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.

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