Table 5.2.7.1. *Centroid displacement* $\langle \Delta E/E \rangle$ *and variance* W *of certain aberrations of an energy-dispersive diffractometer [mainly from Wilson (1973), where more detailed results are given for the aberrations marked with an asterisk]*

The Soller slits are taken to be in the original orientation (Soller, 1924). For the notation, see the footnote.

Aberration	$\langle \Delta E/E \rangle$	W
Specimen displacement	~ 0	Included in equatorial divergence
Specimen transparency*	~ 0	?
Equatorial divergence*	~ 0	$\cot^2\theta(A^2 + B^2)/24$ for narrow Soller slits
Axial divergence	$-R^{-2}\,\mathrm{cosec}^2\,\theta[X^2\cos 2\theta + 4Y^2\cos^2\theta + Z^2\cos 2\theta]/24$	$R^{-4}\,\mathrm{cosec}^4\,\theta[X^4\cos^2 2\theta + 4Y^4(1+\cos 2\theta)^2 + Z^4\cos^2 2\theta + 5X^2Z^2 + 5Y^2(X^2+Z^2) \times (1+\cos 2\theta)^2]/720$
Refraction*	Probably negligible at the present stage of technique	
Response variations Centroid	$[Vf' + f''(\mu_3/2 - V^2f'/f)]/Ef$	?
Peak	$-f'I/EfI''$	?
Interaction of Lorentz *etc.* factors and geometrical aberrations	$\langle(\Delta\theta)^2\rangle/2 - \cot\theta[\langle\Delta\theta\rangle + (g'/g)\langle(\Delta\theta)^2\rangle] + \cot^2\theta(EI'/I)\langle(\Delta\theta)^2\rangle$	$-\cot\theta[\langle(\Delta\theta)^3\rangle - \langle\Delta\theta\rangle\langle(\Delta\theta)^2\rangle] + \cot^2\theta\{\langle(\Delta\theta)^2\rangle - \langle\Delta\theta\rangle^2 + (2g'/g)[\langle(\Delta\theta)^3\rangle - \langle\Delta\theta\rangle\langle(\Delta\theta)^2\rangle]\}$

Notation: A and B are the angular apertures (possibly equal) of the two sets of Soller slits; E is the energy of the detected photon; $f(E)$ is the variation of a response (energy of the continuous radiation, absorption in the specimen *etc.*) with E; $g(\theta)$ is an angle-dependent response (Lorentz factor *etc.*); $I(E - E_1)\,\mathrm{d}E$ is the counting rate recorded at E when the energy of the incident photons is actually E_1; R is the diffractometer radius; V is the variance and μ_3 is the third central moment of the energy-resoluton function I; $2X, 2Y, 2Z$ are the effective dimensions (possibly equal) of the source, specimen, and detector; the primes indicate differentiation; the averages $\langle(\Delta\theta)^2\rangle$ *etc.* are over the range of Bragg angles permitted by the slits *etc.*

A diffractometer can be converted from angle-dispersive to energy-dispersive by (i) replacing the usual counter by a solid-state detector, (ii) replacing the usual electronic circuits by a multichannel pulse-height analyser, and (iii) keeping the specimen and detector stationary while the counts are accumulated. When so used, the geometrical aberrations are essentially the same as those of an angle-dispersive diffractometer, though the greater penetrating power of the higher-energy X-rays means that greater attention must be paid to the irradiated volume and the specimen transparency (Langford & Wilson, 1962; Mantler & Parrish, 1977). As Sparks & Gedcke (1972)* emphasize, spacing measurements made with such an arrangement are subject to large specimen-surface displacement and transparency aberrations, and the corrections required to allow for them are difficult to make. Fukamachi, Hosoya & Terasaki (1973) and Nakajima, Fukamachi, Terasaki & Hosoya (1976) showed that this difficulty can be avoided if the Soller slits are rotated about the beam directions by 90°, so that they limit the equatorial divergence instead of the axial; this was, of course, the orientation used by Soller (1924) himself. Any effect of specimen-surface displacement and transparency is then negligible if ordinary care in adjustment is used, and the specimen may be placed in the reflection, or the symmetrical transmission, or the unsymmetrical transmission position (Wilson, 1973). The geometrical aberrations are collected in Table 5.2.7.1, and apply to the original orientation of the Soller slits; in the Sparks & Gedcke (1972) orientation, the usual ones apply. In general, the physical aberrations are the same for both orientations. The most difficult correction is that for the energy distribution in the incident X-ray beam; aspects of this have been discussed by Bourdillon, Glazer, Hidaka & Bordas (1978), Glazer, Hidaka & Bordas (1978), Buras, Olsen, Gerward, Will & Hinze (1977), Fukamachi, Hosoya & Terasaki (1973), Laguitton & Parrish (1977) and Wilson (1973). Only the last of these is directly relevant to the lattice-spacing problem. The best results reported so far seem to be those of Fukamachi, Hosoya & Terasaki (1973) (0.01% in the lattice parameter).

Okazaki & Kawaminami (1973) have suggested the use of a stationary specimen followed by analysis of the diffracted X-rays with a single-crystal spectrometer. This would give some of the advantages of energy-dispersive diffractometry (easy control of temperature *etc.*, because only small windows would be needed), but there would be no reduction in the time required for recording a pattern.

5.2.8. Camera methods

The types of powder camera frequently used in the determination of lattice parameters are described in Section 2.3.4. The main geometrical aberrations affecting measurements made with them are summarized in Table 5.2.8.1. At high angles, most of them vary *approximately* as $(\pi - 2\theta)^2$, and one would thus expect to obtain an approximately straight-line extrapolation if the apparent values of the lattice parameter were plotted against a function something like $(\pi - 2\theta)^2$. A function that has been

* There seems to be an error in their equation (5), which carries over into the equations they derive from it.

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	 $-$ $+$ ~ 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*)]:

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

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.

references