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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, 1965*c*, 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:

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

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

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

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

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

where a, b, c are the edges of the unit cell, and $A, \ldots, G$ 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

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

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

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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 (c unique)	Rhombohedral	Triclinic
A	1	1	1	$\sin^2\alpha$	$\sin^2\alpha$
B	1	1	1	$\sin^2\alpha$	$\sin^2\beta$
C	1	$\frac{3}{4}$	$\sin^2\gamma$	$\sin^2\alpha$	$\sin^2\gamma$
D	0	0	0	$\cos^2\alpha-\cos\alpha$	$\cos\beta\cos\gamma-\cos\alpha$
E	0	0	0	$\cos^2\alpha-\cos\alpha$	$\cos\gamma\cos\alpha-\cos\beta$
F	0	$\frac{1}{2}$	$-\cos\gamma$	$\cos^2\alpha-\cos\alpha$	$\cos\alpha\cos\beta-\cos\gamma$
G	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 ordinary 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.

references