and (II)
(V) Alexander and Klug (1950)	Correction curves relating β/B to b/B	$I(x)$ assumed to be $(1 + a^2 x^2)^{-1}$ and X-ray source contour of form $\exp(-k^2 x^2)$
(VI) Schoening, van Niekirk, and Haul (1952)	Correction curves relating β/B to b/B	$(1 + c^2 x^2)^{-2}$

TABLE 3
CORRECTION FORMULAE FOR DIFFERENT TYPES OF PARTICLE SIZE BROADENING AND DIFFERENT INSTRUMENTAL CONTOURS $g(x)$

$p(M)$	β	Relationship between B , b , and β	
		$g(x) = \exp(-k^2 x^2)$, $b = \pi^{\frac{1}{2}}/k$	$g(x) = (1 + c^2 x^2)^{-2}$, $b = \pi/2c$
$\frac{2\pi}{aT} \exp\left(-\frac{2\pi}{aT} M\right)$	$\frac{\pi}{a}$	$\frac{b}{B} = \exp \frac{\beta^2}{\pi b^2} \operatorname{erfc} \frac{\beta}{\pi^{\frac{1}{2}} b}$	$\frac{\beta}{B} = \frac{1}{2} - \frac{2b}{B} + \frac{1}{2} \left(1 + \frac{8b}{B}\right)^{\frac{1}{2}}$
$\delta \left(M - \frac{nT}{\pi}\right)$	$\frac{\pi}{n}$	$\frac{b}{B} = \operatorname{erf} \frac{\pi^{\frac{1}{2}} b}{\beta} - \frac{\beta}{\pi b} \left[1 - \exp\left(-\frac{\pi b^2}{\beta^2}\right)\right]$	$\frac{b}{B} = \frac{\beta}{8b} \left[\left(3 + \frac{4b}{\beta}\right) \exp\left(-\frac{4b}{\beta}\right) - 3 + \frac{8b}{\beta}\right]$
$\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \cdot \frac{1}{\sigma} \cdot \exp\left(-\frac{M^2}{2\sigma^2}\right)$	$\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \cdot \frac{T}{\sigma}$	$\frac{\beta}{B} = 1 - \frac{b^2}{B^2}$	$\frac{\beta}{B} = -\frac{3\pi\beta^2}{16b^2} + \frac{3\beta}{2b} + \left(\frac{9\pi\beta^2}{16b^2} - 2\right) \exp \frac{16b^2}{\pi\beta^2} \operatorname{erfc} \frac{4b}{\pi^{\frac{1}{2}}\beta}$
$\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \cdot \frac{M^2}{S^3} \exp\left(-\frac{M^2}{2S^2}\right)$	$\left(\frac{8}{\pi}\right)^{\frac{1}{2}} \cdot \frac{T}{3S}$	$\frac{b}{B} = \frac{1}{8b} \left[\frac{9\beta^2 + 32b^2}{(9\beta^2 + 16b^2)^{\frac{1}{2}}} - 3\beta \right]$	$\frac{\beta}{B} = -\frac{9\pi\beta^2}{64b^2} + \frac{3\beta}{4b} + \frac{32b}{9\pi\beta} + \left(\frac{9\pi\beta^2}{64b^2} - \frac{256b^2}{27\pi\beta^2}\right) \exp \frac{64b^2}{9\pi\beta^2} \operatorname{erfc} \frac{8b}{3\pi^{\frac{1}{2}}\beta}$

The observed intensity distribution $h(x)$ in the presence of size broadening is then found from

$$h(x) = \int_{-\infty}^{\infty} H(m) \exp(-2\pi i m x) dm.$$

Finally

$$B = \int_{-\infty}^{\infty} h(x) dx / h(0) = H(0) / h(0),$$

or

$$B = G(0) / \int_{-\infty}^{\infty} H(m) dm. \quad \dots\dots\dots (32)$$

(ii) The above method is appropriate if the pure diffraction contour $I(x)$ is known directly. If, however, the size distribution function $p(|m|)$ is adopted as a starting-point, it is more convenient to derive an expression for the breadth B in terms of this distribution function. The analysis is too lengthy to set out here, but it can be shown that

$$B = \overline{M} G(0) / \int_{-\infty}^{\infty} t(Tm) G(m) dm, \quad \dots\dots\dots (33)$$

where the parameters have the significance defined previously.

As pointed out already, B will depend upon the functions chosen to represent $I(x)$ and $g(x)$. In practice, it is generally found that the instrumental contour $g(x)$ may be represented quite closely, either by $\exp(-k^2 x^2)$ (Taylor and Sinclair 1945; Shull 1946; Alexander 1950), or by a function of the type $(1 + c^2 x^2)^{-2}$ (Jones 1938; Schoening, van Niekerk, and Haul 1952).

For both of these forms for $g(x)$, the four types of particle size broadening considered previously have been analysed by the methods outlined above and the results are summarized in Table 3. In Figure 5, the correction curves corresponding to the size distribution function $p(M)$ given by (26) have been plotted in the usual way for the two different forms for $g(x)$. For comparison, the curves corresponding to formulae (I), (II), and (VI) in Table 2 are also included in Figure 5.

III. DISCUSSION

A number of interesting points emerge from the analysis in Section II.

(1) First, the functions $(1 + a^2 x^2)^{-1}$ and $\exp(-k^2 x^2)$, which have previously been used somewhat indiscriminately to represent the pure diffraction contour, can in fact only be identified with line broadening due to *particular* types of particle size and lattice distortion effects respectively. Hence, in any attempt to distinguish between particle size or strain broadening from a particular material, the use of the one or the other of these functions (together with the appropriate relationship between B , b , and β) involves an intrinsic initial assumption about the cause of the broadening, when the object of the investigation is to discover the cause. Such an assumption must inevitably weight the experimental results, partially at least, in favour of one or the other of the two effects.

In this connexion it is therefore perhaps significant that in most previous work on the cause of line broadening from cold-worked metals, those investigators who have used the Warren relationship between B , b , and β have concluded that lattice distortion was the predominant factor, whilst those who have employed the Scherrer correction found that particle size was the main cause. The best procedure in such work therefore is to make no assumptions at all about the shape of the experimental line profiles.

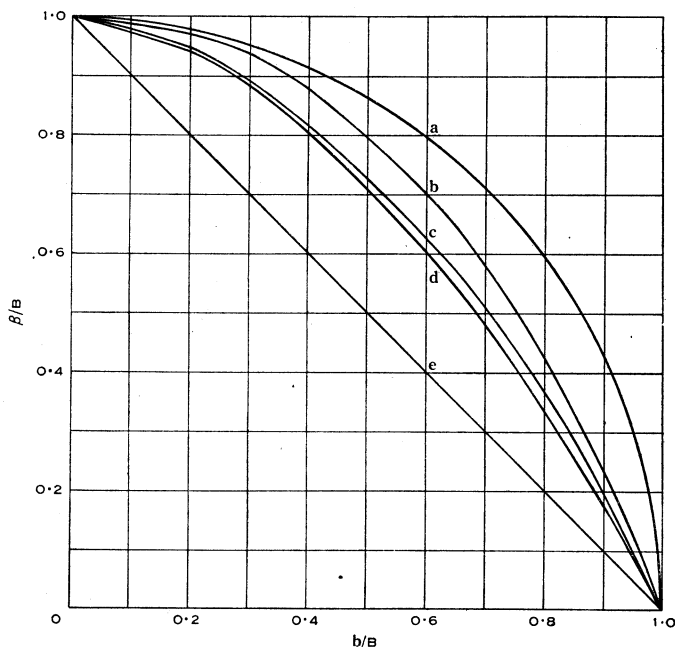


Fig. 5.—Correction curves associated with particle size broadening for various types of size distribution functions and different instrumental contours. *a*, Warren curve; *b*, $p(M)$ given by equation (26), $g(x) = \exp(-k^2x^2)$; *c*, $p(M)$ given by equation (26), $g(x) = (1 + c^2x^2)^{-2}$; *d*, Schoening, van Niekerk, and Haul curve; *e*, Scherrer curve.

(2) Secondly, as would be expected, the pure diffraction contour depends not only upon the cause of the broadening but also upon the nature of the size and strain distribution functions. In cases where the size effect is negligible, Eastabrook and Wilson (1952) have suggested that the Cauchy line profile is possibly a better approximation to the pure diffraction contour encountered in practice than the Gaussian form. At first sight this is in direct contradiction to the results obtained here. It should be noted, however, that different distortion models are considered in the two cases. In the present paper it has been shown that a Gaussian strain distribution corresponds to a Gaussian intensity distribution for the pure diffraction contour. On the other hand, Eastabrook and Wilson have considered the case of crystals large enough for negligible particle size broadening and in which each crystal is *assumed to contain several regions of compression and extension*. In this case, they have shown that for small m

(corresponding to the behaviour of $I(x)$ for large x), $J(m)$ is approximately proportional to $\exp(-2\pi^2 l^2 \bar{e}^2 m^2)$, whereas for large m , $J(m)$ tends more nearly to be proportional to $\exp(-\text{const.} |m|)$. This implies that, for this particular type of distortion broadening, the pure diffraction contour would approximate to a Cauchy form at and near to its peak value, with a gradual transition with progressive increase in x to some other profile (e.g. Gaussian) that is consistent with distortion broadening for small m .

The question as to whether the contour is a closer resemblance to a Cauchy or to a Gaussian profile will depend upon the type of distortion that is operative. For cases of distortion broadening encountered in practice, it seems unlikely that any simple analytic function will truly represent the pure diffraction contour, and for the reasons discussed in (1) above and (4) below, it is dangerous to attempt to assign given functions as "close fits" to the experimental observations when dealing with distortion broadening. For pure particle size broadening on the other hand, such a procedure is often permissible, since determination of the "apparent particle size" from line breadth measurements can only be regarded as approximate in view of a number of other uncertainties.

(3) Thirdly, for pure particle size broadening, Alexander (1950), in discussing the factors affecting determination of crystallite size with a Geiger-counter X-ray spectrometer, concluded that a typical crystal size distribution leads to a pure diffraction contour which bears a closer resemblance to a Cauchy profile than a Gaussian form. The preceding analysis would tend to support this conclusion. At the same time the exact form of the contour depends upon the particular type of size distribution law appropriate to each material.

A point of interest here is that Schoening, van Niekerk, and Haul (1952) have reported recently that the line profiles obtained from small crystals with a Geiger-counter X-ray spectrometer could be represented very closely by functions of the type $(1+c^2x^2)^{-2}$. In this case, although $I(x)$ cannot be conveniently evaluated analytically, by employing the methods described previously it can readily be shown that these functions for $h(x)$ and $g(x)$ cannot truly represent particle size broadening. Assuming that in the samples examined by these authors no distortion broadening occurred, the inconsistency between their experimental observations and the present theoretical treatment presents a problem. It may perhaps be that some other function or functions compatible with particle size broadening could also represent closely their experimental observations. For example, if

$$g(x)/g(0) = (1 + q_1 c_1^2 x^2)(1 + c_1^2 x^2)^{-2}$$

and

$$h(x)/h(0) = (1 + q_2 c_2^2 x^2)(1 + c_2^2 x^2)^{-2}$$

(which approximate to the previous functions if q_1 and q_2 are small), it can be shown that these profiles are compatible with size broadening, giving a non-negative value for the size distribution function $p(|m|)$ provided that

$$0 \leq \frac{1-q_2}{1+q_2} \cdot \frac{1}{c_2} \leq \frac{1-q_1}{1+q_1} \cdot \frac{1}{c_1} + \frac{1}{2} \left(\frac{1}{c_2} - \frac{1}{c_1} \right)^2 \left/ \left(\frac{1}{c_2} - \frac{2q_1}{1+q_1} \cdot \frac{1}{c_1} \right) \right.$$

Examination of Figure 5, however, shows that except in cases where a high accuracy is warranted in the determination of particle size, the differences introduced by using one or other of the correction curves (*b*), (*c*), or (*d*) will not be serious. It is also interesting to note the close agreement between curves (*c*) and (*d*) which are both based upon the same function $(1+c^2x^2)^{-2}$ for $g(x)$. Curve (*d*), given by Schoening, van Niekerk, and Haul, cannot strictly be applicable to particle size broadening, yet is nevertheless a close fit to *their* experimental conditions and observations. On the other hand curve (*c*) corresponds to a particular size distribution which may approximate to typical distributions encountered in practice. It appears therefore that for general application to particle size broadening, curve (*c*) is likely to be a reasonable compromise.

(4) Finally, as pointed out by Eastabrook and Wilson (1952), the original methods developed by Warren and Averbach (1950) for distinguishing between particle size and distortion effects, based upon the shape of the pure diffraction contour rather than its breadth, have certain limitations in practice, particularly if the analysis is restricted to single orders of reflection from given sets of planes in the crystal. It is true, for example, that there is a considerable difference in shape between the Fourier transforms (Fig. 2) corresponding to the contour functions $(1+a^2x^2)^{-1}$ and $\exp(-k^2x^2)$. Comparison of Figures 1 and 2, however, shows that the pure diffraction contours in Figure 1, which produce appreciable changes in Figure 2, only differ appreciably in shape in regions close to their "tails" where percentage errors in measurement are greatest. In consequence, if Fourier methods are used to determine the pure diffraction contour $I(x)$ or its Fourier coefficients, from observations on the shapes of the experimental $h(x)$ and $g(x)$ contours, the shape of the $A(m)$ curve will be critically dependent upon the accuracy of the experimental observations of line intensities at values approaching the general background value due to incoherent scattering. Furthermore, Figures 3 and 4 illustrate how the shape of the curve changes when particle size and distortion effects are both operative. Consequently, although the more recent methods of Warren and Averbach (1952*b*), based on analysis of several orders of reflection from any given set of planes, reduce the chance of ambiguity of interpretation (due to experimental error) of the experimental results, the use of such criteria *alone*, for differentiating between particle size and distortion broadening, would appear to be rather dangerous unless very accurate experimental techniques are employed.

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