5. DETERMINATION OF LATTICE PARAMETERS

Table 5.2.8.1. *Some geometrical aberrations in the Debye–Scherrer method [increase in $\theta = +$, decrease $= -$]*

Source of aberration	Effect on θ	Angle variation of Δd	Remarks

Specimen displacement
  towards exit
  towards entrance
  sideways
	
	$-$
	$+$
	$\sim 0*$
		
		$\cos^2\theta$
		$\cos^2\theta$
		$\sim \theta*$
			Minimized by accurate construction and centring
			Extrapolates to zero

Beam divergence
  perpendicular to axis
  parallel to axis
	
	$+$
	$+$ or $-$
		$\cos\theta\cot\theta$ or $\cos^2\theta/2\theta$
		Complex
			Minimized by reducing collimator dimensions
			See Langford, Pike & Beau (1964)

Film shrinkage	$+$	$(\pi - 2\theta)\cot\theta$	Affects only van Arkel arrangement
Knife-edge calibration	$+$ or $-$	$\theta\cot\theta$	Affects only Bradley–Jay arrangement. Partly eliminated by usual extrapolation
Specimen absorption	$+$	$\cos\theta\cot\theta$ or $\cos^2\theta/2\theta$	Minimized by reducing specimen diameter or dilution. Extrapolates to zero

* For van Arkel and Bradley–Jay arrangements. For Straumanis–Ievins', $+$ or $-$ and $(\pi - 2\theta)\cot\theta$, respectively.

found very satisfactory in practice was suggested by Nelson & Riley (1945) [see also Taylor & Sinclair (1945*a*,*b*)]:

$$\cos^2\theta(\operatorname{cosec}\theta + \theta^{-1})/2. \qquad (5.2.8.1)$$

This function gives linear plots down to quite small values of θ.

5.2.9. Testing for remanent systematic error

Since about 1930, it has been claimed that the lattice parameters of cubic substances could be measured within one part in 50 000. Precision (that is, reproducibility of measurements by one technique within one laboratory) of this order is achieved, but accuracy (agreement between determinations by different techniques or by the same technique in different laboratories) is lower. The IUCr lattice-parameter project (Parrish, 1960) showed a standard deviation of 1 in 30 000 in inter-laboratory comparisons, with some outlying values differing from the mean by one or two parts in 10 000. At that time, therefore, precision was considerably better than accuracy (absence of significant remanent systematic error). Testing for remanent systematic error is thus valuable as an occasional test of methodology, though not undertaken as routine. The principle is outlined here, and more details are given in Chapters 8.4 and 8.5.

When refinement of parameters is performed by least squares, weighted in accordance with the reciprocal of the estimated variance, the expected value of the weighted sum of squares is

$$\langle S \rangle = n - p, \qquad (5.2.9.1)$$

where n is the number of terms summed and p is the number of parameters determined. The standard deviation of the sum S is expected to be

$$\sigma_S = [2(n - p)]^{1/2} \qquad (5.2.9.2)$$

approximately (Wilson, 1980), so that if the actual value of S exceeds

$$\begin{aligned}\langle S \rangle + k\sigma_S &= n - p + k\sigma_S \\ &= n - p + k[2(n - p)]^{1/2} \qquad (5.2.9.3)\end{aligned}$$

(where $k = 2$ or 3), one can reasonably conclude that there are defects in the model (remanent systematic errors). If S is less than this value, one can reasonably conclude that any defects in the model (systematic errors) are at worst of the same order of magnitude as the statistical fluctuations; the sensitivity of the test increases rather slowly with $n - p$. The method was advocated by Beu and his collaborators (Beu, Musil & Whitney, 1962, 1963; Beu, 1964; Beu & Whitney, 1967; Langford, Pike & Beu, 1964; see also Mitra, Ahmed & Das Gupta, 1985) because tests of the hypothesis 'no remaining systematic error' based on likelihood were available; they assumed a normal distribution of errors, possibly without realizing, and certainly without emphasizing, that the method was then equivalent to least squares. Their application of the method to testing for remanent systematic error in lattice-parameter determination was successful: the aberrations of the counter diffractometer were found to be adequately accounted for: additional aberrations were found for the Bond method (see Chapter 5.3); Boom (1966) used it in testing the accuracy of the Debye–Scherrer method.

In statistical literature, the weighted sum of squares S is often called the *scaled deviance*, and

$$E = [S - (n - p)]/[2(n - p)]^{1/2} \qquad (5.2.9.4)$$

is called the *excess*. The test for the absence of significant systematic error is then that the excess should be less than three.

5.2.10. Powder-diffraction standards

The use of properly characterized materials is an important step in determining the performance characteristics of instruments and methods. The best documented and most widely used standards for powder diffraction are those from the [US] National Institute of Standards and Technology* (Dragoo, 1986).

Such standards are used as specimens in diffractometers and cameras for angular calibration to determine systematic errors in the observed 2θ's for profile shapes and in intensities for quantitative analysis and for determining instrumental line profiles. The standard may be used separately as an independent specimen ('external standard'), or mixed with the powder to be investigated ('internal standard'). Some examples of the use of

* http://srmcatalog.nist.gov.

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