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Interpretation of Diffractometer Line Profiles

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A truncation procedure (Ladell, Parrish & Taylor, 1959) has been proposed to circumvent certain practical and theoretical difficulties in the calculation of the moments of diffraction line profiles. The theory of the analysis of line profiles by the method of moments is reviewed. A rigorous formulation of the truncation procedure is given and the truncation error is estimated. An analytic representation of the spectral profile of $K\alpha$ doublets is derived so that the spectral characteristics needed for the analysis of line profiles can be obtained.

Introduction

The line profiles in powder diffractometry are convolutions of the incident X-ray spectral distribution, the various instrumental aberrations and the intrinsic diffraction pattern of the polycrystalline sample. These factors combine in a complex manner to broaden and shift the position of an observed line profile from that which would be observed if the diffractometer were free of aberrations and the specimen were a perfect crystalline powder. The instrumental and geometrical aberrations, which are generally smaller than those that occur in film measurements, can usually be neglected in routine applications. However, they must be taken into account in precision measurements and in special applications that depend upon an accurate analysis of line profiles. A method based upon measuring the first moment or centroid of a line has been developed which makes it possible to correct the data for the aberrations. It was formerly called the center-of-gravity method (Ladell, Parrish & Taylor, 1957, 1959, which are referred to as I in this paper).

Spencer (1931) appears to have been the first to use the concept of moments in X-ray analysis. He used a graphical method to correct the first moment of observed X-ray emission lines to account for the effect of 'vertical' divergence in two-crystal spectrometry. His approach does not appear to have been used subsequently by other spectroscopists or diffractionists, probably because of mathematical difficulties.

Wilson (1950, 1954; Parrish & Wilson, 1954) greatly extended and generalized the application of the method of moments to X-ray powder diffractometry. Wilson showed that it was possible to account for the several instrumental aberrations of the observed line profile in terms of the first and second moments of the aberrational functions. He used the first moment to determine the shift of the line from its correct position, and the variance (involving the second moment) to analyze the broadening. The elegance of this method arises from the fact that the first moment of the observed distribution is the sum of the first moments of the individual instrumental aberrations and the first moment of the dispersed X-ray spectral distribution. The variance similarly has this additive property.

An analysis of all the various instrumental aberrations in terms of the complete aberrational line profiles remains mathematically formidable, but the first and second moments of the aberrational distributions have been derived and most of them have been experimentally confirmed (Wilson, 1950, 1954; Parrish & Wilson, 1954, 1959; Pike, 1957). Although it is convenient and practical to apply the concept of moments to observed line profiles, extensive use of this method is not widespread. Instead, it has been common practice to use other methods to define line positions, which unfortunately lead to measures of central tendency not easily amenable to corrections for instrumental aberrations. In these cases, satisfactory accounts of the effects of the aberrations are either lacking or recourse to questionable extrapolation arguments has been necessary (Ladell, Parrish & Taylor, 1959).

If the full line profiles of the aberrational functions were known, it would be theoretically possible to use them to determine corrections for any measure of central tendency. Tedious and complicated mathematical procedures would be required, because it would be necessary to unfold (Stokes, 1948) all the aberrational functions from the observed line profile. The use of centroids as a measure of central tendency is consequently particularly advantageous, since recourse to unfolding and characterizing complete aberrational distributions is obviated.

Certain theoretical and practical difficulties are, however, encountered in the use of the method of moments. X-ray spectroscopists (Hoyt, 1932; Parratt, 1936; Shacklett & DuMond, 1957) state that the X-ray spectral lines are Cauchy-like in the sense that the decay of the spectral distribution, $I(\lambda-\lambda_0)$, is of the order of $I/(\lambda-\lambda_0)^2$. The first moments of such distributions are indeterminate when the distributions are infinite in extension.

Although observed diffractometer line profiles are

not Cauchy-like in the central region around the peak and in most cases out to several half-widths on either side of the central region, the tails decay very slowly and present the practical difficulty of accurately determining a background level (to define the distribution) in a region where the signal-to-background ratio is approaching zero. Small errors in this region may contribute large uncertain moments in the calculation of the centroid of what is essentially the line profile; moreover, the subjective decision of where the profile begins and ends significantly affects the calculation.

The difficulties have been circumvented by use of a method (I) which truncates the distribution in such a manner that it essentially preserves its basic features and defines an unequivocal centroid. This unequivocally defined centroid is the first moment of the truncated distribution and is indicated in our nomenclature by replacing the overscored dash (—) used for true centroids with the tilde (~).

In view of other approaches to this problem (Pike & Wilson, 1959) and in order to ascertain the precision of this procedure when it is used for lattice parameter determination, we shall review the theory of the analysis of line profiles by the method of moments, give a rigorous formulation for our truncation and estimate the errors implied by this procedure. As was pointed out above, the need for modifying the method of moments with a truncation procedure arises from the mathematical properties of spectral distributions. In order to examine the validity of our procedure and establish the required spectral measures, we have derived an analytic representation of spectral profiles of $K\alpha$ doublets.

The method of moments in line profile analysis

In a diffractometer recording, an observed intensity distribution or line profile, $f(\varepsilon)$, is a function of ε where $\varepsilon/2$ is the glancing angle. The centroid of $f(\varepsilon)$, designated by $\bar{\varepsilon}_f$, is defined as

$$\bar{\varepsilon}_f = \int_{-\infty}^{\infty} \varepsilon f(\varepsilon)\, d\varepsilon \Big/ \int_{-\infty}^{\infty} f(\varepsilon)\, d\varepsilon \,. \tag{1}$$

The mean square broadening or variance of $f(\varepsilon)$, designated by V_f, is defined as

$$V_f = \frac{\int_{-\infty}^{\infty} \varepsilon^2 f(\varepsilon)\, d\varepsilon}{\int_{-\infty}^{\infty} f(\varepsilon)\, d\varepsilon} - (\bar{\varepsilon}_f)^2 \,. \tag{2}$$

An observed line profile results from the convolution of several instrumental aberrational functions with the intrinsic diffraction pattern of the powder and the X-ray spectral distribution. For example, if $z(\varepsilon)$ is the convolution of $u(\varepsilon)$ with $w(\varepsilon)$, we write

$$z(\varepsilon) = u * w(\varepsilon) = \int_{-\infty}^{\infty} u(n) w(\varepsilon - n)\, dn \,. \tag{3}$$

In this notation

$$f(\varepsilon) = h * (j * k(\varepsilon)) \tag{4}$$

where $h(\varepsilon)$ is the X-ray spectral distribution on an angle scale, $j(\varepsilon)$ is the result of a convolution of several instrumental aberrational functions, and $k(\varepsilon)$ is a function representing the intrinsic diffraction pattern of the powder modified by the purely crystallographic effects.

Consider equation (3) which defines a convolution. If the distribution $u(\varepsilon)$ is infinitely narrow, we can write (with appropriate choice of origin) $u(\varepsilon) = \delta(\varepsilon)$ where $\delta(\varepsilon)$ is the Dirac delta function in the vicinity of 0, i.e., $\int u(\varepsilon) = 1$ in the vicinity of 0 and $u(\varepsilon) = 0$ elsewhere. Then

$$z(\varepsilon) = u * w(\varepsilon) = w(\varepsilon) \,. \tag{5}$$

It follows that in an aberrationless instrument

$$f(\varepsilon) = h * k(\varepsilon) \,. \tag{6}$$

Furthermore, if we deal with a well crystallized powder, the particles of which are free of imperfections and not too small, we can consider the spread of $k(\varepsilon)$ to be very small compared to the spread of $h(\varepsilon)$, so that in an ideal experiment using an aberrationless instrument and ideal powder we would have

$$f(\varepsilon) = h(\varepsilon) \,. \tag{7}$$

In the discussion that follows it is convenient to consider an observed line profile as a modified spectral distribution. For this purpose we define a 'generalized' aberrational function $g(\varepsilon)$ given by

$$g(\varepsilon) = j * k(\varepsilon) \,, \tag{8}$$

acting in the vicinity of a specific angle ε_0. Previous work (Wilson, 1950, 1954; Parrish & Wilson, 1954, 1959; Pike, 1957) has shown that the form of $g(\varepsilon)$ does not change rapidly with ε, i.e., $g(\varepsilon)$ in the vicinity of ε_0 is the same as $g(\varepsilon)$ in the vicinity of $\varepsilon_0 + \delta$ where δ is small. Combining equations (4) and (8) we obtain

$$f(\varepsilon) = h * g(\varepsilon) \,. \tag{9}$$

It can be shown that

$$\bar{\varepsilon}_f = \bar{\varepsilon}_g + \bar{\varepsilon}_h \tag{10}$$

and

$$V_f = V_g + V_h = V_j + V_k + V_h \,. \tag{11}$$

Equations (10) and (11) are the basis for the description of line profiles in terms of moments.

The experimental problem which must be solved to interpret line profiles in lattice parameter determinations by the method of moments is to determine $\bar{\varepsilon}_f$ from the measurement of $f(\varepsilon)$ and then to subtract $\bar{\varepsilon}_g$, which is known from aberration studies, to obtain $\bar{\varepsilon}_h$

The relation between $\bar{\varepsilon}_h$ and $\bar{\lambda}$, the centroid of the spectral distribution on a wavelength scale, is then used to determine d, the interplanar spacing sought (Ladell, Mack, Parrish & Taylor, 1959). Similarly, the interpretation of line profiles for crystallographic effects which give rise to line broadening requires the determination of V_k, the variance due to purely crystallographic effects. The latter is obtained by calculating V_f from the measured $f(\varepsilon)$ and subtracting from it the known values of V_j, the variance due to instrumental aberrations, and V_h, the spectral variance.

Unfortunately, theoretical and experimental analyses (Hoyt, 1932; Shacklett & DuMond, 1957) suggest that the spectral distribution $h(\varepsilon)$ is infinite in extension and decays slowly at a rate proportional to $1/\varepsilon^2$. By virtue of equations (7) and (9), these properties are also manifest in the observed distribution. Consequently, $\bar{\varepsilon}_f$ and $\bar{\varepsilon}_h$ are indeterminate since the integral in equation (1) which defines $\bar{\varepsilon}_f$ is logarithmically divergent. Moreover, V_f and V_h are each infinite since the integral in equation (2) which defines V_f diverges. We have therefore developed a truncation procedure to avoid these difficulties and yet retain the concepts stated in equations (10) and (11).

Truncation and error estimate

Our truncation procedure has already been described (I). Here we rigorously formulate the truncation and consider the implications of this procedure.

Let $P(x)$ be a spectral distribution or a distribution formed by convolution of a spectral distribution with an aberrational distribution. The argument is either the angle variable ε or the wavelength variable λ.

The tilde centroid $\tilde{x}_P$ of the distribution $P(x)$ is defined by

$$\tilde{x}_P = \int_{x_1}^{x_2} xP(x)\,dx \Big/ \int_{x_1}^{x_2} P(x)\,dx \qquad (12)$$

where the integration limits x_1 and x_2 are determined by the conditions:

$$P(x_1) = P(x_2) \qquad (13)$$

and

$$\int_{x_1}^{x_2} P(x)\,dx - P(x_1)[x_2 - x_1] = 0{\cdot}9 \int_{-\infty}^{\infty} P(x)\,dx\,. \qquad (14)$$

In basing the truncation upon 90% of the integrated intensity (equation (14)), we have maintained the shape of the distribution essentially intact, yet have excluded portions of the tails which are difficult to measure experimentally because of the low signal-to-background ratio. Because the limits are assigned on the basis of equal ordinate heights (equation (13)), the tilde centroid is relatively insensitive to small deviations from 90% of the integrated intensity. This insensitivity is necessary in practice since there is always a slight indeterminacy in the assignment of the background level.

The tilde variance $\tilde{V}_P(x)$ of the distribution $P(x)$ is defined as

$$\tilde{V}_P(x) = \frac{\int_{x_1}^{x_2} x^2 P(x)\,dx}{\int_{x_1}^{x_2} P(x)\,dx} - (\tilde{x}_P)^2\,. \qquad (15)$$

In using the method of moments we replace the true (but indeterminate) centroids $\bar{x}_P$ by $\tilde{x}_P$ and use the arbitrarily defined variance $\tilde{V}_P$ in place of V_P. In doing this we make the following assumptions:

(1) The decay of $P(x)$ for large values of $|x|$ is at least of the order of $1/x^{2*}$, so that the integral $\int_{-\infty}^{\infty} P(x)\,dx$ converges absolutely. Under these conditions it follows that $\bar{x}_P$ is absolutely convergent or at worst logarithmically divergent.

(2) Even if the first moment of $P(x)$ is absolutely convergent and $\bar{x}_P$ can be evaluated, $\tilde{x}_P$ is a good approximation of $\bar{x}_P$, that is

$$\tilde{x}_P \cong \bar{x}_P\,. \qquad (16)$$

(3) If $\bar{x}_P$ is logarithmically divergent, $\tilde{x}_P$ defines the centroid of the distribution $P(x)$.

On the basis of these assumptions, the summation theorem (equation (10)) still holds approximately, that is,

$$\tilde{\varepsilon}_f \cong \tilde{\varepsilon}_g + \tilde{\varepsilon}_h\,. \qquad (17)$$

The degree of approximation depends upon the exact form of $g(\varepsilon)$ and $h(\varepsilon)$, and an exact evaluation of the error introduced by the method cannot be given unless these functions are specified. It is possible, however, to give a good account of the truncation error by testing a hypothetical case which typifies profiles

* The assertion (see for example, Shacklett & DuMond, 1957) that it has been demonstrated both theoretically and experimentally that X-ray emission lines are Cauchy-like should be accepted with reservations. Since the exact shape of emission lines has never been synthesized from two-crystal spectroscopic work, experimental verification is lacking. The experimental demonstrations to which these authors refer is contingent upon assumptions concerning the exact shape of two-crystal rocking curves which must be removed (by unfolding) before the exact shape of the emission line can be revealed. The shape of the anti-parallel position rocking curve for the Bragg case is complicated and is asymmetric for real crystals. Even for non-absorbing crystals (Zachariasen, 1945) the complexity of the shape of the intrinsic diffraction pattern does not warrant a simple model, as has been assumed by Brogren (1954) for the rocking curve. The difficulty of removing the crystal aberration from an observed two-crystal spectral profile has been discussed in detail (Parratt, Hempstead & Jossem, 1957). Furthermore, the classical dispersion theory of emission line shape (Hoyt, 1932) does not satisfactorily explain reported asymmetries. At present, little is known about the exact nature of the tails of emission lines, so that it is not clear whether the slow decay in observed spectral profiles is due principally to crystal diffraction effects or is inherent in the emission lines.

encountered in practice. To estimate the truncation error we have considered the following problem.

Let $h(x)$ represent a spectral distribution given by

$$\begin{aligned} h(x) &= 1/(1+x^2) && \text{for } x \le 0 \\ h(x) &= 1/(1+\gamma^2 x^2) && \text{for } x \ge 0 \end{aligned} \tag{18}$$

and let $g(x)$ be an aberrational distribution given by

$$\begin{aligned} g(x) &= x+\tau && \text{for } -\tau \le x \le \tau \\ g(x) &= 0 && \text{for } x \le -\tau \\ g(x) &= 0 && \text{for } x > \tau\,. \end{aligned} \tag{19}$$

When $\gamma < 1$, $h(x)$ is representative of the asymmetric profiles obtained in practice using the $K\alpha$ series of the transition elements. Reverse asymmetries ($\gamma > 1$) have been reported for some of the lines ($K\alpha_2$ of V, Ti, etc.). The triangular distribution $g(x)$ is typical of aberrations which occur at very high diffraction angles. At moderately high angles the aberration is represented by a triangular distribution which is the reverse of $g(x)$, i.e., $g(x) = -x+\tau$ in the interval $(-\tau, \tau)$. All cases are thus considered if γ is taken greater and less than unity.

The convolution of $h(x)$ with $g(x)$ is given by

$$\begin{aligned} f(x) = \tfrac{1}{2}\left\{\frac{1}{\xi^2}\ln\left[1+\xi^2(x-\tau)^2\right] - \frac{1}{\varrho^2}\ln\left[1+\varrho^2(x+\tau)^2\right]\right\} \\ +(x+\tau)\left\{\frac{1}{\varrho}\tan^{-1}\varrho(x+\tau) - \frac{1}{\xi}\tan^{-1}\xi(x-\tau)\right\} \end{aligned} \tag{20}$$

where

$$\begin{aligned} \xi = \varrho &= 1 && \text{for } -\infty < x \le -\tau \\ \xi &= 1,\ \varrho = \gamma && \text{for } -\tau \le x \le \tau \\ \xi = \varrho &= \gamma && \text{for } \tau \le x < \infty\,. \end{aligned}$$

The truncation error Δ_T was calculated from

$$\Delta_T = \tilde{x}_f - (\bar{x}_g + \tilde{x}_h)\,. \tag{21}$$

$\tilde{x}_f$ was determined from equation (20) and $\tilde{x}_h$ from equation (18) using the tilde definition given by equations (12), (13) and (14). Thus

$$\tilde{x}_h = 3{\cdot}4088(1-\gamma)/2\gamma\,. \tag{22}$$

An analytic expression was also obtained for $\tilde{x}_f$ in terms of the parameters τ and γ, but this expression, though tractable, is too long for inclusion here. Moreover, it was more expedient to calculate $\tilde{x}_f$ by numerical integration methods and a Royal Precision LGP-30 calculator was used.

The values of $\tilde{x}_f$ obtained for τ ranging from 0·125 to 5·000 and γ from 0·6875 to 1·4532 are listed in the sixth column of Table 1. Also listed in Table 1 are the increment Δx used to approximate the integrals by sums (third column) and the limits of integration x_1 and x_2 (fourth and fifth columns) determined by the truncation procedure defined by equations (12), (13) and (14). $(\bar{x}_g+\tilde{x}_h)$ given in the seventh column was obtained from

$$\bar{x}_g + \tilde{x}_h = \tau/3 + 3{\cdot}4088(1-\gamma/2\gamma)\,, \tag{23}$$

since it follows from equation (19) that

$$\bar{x}_g = \tau/3\,. \tag{24}$$

The results shown in the last column indicate that the truncation error increases as both τ and $1/\gamma$ increase. The magnitudes of the errors are given in units of the width at one-half maximum of the spectral line, $1+(1/\gamma)$.

In order to determine the magnitude of the truncation errors for cases encountered in practice where the centroid of the aberration function is known in degrees ε, it is necessary to determine the width of a spectral line in degrees ε and to convert Table 1 to angle units. Consider a spectral line with width at one-half maximum equal to $0{\cdot}23[1+(1/\gamma)]$ x.u., asymmetry index $1/\gamma$ and peak position at 1540 x.u.; this hypothetical spectral line closely resembles Cu $K\alpha_1$.

Table 1. *Truncation error in the center of gravity determination of* $f(x)$*

γ†	τ‡	Δx	x_1	x_2	$\tilde{x}_f$	$\bar{x}_g+\tilde{x}_h$	Δ_T§
1·0000	0·125	0·03125	−12·7500	12·81250	0·0419	0·0417	0·0002
0·6875	0·25	0·06250	−12·6250	18·5625	0·8603	0·8580	0·0023
0·8125	0·25	0·06250	−12·6250	15·6875	0·4776	0·4766	0·0010
1·0000	0·25	0·03125	−12·71875	12·87500	0·0838	0·0833	0·0005
1·0000	0·25	0·06250	−12·6250	12·7500	0·0838	0·0833	0·0005
0·6875	1·00	0·06250	−12·4375	18·8750	1·1109	1·1080	0·0029
0·8125	1·00	0·06250	−12·3750	15·9375	0·7277	0·7266	0·0011
1·0000	1·00	0·06250	−12·4375	13·0625	0·3338	0·3333	0·0005
1·2344	1·00	0·06250	−12·4375	10·6875	0·0104	0·0097	0·0007
1·4531	1·00	0·06250	−12·4375	9·1250	−0·1983	−0·1981	−0·0002
0·6875	5·00	0·12500	−11·875	20·625	2·4442	2·4414	0·0024
0·8125	5·00	0·12500	−11·875	17·875	2·0628	2·0600	0·0028
1·0000	5·00	0·12500	−11·875	15·000	1·6675	1·6667	0·0007
1·2344	5·00	0·12500	−11·875	12·625	1·3411	1·3431	−0·0020
1·4531	5·00	0·12500	−12·000	11·250	1·1307	1·1352	−0·0045

* All numbers except γ are given in units of the width of the spectral line at one-half peak height, i.e., in terms of $1+(1/\gamma)$.
† γ is the reciprocal of the asymmetry index of the spectral line.
‡ τ is one-half the base width of the right isoceles triangle used to represent the aberration function.
§ These numbers must be multiplied by the *angular* width of the spectral line to obtain the truncation error in °ε.

If we assume that the centroid of this line occurs at 120° (in the absence of aberrations), then the width in degrees ε is $0{\cdot}030[1+(1/\gamma)]$. The effect of the truncation error in degrees ε for aberrational corrections of the order of 0·001° to 0·050° 2ε can be found by multiplying the last column by 0·030°. The second column multiplied by 0·030°/3 is the corresponding aberration correction. The results in Table 1 show that for the cases considered the truncation error is less than 0·0002°. The aberrational corrections are not presumed to be known to better than about 0·001° and since the example is a good model of a practical case, we may conclude that the truncation error is negligible. Although the angular width of the spectral line increases with ε, the aberrational correction decreases up to about 160° ε and the truncation error is negligible in the region 120–160° ε. Above 160° the axial divergence begins to dominate the aberrational correction and below 120°, where other aberrations dominate, truncation errors of the order of 0·001° may occur.

The spectral distribution

In order to follow the procedure for determining lattice parameters (I), estimate the distortions in observed line profiles due to dispersion as well as the Lorentz and polarization factors (Ladell, Mack, Parrish & Taylor, 1959), and in general to employ the method of moments in any analyses of line profiles, it is necessary to have a suitable description of the spectral distribution. Unfortunately, tables of X-ray wavelengths (Cauchois & Hulubei, 1947) do not give sufficient information about the features of spectral profiles from which spectral measures other than the peak position can be inferred. X-ray wavelengths are normally reported in terms of the peak of the spectral distribution (Bearden & Shaw, 1935), but no definitive statement is made in the literature as to the procedure used to establish the position of the peak. In fact it is unlikely that wavelengths derived from measurements of films, photometer tracings or ionization chamber data all refer to the same characteristic of the spectral intensity distribution. Some papers (Bearden & Shaw, 1935; Allison, 1933; Parratt, 1933) report the breadth of the spectral line and the index of asymmetry, but only rarely are full line profiles published (Hoyt, 1932; Spencer, 1931). In view of the difficulties of establishing the background levels and correcting the data for the crystal rocking width and instrumental aberrations (a complete account of which is not always given), it is not possible to determine precise values of $\tilde{\lambda}$ or

The (empirical) analytic representation given here has been compared with unpublished spectral profiles of Cu $K\alpha$ and Fe $K\alpha$ which were obtained with a two-crystal spectrometer and made available to us by Prof. J. A. Bearden of Johns Hopkins University. Except for minor details, our model is reasonably consistent with these experimental spectral profiles. To synthesize our spectral model we have used the parameters of Bearden & Shaw (1935), who have published data for the following characteristics of the K-series of a number of transition elements: λ_{α_1} and λ_{α_2}, the wavelengths of the peaks; w_1 and w_2, the widths at one-half peak height; and u_1 and u_2, the indices of asymmetry of the $K\alpha_1$ and $K\alpha_2$ distributions. In accordance with spectroscopic information cited previously, we assume that the decay of the distributions away from the peaks is Cauchy-like; i.e., of the order of $1/\lambda^2$, and that the integrated intensity of the $K\alpha_1$ distribution is twice that of the $K\alpha_2$ distribution. The latter is valid theoretically for elements whose L-shells are complete. We will ignore the $K\alpha$ satellite lines.

We define the following quantities:

$$\left.\begin{aligned} a &= (1+u_1)/w_1 \\ b &= (1+u_1)/u_1 w_1 \\ c &= (1+u_2)/w_2 \\ m &= (1+u_2)/u_2 w_2 \\ z &= \lambda-\lambda_{\alpha_1} \\ \Delta &= \lambda_{\alpha_2}-\lambda_{\alpha_1} \\ Q &= \tfrac{1}{2}((a+b)/ab)(cm/(c+m)) = \tfrac{1}{2}(w_1/w_2) \end{aligned}\right\} \qquad (25)$$

An analytical expression for the $K\alpha$ distribution based upon the foregoing assumptions is accordingly given by

$$\begin{aligned} I(\lambda, \lambda_{\alpha_1}, \Delta) &= I(z) \\ &= 1/(1+a^2z^2) + Q/(1+c^2(z-\Delta)^2) \quad \text{for} \quad z \le 0 \\ &= 1/(1+b^2z^2) + Q/(1+c^2(z-\Delta)^2) \quad \text{for} \quad 0 \le z \le \Delta \\ &= 1/(1+b^2z^2) + Q/(1+m^2(z-\Delta)^2) \quad \text{for} \quad z \ge \Delta\,. \end{aligned} \qquad (26)$$

On the basis of the definition of the tilde centroid given by equations (12), (13) and (14),

$$\begin{aligned} \tilde{\lambda} = \lambda_{\alpha_1} &+ \tfrac{1}{2}\left\{\frac{\ln(1+b^2z_2^2)}{b^2} - \frac{\ln(1+a^2z_1^2)}{a^2}\right\} \\ &+ \frac{Q}{\Delta}\left\{\frac{\ln[1+m^2(z_2-\Delta)^2]}{m^2} - \frac{\ln[1+c^2(z_1-\Delta)^2]}{c^2}\right\} \end{aligned} \qquad (27)$$

Table 2. *X-ray spectral data**

Line	H.W. obs. (1+1 order) (x.u.)	H.W. corr. w (x.u.)	Index of asymmetry u	λ (kX.)	λ_{α^*} (kX.)	$\tilde{\lambda}$ (kX.)	$(\tilde{\lambda}/\lambda_{\alpha^*})-1$ (%)
Cu $K\alpha_2$	51·5	0·635	1·31	1·541 220			
					1·538 673	1·538 745	0·0047
Cu $K\alpha_1$	39·9	0·471	1·13	1·537 400			
Fe $K\alpha_2$	80·1	0·970	1·26	1·936 000			
					1·933 380	1·933 657	0·0143
Fe $K\alpha_1$	68·4	0·805	1·61	1·932 070			
Cr $K\alpha_2$	90·4	1·031	1·03	2·288 889			
					2·286 296	2·286 450	0·0067
Cr $K\alpha_1$	75·5	0·829	1·37	2·285 000			

* Based on data published by Bearden & Shaw (1935). The width at one-half maximum, H.W., has been corrected for crystal rocking width according to the formula given by Parratt (1935), $W_T = W_0 - 2{\cdot}9W_C^{1{\cdot}7}$ where W_T is the true width, W_0 is the observed width in the (1+1) position and W_C is the rocking width of the crystal used by Bearden & Shaw (1935).

$$\begin{aligned} I(z_1) &= 1/(1+a^2z_1^2) + Q/(1+c^2(z_1-\Delta)^2) \\ &= 1/(1+b^2z_2^2) + Q/(1+m^2(z_2-\Delta)^2) \end{aligned} \tag{29}$$

and

$$A = \frac{1}{b}\tan^{-1} bz_2 - \frac{1}{a}\tan^{-1} az_1 + Q\left\{\frac{\tan^{-1} m(z_2-\Delta)}{m} - \frac{\tan^{-1} c(z_1-\Delta)}{c}\right\}. \tag{30}$$

Similarly the spectral variance is given by

$$\tilde{V} = \frac{\int_{z_1}^{z_2} z^2 I(z)\,dz}{\int_{z_1}^{z_2} I(z)\,dz} - (\tilde{z})^2 . \tag{31}$$

Analytical representations of the Cu $K\alpha$, Fe $K\alpha$ and Cr $K\alpha$ doublet distributions were constructed from these formulations based on the Bearden & Shaw (1935) parameters. Table 2 lists the parameters and differences between λ_{α^*} and $\tilde{\lambda}$ where $\lambda_{\alpha^*} = \lambda_{\alpha_1} + \Delta/3$, often referred to as the 'weighted' mean. The greater difference for Fe $K\alpha$ is due to its greater indices of asymmetry. Fig. 1 shows the constructed Cu $K\alpha$ distribution.

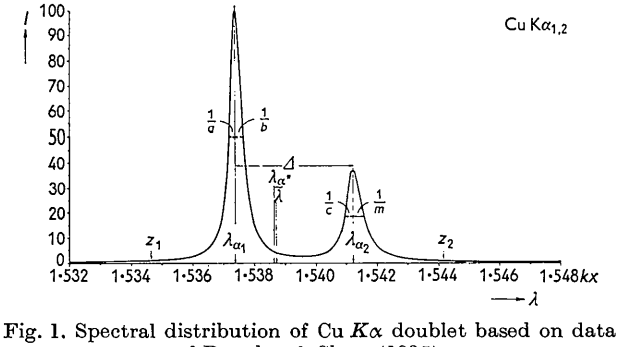

Fig. 1. Spectral distribution of Cu $K\alpha$ doublet based on data of Bearden & Shaw (1935).

If $\tilde{\lambda}$ is used to derive a lattice parameter using the method described, the value of the lattice parameter should be independent of the radiation used. On the other hand, the use of λ_{α^*} will lead to a lattice parameter value which will depend on the radiation used, even though λ_{α^*} is the same characteristic of the spectral distribution for each radiation. The literature contains many examples of different lattice parameters for a given substance obtained with different radiations in which the discrepancy is usually ascribed incorrectly to errors in absorption corrections.

The full implications and utility of our treatment of the method of moments will be better understood when extensive experimental determinations of lattice parameters and other information obtained from the analysis of line profiles are available. To this end a comprehensive program is under way. The preliminary results of this program confirm the effectiveness of our procedures; these will be reported in a separate paper.

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Dispersion, Lorentz and Polarization Effects in the Centroid Method of Precision Lattice Parameter Determination

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It has been found that in the determination of lattice parameters by the method of moments, corrections must be applied to account for the distortion of line profiles caused by the effects of dispersion, Lorentz and polarization factors. These corrections have been calculated as a function of the diffraction angle for Cu $K\alpha$, Fe $K\alpha$ and Cr $K\alpha$ radiations. The corrections presented here are compared to those given by Pike.

In the centroid method of precision lattice parameter determination, the interplanar spacing d is found from Bragg's law by substitution of the centroid of the incident spectral distribution and the centroid of the spectral distribution after diffraction from the set of planes. The latter centroid is determined from the centroid of the observed diffracted line profile by removing the effects of the distortions caused during the diffraction process (Ladell, Parrish & Taylor, 1957, 1959*a*, *b*). The distortions caused by the various instrumental aberrations (flat specimen, axial divergence, etc.) have been discussed (Wilson, 1950; Parrish & Wilson, 1954, 1959; Pike 1957), but even after these have been accounted for, the effects of dispersion, the Lorentz factor and the polarization factor remain.

The effect of dispersion is that the centroid of a dispersed spectral distribution (on an angle scale) deviates from the angle equivalent of the centroid of the incident spectral distribution by an amount Δ_D. Δ_D has been determined from the spectral distribution and is plotted as a function of the diffraction angle ε $(= 2\theta)$ for Cu $K\alpha$, Fe $K\alpha$ and Cr $K\alpha$, Fig. 1. Although the complete spectral distributions have not been published, an analytic representation, derived on the basis of the parameters given in the literature (Hoyt, 1932; Bearden & Shaw, 1935; Parratt, 1936), has been used for computing the graphs in Fig. 1.

The expression for $I(\lambda)$, used for the spectral distribution, is

$$\left.\begin{aligned} I(\lambda) &= \frac{1}{1+a^2(\lambda-\lambda_{\alpha_1})^2}+\frac{Q}{1+c^2(\lambda-\lambda_{\alpha_1}-\Delta)^2} \\ &\qquad\qquad \text{for } \lambda \le \lambda_{\alpha_1} \\ &= \frac{1}{1+b^2(\lambda-\lambda_{\alpha_1})^2}+\frac{Q}{1+c^2(\lambda-\lambda_{\alpha_1}-\Delta)^2} \\ &\qquad\qquad \text{for } (\lambda_{\alpha_1}+\Delta) \ge \lambda \ge \lambda_{\alpha_1} \\ &= \frac{1}{1+b^2(\lambda-\lambda_{\alpha_1})^2}+\frac{Q}{1+m^2(\lambda-\lambda_{\alpha_1}-\Delta)^2} \\ &\qquad\qquad \text{for } \lambda \ge (\lambda_{\alpha_1}+\Delta)\,. \end{aligned}\right\} \quad (1)$$

The values of the constants used are given in Table 1; a complete discussion of the representation of the spectral profile has been reported (Ladell, Parrish & Taylor, 1959*b*).