A METHOD OF CORRECTING THE BROADENING OF X-RAY LINE PROFILES

By R. N. BRACEWELL*

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Summary

A numerical method is presented which allows X-ray line profiles to be corrected for instrumental broadening. It provides an alternative to the use of Fourier analysis as described by Stokes. A special development of the method (as hitherto used) is necessary to permit its application to X-ray analysis where the Kα doublet constitutes a complication.

I. INTRODUCTION

X-ray powder photographs taken with characteristic X-radiation reveal facts about the powdered material, such as size of particle and condition of the crystal lattice structure, which have given rise to the developing subject of X-ray metallography (see Taylor 1945). The information is contained in the shape of the line profile as measured from the X-ray photograph with a microphotometer or directly with a Geiger counter spectrometer. However, the profile is subject to influences other than that under study and it is necessary to make allowance. For example, if the size of the particles is of interest, allowance must be made for the geometrical details of the X-ray camera and a number of other factors which combine to produce appreciable broadening; and if the state of strain of the lattice is under study then it is necessary to allow, in addition, for the broadening due to the finite size of the particle. Furthermore, Kα radiation, commonly used in X-ray powder diffraction, is in fact a doublet which causes further complication when conditions are such that it is neither fully resolved nor fully unresolved.

In early work Scherrer corrected the width of the observed line by subtracting the width obtained when the phenomenon under study was absent. This is hardly reasonable (although there is a special case in which it is valid), and subsequently Taylor (1941) considered the modifications which arise if the line profiles are Gaussian. In this work the observations were not deemed adequate to yield more than one parameter, the line width. It has since become desirable to calculate the line profiles without initial assumptions as to shape. The Fourier analysis method for this has been described by Stokes (1948) and a relaxation method has been given by Paterson (1950).

The basic problem arises in very many connexions and has been recently discussed, with respect particularly to radio astronomy, by Bracewell and

* Division of Radiophysics, C.S.I.R.O., University Grounds, Sydney.

Roberts (1954). The process of successive substitutions, which they describe, ought to be applicable in X-ray analysis, bringing with it its advantages. Direct application is, however, usually impossible since the splitting of the $K\alpha$ line causes the process to diverge. This difficulty has been overcome by the introduction of a simple method of removing the effect of the doublet.

The present method is free from the subjective element of Paterson's method and rather shorter. It is much less laborious than Stokes's method. The latter method is, however, the appropriate one where, as in lattice distortion studies (cf. Averbach and Warren 1949), one requires the Fourier transform of the corrected profile.

II. The Problem

Let $A(\xi)$ be the apparatus function or instrumental profile. In the typical case shown in Figure 1, $A(\xi)$ has two humps corresponding to the two components of the doublet, and the broadening of each component is due to the geometry of the camera, etc. This profile was determined experimentally on annealed aluminium. If the aluminium is now subjected to cold work which would broaden an infinitely narrow line into a profile $F(\xi)$, then the distribution actually observed would be $G(\xi)$.

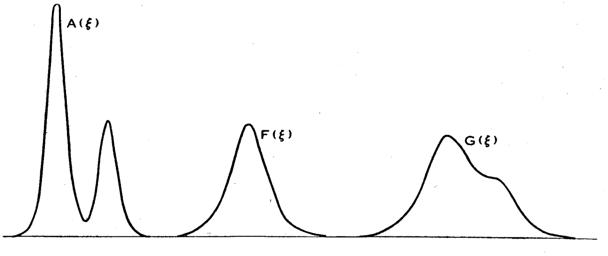

Fig. 1

The actual case illustrated in Figure 1 and tabulated in Table 1, has been taken from Paterson (1950), with small changes in normalization and interval of tabulation.

The relation between the three functions is

$$G(\xi)=\int_{-\infty}^{\infty} A(\xi-u)F(u)\mathrm{d}u. \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Given $G(\xi)$, and knowing the effect of the apparatus $A(\xi)$, it is required to find $F(\xi)$.

Now $A(\xi)$ and $G(\xi)$ may be expressed in the following form

$$A(\xi)=\int_{-\infty}^{\infty} \alpha(\xi-u)\mathrm{II}(u)\mathrm{d}u, \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$G(\xi)=\int_{-\infty}^{\infty} \gamma(\xi-u)\mathrm{II}(u)\mathrm{d}u, \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where $\mathrm{II}(\xi)=\delta(\xi)+\frac{1}{2}\delta(\xi-\sigma)$, $\delta(\xi)$ is the unit impulse function, and σ is the separation of the two components of the $K\alpha$ doublet. We are here using the fact that the intensities of the two components are in the ratio of 2 to 1. Solving these integral equations would yield $\alpha(\xi)$ and $\gamma(\xi)$, which are the forms that would be taken by $A(\xi)$ and $G(\xi)$ if the doublet were a single line. This is not a difficult step, but to clarify the exposition we shall defer the explanation to Appendix I, meanwhile assuming that $\alpha(\xi)$ and $\gamma(\xi)$ have been obtained from $A(\xi)$ and $G(\xi)$. Figure 2 shows $\alpha(\xi)$ and $\gamma(\xi)$.

TABLE 1

$A(\xi)\times 10^3$	$F(\xi)\times 10^3$	$G(\xi)\times 10^3$
2	0	1
9	3	3
42	4	5
114	7	8
228	8	12
314	12	19
192	20	30
68	41	50
28	58	70
28	91	98
59	129	124
114	151	138
157	145	135
96	115	120
34	85	105
11	53	89
3	33	84
1	18	82
	12	80
	8	72
	6	58
	3	43
	0	28
		18
		11
		7
		4
		3
		2
		1

From equations (**1**), (**2**), and (**3**),

$$\int_{-\infty}^{\infty}\gamma(\xi-u)\mathrm{I}_1(u)\mathrm{d}u=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}F(\xi-u)\alpha(u-w)\mathrm{I}_1(w)\mathrm{d}u\mathrm{d}w,$$

and from this it may be shown that

$$\gamma(\xi)=\int_{-\infty}^{\infty}\alpha(\xi-u)F(u)\mathrm{d}u, \quad \ldots\ldots\ldots\ldots\ldots \quad (\mathbf{4})$$

provided that the Fourier transform of $\mathrm{II}(\xi)$ has no zeros, a property which may readily be verified. Equation (**4**) shows that the relationship between γ, α, and F is the same as that between G, A, and F as in equation (**1**).

The method of successive substitutions yields the solution of (**4**) as the following series :

$$F(\xi)=\gamma(\xi)+\varepsilon_1+\varepsilon_2+\ldots,$$

where

$$\varepsilon_1=\int_{-\infty}^{\infty}\gamma(\xi-u)[\delta(u)-\alpha(u)]\mathrm{d}u,$$

$$\varepsilon_2=\int_{-\infty}^{\infty}\varepsilon_1(\xi-u)[\delta(u)-\alpha(u)]\mathrm{d}u, \text{ etc.}$$

This series converges if $|1-\bar{\alpha}(s)|<1$ for all s for which $\bar{\gamma}(s)\neq 0$, where $\bar{\alpha}(s)$ and $\bar{\gamma}(s)$ are the Fourier transforms of $\alpha(\xi)$ and $\gamma(\xi)$ (see Bracewell and Roberts 1954). When the condition is not met, the series may still give an asymptotic representation of $F(\xi)$, even though ultimately divergent (Bracewell, unpublished

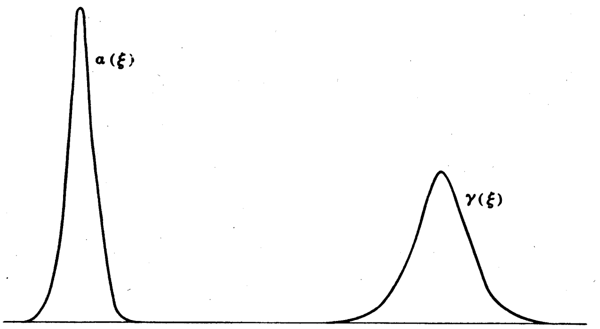

Fig. 2

data). It will be found that $A(\xi)$ fails to fulfil the convergence condition, on account of the violent disturbance due to the doublet. But in equation (**4**) this effect has been removed and, although technically the condition is still not met, it fails only for large values of s which do not play an important part if only a few stages of correction are required. The series is thus asymptotic to $F(\xi)$.

The working is shown in full in Table 2 for the present case. In the first column appear the values of α (Fig. 2), the instrumental profile corrected for doublet effect by the method of Appendix I. The column $\delta-\alpha$ is derived from the first column by subtracting the latter from the sequence . . . 0 0 1 0 0 . . . . It is written on a movable strip of paper and *in the reverse sense.* (The necessity for the reversal of sense will be found in the occurrence of the variable u with opposite signs in equations such as (**1**).) The column γ (Fig. 2) is obtained from the observed distribution by correction for doublet effect. The values of the first correction term ε_1 are then calculated by summing products of corresponding numbers in the second and third columns ; e.g. the value marked with an asterisk is equal to $(-2)\times 1+(-7)\times 3+(-23)\times 5+\ldots$, and is written opposite the arrow. The remaining values are obtained by sliding the movable strip up and down. Succeeding correction columns are obtained from their predecessors in exactly the same way.

Corrections up to 12 per cent. are introduced by ε_1, and up to 3 per cent. by ε_2. The next set of corrections, if calculated, will be found to be all less than 2 per cent., which, in the present case, is negligible. The last column, $\gamma+\varepsilon_1+\varepsilon_2$, is thus the approximate solution yielded by the method of successive substitutions, and is shown as $F(\xi)$ in Figure 1.

TABLE 2

$\alpha \times 10^3$	$(\delta—\alpha) \times 10^3$ (read upwards)	$\gamma \times 10^3$	$\varepsilon_1 \times 10^3$	$\varepsilon_2 \times 10^3$	$\gamma+\varepsilon_1+\varepsilon_2$
2	—2	1	—1	0	0
9	—7	3	—1	+1	3
42	—23	5	—2	+1	4
114	—67	8	—2	+1	7
228	—192	12	—4	0	8
314	+686 →	19	—6*	—1	12
192	—228	30	—8	—2	20
67	—114	49	—7	—1	41
23	—42	69	—7	—4	58
7	—9	95	—1	—3	91
2	—2	120	+8	+1	129
		132	+15	+4	151
		126	+15	+4	145
		105	+9	+1	115
		80	—5	0	85
		55	—0	—2	53
		36	—2	—1	33
		22	—3	—1	18
		14	—2	0	12
		9	—1	0	8
		6	—0	0	6
		3	—0	0	3
		1	—1	0	0

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APPENDIX I

Removal of Doublet Effect

To solve

$$A(\xi)=\int_{-\infty}^{\infty}\alpha(\xi-u)\mathrm{I}_{\mathrm{I}}(u)\mathrm{d}u$$

for $\alpha(\xi)$ when $A(\xi)$ is given and $\mathrm{I}_{\mathrm{I}}(\xi)=\delta(\xi)+\frac{1}{2}\delta(\xi-\sigma)$, we apply the method of successive substitutions.

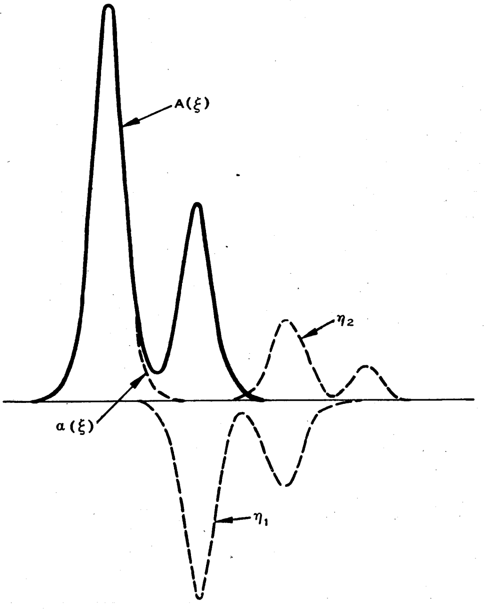

Fig. 3

Then

$$\alpha(\xi)=A(\xi)+\eta_1+\eta_2+\cdot\ .\ .\ ,$$

where

$$\eta_1=\int_{-\infty}^{\infty}A(\xi-u)[\delta(u)-\mathrm{I}_{\mathrm{I}}(u)]\mathrm{d}u,\ \text{etc.}$$

But this reduces to

$$\begin{aligned}\eta\ &=-\tfrac{1}{2}\int_{-\infty}^{\infty}A(\xi-u)\delta(u-\sigma)\mathrm{d}u\\&=-\tfrac{1}{2}A(\xi-\sigma),\end{aligned}$$

which is the same as $A(\xi)$ but changed in sign, halved, and shifted by σ. And η_2 must be obtained from η_1 in the same way. Hence finally

$$\alpha(\xi)=A(\xi)-\tfrac{1}{2}A(\xi-\sigma)+\tfrac{1}{4}A(\xi-2\sigma)-\ldots \qquad \ldots\ldots (5)$$

Once this simple formula has been obtained, it is easy to understand (see Fig. 3). A sufficient condition that it should converge is that $|1-\overline{\mathrm{I}\mathrm{I}}(s)|<1$, where $\overline{\mathrm{I}\mathrm{I}}(s)$ is the Fourier transform of $\mathrm{I}\mathrm{I}(\xi)$, and this condition is met for all s.

In obtaining $\alpha(\xi)$ from $A(\xi)$ only one correction term need be taken, and in obtaining $\gamma(\xi)$ from $G(\xi)$ only two.

Equation (**5**) has been given by DuMond and Kirkpatrick (1931) who derived it by a direct argument. They state that the series converges, adducing the (insufficient) fact that the terms tend to zero. A process formally equivalent to equation (**5**), but adapted for greater convenience in use, has been given by Rachinger (1948),* and practical hints are contained in a note by Pease (1948). The present posing of the problem as an integral equation appears to be novel; it readily yields the proof of convergence, and shows that $\alpha(\xi)$ is not restricted to functions which fall to zero outside a finite range of ξ, nor even to functions which approach zero at all.

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