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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, 1959a, 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 (= 2θ) 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

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

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, 1959b).

Table 1. *Spectral constants*

	$\lambda_{\alpha 1}$ (x.u.)	Q	a (x.u.$^{-1}$)	b (x.u.$^{-1}$)	c (x.u.$^{-1}$)	m (x.u.$^{-1}$)	Δ (x.u.)
Cu	1537·400	0·3709	4·522	4·002	3·638	2·777	3·820
Fe	1932·070	0·4150	3·242	2·014	2·330	1·849	3·930
Cr	2285·000	0·4020	2·859	2·087	1·969	1·912	3·889
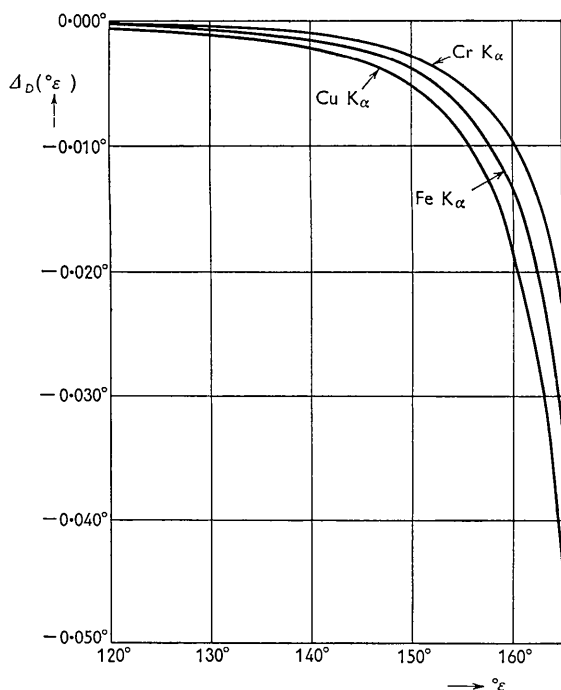
Fig. 1. Calculated values of the dispersion correction Δ_D for Cu $K\alpha$, Fe $K\alpha$ and Cr $K\alpha$ radiations.

For the derivation of Δ_D, the following notation* was used:

$\tilde{\lambda}$, the centroid of $I(\lambda)$, computed between the limits λ_1, λ_2,

$h(\varepsilon)$, the dispersed spectral distribution (on an angle scale),

$\tilde{\varepsilon}_h$, the centroid of $h(\varepsilon)$ computed between the limits ε_1, ε_2 (related to λ_1, λ_2 by Bragg's law),

ε_B, the angle equivalent of $\tilde{\lambda}$.

Using this notation,

$$\Delta_D = \varepsilon_B - \tilde{\varepsilon}_h \qquad (2)$$

where

$$\varepsilon_B = 2 \sin^{-1} \frac{\tilde{\lambda}}{2d}$$

$$= 2 \sin^{-1} \left[\int_{\varepsilon_1}^{\varepsilon_2} h(\varepsilon) \sin (\varepsilon/2) \, d\varepsilon \Big/ \int_{\varepsilon_1}^{\varepsilon_2} h(\varepsilon) \, d\varepsilon \right] \qquad (3)$$

and

---

* The tilde ($\sim$) notation refers to the centroid of a distribution calculated between limits determined by a truncation procedure previously described (Ladell, Parrish & Taylor, 1957, 1959a).

$$\tilde{\varepsilon}_h = \int_{\varepsilon_1}^{\varepsilon_2} \varepsilon h(\varepsilon) \, d\varepsilon \Big/ \int_{\varepsilon_1}^{\varepsilon_2} h(\varepsilon) \, d\varepsilon . \qquad (4)$$

Since

$$h(\varepsilon) \, d\varepsilon = I(\lambda) \, d\lambda = I(\lambda) \mathrm{d} \cos (\varepsilon/2) \, d\varepsilon , \qquad (5)$$

it follows that

$$\tilde{\varepsilon}_h = \int_{\varepsilon_1}^{\varepsilon_2} \varepsilon I(\lambda) \cos \varepsilon/2 \, d\varepsilon \Big/ \int_{\varepsilon_1}^{\varepsilon_2} I(\lambda) \cos (\varepsilon/2) \, d\varepsilon . \qquad (6)$$

The calculation was made by choosing a value of ε_B and computing the corresponding value of d from equation (3) to be used to carry out the transformation of equation (5) required in equation (6). The integrations in equation (6) were performed numerically on a Royal Precision Company LGP-30 electronic digital computer.

The effect of the Lorentz and polarization factors has been discussed and a formulation for the correction Δ_{LP} has been given (Ladell, Parrish & Taylor, 1959a). The values of Δ_{LP} have been calculated using the spectral model given by equation (1). Δ_{LP} contains the corrections for the distortions due to the Lorentz factor csc 2θ, the polarization factor $0.5(1+\cos^2 2\theta)$ and the geometric factor csc θ, which accounts for the
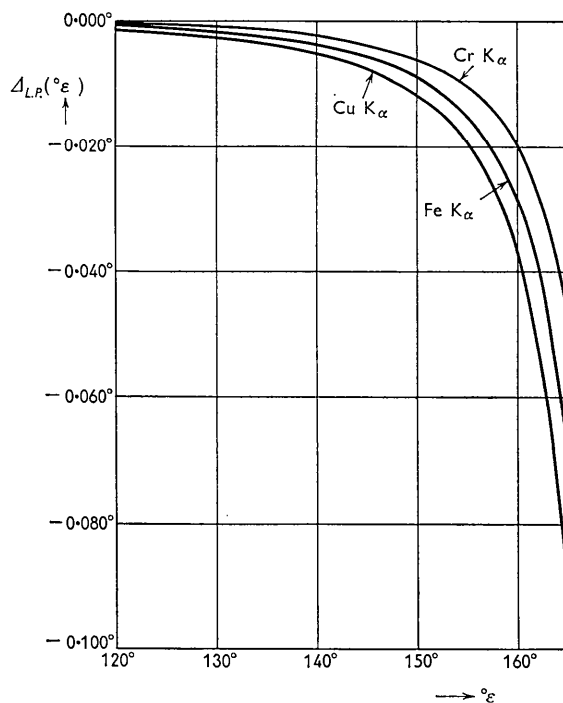
Fig. 2. Calculated values of the Lorentz and polarization correction Δ_{LP} for Cu $K\alpha$, Fe $K\alpha$ and Cr $K\alpha$ radiations.

variation in curvature of the powder rings as intercepted by the receiving slit. For the diffractometer, the latter may be considered as part of the Lorentz factor. The calculated values of Δ_{LP} for Cu $K\alpha$, Fe $K\alpha$ and Cr $K\alpha$ radiations are shown in Fig. 2.

The appropriate values of Δ_D and Δ_{LP} must be added to an aberration-corrected centroid before the latter can be used with $\bar{\lambda}$ to determine the desired interplanar spacing.

The effect of dispersion, Lorentz and polarization factors in the centroid method has been treated differently by Lang (1956) and Pike (1959). The limitations of Lang's method have been discussed by Pike (1959). In his treatment of this problem, Pike infers the combined correction $(\Delta_D+\Delta_{LP})$ from the properties of the spectral variance, which, because of the slow decay of spectral profiles, is arbitrarily defined as a function of an assigned range, $2A$. In his formulation

$$(\Delta_D+\Delta_{LP})_{\text{Pike}} = \frac{180}{\pi\langle\lambda\rangle_A^2} V_A \tan^3\theta$$
$$\times \left\{3 + \cot^2\theta - \frac{8\cos^2\theta\cos 2\theta}{1+\cos^2 2\theta}\right\} \qquad (7)$$

where $\langle\lambda\rangle_A$ is the centroid and V_A the variance of the spectral profile calculated over the range $2A$ according to his truncation procedure (Pike & Wilson, 1959).

A comparison of our results with those given by Pike was made by evaluating his correction, equation
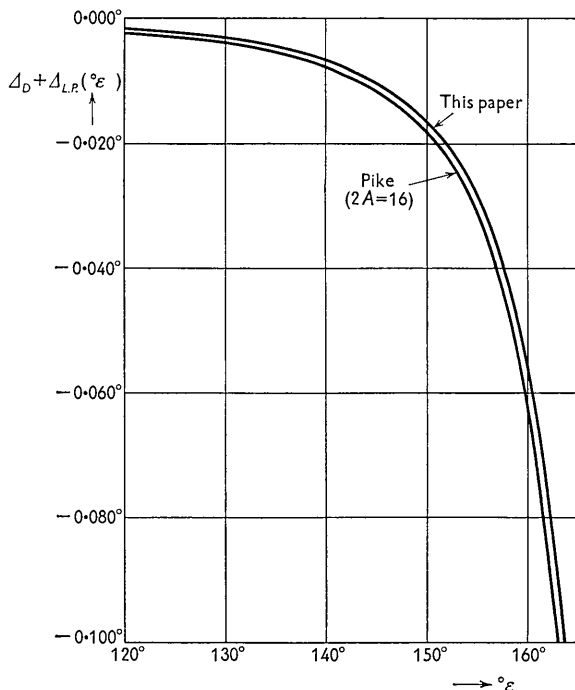

Fig. 3. The combined correction $\Delta_D+\Delta_{LP}$ for Cu $K\alpha$ radiation. The same correction using Pike's method is shown for comparison.
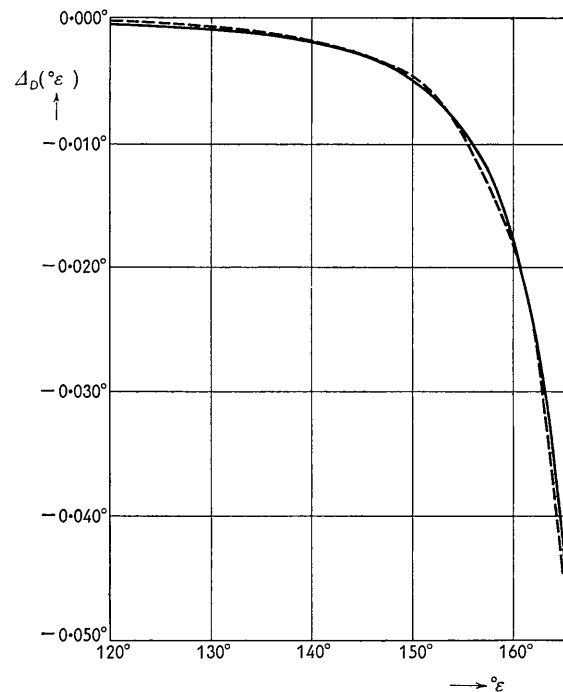

Fig. 4. The dispersion correction Δ_D for Cu $K\alpha$ radiation computed by the procedure described in this paper using the asymmetric spectral distribution (solid line) and an assumed symmetric spectral distribution (dashed line).

(7), for the range $2A = 16$ units of half-width, which is equivalent to the range implied in our truncation procedure (see footnote). This calculation was performed using Pike's spectral model and method of approximating the variance, and the results are shown in Fig. 3. Our curve for the same corrections $(\Delta_D+\Delta_{LP})$ is also shown in Fig. 3. His corrections are approximately 8% larger in magnitude than ours. To test whether the discrepancy is due to his less restrictive spectral model, the dispersion corrections have been calculated by applying our procedure to his model. The results for Cu $K\alpha$ are shown in Fig. 4. For comparison, the Cu $K\alpha$ dispersion curve from Fig. 1 is also shown. These results indicate that the difference between our calculations cannot reasonably be ascribed to the difference in spectral models. Also, it appears that the dispersion correction is relatively insensitive to spectral asymmetries.

In view of the approximations made by Pike in calculating the spectral variance, we have recalculated this quantity on his spectral model using our truncation procedure. For the equivalent range, i.e., $2A = 16$, our calculation leads to a value that is 8% lower than his. It is clear that Pike's corrections would be more consistent with ours had he used the exact expression for calculating the spectral variance by his truncation procedure. It is interesting to note that despite the different approaches to the problem, the results are essentially the same.

We have had a stimulating correspondence on this subject with Prof. A. J. C. Wilson and Dr E. R. Pike, University College, Cardiff, Wales.

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V. Algèbre des Facteurs de Structure

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The possibility of writing the structure invariant $|E(\mathbf{H_1})E(\mathbf{H_2})E(\mathbf{H_3})|\cos\alpha$ as a function of absolute values of structure factors is investigated in each space group. Hauptman & Karle's affirmative result (1957) in $P1$ may be extended to non-centrosymmetric space groups of order 2. In the present status of structure factor algebra it is not possible to generalize this result to further space groups.

Introduction

La méthode suivie et les notations sont celles du mémoire précédent (Bertaut, 1959), abrégé (IV). On étudie la relation entre le triple produit $E(\mathbf{H_1})E(\mathbf{H_2})E(\mathbf{H_3})$ et la moyenne M_{222} (V–1) du texte.

Des relations générales sont données dans le cas de groupes sans centre (V–27) et avec centre de symétrie (V–32). Elles se réduisent aux relations données par Hauptman & Karle (1957a, b) dans les groupes $P1$ et $P\bar{1}$.

Etude du triple produit

$$M_{222} = \big\langle(|E(\mathbf{h_1+h})|^2-1)(|E(\mathbf{h_2+h})|^2-1)$$
$$\times(|E(\mathbf{h_3+h})|^2-1)\big\rangle. \quad (\text{V–1})$$

Groupes sans centre de symétrie

$P1$. Nous envisageons d'abord le groupe $P1$ où l'on a

$$|E(\mathbf{h_1})|^2-1 = \varphi^2 \sum_{j_1 \ne k_1} \xi_{j_1}(\mathbf{h_1})\xi_{k_1}(\mathbf{\bar{h}_1}). \quad (\text{V–2})$$

Ecrivons la même relation (V–2) avec un vecteur $\mathbf{h_2}$, puis avec un vecteur $\mathbf{h_3}$. Appelons les indices de sommation respectifs j_2, k_2 et j_3, k_3. Multipliant les trois relations membre à membre, on obtiendra des termes dépendant de 2, 3, 4, 5 et 6 atomes différents. Nous n'envisagerons que ceux des termes qui font apparaître les différences suivantes de vecteurs

$$\mathbf{H_1} = \mathbf{h_1-h_2}; \quad \mathbf{H_2} = \mathbf{h_2-h_3}; \quad \mathbf{H_3} = \mathbf{h_3-h_1}. \quad (\text{V–3})$$

Entre les vecteurs $\mathbf{H_j}$ ($j = 1, 2, 3$) on a la relation suivante

$$\mathbf{H_1+H_2+H_3} = 0. \quad (\text{V–4})$$

Les termes correspondants dépendent de trois atomes différents. On les obtient en posant d'abord

$$j_1 = k_2; \quad j_2 = k_3; \quad j_3 = k_1 \quad (\text{V–5})$$

ce qui donne lieu à (cf. (II–12), (IV))

$$A = \varphi^6 \sum_{j_1 j_2 j_3} \xi_{j_1}(\mathbf{H_1})\xi_{j_2}(\mathbf{H_2})\xi_{j_3}(\mathbf{H_3}) \ (= \varphi^3 S_{jkl}) \quad (\text{V–6})$$

et en posant ensuite

$$j_1 = k_3; \quad j_2 = k_1; \quad j_3 = k_2 \quad (\text{V–7})$$

ce qui donne lieu au terme complexe conjugué A^* de (V–6). Tout autre terme dépendra en plus soit de sommes de vecteurs $\mathbf{h_j}$ ($j = 1, 2, 3$), soit des vecteurs $\mathbf{h_j}$ seuls. L'intérêt de cette remarque réside en ce que les relations (V–3) à (V–7) subsistent si l'on remplace $\mathbf{h_j}$ ($j = 1, 2, 3$) par $\mathbf{h_j+h}$ de sorte qu'en faisant une moyenne sur $\mathbf{h}$ et en maintenant fixes $\mathbf{h_j}$ ($j = 1,2,3$) tous les termes autres que A et A^* (V–6) disparaissent. On obtient donc finalement dans le groupe $P1$

$$M_{222} = A+A^* \quad (\text{V–8})$$

où A est donné par (V–6), $\mathbf{H_j}$ par (V–3) et M_{222} par