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	$-R^{-2}\operatorname{cosec}^2\theta[X^2\cos 2\theta+4Y^2\cos^2\theta+Z^2\cos 2\theta]/24$	$R^{-4}\operatorname{cosec}^4\theta[X^4\cos^2 2\theta+4Y^4(1+\cos 2\theta)^2$ $+Z^4\cos^2 2\theta+5X^2Z^2+5Y^2(X^2+Z^2)$ $\times(1+\cos 2\theta)^2]/720$
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.*); $I(E-E_1)\,dE$ 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).

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

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

references