

5.2. X-ray diffraction methods: polycrystalline

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5.2.1. Introduction

5.2.1.1. The techniques available

X-ray powder methods for the accurate determination of lattice parameters can be divided broadly into four groups, depending on the type of dispersion, type of source, and the type of detector. They are:

(1) angle-dispersive: diffractometer methods, conventional tube source (Section 2.3.2);

(2) angle-dispersive: diffractometer methods, synchrotron sources (Subsections 2.3.3.1, 2.3.3.2);

(3) energy-dispersive: diffractometer methods (Subsection 2.3.3.3, Chapter 2.5);

(4) angle-dispersive: camera methods (Section 2.3.4).

The geometry, advantages, and some practical details of the methods are given in the sections whose numbers are given in parentheses. The techniques will be discussed in the above order in Sections 5.2.4–5.2.8. More details of systematic errors in diffractometry are given in Wilson (1963, 1965c, 1974). Some general points on checking precision and accuracy were made in Chapter 5.1. Many of them are treated in greater detail in Section 2.3.5, and are recapitulated in Section 5.2.13.

The technique of choice will depend on the accuracy required and on the nature and quantity of the material available. At present, the technique most frequently used for the purposes of this chapter is angle-dispersive diffractometry with a conventional tube source (1). Angle-dispersive diffractometry with synchrotron radiation (2) is capable of greater precision and accuracy, but access to the synchrotron sources is cumbersome and may involve long waiting periods. Energy-dispersive methods (3) would ordinarily be adopted only if the required environmental conditions (high or low temperatures, high pressures, ...) can be achieved most readily by means of a fixed-angle diffractometer. Camera methods (4) are adaptable to small quantities of material, but microdiffractometers (Subsection 2.3.1.5) can be used with similar or even smaller quantities.

5.2.1.2. Errors and aberrations: general discussion

The relation between the lattice spacing d , the angle of incidence (Bragg angle) θ , and the wavelength λ is Bragg's law:

$$\lambda = 2d \sin \theta. \quad (5.2.1.1)$$

The lattice spacing d is related to the lattice parameters a , b , c , α , β , γ and the indices of reflection h , k , l . In the simple case of cubic crystals, the relation is

$$d^{-2} = a^{-2}(h^2 + k^2 + l^2), \quad (5.2.1.2)$$

where a is the single lattice parameter. The general relation is

$$d^{-2} = G^{-1}(abc)^{-2}[A(hbc)^2 + B(kca)^2 + C(lab)^2 + 2abc(Dkla + Elhb + Fhkc)], \quad (5.2.1.3)$$

where a , b , c are the edges of the unit cell, and A , ..., G are the functions of the angles of the unit cell given in Table 5.2.1.1.

Differentiation of (5.2.1.1) shows that the errors in the measurement of d are related to the errors in the measurement of λ and θ by the equation

$$(\Delta d)/d = (\Delta \lambda)/\lambda - \cot \theta (\Delta \theta). \quad (5.2.1.4)$$

Wavelength and related problems are discussed in Section 5.2.2 and geometrical and other aberration problems in Section 5.2.3.

5.2.1.3. Errors of the Bragg angle

The error in the Bragg angle, $\Delta\theta$, will ordinarily consist of both random and systematic components. The random components (as the name implies) have an expected value zero, but the systematic errors will affect all measurements consistently to a greater or lesser extent. The systematic errors may be, and usually are, functions of θ and/or λ . Such errors would ordinarily reveal themselves in checks of internal consistency: the values of the apparent lattice parameter, plotted as a function of θ , would show a systematic drift, not a random scatter. The success or otherwise of attempts to eliminate or account for them would be subject to statistical tests (Section 5.2.9 and Chapter 8.5). There is an exception to the 'ordinarily'; if the variation of $\Delta\theta$ with θ happens to be of the form $K \tan \theta$, where K does not depend on θ either explicitly or through λ , the resultant fractional error $(\Delta d)/d$ is a constant, and would not be revealed either by systematic drift of the apparent lattice parameter with θ or by statistical tests.

5.2.1.4. Bragg angle: operational definitions

The Bragg angles are determined from the observations by a series of operations that are often quite complex.

For film cameras of diameter 57.3 or 114.6 mm, a simple measurement with a millimetre scale gives θ in degrees ($1 \text{ mm} = 1$ or 0.5°). This determination is crude, and ordinarily the lines on the film would be measured with a low-power travelling microscope or a densitometer. The effective camera diameter is found from measurements of fiducial marks imprinted on the film, or by use of the Straumanis film mounting. References to detailed descriptions are given in Section 2.3.4.

For Bragg–Brentano (Parrish) and Seemann–Bohlin diffractometers, rate-meter measurements with strip-chart recordings have time-constant errors, and precision measurements require step-scanning (Subsection 2.3.3.5). The data may be analysed to give one or more of the following measures of position:

(a) The centroid of the reflection (Subsection 2.3.3.3).

(b) The peak of the reflection (Subsection 2.3.3.3). The extrapolated mid-point of chords is a kind of modified peak determination, but the best method of locating peaks so far in operation is that called 'peak search' (Subsection 2.3.3.7).

(c) Profile fitting (Subsection 2.3.3.8). In principle, profile fitting could give the Bragg angle corresponding to any desired feature of the diffraction maximum (centroid peak, median, ...), but it has been used in practice mainly for locating the Bragg angle corresponding to the peak.

As usual, it is necessary to distinguish between the precision (reproducibility) of a measurement and its accuracy (extent to which it is affected by systematic errors). In principle, it does not matter if the Bragg angle obtained by any of the above operations is affected by systematic errors, as these can be calculated and allowed for, as described in the following paragraphs. The most precise methods are the peak-search and individual profile-fitting computer procedures. They are routinely capable of a precision of about $0.001^\circ(2\theta)$ for reasonably sharp reflections, and are free from the subjective effects that may influence, for example, film measurements or the graphical extrapolation of the mid-points of chords. As well as a measure of the peak position, the peak-search procedure gives a measure of the peak intensity, and the

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, Travennier & 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 λ , so that *relative* spacings can be determined without regard to the accuracy of λ , 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 θ the fractional error in the spacing d approaches zero as θ approaches 90° . The errors in θ – expressed as $\Delta(2\theta) = KF(2\theta)$ in (5.2.3.2) – arising from any specified aberration may increase as θ 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

5. DETERMINATION OF LATTICE PARAMETERS

Table 5.2.4.1. Centroid displacement $\langle \Delta\theta/\theta \rangle$ and variance W of certain aberrations of an angle-dispersive diffractometer; for references see Wilson (1963, 1965c, 1974) and Gillham (1971)

For the Seemann–Bohlin arrangement, S and R are given by equations (5.2.4.1) and (5.2.4.2); for the symmetrical arrangement, they are equal to R_0 . Other notation is explained at the end of the table.

Aberration	$\langle \Delta(2\theta) \rangle$	W
Zero-angle calibration	Constant	0
Specimen displacement	$-s\{R^{-1} \cos(2\theta - \varphi) + S^{-1} \cos \varphi\}$	0
Specimen transparency Thick specimen	$-\sin 2\varphi/\mu(R + S)$	$\sin^2 2\varphi/\mu^2(R + S)^2$
Thin specimen	See Wilson (1974, p. 547)	
2:1 mis-setting	Zero if centroid of illuminated area is centred	$\beta^2 A^2 [R^{-1} \cos(2\theta - \varphi) + S^{-1} \cos \varphi]^2 / 3$
Inclination of plane of specimen to axis of rotation	Zero if centroid of illuminated area on equator of specimen	$\gamma^2 h^2 [R^{-1} \cos(2\theta - \varphi) + S^{-1} \cos \varphi]^2 / 3$ for uniform illumination
Flat specimen	$-A^2 \sin 2\theta / 3RS$	$4A^4 \sin^2 2\theta / 45 R^2 S^2$
Focal-line width	Small	$\sim f_1^2 / 12S^2$
Receiving-slit width	Small	$\sim r_1^2 / 12R^2$
Interaction terms	Small if adjustment reasonably good	See Wilson (1963, 1974)
Axial divergence No Soller slits, source, specimen and receiver equal	$-h^2[(S^{-2} + R^{-2}) \cot 2\theta + (RS)^{-1} \operatorname{cosec} 2\theta] / 3$	$h^4 \{ [7S^{-4} + 2(RS)^{-2} + 7R^{-4}] \cot^2 2\theta + 14(RS)^{-1} (S^{-2} + R^{-2}) \cot 2\theta \operatorname{cosec} 2\theta + 19(RS)^{-2} \operatorname{cosec}^2 2\theta \} / 45$
Narrow Soller slits One set in incident beam	$-\Delta^2 / 12 + h^2 / 3R^2 \cot 2\theta$	$7[\Delta^4 / 720 + h^4 / 45R^2] \cot^2 2\theta + h^2 \operatorname{cosec}^2 2\theta / 9R^2$
One set in diffracted beam	Replace R by S in the above	
Two sets	$-(\Delta^2 \cot 2\theta) / 6$	$\Delta^4 (10 + 17 \cot^2 2\theta) / 360$
Wide Soller slits	Complex. See Pike (1957), Langford & Wilson (1962), Wilson (1963, 1974), and Gillham (1971)	
Refraction	$\sim -2\delta \tan \theta$	$\sim \delta^2 [-6 \ln(\Delta/2) + 25] / 4\mu p$
Physical aberrations	See Wilson (1963, 1965c, 1970a, 1974) and Gillham & King (1972)	

Notation: $2A$ = illuminated length of specimen; β = angle of equatorial mis-setting of specimen; γ = angle of inclination of plane of specimen to axis of rotation; Δ = angular aperture of Soller slits; μ = linear absorption coefficient of specimen; r_1 = width of receiving slit (varies with θ in some designs of diffractometer); s = specimen-surface displacement; f_1 = projected width of focal line; h = half height of focal line, specimen, and receiving slit, taken as equal; $1 - \delta$ = index of refraction; p = effective particle size.

extrapolation is quick and easy for cubic substances, and by the use of successive approximations it can be applied to hexagonal (Wilson & Lipson, 1941), tetragonal, and even orthorhombic materials. It is, however, very cumbersome for non-cubic substances, and impracticable if the symmetry is less than orthorhombic.

Analytic extrapolation seems to have been first used by Cohen (1936a,b). It is now usual even in the cubic case: programs are often included in the software accompanying powder diffractometers, and many others are available separately. Some

programs that are frequently referred to are described by Appleman & Evans (1973), Mighell, Hubbard & Stalick (1981), and Ferguson, Rogerson, Wolstenholme, Hughes & Huyton (1987); for a comparison, see Kelly (1988). If the precision warrants it, the single function $KF(\theta)$ may be replaced by a sum of functions $K_i F_i(\theta)$, one for each of the larger aberrations listed in Tables 5.2.4.1, 5.2.7.1, and 5.2.8.1. Two – the zero error and a function corresponding to specimen-surface displacement and transparency – must be used routinely; one or two more may be added if the precision warrants it.

5.2.4. Angle-dispersive diffractometer methods: conventional sources

The symmetrical Bragg–Brentano (Parrish) and the Seemann–Bohlin angle-dispersive diffractometers are fully described in Chapter 2.3. The centroid and peak displacements and the variances of the aberrations of the symmetrical diffractometer have been collected by Wilson (1961, 1963, 1965*c*, 1970*a*, 1974). For the Seemann–Bohlin type, they are collected in Table 5.2.4.1, mainly from Wilson (1974). They are expressed in inverse powers of the source–specimen distance S and the specimen–detector distance R , and tend to be larger for the Seemann–Bohlin arrangement than for the symmetrical arrangement. For the latter, S and R are constant and equal to the radius, say R_0 , of the diffractometer, whereas, for the former,

$$S = 2R_0 \sin \varphi \quad (5.2.4.1)$$

and

$$R = 2R_0 \sin (2\theta - \varphi), \quad (5.2.4.2)$$

where φ is the constant angle that the incident X-rays make with the specimen surface. In the Seemann–Bohlin case, S will be constant at a value depending on the choice of angle φ , but usually less than R_0 , and R will vary with 2θ , approaching zero as θ approaches $\varphi/2$. There will thus be a range of 2θ for which the Seemann–Bohlin aberrations containing R become very large. Mack & Parrish (1967) have confirmed experimentally the expected differences in favour of the symmetrical arrangement for general use, even though the effective equatorial divergence ('flat-specimen error') can be greatly reduced by curving the specimen appropriately in the Seemann–Bohlin arrangement. The aberrations for the symmetrical arrangement are found by putting $R = S = R_0$, $\varphi = \theta$ in the expression in Table 5.2.4.1; they are given explicitly by Wilson (1963, 1965*c*, 1970*a*).

5.2.5. Angle-dispersive diffractometer methods: synchrotron sources

Lattice-parameter determination with synchrotron radiation has a number of advantages over focusing methods (Parrish, Hart, Huang, & Bellotto, 1987; Parrish, 1988; Huang, 1988). The $K\alpha$ -doublet problem does not arise; the symmetrical single profiles greatly simplify the accurate angular measurement of peaks. The higher intensity and low uniform background out to the highest θ values give a higher statistical counting precision, an important factor in accurate measurements. Short wavelengths (0.65 to 1.4 Å) can be used to increase greatly the number of reflections without compromising the accuracy of the peak measurements. If desired, the patterns can be recorded with two or more wavelengths of about the same intensity, instead of being confined to the $K\alpha$ and $K\beta$ lines (Popović, 1973). The large specimen-surface-displacement and flat-specimen errors associated with most other methods do not occur, so that systematic errors are small or absent. The wavelength can be selected to obtain the desired dispersion, to avoid fluorescence, and to reduce specimen transparency.

The reflections are virtually symmetrical narrow peaks (Subsection 2.3.2.1), with widths of the order of 0.02 – $0.04^\circ (2\theta)$ when an analysing crystal is used instead of a receiving slit, and of the order of 0.05° when a long Soller slit is used as a collimator. These increase with increasing 2θ because of wavelength dispersion and small particle size. The angular positions of the peaks can be determined with high precision by the use of profile-fitting or peak-search measurements, and the only significant geometrical aberration is axial divergence.

There are no lines in the synchrotron-radiation spectrum, and this creates the problem of determining the wavelength selected by the monochromator. If a highly accurate diffractometer were used for the monochromator and the monochromator d spacing were known accurately, the wavelength could be determined directly from θ_M . The angular accuracy of the diffractometer would have to be 0.0002° to achieve an accuracy of one part in 10^6 in the wavelength at $\lambda = 1.54$ Å.

In practice, the wavelengths can often be determined by scanning the absorption edges of elements in the specimen or a metal foil placed in the beam. There is no feature of the absorption edge that is accurately measurable, and the wavelengths are usually listed to one or two decimal places fewer than those for the emission lines.

The wavelength problem could be avoided by using the ratio of the lattice parameter of the specimen to that of an accurately known standard measured with the same experimental conditions (Parrish *et al.*, 1987). The standard may be mixed with the specimen or measured separately, as there is no specimen-surface displacement shift. Mixing reduces the intensity of both patterns and worsens the peak-to-background ratio. The limitation is the accuracy of the lattice parameter of the standard. The only widely available one is the National Institute of Standards and Technology [NIST, formerly National Bureau of Standards (NBS)] silicon powder 640b (see Section 5.2.10). This accuracy may not be sufficient for measuring doping levels, stoichiometry, and similar analyses now possible with synchrotron-radiation methods and the wavelength is normally determined directly from data for a standard whose lattice parameter is known with a high degree of precision, such as NIST SRM silicon 640b.

The most promising method is to use a high-quality single-crystal plate of float-zoned oxygen-free silicon, now widely available. Its lattice parameter is known to about one part in 10^7 (Hart, 1981), which is much higher accuracy than that of the published lists of X-ray wavelengths. Several orders of reflection (for example 111, 333, 444) should be used to improve the accuracy of the measurement.

Data are usually collected by step-scanning with selected constant angular increments and count times. To avoid interruptions due to refilling of the synchrotron ring, it is better to make a number of short runs rather than one long one. The data can then be added together and treated as a single data set. A shift in the orbit may cause a change in the wavelength reflected by the monochromator, and it is important to be aware of this in accurate lattice-parameter determination. The peaks are narrow, and the angle increments should be small enough to produce at least a dozen points in each peak. In practice, the scans may be made to cover a range of one to two half-widths (full widths at half height) on both sides of the peak, with increments of about 0.1 to 0.2 of the half-width, in order to record a sufficient number of data points for accurate profile fitting. The count time, which depends on the intensity, should be checked by determining the goodness-of-fit of the calculated profiles and the experimental points (Subsection 2.3.3.8 and Chapters 8.4 and 8.6).

The lower-angle peaks generally have higher intensities and are therefore preferred to the higher-angle peaks because of the better counting statistics. If the diffractometer can scan to negative angles, the number of strong peaks can be doubled by measuring the reflections on both sides of the zero position. The specimen can be used in either reflection or transmission, but reflection generally gives higher intensity. The lattice parameters are determined by a least-squares analysis of the peak angles determined by profile fitting, and it is therefore necessary to measure a sufficient number of reflections to give a statistically

5. DETERMINATION OF LATTICE PARAMETERS

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 $\lambda = 1 \text{ \AA}$ 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-Voigt 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.

5.2. X-RAY DIFFRACTION METHODS: POLYCRYSTALLINE

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	$-R^{-2} \operatorname{cosec}^2 \theta [X^2 \cos 2\theta + 4Y^2 \cos^2 \theta + Z^2 \cos 2\theta]/24$	$R^{-4} \operatorname{cosec}^4 \theta [X^4 \cos^2 2\theta + 4Y^4 (1 + \cos 2\theta)^2 + Z^4 \cos^2 2\theta + 5X^2 Z^2 + 5Y^2 (X^2 + Z^2) \times (1 + \cos 2\theta)^2]/720$
Refraction*	Probably negligible at the present stage of technique	
Response variations Centroid	$[Vf' + f''(\mu_3/2 - V^2 f'/f)]/Ef$?
Peak	$-f'I/EfI''$?
Interaction of Lorentz <i>etc.</i> 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-resolution 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.

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 (1945a,b)]:

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

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

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

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

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

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

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

(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

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

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://srncatalog.nist.gov>.

5.2. X-RAY DIFFRACTION METHODS: POLYCRYSTALLINE

 Table 5.2.10.1. NIST values for silicon standards ($\lambda = 1.5405929 \text{ \AA}$, $T = 298 \text{ K}$ for 640, 640a and 640b, $T = 295.6 \text{ K}$ for 640c, $a_0 \pm 0.000035 \text{ \AA}$, no refraction correction)

Standard	Year issued	a_0 (Å)	Cu $K\alpha_1$	
			111 (2θ)	444 (2θ)
640	1974*	5.43086	28.4427	158.6382
640a	1982†	5.430806	28.4430	158.6443
640b	1987	5.430922	28.4424	158.6315
640c	2000	5.4311946	28.4410	158.6031

*Hubbard, Swanson & Mauer (1975). † Hubbard (1983).

standards are given by Hubbard (1983) and Wong-Ng & Hubbard (1987).

The current silicon-powder standard for 2θ calibration is Standard Reference Material (hereinafter abbreviated SRM) 640c; SRM 640, SRM 640a and SRM 640b are no longer available, but data for all four are listed in Table 5.2.10.1 for the use of workers who may still have stocks of the earlier standards. The median particle size (mass-weighted distribution) is about $5 \mu\text{m}$, and 95% of the particles are $< 10 \mu\text{m}$. There is a wide range of particle sizes in SRM 640, and sieving is necessary to remove the larger particles. The agreement between SRM's 640 and 640a and between 640 and 640b is one part in 10^{-5} , and between 640a and 640b is two parts in 10^{-5} . The accuracy is given as 3.5×10^{-5} for each. All were calculated by the use of the Deslattes & Henins (1973) Cu $K\alpha_1$ wavelength of 1.5405981 \AA , without refraction correction, and corrected to 298 K . Because this wavelength was later found to have a systematic error (see Section 4.2.2), and a more accurate value, $1.5405929(5) \text{ \AA}$ (see Table 4.2.2.1), is now available, this wavelength was used for SRM 640c, with the temperature adjusted to 295.6 K . The data for the earlier SRMs have also been adjusted to reflect this more accurate wavelength.

Table 5.2.10.2 lists the reflection angles for silicon 640c, silver and tungsten calculated from the adjusted NIST lattice parameters and the Table 4.2.2.1 value for the Cu $K\alpha_1$ wavelength. Table 5.2.10.3 lists the reflection angles of silicon 640c calculated from the Table 4.2.2.1 wavelengths for Mo $K\alpha_1$, Cr $K\alpha_1$ and other wavelengths selected for synchrotron radiation users. The high-angle reflections of silicon for Mo $K\alpha_1$ are listed in Table 5.2.10.4. NIST does not provide a tungsten standard, but reflection angles calculated from $a = 3.16523(4) \text{ \AA}$ at 298 K for Cu $K\alpha_1 = 1.5405929 \text{ \AA}$ are given in Table 5.2.10.2 and in Table 5.2.10.5 for a number of other wavelengths.

For calibration at small diffraction angles, NIST provides fluorophlogopite, a synthetic mica, as SRM 675. The (001) lattice spacing, adjusted for the revised wavelength of Cu $K\alpha_1$, is $9.98101(7) \text{ \AA}$ at 298 K . Table 5.2.10.6 lists the diffraction angles for Cu $K\alpha_1$. NIST advises mixing it with silicon because the higher-angle reflections may be in error because of specimen transparency. SRM 675 was purposely prepared as large particles (up to $75 \mu\text{m}$) to encourage preferred orientation of the mica flakes; only the 00l reflections are then observed. The first reflection with Cu $K\alpha_1$ radiation for SRM 675 occurs at $8.853^\circ(2\theta)$ (Table 5.2.10.6) and a material that extends the coverage of NIST SRMs down to very low angles is silver behenate (Huang, Toraya, Blanton & Wu, 1993). The long spacing for this material, obtained with synchrotron radiation and by using SRM 640a as an internal standard, is $d_{001} = 58.380(3) \text{ \AA}$ and, for Cu $K\alpha_1$ radiation, there are 13

 Table 5.2.10.2. Reflection angles ($^\circ$) for tungsten, silver, and silicon ($\lambda = 1.5405929 \text{ \AA}$, $T = 298 \text{ K}$ for tungsten and silver, $T = 295.6 \text{ K}$ for silicon)

hkl	Tungsten	Silver	Silicon
	$a_0 = 3.16523(4) \text{ \AA}$	$a_0 = 4.08650(2) \text{ \AA}$	$a_0 = 5.431195(9) \text{ \AA}$ (SRM 640c)
110	40.262		
111		38.112	28.441
200	58.251	44.295	
211	73.184		
220	86.996	64.437	47.300
310	100.632		
311		77.390	56.120
222	114.923	81.533	
321	131.171		
400	153.535	97.875	69.126
331		110.499	76.372
420		114.914	
422		134.871	88.025
511/333		156.737	94.947
440			106.701
531			114.084
620			127.534
533			136.880
444			158.603

well defined and evenly spaced 00l reflections in the range 1.5 to $20^\circ(2\theta)$ (Table 5.2.10.7). This material is suitable for use as an external or an internal low-angle calibration standard for the analysis of materials with large unit-cell dimensions and modulated multilayers with large layer periodicity.

Although the reflection angles are given to three decimal places in the tables in this section, the accuracy is lower by an amount that is not known with certainty. The lower accuracy arises from three factors: uncertainties in the lattice parameters of the W and Ag internal standards, the experimental precision, and the methods used. The wavelength given in Table 4.2.2.1 is far more accurate than these factors. The tables can probably be used to two places of decimals, the 2θ errors increasing with increasing 2θ .

In using an external standard for calibrating an instrument (without a wide receiving slit), it is essential to minimize specimen-surface displacement, which shifts the measured position of the reflection (Subsection 5.2.3.1). The amount of the shift and even its direction may vary when the specimen is remounted, and it is advisable to make several measurements after removal and replacement, in order to determine the degree of reproducibility. Specimen transparency is equivalent to a variable specimen-surface displacement, since the effective depth of penetration varies with the angle of incidence of the beam. The maximum shift occurs at 2θ equal to 90° , and it vanishes at 0 and 180° . For example, for silicon, the linear absorption coefficient is 133 cm^{-1} for $\lambda = 1.54 \text{ \AA}$ and 15 cm^{-1} for 0.7 \AA , shifting the 422 reflection by -0.01° at 88° and -0.05° at 37° , respectively. It should be noted that SRM silicon 640b, as supplied by NIST, exhibits measurable sample broadening (van Berkum, Sprong, de Keijser, Delhez & Sonneveld, 1995) and is thus not suitable for determining instrumental line profiles.

5. DETERMINATION OF LATTICE PARAMETERS

Table 5.2.10.3. Silicon standard reflection angles ($^{\circ}$) (NIST SRM 640c, $a_0 = 5.431195 \text{ \AA}$, $T = 295.6 \text{ K}$)

$h \ k \ l$	$d \text{ (\AA)}$	I	Mo $K\alpha_1$ 0.709317 \AA	1.000000 \AA	1.250000 \AA	1.500000 \AA	1.750000 \AA	Cr $K\alpha_1$ 2.289746 \AA
1 1 1	3.13570	100.0	12.988	18.350	22.994	27.676	32.406	42.829
2 2 0	1.92022	71.1	21.287	30.186	37.990	45.981	54.217	73.202
3 1 1	1.63757	43.5	25.016	35.556	44.873	54.516	64.597	88.714
4 0 0	1.35780	11.8	30.283	43.215	54.813	67.059	80.245	114.955
3 3 1	1.24600	17.4	33.074	47.317	60.213	74.016	89.215	133.514
4 2 2	1.10864	22.3	37.314	53.616	68.635	85.142	104.232	
5 1 1]	1.04523	8.7	39.670	57.157	73.447	91.704	113.678	
3 3 3]	1.04523	2.9	39.670	57.157	73.447	91.704	113.678	
4 4 0	0.96011	6.0	43.356	62.768	81.229	102.734	131.386	
5 3 1	0.91804	9.8	45.452	66.000	85.812	109.563	144.772	
6 2 0	0.85871	7.1	48.789	71.221	93.411	121.713		
5 3 3	0.82825	2.9	50.707	74.268	97.981	129.788		
4 4 4	0.78393	1.5	53.797	79.258	105.739	146.162		
7 1 1]	0.76052	1.9	55.594	82.211	110.532	160.918		
5 5 1]	0.76052	1.9	55.594	82.211	110.532	160.918		
6 4 2	0.72577	5.7	58.506	87.090	118.893			
7 3 1]	0.70708	2.4	60.209	90.004	124.237			
5 5 3]	0.70708	1.2	60.209	90.004	124.237			
8 0 0	0.67890	0.5	62.987	94.866	134.030			
7 3 3	0.66353	0.8	64.620	97.797	140.757			
6 6 0]	0.64007	0.7	67.297	102.735	155.085			
8 2 2]	0.64007	1.3	67.297	102.735	155.085			
7 5 1]	0.62714	1.7	68.876	105.740	170.531			
5 5 5]	0.62714	0.2	68.876	105.740	170.531			
8 4 0	0.60723	0.9	71.473	110.855				
9 1 1]	0.59615	0.4	73.013	114.009				
7 5 3]	0.59615	0.8	73.013	114.009				
6 6 4	0.57897	0.7	75.551	119.447				
9 3 1	0.56934	0.6	77.061	122.854				
8 4 4	0.55432	0.5	79.555	128.846				
9 3 3]	0.54586	0.2	81.042	132.692				
7 7 1]	0.54586	0.2	81.042	132.692				
7 5 5]	0.54586	0.2	81.042	132.692				
10 2 0]	0.53257	0.4	83.509	139.717				
8 6 2]	0.53257	0.8	83.509	139.717				
9 5 1]	0.52505	0.4	84.982	144.460				
7 7 3]	0.52505	0.2	84.982	144.460				
9 5 3	0.50646	0.3	88.897	161.678				
10 4 2	0.49580	0.5	91.340					
11 1 1]	0.48971	0.1	92.808					
7 7 5]	0.48971	0.1	92.808					
8 8 0	0.48005	0.1	95.258					
11 3 1]	0.47453	0.2	96.729					
9 7 1]	0.47453	0.2	96.729					
9 5 5]	0.47453	0.1	96.729					

5.2.11. Intensity standards

The measurement of intensity falls within the scope of Parts 6 and 7. However, powder methods are much used in quantitative analysis, and the National Institute of Standards and Technology provides five standards for use as internal standards for this purpose and for checking the accuracy of diffractometer and camera intensity measurements. The five materials, certified as SRM 674, are $\alpha\text{-Al}_2\text{O}_3$ (corundum), ZnO, TiO_2 (rutile), Cr_2O_3 , and CeO_2 . Table 5.2.11.1, taken from the NIST certificate, is a

partial list of pertinent data. The lattice parameters have an uncertainty of 3 parts in 10^5 , which must be increased by a factor of 2 or 3 because of uncertainty in internal standards and thermal expansion. The five materials have a wide range of absorption coefficient and the crystallite size (about $2 \mu\text{m}$) causes a small profile broadening. The table gives the intensities of the second- and third-strongest lines relative to the strongest = 100, and the final column gives the ratio of the strongest peak to the strongest peak of Al_2O_3 .

5.2. X-RAY DIFFRACTION METHODS: POLYCRYSTALLINE

 Table 5.2.10.4. Silicon standard high reflection angles ($^{\circ}$) (NIST SRM 640c, $a_0 = 5.431195 \text{ \AA}$, $T = 295.6 \text{ K}$, $\lambda = 0.709317 \text{ \AA}$)

h	k	l	d (\AA)	2θ	h	k	l	d (\AA)	2θ
10	6	0	0.46572	99.198	9	9	5	0.39717	126.497
8	6	6	0.46572	99.198	8	8	8	0.39196	129.600
11	3	3	0.46067	100.686	13	5	1	0.38894	131.530
9	7	3	0.46067	100.686	11	7	5	0.38894	131.530
12	0	0	0.45260	103.183	10	10	0	0.38404	134.882
8	8	4	0.45260	103.183	10	8	6	0.38404	134.882
11	5	1	0.44796	104.694	14	2	0	0.38404	134.882
7	7	7	0.44796	104.694	13	5	3	0.38120	136.990
12	2	2	0.44053	107.235	11	9	1	0.38120	136.990
10	6	4	0.44053	107.235	12	8	0	0.37659	140.703
11	5	3	0.43624	108.777	11	9	3	0.37390	143.079
9	7	5	0.43624	108.777	9	9	7	0.37390	143.079
12	4	0	0.42937	111.378	12	6	6	0.36955	147.363
9	9	1	0.42540	112.961	10	10	4	0.36955	147.363
10	8	2	0.41903	115.642	14	4	2	0.36955	147.363
9	9	3	0.41533	117.279	13	7	1	0.36701	150.191
11	7	1	0.41533	117.279	11	7	7	0.36701	150.191
11	5	5	0.41533	117.279	13	5	5	0.36701	150.191
13	1	1	0.41533	117.279	12	8	4	0.36289	155.551
12	4	4	0.40939	120.064	11	9	5	0.36048	159.376
11	7	3	0.40595	121.773	15	1	1	0.36048	159.376
13	3	1	0.40595	121.773	13	7	3	0.36048	159.376
9	7	7	0.40595	121.773	14	6	0	0.35658	168.113
12	6	2	0.40039	124.694					
13	3	3	0.39717	126.497					

5.2.12. Instrumental line-profile-shape standards

The need for standard reference materials to determine instrumental line profiles arose from the increased use in recent years of whole-pattern methods (Section 5.2.6) in several applications of powder diffraction. Instrumental line-profile standards are required to determine resolution, as a check that alignment has been optimized, or to compare the performance of different diffractometers, and to obtain sample contributions from observed data in line-profile analysis. Different standards may therefore be required if samples of interest do not have a high absorption coefficient for the radiation used.

In addition to the usual requirements for SRMs, suitable substances for instrument characterization clearly should not exhibit any measurable sample broadening, even when used with high-resolution diffractometers. Various materials were considered by the Technical Committee of the JCPDS-ICDD, in association with NIST, and lanthanum hexaboride [LaB_6 ; $a_0 = 4.15695(6) \text{ \AA}$ at $T = 299 \text{ K}$] was selected for use as an instrumental standard (Fawcett *et al.*, 1988). This was subsequently marketed by NIST as SRM 660 and it also serves as a line position standard. Other materials used as instrumental standards include BaF_2 (Louër & Langford, 1988) and KCl (Scardi, Lutterotti & Maistrelli, 1994). Both are low-cost materials, are available in large quantities, and can readily be annealed to minimize sample broadening. Although KCl introduces a measurable contribution to line breadth owing to sample transparency, it can be used to advantage for correcting data from materials having a similar absorption coefficient, such as many ceramics. van Berkum, Sprong, de Keijser, Delhez & Sonneveld (1995) selected a 5–10 μm size fraction from silicon SRM 640b, deposited about 1.5 Mg m^{-2} uniformly on a (510)-

oriented single-crystal silicon wafer and annealed the whole assemblage to produce an instrument line-profile standard. The resulting line-profile widths were found to be slightly less than for LaB_6 at angles below about $100^{\circ}(2\theta)$ with $\text{Cu K}\alpha$ radiation.

5.2.13. Factors determining accuracy

Many factors influencing accuracy in lattice-parameter determination have been mentioned in passing or discussed at length in this and previous chapters. This section attempts to summarize them and put them into perspective. Accuracy in the range of 1 to 0.1% can now be achieved routinely with average care. Increasing the accuracy to 0.01% requires considerable care in specimen preparation, data collection, instrument alignment, and calibration. The range 0.001 to 0.0001% is rarely reached and each determination is virtually a research project. The more important factors are:

- (1) Differentiation of the Bragg equation, as in (5.2.1.4), shows the advantage of using the highest-angle reflections; because of the $\cot\theta$ term, the error in Δd is smaller for a given angular accuracy $\Delta\theta$. The gain is not as great as one might expect at first, as the experimental accuracy of the back reflections is lowered because of (i) their lower intensity, (ii) their lower peak-to-background ratio, (iii) their broadening by wavelength dispersion and crystallite imperfection, and (iv) problems of overlapping.
- (2) The lower-angle reflections show the converse effects of (i) higher intensity, (ii) higher peak-to-background ratio, (iii) less broadening, and (iv) fewer problems of overlapping. In any particular case, a balance of advantage must be sought.

5. DETERMINATION OF LATTICE PARAMETERS

Table 5.2.10.5. Tungsten reflection angles ($^{\circ}$) ($a_0 = 3.16523 \text{ \AA}$, $T = 298 \text{ K}$)

$h \ k \ l$	$d \text{ (\AA)}$	I	Mo $K\alpha_1$ 0.709317 \AA	1.000000 \AA	1.250000 \AA	1.500000 \AA	1.750000 \AA	Cr $K\alpha_1$ 2.289746 \AA
1 1 0	2.23816	100.0	18.235	25.817	32.431	39.157	46.027	61.531
2 0 0	1.58262	18.1	25.899	36.834	46.521	56.575	67.130	92.672
2 1 1	1.29220	37.0	31.860	45.528	57.851	70.958	85.241	124.747
2 2 0	1.11908	11.1	36.953	53.076	67.903	84.164	102.868	
3 1 0	1.00093	14.4	41.505	59.938	77.279	97.059	121.896	
2 2 2	0.91372	3.3	45.679	66.352	86.316	110.333	146.518	
3 2 1	0.84594	14.2	49.574	72.464	95.262	124.894		
4 0 0	0.79131	1.3	53.255	78.376	104.339	142.810		
3 3 0]	0.74605	2.0	56.768	84.164	113.805			
4 1 1]	0.74605	4.0	56.768	84.164	113.805			
4 2 0	0.70777	3.1	60.145	89.893	124.027			
3 3 2	0.67483	2.5	63.411	95.621	135.687			
4 2 2	0.64610	2.0	66.586	101.406	150.632			
5 1 0]	0.62075	1.6	69.687	107.312				
4 3 1]	0.62075	3.2	69.687	107.312				
5 2 1	0.57789	2.2	75.717	119.815				
4 4 0	0.55954	0.5	78.668	126.656				
5 3 0]	0.54283	0.8	81.589	134.172				
4 3 3]	0.54283	0.8	81.589	134.172				
6 0 0]	0.52754	0.2	84.488	142.810				
4 4 2]	0.52754	0.7	84.488	142.810				
6 1 1]	0.51347	0.6	87.373	153.695				
5 3 2]	0.51347	1.2	87.373	153.695				
6 2 0	0.50047	0.5	90.251	175.042				
5 4 1	0.48841	1.0	93.129					
6 2 2	0.47718	0.4	96.016					
6 3 1	0.46669	0.8	98.919					
4 4 4	0.45686	0.1	101.845					
5 5 0]	0.44763	0.2	104.802					
7 1 0]	0.44763	0.3	104.802					
5 4 3]	0.44763	0.7	104.802					
6 4 0	0.43894	0.3	107.800					
5 5 2]	0.43073	0.3	110.851					
6 3 3]	0.43073	0.3	110.851					
7 2 1]	0.43073	0.6	110.851					
6 4 2	0.42297	0.6	113.963					
7 3 0	0.41562	0.3	117.150					
7 3 2]	0.40198	0.5	123.837					
6 5 1]	0.40198	0.5	123.837					
8 0 0	0.39565	0.1	127.376					
7 4 1]	0.38961	0.5	131.091					
8 1 1]	0.38961	0.3	131.091					
5 5 4]	0.38961	0.3	131.091					
8 2 0]	0.38384	0.3	135.029					
6 4 4]	0.38384	0.3	135.029					
6 5 3	0.37832	0.6	139.257					
8 2 2]	0.37303	0.3	143.877					
6 6 0]	0.37303	0.1	143.877					
7 4 3]	0.36795	0.6	149.106					
7 5 0]	0.36795	0.3	149.106					
8 3 1]	0.36795	0.6	149.106					
6 6 2	0.36308	0.4	155.271					
7 5 2	0.35839	1.1	163.450					

5.2. X-RAY DIFFRACTION METHODS: POLYCRYSTALLINE

Table 5.2.10.6. *Fluorophlogopite 00l standard reflection angles* [NIST SRM 675, $d(00l) = 9.98104(7) \text{ \AA}$, $T = 298 \text{ K}$, $\lambda = 1.5405929 \text{ \AA}$]

l	2θ ($^\circ$)
1	8.853
2	17.759
3	26.774
4	35.962
5	45.397
6	55.169
7	65.399
8	76.255
10	101.025
11	116.193
12	135.674

Table 5.2.10.7. *Silver behenate 00l standard reflection angles* [$d(00l) = 58.380(3) \text{ \AA}$, $\lambda = 1.5405929 \text{ \AA}$ (Huang, Toraya, Blanton & Wu, 1993)]

l	2θ ($^\circ$)
1	1.512
2	3.024
3	4.537
4	6.051
5	7.565
6	9.081
7	10.599
8	12.118
9	13.640
10	15.164
11	16.691
12	18.221
13	19.754

The forward reflections have been used in parallel-beam synchrotron-radiation lattice-parameter studies (Parrish *et al.*, 1987).

- (3) The profile shape has a strong influence on the accuracy of the angle measurement. The geometrical aberrations produce asymmetries that reduce the accuracy; the effects can be minimized by a proper selection of slit sizes. In most cases, it is inadvisable to use $K\beta$ radiation to avoid $K\alpha$ -doublet splitting, as the intensity is reduced by a factor of seven. Symmetrical profiles are obtained with parallel-beam optics, but it is usually necessary to use synchrotron radiation to achieve sufficient intensity.

- (4) The largest and commonest source of systematic error in focusing geometry is the specimen-surface displacement. Several remountings of the specimen in the diffractometer and measurement of some low-angle reflections may be helpful in determining and minimizing the error. This aberration does not occur in parallel-beam geometry unless a receiving slit is used.
- (5) The precision of the diffractometer gears (or the equivalent) may be the limiting factor in high-precision measurements. The use of an electromagnetic encoder mounted on the 2θ -output shaft can increase the precision considerably. It is not normally included in commercial diffractometers because of its cost, but it is essential for adequate accuracy when the 2θ angles must be determined to better than 0.001° . The various types of mechanical error have been described by Jenkins & Schreiner (1986).

The diffractometer must be carefully adjusted to avoid mechanical problems. The effect of backlash can be minimized by slewing beyond and then returning to the starting angle, and by always scanning in the same direction. It is essential to avoid over-tight worm-and-gear meshing, as it causes jerky rather than smooth movement.

- (6) The beam must be precisely centred, the slits and monochromator (if used) must be parallel to the line focus of the X-ray tube, and the scanning plane must be perpendicular to the line focus.
- (7) The use of standard specimens with accurately known lattice parameters (Section 5.2.10) and ideally free of line broadening is strongly recommended as a test of the overall precision of the instrumentation and method.
- (8) For a given total time available for an experiment, it is necessary to strike a balance between numerous short steps with short counting times and fewer longer steps with longer counting times. The former alternative may give a better definition of the line shape; the latter may give lower calculated standard uncertainties (formerly called estimated standard deviations) in any derived parameters. Obviously, the step length must be considerably shorter than the width of any feature of the profile that is considered to be of importance.
- (9) Least-squares refinement is discussed in Subsection 5.2.3.2. The programs and the methods of handling the data should be carefully checked, as various programs have been found to give slightly different values from the same experimental data (see, for example, JCPDS – International Centre for Diffraction Data, 1986; Kelly, 1988).
- (10) Specimen preparation is very important; the particle size should preferably be less than $10 \mu\text{m}$, and a flat smooth surface normal to the diffraction vector is essential. The linearity of the detector and the temperature of the

Table 5.2.11.1. *NIST intensity standards, SRM 674*

Standard	Crystal system	a_0 (\AA)	c_0 (\AA)	$I_{\text{rel}} \text{ hkl}$		$I_1/I_c(113)$
				2	3	
Al_2O_3 (corundum)	Trigonal	4.75893 (10)	12.9917 (7)	92.5 (26) 116	87.4 (19) 104	—
ZnO	Hexagonal	3.24981 (12)	5.20653 (13)	57.6 (11) 100	40.2 (14) 002	5.17 (13) 101
TiO_2 (rutile)	Tetragonal	4.59365 (10)	2.95874 (8)	56.9 (28) 211	44.0 (17) 101	3.39 (12) 110
Cr_2O_3	Trigonal	4.95916 (12)	13.5972 (6)	94.5 (22) 116	87.1 (23) 110	2.10 (5) 104
CeO_2	Cubic	5.41129 (8)	—	53.5 (20) 220	43.4 (23) 311	7.5 (2) 111

5. DETERMINATION OF LATTICE PARAMETERS

specimen must be properly controlled during the collection of the experimental data.

- (11) The accuracy of the 2θ measurements is directly dependent on the individual step-scanned points. The counting statistical accuracy is determined by the intensity and the background level, and is a major factor in lattice-parameter precision. Preliminary tests on typical profiles ensure that fullest advantage can be taken of the experimental conditions.
- (12) At present (2003), the best approach to precision lattice-parameter determination is to follow the suggestions listed above, and to use peak search or profile fitting to calculate the observed 2θ positions. All the well determined peaks are used in the least-squares refinement against 2θ to obtain the zero-angle calibration correction, and in the case of focusing methods the specimen-surface displacement is added. The use of standards is recommended.

5.5. Neutron methods

BY B. T. M. WILLIS

In general, one would not expect to measure lattice parameters as precisely with neutrons as with X-rays. The main reason for this is the need to relax the resolution of the diffraction peaks observed in neutron diffraction, in order to obtain reasonable count rates. However, the high-resolution powder diffractometer D2B (on the reactor source at the Institut Laue-Langevin) and the high-resolution powder instrument HRPD (on the pulsed source at the Rutherford Appleton Laboratory) have resolutions approaching that of X-ray diffractometers. Using Rietveld refinement, lattice parameters can be deter-

mined to a precision of a few parts in 10^4 (Fischer *et al.*, 1986).

Neutron methods are better suited to the indexing of the powder pattern. This requires the accurate measurement of the d spacings of the lowest-index lines in the pattern. Whereas d spacings measured with X-rays at low values of $(\sin \theta)/\lambda$ tend to have systematic errors, this is not such a serious problem with neutrons. It is relatively straightforward, using the time-of-flight pulsed-neutron method, to measure the d spacings of the first 20–30 lines of a powder pattern to better than 0.1%.

References

5.1

- Block, S. & Hubbard, C. R. (1980). Editors. *Accuracy in powder diffraction*. Natl Bur. Stand. US Spec. Publ. No. 567. CSIRO (1988). Papers presented at the International Symposium on X-ray Powder Diffractometry, Fremantle, Australia, 20–23 August 1987. *Aust. J. Phys.* **41**(2), iv, 101–335.
- Hubbard, C. R. (1983). *New standard reference materials for X-ray powder diffraction*. *Adv. X-ray Anal.* **26**, 45–51.
- Klug, H. P. & Alexander, L. E. (1974). *X-ray diffraction procedures for polycrystalline and amorphous materials*, 2nd ed. New York: John Wiley.
- Okada, Y. & Tokumaru, Y. (1984). *Precise determination of lattice parameter and thermal expansion coefficient of silicon between 300 and 1500 K*. *J. Appl. Phys.* **56**, 314–320.
- Peiser, H. S., Rooksby, H. P. & Wilson, A. J. C. (1960). Editors. *X-ray diffraction by polycrystalline materials*, 2nd ed. London: Chapman & Hall.
- Prince, E. & Stalick, J. K. (1992). Editors. *Accuracy in powder diffraction. II. NIST Spec. Publ. No. 846*.
- Wilson, A. J. C. (1980). *Accuracy in methods of lattice-parameter measurement*. *Accuracy in powder diffraction*. Natl Bur. Stand. US Spec. Publ. No. 567.

5.2

- Alexander, L. (1948). *Geometrical factors affecting the contours of X-ray spectrometer maxima. I. Factors causing asymmetry*. *J. Appl. Phys.* **19**, 1068–1071.
- Alexander, L. (1950). *Geometrical factors affecting the contours of X-ray spectrometer maxima. II. Factors causing broadening*. *J. Appl. Phys.* **21**, 126–136.
- Alexander, L. (1953). *The effect of vertical divergence on X-ray powder diffraction lines*. *Br. J. Appl. Phys.* **4**, 92–93.
- Alexander, L. (1954). *The synthesis of X-ray spectrometer line profiles with application to crystallite size measurements*. *J. Appl. Phys.* **25**, 155–161.
- Appleman, D. E. & Evans, H. T. (1973). *Indexing and least-squares refinement of powder diffraction data*. US Department of Commerce, National Technical Information Service, 5286 Port Royal Rd, Springfield, VA 22151, USA.
- Barth, H. (1960). *Möglichkeit der Präzisionsgitterkonstantenmessungen mit hochmonochromatischer Röntgenstrahlung*. *Acta Cryst.* **13**, 830–832.

- Bearden, J. A. (1964). *X-ray wavelengths*. US AEC Division of Technical Information Ext., Oak Ridge, Tennessee, USA. [The tables are reprinted more accessibly in *International tables for X-ray crystallography* (1974). Vol. IV, pp. 6–43. Birmingham: Kynoch Press. Present distributor: Kluwer Academic Publishers.]
- Berkum, J. van, Sprong, G. J. M., de Keijser, Th. H., Delhez, R. & Sonneveld, E. J. (1995). *The optimum standard specimen for X-ray diffraction line-profile analysis*. *Powder Diffr.* **10**, 129–139.
- Beu, K. E. (1964). *The evaluation of centroid lattice parameter data for tungsten by the likelihood ratio method*. *Acta Cryst.* **17**, 1149–1164.
- Beu, K. E., Musil, F. J. & Whitney, D. R. (1962). *Precise and accurate lattice parameters by film powder methods. I. The likelihood ratio method*. *Acta Cryst.* **15**, 1292–1301.
- Beu, K. E., Musil, F. J. & Whitney, D. R. (1963). *The likelihood ratio method for the precise and accurate determination of lattice parameters for tetragonal and hexagonal crystals*. *Acta Cryst.* **16**, 1241–1242.
- Beu, K. E. & Whitney, D. R. (1967). *Further developments in a likelihood ratio method for the precise and accurate determination of lattice parameters*. *Acta Cryst.* **22**, 932–933.
- Boom, G. (1966). *Accurate lattice parameters and the LPC method*. Groningen: van Denderen.
- Boom, G. & Smits, D. W. (1965). *Calculation of Debye-Scherrer diffraction line profiles and their applications in precision determination of lattice parameters*. *Proc. K. Ned. Akad. Wet. Ser. B*, **68**, 46–52.
- Bourdillon, A. J., Glazer, A. M., Hidaka, M. & Bordas, J. (1978). *High-resolution energy-dispersive diffraction using synchrotron radiation*. *J. Appl. Cryst.* **11**, 684–687.
- Buras, B., Olsen, J. S., Gerward, L., Will, G. & Hinze, E. (1977). *X-ray energy-dispersive diffractometry using synchrotron radiation*. *J. Appl. Cryst.* **10**, 431–438.
- Cheary, R. W. & Coelho, A. (1992). *A fundamental parameters approach to X-ray line-profile fitting*. *J. Appl. Cryst.* **25**, 109–121.
- Cheary, R. W. & Coelho, A. (1994). *Synthesizing and fitting linear position-sensitive detector step-scanned line profiles*. *J. Appl. Cryst.* **27**, 673–681.
- Chevallier, P., Travenier, M. & Briand, J. P. (1978). *On the natural width of the K_{α} x-ray [sic] line observed at the energy threshold*. *J. Phys. B*, **11**, L171–L179.

5. DETERMINATION OF LATTICE PARAMETERS

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- Cohen, M. U. (1936a). *Elimination of systematic errors in powder photographs*. *Z. Kristallogr.* **94**, 288–298.
- Cohen, M. U. (1936b). *Calculation of precise lattice constants for X-ray powder photographs*. *Z. Kristallogr.* **94**, 306–310.
- Deslattes, R. D. & Henins, A. (1973). *X-ray to visible wavelength ratios*. *Phys. Rev. Lett.* **31**, 972–975.
- Deslattes, R., Henins, A. & Kessler, E. G. (1980). *Accuracy in X-ray wavelengths. Accuracy in powder diffraction*, edited by S. Block & C. R. Hubbard, pp. 55–71. *Natl Bur. Stand. (US) Spec. Publ. No. 567*.
- Dragoo, A. L. (1986). *Standard reference materials for X-ray diffraction. Part I. Overview of current and future standard reference materials*. *Powder Diffr.* **1**, 294–304.
- Edwards, H. J. & Toman, K. (1970). *The additivity of variances in powder diffraction profile analysis*. *J. Appl. Cryst.* **3**, 165–171.
- Fawcett, T. G., Crowder, C. E., Brownell, S. J., Zhang, Y., Hubbard, C., Schreiner, W., Hamill, G. P., Huang, T. C., Sabino, E., Langford, J. I., Hamilton, R. & Louër, D. (1988). *Establishing an instrumental peak profile calibration standard for powder diffraction analyses: international round robin conducted by the JCPDS-ICDD and the US National Bureau of Standards*. *Powder Diffr.* **3**, 209–218.
- Ferguson, I. F., Rogerson, I. F., Wolstenholme, J. F. R., Hughes, T. E. & Huyton, A. (1987). *FIRESTAR-2. A computer program for the evaluation of X-ray powder measurements and the derivation of crystal lattice parameters*. United Kingdom Atomic Energy Authority, Northern Division Report ND-R-909(S). London: HMSO, February 1987.
- Fukamachi, T., Hosoya, S. & Terasaki, D. (1973). *The precision of interplanar distances measured by an energy-dispersive X-ray diffractometer*. *J. Appl. Cryst.* **6**, 117–122.
- Gale, B. (1963). *The positions of Debye diffraction line peaks*. *Br. J. Appl. Phys.* **14**, 357–364.
- Gale, B. (1968). *The aberrations of a focusing X-ray diffraction instrument: second-order theory*. *Br. J. Appl. Phys. (J. Phys. D)*, **1**, 393–408.
- Giessen, B. C. & Gordon, G. E. (1968). *X-ray diffraction: new high-speed technique based on X-ray spectroscopy*. *Science*, **159**, 973–975.
- Gillham, C. J. (1971). *Centroid shifts due to axial divergence and other geometrical factors in Seemann-Bohlin diffractometry*. *J. Appl. Cryst.* **4**, 498–506.
- Gillham, C. J. & King, H. W. (1972). *Measurements of centroid and peak shifts due to dispersion and the Lorentz factor at very high Bragg angles*. *J. Appl. Cryst.* **5**, 23–27.
- Glazer, A. M., Hidaka, M. & Bordas, J. (1978). *Energy-dispersive powder profile refinement using synchrotron radiation*. *J. Appl. Cryst.* **11**, 165–172.
- Greenberg, B. (1989). *Bragg's law with refraction*. *Acta Cryst.* **A45**, 238–241.
- Hart, M. (1981). *Bragg angle measurement and mapping*. *J. Cryst. Growth*, **55**, 409–427.
- Hart, M., Cernik, R., Parrish, W. & Toraya, H. (1990). *Lattice-parameter determination for powders using synchrotron radiation*. *J. Appl. Cryst.* **23**, 286–291.
- Hart, M., Parrish, W., Bellotto, M. & Lim, G. S. (1988). *The refractive-index correction in powder diffraction*. *Acta Cryst.* **A44**, 193–197.
- Huang, T. C. (1988). *Precision peak determination in X-ray powder diffractometry*. *Aust. J. Phys.* **41**, 201–212.
- Huang, T. C., Toraya, H., Blanton, T. N. & Wu, Y. (1993). *X-ray powder diffraction analysis of silver behenate, a possible low-angle diffraction standard*. *J. Appl. Cryst.* **26**, 180–184.
- Hubbard, C. R. (1983). *New standard reference materials for X-ray powder diffraction*. *Adv. X-ray Anal.* **26**, 45–51.
- Hubbard, C. R., Swanson, H. É. & Mauer, F. A. (1975). *A silicon powder diffraction standard reference material*. *J. Appl. Cryst.* **8**, 45–48.
- JCPDS-International Centre for Diffraction Data (1986). *Task group on cell parameter refinement*. *Powder Diffr.* **1**, 66–76.
- Jenkins, R. & Schreiner, W. N. (1986). *Considerations in the design of goniometers for use in X-ray powder diffraction*. *Powder Diffr.* **1**, 305–319.
- Kelly, E. H. (1988). *A summary of a 'round-robin' exercise comparing the output of computer programs for lattice-parameter refinement and calculations*. British Crystallographic Association.
- Kogan, V. A. & Kupriyanov, M. F. (1992). *X-ray powder diffraction line profiles by Fourier synthesis*. *J. Appl. Cryst.* **25**, 16–25.
- Ladell, J., Parrish, W. & Taylor, J. (1959). *Interpretation of diffractometer line profiles*. *Acta Cryst.* **12**, 561–567.
- Laguitton, D. & Parrish, W. (1977). *Experimental spectral distribution versus Kramers' law for quantitative X-ray fluorescence by the fundamental parameters method*. *X-ray Spectrom.* **6**, 201–203.
- Langford, J. I., Louër, D., Sonneveld, E. J. & Visser, J. W. (1986). *Applications of total pattern fitting to a study of crystallite size and strain in powder zinc oxide*. *Powder Diffr.* **1**, 211–221.
- Langford, J. I., Pike, E. R. & Beu, K. E. (1964). *Precise and accurate lattice parameters by film powder methods. IV. Theoretical calculation of axial (vertical) divergence profiles, centroid shifts, and variances for cylindrical powder diffraction cameras*. *Acta Cryst.* **17**, 645–651.
- Langford, J. I. & Wilson, A. J. C. (1962). *Counter diffractometer: the effect of specimen transparency on the intensity, position and breadth of X-ray powder diffraction lines*. *J. Sci. Instrum.* **39**, 581–585.
- Louër, D. & Langford, J. I. (1988). *Peak shape and resolution in conventional diffractometry with monochromatic X-rays*. *J. Appl. Cryst.* **21**, 430–437.
- Mack, M. & Parrish, W. (1967). *Seeman-Bohlin X-ray diffractometry. II. Comparison of aberrations and intensity with conventional diffractometer*. *Acta Cryst.* **23**, 693–700.
- Mack, M. & Spielberg, N. (1958). *Statistical factors in X-ray intensity measurements*. *Spectrochim. Acta*, **12**, 169–178.
- Mantler, M. & Parrish, W. (1977). *Energy dispersive X-ray diffractometry*. *Adv. X-ray Anal.* **20**, 171–186.
- Mighell, A. D., Hubbard, C. R. & Stalick, J. K. (1981). *NBS*EXAIDS83. A Fortran program for crystallographic data evaluation*. *Natl Bur. Stand. (US) Tech. Note*, No. 1141, April 1981.
- Mitra, G. B., Ahmed, A. & Das Gupta, P. (1985). *Precise and accurate estimation of crystallographic parameters by maximum-likelihood and min-max methods. Structure and statistics in crystallography*, edited by A. J. C. Wilson, pp. 151–181. Guilderland, NY: Adenine Press.
- Nakajima, T., Fukamachi, T., Terasaki, O. & Hosoya, S. (1976). *The detection of small differences in lattice constant at low temperature by an energy-dispersive X-ray diffractometer*. *J. Appl. Cryst.* **9**, 286–290.

REFERENCES

5.2 (cont.)

- Nelson, J. B. & Riley, D. P. (1945). *An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals*. *Proc. Phys. Soc. London*, **57**, 160–177, 477–495.
- Okazaki, A. & Kawaminami, M. (1973). *Accurate measurement of lattice constant in a wide range of temperature: use of white X-rays and double-crystal diffractometry*. *Jpn. J. Appl. Phys.* **12**, 783–789.
- Parrish, W. (1960). *Results of the IUCr precision lattice-parameter project*. *Acta Cryst.* **13**, 838–850.
- Parrish, W. (1988). *Advances in synchrotron X-ray polycrystalline diffraction*. *Aust. J. Phys.* **41**, 101–112.
- Parrish, W. & Hart, M. (1987). *Advantages of synchrotron radiation for polycrystalline diffractometry*. *Z. Kristallogr.* **179**, 161–173.
- Parrish, W., Hart, M., Huang, T. C. & Bellotto, M. (1987). *Lattice-parameter determination using synchrotron powder data*. *Adv. X-ray Anal.* **30**, 373–382.
- Parrish, W. & Huang, T. C. (1980). *Accuracy of the profile fitting method for X-ray polycrystalline diffractometry*. *Natl Bur. Stand. (US) Spec. Publ. No. 457*, pp. 95–110.
- Pawley, G. S. (1981). *Unit-cell refinement from powder diffraction scans*. *J. Appl. Cryst.* **14**, 357–361.
- Pike, E. R. (1957). *Counter diffractometer – the effects of vertical divergence on the displacement and breadth of powder diffraction lines*. *J. Sci. Instrum.* **34**, 355–361.
- Pike, E. R. & Wilson, A. J. C. (1959). *Counter diffractometer – the theory of the use of centroids of diffraction profiles for high accuracy in the measurement of diffraction angles*. *Br. J. Appl. Phys.* **10**, 57–68.
- Popović, S. (1973). *Unit-cell dimension measurements from pairs of X-ray diffraction lines*. *J. Appl. Cryst.* **6**, 122–128.
- Rietveld, H. M. (1967). *Line profiles of neutron powder-diffraction peaks for structure refinement*. *Acta Cryst.* **22**, 151–152.
- Rietveld, H. M. (1969). *A profile refinement method for nuclear and magnetic structures*. *J. Appl. Cryst.* **2**, 65–71.
- Sandström, A. E. (1957). *Experimental methods of X-ray spectroscopy: ordinary wavelengths*. *Handbuch der Physik*, pp. 78–245 (esp. p. 157). Berlin: Springer.
- Scardi, P., Lutterotti, L. & Maistrelli, P. (1994). *Experimental determination of the instrumental broadening in Bragg-Brentano geometry*. *Powder Diffr.* **9**, 180–186.
- Soller, W. (1924). *A new precision X-ray spectrometer*. *Phys. Rev.* **24**, 158–167.
- Sparks, C. J. & Gedcke, D. A. (1972). *Rapid recording of powder diffraction patterns with Si(Li) X-ray energy analysis system: W and Cu targets and error analysis*. *Adv. X-ray Anal.* **15**, 240–253.
- Spencer, R. C. (1931). *Additional theory of the double X-ray spectrometer*. *Phys. Rev.* **38**, 618–629.
- Spencer, R. C. (1935). *The effect of the spectrometer on the width of spectral lines*. *Phys. Rev.* **48**, 473.
- Spencer, R. C. (1937). *A theorem on the effect of vertical divergence*. *Phys. Rev.* **52**, 761.
- Spencer, R. C. (1939). *The correction of experimental curves for the resolving power of the apparatus*. *Phys. Rev.* **55**, 239.
- Spencer, R. C. (1941). *Optimum design of physical apparatus*. *Phys. Rev.* **60**, 172.
- Spencer, R. C. (1949). *Discussion of “Geometrical factors affecting X-ray spectrometer maxima”*. *J. Appl. Phys.* **20**, 413–414.
- Taylor, A. & Sinclair, H. B. (1945a). *The influence of absorption on the shapes and positions of lines in Debye-Scherrer powder photographs*. *Proc. Phys. Soc. London*, **57**, 108–125.
- Taylor, A. & Sinclair, H. B. (1945b). *On the determination of lattice parameters by the Debye-Scherrer method*. *Proc. Phys. Soc. London*, **57**, 126–135.
- Thomsen, J. S. (1974). *High-precision X-ray spectroscopy*. *X-ray spectroscopy*, edited by L. V. Azaroff, pp. 26–132. New York: McGraw-Hill.
- Thomsen, J. S. & Yap, F. Y. (1968a). *Effect of statistical counting errors on wavelength criteria for X-ray spectra*. *J. Res. Natl Bur. Stand. Sect. A*, **72**, 187–205.
- Thomsen, J. S. & Yap, F. Y. (1968b). *Simplified method of computing centroids of X-ray profiles*. *Acta Cryst.* **A24**, 702–703.
- Timmers, J., Delhez, R., Tuinstra, F. & Peerdeman, F. (1992). *X-ray tracing; a tool for improved accuracy in powder diffractometry*. *Accuracy in powder diffraction II*. NIST Spec. Publ. No. 846, edited by E. Prince & J. K. Stalick, p. 217.
- Toraya, H. (1986). *Whole-powder-pattern fitting without reference to a structural model: application to X-ray powder diffractometer data*. *J. Appl. Cryst.* **19**, 440–447.
- Toraya, H. (1988). *The deconvolution of overlapping reflections by the procedure of direct fitting*. *J. Appl. Cryst.* **21**, 192–196.
- Wilkens, M. (1960). *Zur Brechungskorrektur bei Gitterkonstantmessungen an Pulverpräparaten*. *Acta Cryst.* **13**, 826–828.
- Wilson, A. J. C. (1940). *On the correction of lattice spacings for refraction*. *Proc. Cambridge Philos. Soc.* **36**, 485–489.
- Wilson, A. J. C. (1950). *Geiger-counter X-ray spectrometer – influence of the size and absorption coefficient of the specimen on position and shape of powder diffraction maxima*. *J. Sci. Instrum.* **27**, 321–325.
- Wilson, A. J. C. (1958). *Effect of absorption on mean wavelength of X-ray emission lines*. *Proc. Phys. Soc. London*, **72**, 924–925.
- Wilson, A. J. C. (1961). *A note on peak displacements in X-ray diffractometry*. *Proc. Phys. Soc. London*, **78**, 249–255.
- Wilson, A. J. C. (1962). *Refraction broadening in powder diffractometer*. *Proc. Phys. Soc. London*, **80**, 303–305.
- Wilson, A. J. C. (1963). *Mathematical theory of X-ray powder diffractometry*. Eindhoven: Centrex.
- Wilson, A. J. C. (1965a). *On variance as a measure of line broadening in diffractometry. IV. The effect of physical aberrations*. *Proc. Phys. Soc. London*, **85**, 171–176.
- Wilson, A. J. C. (1965b). *The location of peaks*. *Br. J. Appl. Phys.* **16**, 665–674.
- Wilson, A. J. C. (1965c). *Röntgenstrahlpulverdiffractometrie. Mathematische Theorie*. Eindhoven: Centrex.
- Wilson, A. J. C. (1967). *Statistical variance of line-profile parameters. Measures of intensity, location and dispersion*. *Acta Cryst.* **23**, 888–898. *Addenda and Corrigenda, ibid.*, **A24**, 478 and **A25**, 584–585.
- Wilson, A. J. C. (1970a). *Elements of X-ray crystallography*. Reading, MA: Addison-Wesley.
- Wilson, A. J. C. (1970b). *Limitations on the additivity of moments in line-profile analysis*. *J. Appl. Phys.* **3**, 71–73.
- Wilson, A. J. C. (1971). *Some statistical considerations in the location of Mössbauer lines*. *Nucl. Instrum. Methods*, **94**, 225–227.
- Wilson, A. J. C. (1973). *Note on the aberrations of a fixed-angle energy-dispersive diffractometer*. *J. Appl. Cryst.* **6**, 230–237.

5. DETERMINATION OF LATTICE PARAMETERS

5.2 (cont.)

- Wilson, A. J. C. (1974). *Powder diffractometry. X-ray diffraction*, by L. V. Azaroff, R. Kaplow, N. Kato, R. Weiss, A. J. C. Wilson & R. A. Young, Chap. 6. New York: McGraw-Hill.
- Wilson, A. J. C. (1980). *Accuracy in methods of lattice-parameter measurement. Natl Bur. Stand. (US) Spec. Publ.* No. 567, pp. 325–351.
- Wilson, A. J. C. & Delf, B. W. (1961). *Effects of variations in the quantum counting efficiency of detectors on the mean wavelengths of emission lines. Proc. Phys. Soc. London*, **78**, 1256–1258.
- Wilson, A. J. C. & Lipson, H. (1941). *The calibration of Debye-Scherrer X-ray powder cameras. Proc. Phys. Soc. London*, **53**, 245–250.
- Wilson, A. J. C., Thomsen, J. S. & Yap, F. Y. (1965). *Minimization of the variation of parameters derived from X-ray powder diffractometer line profiles. Appl. Phys. Lett.* **7**, 163–165.
- Wong-Ng, W. & Hubbard, C. R. (1987). *Standard reference materials for X-ray diffraction. Part II. Calibration using d-spacing standards. Powder Diffr.* **2**, 242–248.
- Young, R. A. (1988). *Pressing the limits of Rietveld refinement. Aust. J. Phys.* **41**, 294–310.
- Zevin, L. S., Umanskij, M. M., Khejker, D. M. & Pančenko, J. M. (1961). *The question of diffractometer methods of precision measurement of unit-cell parameters. Sov. Phys. Crystallogr.* **6**, 277–283.
- Aristov, V. V., Shekhtman, V. Sh. & Shmytko, I. M. (1973). *Precision measurement of crystallographic parameters by the X-ray divergent-beam technique. (In Russian.) Kristallografiya*, **18**, 706–709. (English transl: *Sov. Phys. Crystallogr.* **18**, 445–446.)
- Aristov, V. V. & Shmytko, I. M. (1978). *Precision lattice parameter measurement by the X-ray divergent-beam technique. J. Appl. Cryst.* **11**, 662–668.
- Aristov, V. V., Shmytko, I. M. & Shulakov, E. V. (1974a). *Application of the X-ray divergent-beam technique for the determination of the angles between crystal blocks. I. Reflexion from the planes parallel to the crystal surface. J. Appl. Cryst.* **7**, 409–413.
- Aristov, V. V., Shmytko, I. M. & Shulakov, E. V. (1974b). *Application of the X-ray divergent-beam technique for the determination of the angles between crystal blocks. II. Determination of the total misorientation angle between blocks. J. Appl. Cryst.* **7**, 413–416.
- Arndt, U. W. & Willis, B. T. M. (1966). *Single crystal diffractometry*. Cambridge University Press.
- Åsbrink, S., Wołczyr, M. & Hong, S.-H. (1985). *X-ray Bond-type diffractometric investigations on V₃O₅ in the temperature interval 298 to 480 K including the phase transition temperature T_i = 428 K. Phys. Status Solidi A*, **87**, 135–140; erratum: **89**, 415.
- Azáróff, L. V. (1974). *X-ray spectroscopy*, Chap. 2. New York: McGraw-Hill.
- Báčkovský, J. (1965). *On the most accurate measurements of the wavelengths of X-ray spectral lines. Czech. J. Phys.* **B15**, 752–759.
- Baker, J. A., Tucker, T. N., Moyer, N. E. & Buschert, R. C. (1968). *Effects of carbon on the lattice parameter of silicon. J. Appl. Phys.* **39**, 4365–4368.
- Baker, J. F. C. & Hart, M. (1975). *An absolute measurement of the lattice parameter of germanium using multiple-beam X-ray diffractometry. Acta Cryst.* **A31**, 364–367.
- Baker, J. F. C., Hart, M., Halliwell, M. A. G. & Heckingbottom, R. (1976). *Precise lattice parameter determination of dislocation-free gallium arsenide. I. X-ray measurements. Solid-State Electron.* **19**, 331–334.
- Baker, T. W., George, J. D., Bellamy, B. A. & Causer, R. (1966). *Very high precision X-ray diffraction. Nature (London)*, **210**, 720–721.
- Baker, T. W., George, J. D., Bellamy, B. A. & Causer, R. (1968). *Fully automated high-precision X-ray diffraction. Adv. X-ray Anal.* **11**, 359–375.
- Barla, K., Herino, R., Bomchil, G. & Pfister, J. C. (1984). *Determination of lattice parameter and elastic properties of porous silicon by X-ray diffraction. J. Cryst. Growth*, **68**, 727–732.
- Barns, R. L. (1972). *A strategy for rapid and accurate (p.p.m.) measurement of lattice parameters of single crystals by Bond's method. Adv. X-ray Anal.* **15**, 330–338.
- Bartels, W. J. (1983). *Characterization of thin layers on perfect crystals with a multipurpose high-resolution X-ray diffractometer. J. Vac. Sci. Technol.* **B1**, 338–345.
- Batchelder, D. N. & Simmons, R. O. (1965). *X-ray lattice constant of crystals by a rotating-camera method: Al, Ar, Au, CaF₂, Cu, Ge, Ne, Si. J. Appl. Phys.* **36**, 2864–2868.
- Bearden, J. A. (1933). *The wavelengths of the silver, molybdenum, copper, iron and chromium K α_1 lines. Phys. Rev.* **43**, 92–97.
- Bearden, J. A. (1965). *Selection of W K α_1 as the X-ray wavelength standard. Phys. Rev.* **137**, BY55–BY61.

5.3

- Abrahams, S. C., Liminga, R., Marsh, P., Schrey, F., Albertsson, J., Svensson, C. & Kvik, A. (1983). *Thermal expansivity of α -LiIO₃ between 20 and 520 K. J. Appl. Cryst.* **16**, 453–457.
- Alcock, N. W. & Sheldrick, G. M. (1967). *The determination of accurate unit-cell dimensions from inclined Weissenberg photographs. Acta Cryst.* **23**, 35–38.
- Alexander, L. (1948). *Geometrical factors affecting the contours of X-ray spectrometer maxima. I. Factors causing asymmetry. J. Appl. Phys.* **19**, 1068–1071.
- Alexander, L. (1950). *Geometrical factors affecting the contours of X-ray spectrometer maxima. II. Factors causing broadening. J. Appl. Phys.* **21**, 126–136.
- Alexander, L. (1954). *The synthesis of X-ray spectrometer line profiles with application to crystallite size measurements. J. Appl. Phys.* **25**, 155–161.
- Alexander, L. E. & Smith, G. (1962). *Single-crystal intensity measurements with the three-circle counter diffractometer. Acta Cryst.* **15**, 983–1004.
- Amorós, J. L., Buerger, M. J. & Amorós, M. C. (1975). *The Laue method*. New York: Academic Press.
- d'Amour, H., Denner, W., Schulz, H. & Cardona, M. (1982). *A uniaxial stress apparatus for single-crystal X-ray diffraction on a four-circle diffractometer: Application to silicon and diamond. J. Appl. Cryst.* **15**, 148–153.
- Ando, M., Bailey, D. & Hart, M. (1978). *A simple Bragg-spacing comparator. Acta Cryst.* **A34**, 484–489.
- Ando, M., Hagashi, Y., Usuda, K., Yasuami, S. & Kawata, H. (1989). *A precision Bond method with SR. Rev. Sci. Instrum.* **60**, 2410–2413.