

## 5. DETERMINATION OF LATTICE PARAMETERS

Table 5.2.1.1. Functions of the cell angles in equation (5.2.1.3) for the possible unit cells

| Function | Cell                          |               |                               |   |   |
|----------|-------------------------------|---------------|-------------------------------|---|---|
|          | Cubic tetragonal orthorhombic | Hexagonal     | Monoclinic ( <i>c</i> unique) | Rhombohedral                            | Triclinic   |
| <i>A</i> | 1                             | 1             | 1                             | $\sin^2 \alpha$                         | $\sin^2 \alpha$   |
| <i>B</i> | 1                             | 1             | 1                             | $\sin^2 \alpha$                         | $\sin^2 \beta$  |
| <i>C</i> | 1                             | $\frac{3}{4}$ | $\sin^2 \gamma$               | $\sin^2 \alpha$                         | $\sin^2 \gamma$   |
| <i>D</i> | 0                             | 0             | 0                             | $\cos^2 \alpha - \cos \alpha$           | $\cos \beta \cos \gamma - \cos \alpha$  |
| <i>E</i> | 0                             | 0             | 0                             | $\cos^2 \alpha - \cos \alpha$           | $\cos \gamma \cos \alpha - \cos \beta$  |
| <i>F</i> | 0                             | $\frac{1}{4}$ | $-\cos \gamma$                | $\cos^2 \alpha - \cos \alpha$           | $\cos \alpha \cos \beta - \cos \gamma$  |
| <i>G</i> | 1                             | $\frac{3}{4}$ | $\sin^2 \gamma$               | $1 + 2 \cos^3 \alpha - 3 \cos^2 \alpha$ | $1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma$ |

profile-fitting procedure gives a measure of the peak intensity and (if desired) a measure of the integrated intensity.

### 5.2.2. Wavelength and related problems

#### 5.2.2.1. Errors and uncertainties in wavelength

In diffractometry, the errors in wavelength,  $\Delta\lambda$ , are usually entirely systematic; the crystallographer accepts whatever wavelength the spectroscopist provides, so that an error that was random in the spectroscopy becomes systematic in the diffractometry. One or two exceptions to this rule are noted below, as they are encountered in the discussion of the various techniques. Equation (5.2.1.4) shows that such a systematic error in wavelength, arising either from uncertainty in the wavelength scale (affecting all wavelengths) or from a systematic error in one wavelength (possibly arising from a random error in its determination) produces a constant fractional error in the spacing, an error that is not detectable by any of the usual tests for systematic error.

Ordinarily, the wavelength to be inserted in (5.2.1.1) is not known with high accuracy. The emission wavelengths given by spectroscopists – the exact feature to which they refer is usually not known, but is probably nearer to the peak of the wavelength distribution than to its centroid – are subject to uncertainties of one part in 50 000 [see, for example, Sandström (1957, especially p. 157)], though this uncertainty is reduced by a factor of ten for some more recent measurements known to refer to the peak defined by, say, the extrapolated mid-points of chords (Thomsen, 1974). Energy-dispersive and synchrotron devices are usually calibrated by reference to such X-ray wavelengths, and thus their scales are uncertain to at least the same extent. Use of a standard silicon sample (Sections 5.2.5 and 5.2.10) will ordinarily give greater accuracy. There are a few wavelengths determined by interferometric comparison with optical standards where the uncertainty may be less than one part in a million (Deslattes, Henins & Kessler, 1980); see Section 4.2.2.

The wavelength distributions in the emission spectra of the elements ordinarily used in crystallography are not noticeably affected by the methods used in preparing targets. There is a slight dependence, at about the limit of detectability, on operating voltage, take-off angle, and degree of filtration (Wilson, 1963, pp. 60–63), and even the fundamental emission profile is affected somewhat by the excitation conditions (Chevallier, Travenier & Briand, 1978). Effective monochromators, capable of separating the  $K\alpha_1$  and  $K\alpha_2$  components (Barth, 1960), produce large variations. However, (5.2.1.1)

depends only on the ratio of  $d$  to  $\lambda$ , so that *relative* spacings can be determined without regard to the accuracy of  $\lambda$ , provided that nothing is done that alters the wavelength distribution between measurements, and that the same identifiable feature of the distribution (peak, centroid, mid-point of chord, ...) is used throughout.

#### 5.2.2.2. Refraction

X-rays, unless incident normally, are refracted away from the normal on entering matter, and while inside matter they have a longer wavelength than *in vacuo*. Both effects are small, but the former leads to a measurable error for solid specimens (that is, specimens without voids or binder) with flat surfaces (single crystals or polished metal blocks). This effect becomes prominent at grazing incidence, and may lead to total external reflection. For the usual powder compacts (Section 2.3.4), refraction leads to a broadening rather than a displacement (Wilson, 1940, 1962; Wilkens, 1960; Hart, Parrish, Bellotto & Lim, 1988; Greenberg, 1989). The greater wavelength within the powder grain leads to a pseudo-aberration; the actual wavelength ought to be used in (5.2.1.1), and if the *in vacuo* wavelength is used instead the lattice spacing obtained will be too small by a fraction equal to the amount by which the refractive index differs from unity. The difference is typically in the fourth decimal place in the lattice parameter expressed in Å. The need for any refraction correction for very fine powders has been questioned.

#### 5.2.2.3. Statistical fluctuations

Statistical fluctuations in the number of counts recorded are not aberrations, but random errors. They influence the precision with which the angles of diffraction, and hence the lattice parameters, can be determined. The fluctuations arise from at least two sources: emission of X-ray quanta from the source is random, and the number of crystallites in an orientation to reflect varies with position within the specimen and with the relative orientations of the specimen and the incident beam. The theory of fluctuations in recording counts is discussed in Chapter 7.5; their effect can be reduced as much as is desired by increases in the counting times. Fluctuations in particle orientation are more difficult to control; use of smaller particles, larger illuminated volumes, and rotation of the specimen are helpful, but may conflict with other requirements of the experiment. The section on specimen preparation in Chapter 2.3 should be consulted.

## 5.2. X-RAY DIFFRACTION METHODS: POLYCRYSTALLINE

Among the many papers relevant to the problem are Mack & Spielberg (1958), Pike & Wilson (1959), Thomsen & Yap (1968*a,b*), Wilson (1965*a,b,c*, 1967, 1971), Wilson, Thomsen & Yap (1965), and Zevin, Umanskij, Khejker & Pančenko (1961). The formulae are complicated, and depend on the measure of location that is adopted for the diffraction profile. In general, however, the variance of the angle is inversely proportional to the number of counts accumulated.

### 5.2.3. Geometrical and physical aberrations

#### 5.2.3.1. Aberrations

The systematic errors are generally called aberrations; they differ from random errors in that in principle they can be calculated for any particular experimental arrangement and the observations corrected for them, leaving only the random error. In practice, of course, the calculation may be difficult. Aberrations can be divided broadly into two classes: (i) geometrical and (ii) physical. The geometrical aberrations are those that depend on the dimensions of the source, specimen, and detector (or of the slits that limit their effective dimensions). In angle-dispersive techniques, the physical aberrations depend on the intensity distribution in the range of wavelengths used, and in both angle- and energy-dispersive techniques they depend on the response characteristics of the detector and associated circuits.

The aberrations shift and distort the diffraction maxima. The study of their effects can be divided into four stages, corresponding to four levels of mathematical difficulty, and the stage to which it is necessary to carry the calculation depends on the purpose in view and the identifiable feature (Subsection 5.2.2.1) of the wavelength distribution that it is intended to adopt as a measure of the position of the line profile. The three usual features are:

- (i) the centroid (centre of gravity, mean, average) of the wavelength distribution;
- (ii) the peak (mode, maximum); and
- (iii) the best overall fit between the observed and the synthesized line profile.

The first of these, the centroid, requires only the first stage of the calculation for the geometrical aberrations and the first and second for the physical; the second, the peak, logically requires all four stages, but approximations can be obtained at the second stage; and the third, the best overall fit, requires all four stages.

The first stage of the calculation is the determination of the effect of the aberration on the centroid of the diffraction maximum, and ordinarily this gives rise to no insurmountable difficulty (Spencer, 1931, 1935, 1937, 1939, 1941, 1949; Wilson, 1950; Ladell, Parrish & Taylor, 1959; Pike & Wilson, 1959). It is all that is required for the correction of centroid positions for geometrical aberrations, which should be strictly additive. There is some limitation for physical aberrations (Edwards & Toman, 1970; Wilson, 1970*b*).

The second stage is the calculation of the mean-square broadening (variance). This can be used to obtain a reasonable approximation to the correction of peak positions over a wide range of Bragg angle (Wilson, 1961; Gale, 1963, 1968). To this approximation, the position of the observed peak is given by

$$(2\theta)_{\text{obs}} = (2\theta)_{\text{true}} + \langle \Delta(2\theta) \rangle + WI'''/2I'', \quad (5.2.3.1)$$

where  $\langle \Delta(2\theta) \rangle$  is the centroid and  $W$  the variance of the geometrical aberrations and  $I''$  and  $I'''$  are second and third derivatives of the observed line profile evaluated at its maximum. The physical aberrations of the centroid depend on the variance of the part of the wavelength distribution used in

determining the centroid (Wilson, 1958, 1963; Wilson & Delf, 1961). Those of the peak depend on the ratio of the peak intensity  $I$  to its second derivative  $I''$  (Wilson, 1961, 1963, 1965*c*).

Often an aberration can be expressed in the form

$$\Delta(2\theta) = KF(2\theta), \quad (5.2.3.2)$$

where the function  $F$  gives the angular variation of the aberration and  $K$  depends only on dimensions *etc.* that are fixed for a particular experiment but whose actual measurement is too difficult or tedious. The constant  $K$  can then be treated along with the lattice parameters as an adjustable parameter in least-squares refinement (analytical extrapolation; see Subsection 5.2.3.2).

The third stage is the calculation of the line profile corresponding to each geometrical aberration. These aberration profiles can be combined by convolution (folding), either directly or by Fourier methods, and, in the fourth stage, the combined aberration profile can be convoluted with the emission profile of the X-ray source (or the emission profile as trimmed by a monochromator, pulse-height analyser, filter *etc.*) and with the diffraction profile corresponding to the state of strain, crystallite size, *etc.* of the specimen. This calculation of the composite line profile would be a necessary preliminary to an exact use of peak positions or of overall-profile fitting in lattice-parameter determination.

Such calculations were proposed many years ago (for example, by Alexander, 1948, 1950, 1953, 1954), and have been used by Beu and co-workers (see Section 5.2.9), and also by Boom and Smits (Boom & Smits, 1965; Boom, 1966). With the development of more powerful computer methods, such calculations can now be carried out routinely (*e.g.* Cheary & Coelho, 1992, 1994; Kogan & Kupriyanov, 1992; Timmers, Delhez, Tuinstra & Peerdeman, 1992). However, not all the relevant instrumental parameters can in general be determined with sufficient accuracy and overall instrumental line profiles are normally obtained by means of a suitable standard material, for which sample broadening is negligible (Section 5.2.12). There is, however, a related common approach, empirical rather than fundamental, based on the proposal of Rietveld (1967, 1969). Its use in structure determination is treated in detail in Chapter 8.6, and its use in lattice-parameter determination in Section 5.2.6. There seems to be no detailed published study of the accuracy attainable for lattice parameters, but the estimated standard deviations quoted (see, for example, Young, 1988) are comparable with those obtained for simpler structures giving resolved reflections.

#### 5.2.3.2. Extrapolation, graphical and analytical

Equation (5.2.1.4) indicates that for a given error in  $\theta$  the fractional error in the spacing  $d$  approaches zero as  $\theta$  approaches  $90^\circ$ . The errors in  $\theta$  – expressed as  $\Delta(2\theta) = KF(2\theta)$  in (5.2.3.2) – arising from any specified aberration may increase as  $\theta$  increases, but ordinarily this increase is insufficient to outweigh the effect of the  $\cot \theta$  factor. In the simple cubic case, one can write

$$a_{\text{true}} = [(h^2 + k^2 + l^2)^{1/2} \lambda / 2 \sin \theta] + KF(\theta), \quad (5.2.3.3)$$

where  $K$  is a proportionality factor and  $F(\theta)$  represents the angular variation of the systematic errors in the lattice parameter. The functions  $F$  in (5.2.3.2) and (5.2.3.3) are not exactly the same; they are transformed into one another by the use of (5.2.1.4). Functions suitable for different experimental arrangements are quoted in the following sections; see, for example, equation (5.2.8.1) for the Debye–Scherrer camera and Tables 5.2.4.1 and 5.2.7.1 for diffractometers. Simple graphical