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 (1945*a,b*)]:

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

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

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

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

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

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

$$\langle S \rangle + k\sigma_S = n - p + k\sigma_S$$
$$= n - p + k[2(n - p)]^{1/2} \qquad (5.2.9.3)$$

(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

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

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://srmcatalog.nist.gov.

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

			Cu $K\alpha_1$	
Standard	Year issued	a_0 (Å)	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 μm, and 95% of the particles are < 10 μm. 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 Å, 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) Å (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 $a = 3.16523(4)$ Å at 298 K for Cu $K\alpha_1 = 1.5405929$ Å 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) Å 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 μm) 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°(2θ) (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 $d_{001} = 58.380\,(3)$ Å and, for Cu $K\alpha_1$ radiation, there are 13

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

hkl	Tungsten $a_0 = 3.16523\,(4)$ Å	Silver $a_0 = 4.08650\,(2)$ Å	Silicon $a_0 = 5.431195\,(9)$ Å (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°(2θ) (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 $133\,\text{cm}^{-1}$ for $\lambda = 1.54$ Å and $15\,\text{cm}^{-1}$ for 0.7 Å, 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.

references