valid result. The zero-angle position should be included as a variable parameter in the least-squares calculation.

A precision of a few parts per million in the lattice parameter of NIST silicon has been reached with the high-precision diffractometer in the Daresbury Laboratory (Hart, Cernik, Parrish & Toraya, 1990). This instrument has an accurate gear and an incremental encoder driven by a DC servomotor with a feedback servoloop capable of positioning the detector arm within 0.36″. A large number of repeated measurements showed a statistical accuracy of $0.0001^\circ(2\theta)$, corresponding to 1 in the fifth decimal place of d for $\lambda = 1$ Å and $2\theta = 20^\circ$.

5.2.6. Whole-pattern methods

The recent large increase in the use of powder samples for crystal-structure refinement and analysis has also stimulated interest in lattice-parameter determinations, which are derived during the course of the calculation. The most frequently used method is that of Rietveld (1967, 1969) described in Chapter 8.6. In outline, a profile-fitting function containing adjustable parameters to vary the width and shape with 2θ is selected. The parameters corresponding to the atomic positions, multiplicity, lattice parameters, *etc*. of the selected structure model are varied until the best least-squares fit between the whole observed diffraction pattern and the whole calculated pattern of the model is obtained. There is no detailed published study of the accuracy of the lattice parameters that is attained but the estimated standard deviations quoted in a number of papers (see, for example, Young, 1988) appear to be comparable with those published for simple structures having no overlapped reflections. In this type of calculation, the accuracy of the lattice parameters is tied to the accuracy of the refined structure because it includes the model errors in the least-squares residuals.

An alternative to the Rietveld method is the pattern-decomposition method in which the integrated intensities are derived from profile fitting and the data used in a powder least-squares-refinement program. The reflections may be fitted individually or in small clusters (Parrish & Huang, 1980) or the whole pattern can be fitted (Pawley, 1981; Langford, Louër, Sonneveld & Visser, 1986; Toraya, 1986, 1988); unlike the Rietveld method, no crystal-structure model is required and only the first stage is used for lattice parameters. The Pawley method was developed for neutron-diffraction data and uses slack constraints to handle the problem of least-squares ill-conditioning due to overlapping reflections, and the positions of the reflections are constrained by the lattice parameters. The refinement also determines the zero-angle calibration correction.

Toraya extended the Pawley method to X-ray powder diffractometry. He first determined the profile shapes and peak positions of several standard samples by individual profile fittings to generate a curve relating the peak shifts to 2θ. A pair of split Pearson VII profiles was used for conventional patterns to handle the $K\alpha$ doublets and the profile asymmetries, and a pseudo-Voight function for the nearly symmetrical synchrotron-radiation profiles. The program is set up so that the parameters of the fitting function are varied with 2θ to account for the increasing widths and the peak shifts and the whole pattern is automatically fitted. The positions of the individual reflections are a function of the calculated lattice parameters, which are refined together with the integrated intensities as independent variables. This method also permits simultaneous refinement of several phases present in the pattern. Unit cells calculated from whole-pattern profile fitting and incorporating the peak-shift corrections had estimated standard deviations an order of magnitude smaller than those not using the systematic error correction. It is also possible to use an internal standard and to make the corrections by refining the cell parameters of the sample and holding constant the parameters of the standard.

Good results can also be obtained using selected peaks rather than the whole pattern (Parrish & Huang, 1980). Peak search or profile fitting is used to determine the observed peak positions. The least-squares refinement is used to minimize $\Delta(2\theta)$ (observed − calculated). It also determines the average and the standard deviation of all the d's and 2θ's. In principle, all the aberrations causing shifts can be incorporated in the refinement. There are, however, large correlations between aberrations with similar angular dependencies. In practice, the zero-angle calibration correction is always determined, and the specimen-surface displacement shift is usually included.

The lattice-parameter determination requires an indexed pattern in which the peak angles have been determined by peak search or profile fitting. Reflections known to have poor precision because of very low intensity or close overlapping should be omitted. The estimated standard deviation is dependent on the number of reflections used and it is better to use all the well measured peaks. There is the question of using a weighting scheme in which the high-angle reflections are given greater weight because of their higher accuracy for a given 2θ error. As noted in Subsection 5.2.13, higher-order reflections usually have low intensities and much overlapping. Some judgement and critical tests are often required.

5.2.7. Energy-dispersive techniques

There are now two basic energy-dispersive techniques available. In both, the specimen and detector are fixed in a selectable θ–2θ setting. The method (Giessen & Gordon, 1968) first described and most widely used requires a solid-state detector and a multichannel pulse-height analyser (Section 2.3.2 and Chapter 2.5). The resolution of the pattern is determined by the energy resolution of the detector and is considerably poorer than that of conventional angle-dispersive techniques, thereby greatly limiting its applications. The second method uses an incident-beam monochromator, a conventional scintillation counter, and a single-channel pulse-height analyser. The monochromator is step-scanned to select a gradually increasing (or decreasing) single wavelength (Parrish & Hart, 1987). This method permits much higher count rates, thereby reducing the time required for the experiment. Since the resolution is determined by the X-ray optics, the resolution is the same as in angle-dispersive diffractometry (Subsection 2.3.2.4). The method has, however, the disadvantage that the widths of the profiles vary with energy, and unless care is taken with the step size there may be too few points per reflection to define the profile adequately. The method is particularly applicable to synchrotron radiation, but there have been no publications to date on its use for lattice-parameter determination.

Energy-dispersive techniques (Section 2.2.3 and Chapter 2.5) are not ordinarily the method of choice for lattice-parameter determination. Relative to angle-dispersive techniques, they suffer from the following disadvantages:

(1) lower resolution;

(2) need for absolute energy calibration of the multichannel pulse-height analyser;

(3) need to know the energy distribution in the incident beam;

(4) specimen transparency varies with energy; even tungsten becomes transparent for 35 keV radiation.

Nevertheless, the advantage of stationary specimen and detector may outweigh these disadvantages for special applications.

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.

references