

5.2. X-RAY DIFFRACTION METHODS: POLYCRYSTALLINE

**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

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.