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A method for the determination of the centroid of an X-ray distribution.*

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The centroid θ_C of an X-ray distribution is defined by the expression

$$\theta_C = \int_{-\infty}^{\infty} \theta P(\theta) d(\theta) \Big/ \int_{-\infty}^{\infty} P(\theta) d(\theta) \qquad (1)$$

where $P(\theta)$ is the intensity distribution. The impossibility of using infinite limits has been discussed and various truncation procedures for determining acceptable finite limits have been proposed by Ladell, Parrish & Taylor (1959); Pike & Wilson (1959); Zevin, Umanskii, Kheiker & Panchenko (1961). Difficulties were encountered in applying each of these procedures to $K\alpha$ reflections primarily because of the presence of $K\alpha$ satellites near the truncation limit on the low angle side of the $K\alpha_1$ line (Parrish, Mack & Taylor, 1963), and consequently it was necessary to develop a more satisfactory procedure. The method described below has points of similarity to both the 'simplified' and 'unsimplified' methods of Pike & Wilson (1959), but eliminates their horizontal truncation and defines the background as in the methods of Ladell, Parrish & Taylor (1959) and Zevin *et al.* (1961). A detailed comparison of the various methods is being prepared for publication.

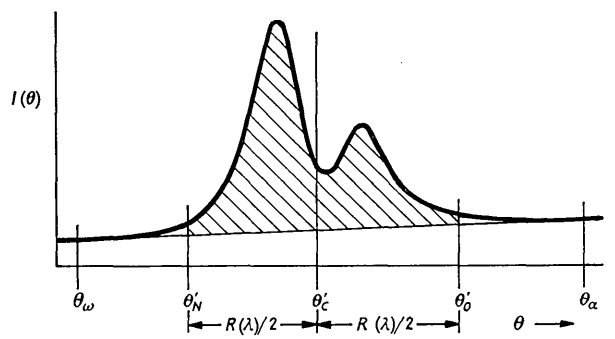

Fig. 1. Truncation limits and the resultant centroid shown schematically for an X-ray powder diffraction profile. For convenience the distribution is shown as a smooth curve, but in practice the line is step-scanned in equal angular increments $\Delta\theta$. The hatched portion denotes the area $\Sigma[I(\theta)-B(\theta)]\Delta\theta$ used in the calculation of the centroid.

We define the intensity distribution $P(\theta)=I(\theta)-B(\theta)$, where $I(\theta)$ is the observed line profile intensity distribution, and $B(\theta)$ is the background intensity distribution. In our experimental arrangement we record $I(\theta)$ by step-scanning with equal angular increments $\Delta 2\theta$ which can be varied from 0·01 to 0·05° (2θ) but must be small compared with the breadth of the profile. We establish the background by measuring the intensities B_α and B_ω at the angles θ_α and θ_ω and assuming a linear variation of $B(\theta)$ with θ; the angles θ_α and θ_ω lie beyond the region where the profile merges into the background (Fig. 1).

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Since $\Delta\theta$ is small compared with the range over which the continuous function $I(\theta)$ has appreciable value, the integrals of equation (1) may be replaced by summations:

$$\theta_C = \sum_{j=0}^{N} \theta_j [I(\theta_j) - B(\theta_j)] \Big/ \sum_{j=0}^{N} [I(\theta_j) - B(\theta_j)] \qquad (2)$$

where $\theta_j = \theta_{j-1} + \Delta\theta$. Equation (2) defines the unique centroid of $P(\theta)$ consistent with equation (1) whenever the distribution $P(\theta)$ is such that $P(\theta_p) \cong 0$ for $p > N$ and $p < 0$.

As in the other approximations based upon truncation procedures, we determine limits of integration θ'_{0n} and θ'_{Nn} (in place of θ_0 and θ_N) and calculate a centroid θ_{Cn} in such a manner as to characterize uniquely the distribution $P(\theta)$ in terms of a corresponding range $R(\lambda)$ of the incident wavelength distribution.*

In our procedure the limits of integration must be symmetric (with respect to a wavelength scale) about the centroid. The centroid of an X-ray diffractometer profile is determined by a successive approximation process as follows:

1. A wavelength range $R(\lambda)$ is selected so that the value of $P(\theta)$ at the limits is approximately 1% of the $K\alpha_1$ peak intensity. This criterion ensures that the range is sufficiently large to include the significant details of the profile. The value of $R(\lambda)$ used for a powder line depends upon the radiation, the aberrations, and the diffraction angle and is of the order of 0·015 Å at 160° (2θ) and 0·030 Å at 70° (2θ).

2. The range and the requirement of symmetry on a wavelength scale establish wavelength values

$$\lambda_0 = \lambda_C + R(\lambda)/2 \text{ and } \lambda_N = \lambda_C - R(\lambda)/2\,, \qquad (3)$$

where λ_C is the centroid of the spectral distribution for the selected range $R(\lambda)$. These wavelength values can be transformed to angular limits θ_0, θ_N by means of the relation

$$\lambda_C/\sin\theta_C = \lambda_0/\sin\theta_0 = \lambda_N/\sin\theta_N = 2d_{hkl}\,. \qquad (4)$$

Since d_{hkl} is not known, tentative limits are calculated using an approximate value of θ_C (denoted below by θ_{C0}). The effect of aberrations is to displace the observed profile and therefore a modification is required to preserve the correspondence between the angle and wavelength scales explicit in equation (4) (Pike & Wilson, 1959). The relation between limits θ'_0, θ'_N on the observed scale and the limits θ_0, θ_N on the 'true' scale is:

$$\theta'_0 = \theta_0 - \Delta_G \text{ and } \theta'_N = \theta_N - \Delta_G \qquad (5)$$

where Δ_G is the sum of the zero-angle and goniometer angle corrections (Parrish & Lowitzsch, 1959) and

* In the following discussion, unprimed quantities refer to 'true' values (*i.e.* free of aberrations and displacements) and primed quantities refer to the experimentally observed values. The first subscript indicates the variable (*i.e.* truncation limit or centroid) and the second subscript denotes the step in the iteration.

the corrections for all the aberrations (see for example, Wilson, 1963) except for dispersion and the Lorentz-polarization factor.

Thus for the first iteration, we obtain the limits

$$\theta'_{01} = \sin^{-1}\left\{\frac{[\lambda_C + R(\lambda)/2]\sin\theta_{C0}}{\lambda_C}\right\} - \Delta_G$$

$$\theta'_{N1} = \sin^{-1}\left\{\frac{[\lambda_C - R(\lambda)/2]\sin\theta_{C0}}{\lambda_C}\right\} - \Delta_G . \qquad (6)$$

The angles θ'_{01}, θ'_{N1} are rounded to the nearest θ'_j values; because of this rounding an exact knowledge of the spectral distribution is not required and only an approximate value of λ_C need be used in equations (6). The accuracy of λ_C required for equations (6) depends of course both on the Bragg angle and on the magnitude of $\Delta\theta$; the weighted mean of the published peak values of α_1 and α_2 is sufficiently accurate for the back reflection region and the $\Delta\theta$ values given above.

3. The centroid θ'_{C1} of the distribution between the (rounded) limits θ'_{01} and θ'_{N1} is calculated from equation (2) (replacing the unprimed by the primed values) and an adjusted centroid θ_{C1} is found from

$$\theta_{C1} = \theta'_{C1} + \Delta_G . \qquad (7)$$

4. If $\theta_{C1} \neq \theta_{C0}$, then θ_{C1} replaces θ_{C0} in equations (6) to calculate new limits θ'_{02}, θ'_{N2}. A new centroid θ_{C2} is then calculated as in step 3.

5. The process is iterated i times until $\theta_{Ci} = \theta_{C(i-1)} = \theta_{Cn}$, at which point the limits are symmetric on a wavelength scale about the centroid. In practice, i is small — at most two or three iterations are required.

6. Finally, the corrected centroid $\theta_C(R)$ is found from

$$\theta_C(R) = \theta_{Cn} + \Delta_L \qquad (8)$$

where Δ_L is the correction of the centroid to account for the effects of dispersion and the Lorentz-polarization factor (Ladell, Mack, Parrish & Taylor, 1959).

The necessity of using an equivalent measure of line position for the powder diffraction line and the spectral line has been discussed by Ladell, Parrish & Taylor (1959) and Pike & Wilson (1959). Because of this requirement, the centroid λ_C of the incident spectral distribution for the same wavelength range as that used in determining $\theta_C(R)$ must be known accurately in order to solve the Bragg equation for d_{hkl}.

To determine λ_C for a selected wavelength range $R(\lambda)$, the procedure is as follows:

1. An approximate centroid λ_{C0} is chosen and the centroid λ_{C1} of the spectral distribution between the limits $\lambda_{01} = \lambda_{C0} + R(\lambda)/2$ and $\lambda_{N1} = \lambda_{C0} - R(\lambda)/2$ is calculated.

2. The difference $D_1 = \lambda_{C1} - \lambda_{C0}$ is used to determine new limits $\lambda_{02} = \lambda_{01} + D_1$ and $\lambda_{N2} = \lambda_{N1} + D_1$, and a new centroid λ_{C2} is calculated.

3. The process is iterated i times until $D_i = D_n = \lambda_{Cn} - \lambda_{C(n-1)} = 0$, at which point the centroid λ_{Cn} lies midway between the limits. Then $\lambda_{Cn} = \lambda_C$ is the spectral centroid for the range $R(\lambda)$.

It should be noted that experimental two-crystal spectrometer spectral distributions may require corrections for aberrations and that these corrections, if known, may be applied in a manner similar to that used for $\theta_C(R)$. Standard values of λ_C for a given radiation need be tabulated only once for a series of ranges for use in solving the Bragg equation. Results of the determination of λ_C for various ranges for Cu $K\alpha$ and Fe $K\alpha$ spectral distributions and the application of the above method to the determination of lattice parameters are being prepared for publication.

References

LADELL, J., MACK, M., PARRISH, W. & TAYLOR, J. (1959). *Acta Cryst.* **12**, 567.

LADELL, J., PARRISH, W. & TAYLOR, J. (1959). *Acta Cryst.* **12**, 561.

PARRISH, W. & LOWITZSCH, K. (1959). *Amer. Min.* **44**, 765.

PARRISH, W., MACK, M. & TAYLOR, J. (1963). *J. Appl. Phys.* **34**, 2544.

PIKE, E. R. & WILSON, A. J. C. (1959). *Brit. J. Appl. Phys.* **10**, 57.

WILSON, A. J. C. (1963). *Mathematical Theory of X-Ray Powder Diffractometry*. Eindhoven: Centrex Publ. Co.

ZEVIN, L. S., UMANSKII, M. M., KHEIKER, D. M. & PANCHENKO, YU. M. (1961). *Kristallografiya*, **6**, 348.

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Étude cristallographique préliminaire du perfluoxymolybdate monohydraté de potassium, $K_2MoO_3F_4,H_2O$.

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Le perfluoxymolybdate monohydraté de potassium (Piccini, 1892) cristallise en lamelles monocliniques; les formes les plus courantes sont: {001}, {301}, {$\bar{3}$01}, {021}, {031}.

L'interprétation des diagrammes de cristal tournant et du diagramme de poudre de $K_2MoO_3F_4,H_2O$, conduit à une maille monoclinique de paramètres:

$$a = 6{,}31 \pm 0{,}015,\ b = 6{,}28 \pm 0{,}015,\ c = 18{,}15 \pm 0{,}015\ \text{Å};$$
$$\beta = 98°\ 09' \pm 10'.$$
$$a:b:c = 1{,}0048:1:2{,}8901$$
$$\lambda\ \text{Cu}\ K\alpha = 1{,}5418\ \text{Å}.$$

Cette maille est reliée à celle trouvée par étude mor-