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An Experimental Investigation of the Truncation Errors Incurred in Single-Crystal Diffractometry

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Integrated intensity measurements depend on the wavelength range of integration. In conventional X-ray measurement procedures this range decreases with increasing diffraction angle, which results in a systematic intensity error for which normally no correction is applied. This paper presents an experimental investigation of this error for standard integration scans. A correction formula is derived and tested, and it is shown that failure to take account of this error has led to spuriously high temperature factors in most X-ray structure analyses.

Introduction

Alexander & Smith (1962) observed that the natural width of characteristic X-ray lines cannot be neglected when measuring integrated intensities with a single-crystal diffractometer. The wavelength dispersing power for a Bragg reflexion, $d\theta/d\lambda$, is $(\tan\theta)/\lambda$ but in practice the angular integration range used is almost independent of θ (even if the α_1–α_2 splitting is added to a constant scan range). The wavelength limits of the integral therefore decrease with diffraction angle. Fig. 1 shows diagrammatically how this can result in significant intensity errors. Alexander & Smith pointed out that these errors would be quite substantial. In spite of their work, subsequent references to it (*e.g.* Kheiker, 1968; Young, 1968, 1974; Einstein, 1974) and the awareness of truncation errors in powder diffractometry, the effect seems to have been largely ignored in single-crystal intensity measurements.

The reason for this is probably twofold. Firstly, it is not possible to separate spectral and diffraction effects in the tails of the double-crystal spectrometer rocking curves (Ladell, Parrish & Taylor, 1959). Alexander & Smith therefore had to assume a profile for the spectral line shape. Secondly, so many other factors dominate the shape of the single-crystal diffractometer rocking curves, that the existence of truncation errors is not very obvious experimentally.

This paper presents an experimental investigation of the characteristic line shape and of truncation errors.

The characteristic line shape

From spectroscopic theory (*e.g.* Heitler, 1957), the natural X-ray line shape is expected to be a Cauchy distribution. The spectrum observed in an X-ray diffraction experiment will be the natural spectrum convoluted with the diffraction function; but as Ladell, Parrish & Taylor (1959) have observed, it is impossible to deconvolute the two. Alexander & Smith (1962) therefore assumed that diffraction effects would be negligible and took a Cauchy line profile for their calculations. In the present work, a spectrum was taken from a single-crystal diffractometer so that the diffraction effects would be identical with those encountered when measuring integrated intensities.

Fig. 2 shows a Cu $K\alpha$ spectrum taken from the 004 reflexion of a small diamond. An $\omega/2\theta$ scan was used with restricted counter slits to minimize broadening by the source. A Cauchy distribution has been fitted to the spectrum by using the linewidth and relative

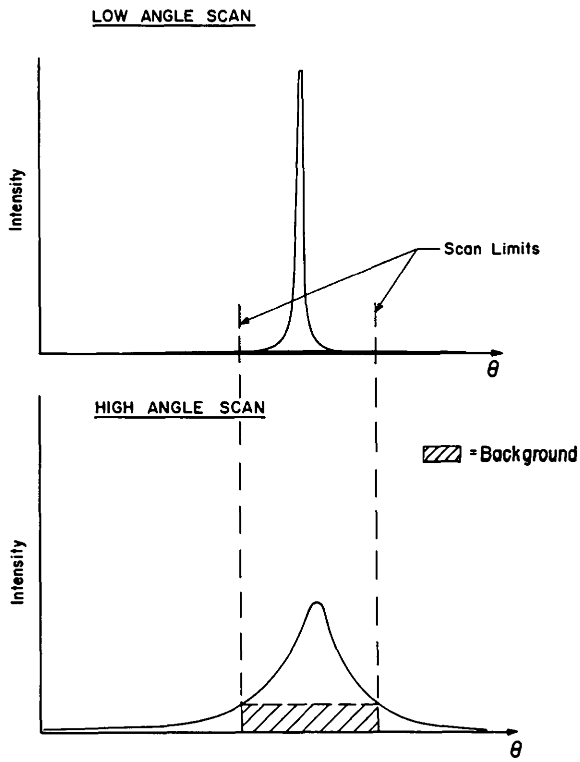

Fig. 1. A diagrammatic representation of truncation errors.

intensity data from Compton & Allison (1935),* convoluting with a rectangular resolution function and varying the scale. The fit is good and discrepancies could well be due to errors in the linewidths or choice of resolution function. Alexander & Smith's assumption of Cauchy-shaped characteristic lines was therefore justified. [The work of Edwards & Langford (1971) confirms this and also shows the existence of a $K\alpha$ satellite line. Since the relative intensity of this satellite is only 0·6% of the $K\alpha$ doublet its effect may be ignored.]

* Full width at half height = 0·58 X.U. ($K\alpha_1$), 0·77 X.U. ($K\alpha_2$); $I\alpha_2/I\alpha_1 = 0{\cdot}497$.

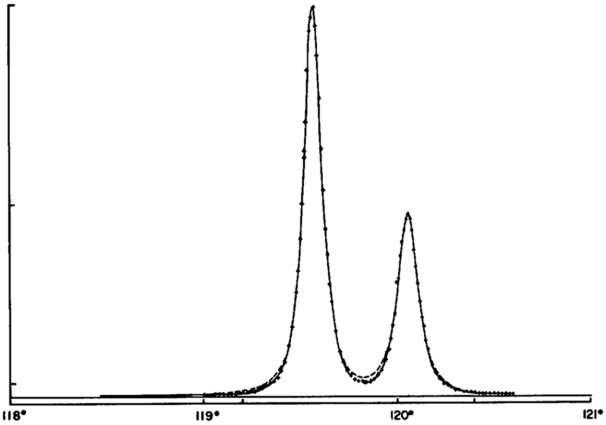

Fig. 2. A high-resolution spectrum of the Cu $K\alpha$ doublet using the 004 reflexion of a small diamond mounted on a single-crystal diffractometer.

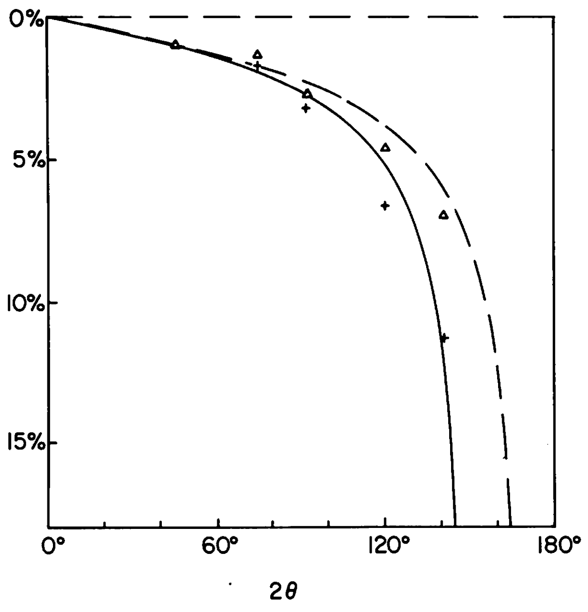

Fig. 3. Experimentally determined truncation errors. The experimental points represent the ratio of $\omega/2\theta$ integrated intensities to normalized ω/θ integrated intensities. The crosses and the continuous line are for a 2° $\omega/2\theta$ scan; the triangles and the dashed line are for an $\omega/2\theta$ scan of 2° plus the $K\alpha_1$–$K\alpha_2$ splitting.

Experimental measurement of truncation errors

To establish the magnitude of typical truncation errors, the following experiments were carried out. Integrated intensities were measured for a series of reflexions from a small diamond. First they were measured with an $\omega/2\theta$ scan with a constant range of 2°, then with an $\omega/2\theta$ scan of 2° plus the $K\alpha_1$–$K\alpha_2$ splitting. The same reflexions were measured a third time using a recently developed high-resolution monochromation technique which entails an ω/θ scan and restricted counter slits (Denne, 1977). For the last series, a constant bandpass of three times the $K\alpha_1$–$K\alpha_2$ splitting was used; this corresponds to 96·1% of the total Cu $K\alpha$ spectrum as represented by Cauchy profiles; the ω/θ intensities were therefore normalized by multiplying by 1/0·961.

Fig. 3 shows the ratio of the $\omega/2\theta$ measurements to the ω/θ estimates of integrated intensity. It is evident that the $\omega/2\theta$ intensities are all less than the normalized ω/θ measurements; the constant-scan $\omega/2\theta$ intensities are consistently less than those obtained with a scan that increased with angle. All differences increase as the diffraction angle increases. The ratio tends to 1 as 2θ tends to 0, confirming that the $\omega/2\theta$ scan can only measure the entire natural line when the dispersion is zero.

The experimental points of Fig. 3 confirm in a quantitative way the predictions of Alexander & Smith and show that truncation errors are indeed a serious error source in integrated intensity measurement.

Theoretical calculation of truncation errors

The equation for the Cauchy distribution is:

$$I(\lambda) = (w_0/2\pi)/\{(\lambda-\lambda_0)^2 + (w_0/2)^2\} \tag{1}$$

where λ_0 is the mean wavelength and w_0 is the full width at half height of the distribution. Its definite integral is:

$$\int_a^b I(\lambda)\mathrm{d}\lambda = \left[(1/\pi)\tan^{-1}\frac{2(\lambda-\lambda_0)}{w_0}\right]_a^b \tag{2}$$

$$= C(w_0, \lambda_0, a, b)\,.$$

The wavelengths at the scan limits θ_a, θ_b will be:

$$\lambda_a = 2d\sin(\theta_a) \quad \lambda_b = 2d\sin(\theta_b)\,. \tag{4}$$

The effect of finite source size, finite crystal size and mosaic spread will tend to average out, so the truncation error, T, is:

$$T = 1 - A_1C(w_1, \lambda_1, \lambda_a, \lambda_b) - A_2C(w_2, \lambda_2, \lambda_a, \lambda_b)$$
$$-(\lambda_a-\lambda_b)[I_1(\lambda_a)+I_1(\lambda_b)] + [I_2(\lambda_a)+I_2(\lambda_b)]/2 \tag{5}$$

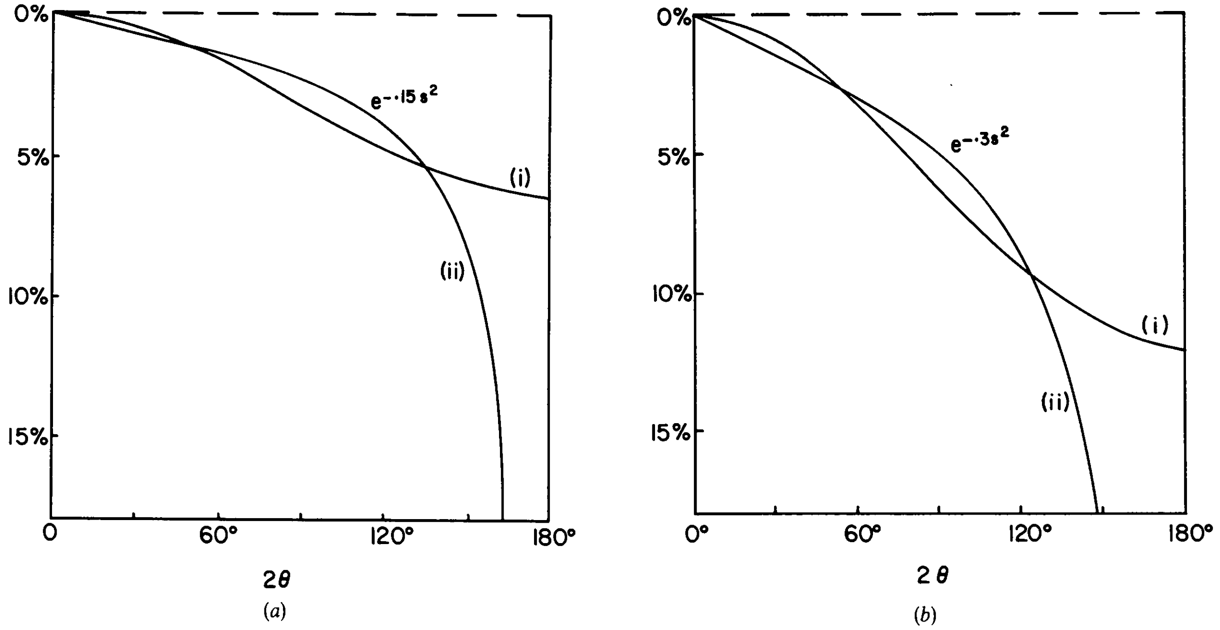

Fig. 4. Isotropic temperature factor curves (i) compared with calculated truncation error curves (ii) for an $\omega/2\theta$ scan of range 2° plus the $K\alpha_1$–$K\alpha_2$ splitting. (*a*) Cu $K\alpha$ radiation, (*b*) Mo $K\alpha$ radiation ($s=\sin\theta/\lambda$).

where

A_1, A_2 = the $K\alpha_1$, $K\alpha_2$ relative intensities,
w_1, w_2 = the $K\alpha_1$, $K\alpha_2$ half widths,
λ_1, λ_2 = the $K\alpha_1$, $K\alpha_2$ mean wavelengths.

T is plotted against 2θ for the $\omega/2\theta$ scans in Fig. 3. It agrees with the experimental values to better than 1% for most points. This agreement both confirms the experimentally determined truncation errors and verifies the correction formula for integrated intensities measured by the $\omega/2\theta$ techniques.

Discussion

Truncation errors have been shown to be a substantial source of experimental error with $\omega/2\theta$ integrated intensity measurements as predicted by Alexander & Smith. Measured intensities are more strongly reduced by truncation errors as the diffraction angle increases, so it is to be expected that this source of error will appear as a spuriously high temperature factor. An estimate of the contribution of truncation error to apparent B factor can be made as follows. The $\omega/2\theta$ scan range generally used appears to be $\sim 2°$ plus the $K\alpha_1$–$K\alpha_2$ splitting. Fig. 4(*a*), (*b*) shows truncation errors for this scan range compared with ΔB factors of 0·075 and 0·15 Å^2 for Cu $K\alpha$ and Mo $K\alpha$ radiation respectively. The curves agree to better than 1% out to $2\theta = 145$ and 132° respectively for the two radiations. This suggests that the temperature factors in most structure analyses are spuriously high by amounts of this order. (*N.B.* TDS errors operate in the opposite sense to truncation errors; in cases where TDS corrections have not been applied, this effect may be reduced or even reversed.)

References

Alexander, L. E. & Smith, G. S. (1962). *Acta Cryst.* **15**, 983–1004.
Compton, H. C. & Allison, S. K. (1935). *X-rays in Theory and Experiment*, p. 744. New York: Van Nostrand.
Denne, W. A. (1977). *Acta Cryst.* To be submitted.
Edwards, A. J. & Langford, J. I. (1971). *J. Appl. Cryst.* **4**, 43–50.
Einstein, J. R. (1974). *J. Appl. Cryst.* **7**, 340–341.
Heitler, W. (1957). *The Quantum Theory of Radiation*, pp. 181–188. Oxford Univ. Press.
Kheiker, D. M. (1968). *Acta Cryst.* A**25**, 82.
Ladell, J., Parrish, W. & Taylor, J. (1959). *Acta Cryst.* **12**, 561–570.
Young, R. A. (1968). *Acta Cryst.* A**25**, 55.
Young, R. A. (1974). *X-ray Diffraction*, by L. V. Azaroff, R. Kaplow, N. Kato, R. J. Weiss, A. J. C. Wilson & R. A. Young, p. 578. New York: McGraw-Hill.