The above experiment was a turning point in accurate measurements of both wavelengths and lattice parameters. Owing to the idea of Deslattes & Henins, it became possible to determine the wavelength in nanometres rather than in troublesome XU or Å* units (*cf.* §4.2.1.1.1). However, the results obtained and the method itself needed verification and some adjustments. These were performed by another group of experimenters with a similar but different measuring device (Becker, Seyfried & Siegert, 1982, and references therein; Siegert, Becker & Seyfried, 1984).

5.3.3.9. *Lattice-parameter and wavelength standards*

An extended series of measurements performed by means of the optical and X-ray interferometry (*cf.* §5.3.3.8) led, among other things, to evaluation of the lattice spacing of a highly perfect silicon sample WASO 4.2.A (Becker *et al.*, 1981). Such silicon samples may be used as reference crystals in successive lattice-spacing comparison measurements – with a double-source double-crystal spectrometer (Windisch & Becker, 1990), for example. The latter measurements provided new excellent lattice-spacing standards (WASO 9, for example) of the well known lattice-parameter values. As shown by the authors, the differences in lattice parameters of different samples of float-zone silicon (due to oxygen or carbon content) were not greater than a few parts in 10^8. Finally, the lattice parameter of silicon, $a = 5.43102088(16)$ Å, has been accepted as the atomic scale length standard (Mohr & Taylor, 2000).

Another reference material reported is crystals of pure rhombohedral corrundum (α-Al_2O_3), *i.e.* of ruby or sapphire (Herbstein, 2000, and references therein; Shvyd'ko *et al.*, 2002).

With silicon standards, measurements or remeasurements of $K\alpha_{1,2}$ and/or $K\beta_{1,3}$ X-ray emission lines and absolute wavelength determinations of most of the 3*d* transition metals (Cr, Mn, Fe, Co, Ni and Cu) have been performed [Härtwig, Grosswig, Becker & Windisch, 1991; Hölzer, Fritsch, Deutsch, Härtwig & Förster, 1997 (see §4.2.2)].

The standard crystals may also be used for determination of such physical quantities as the Avogadro constant (Deslattes *et al.*, 1994; Deslattes, Henins, Schoonover, Caroll & Bowman, 1976). The single accurate wavelength values, on the other hand, may be used both in simple measurements of lattice parameters [based directly on the Bragg law, equation (5.3.1.1)] and for accurate scaling of the wavelength spectra, in order to use them, for example, in high-accuracy lattice-parameter measurements based on complete convolution models [*cf.* §5.3.3.3.1, point(ii)].

Unlike the X-rays emitted from an X-ray tube, for which the spectral line and the characteristic wavelength are known, there are no such characteristic features in synchrotron radiation. Therefore, special energy-selective monochromators should be applied in relative lattice-spacing measurements using synchrotron radiation. Obaidur (2002) proposes two measurement schemes, using two types of high-resolution channel-cut monolithic monochromators. The first scheme (see Fig. 5.3.3.18) is a modification of the Bond method. The second one (see Fig. 5.3.3.19) uses the simultaneous Bragg condition for the indices (5,1,3), $(\bar{5},\bar{1},\bar{3})$, (1,5,3) and $(\bar{1},\bar{5},\bar{3})$. The lattice-spacing differences in Si wafers were determined in the sub-parts in 10^6 range of 0.6 parts in 10^6 (in the first scheme) and of 0.2 parts in 10^6 (second scheme).

Recently, a new atomic scale wavelength standard was proposed by Shvyd'ko *et al.* (2000), instead of the wavelength of the Cu $K\alpha_1$ emission line or of the lattice parameter of a silicon standard. It is the wavelength, λ_M, of the ^{57}Fe Mössbauer radiation, *i.e.* of γ radiation of natural linewidth from nuclear transitions. It has been measured to the sub-parts in 10^6 accuracy: $\lambda_M = 0.86025474(16)$ Å (relative accuracy 0.19 parts in 10^6). Its advantage, in relation to the previous standards, is the high spectral sharpness of the Mössbauer radiation of 3.5×10^{-13} in relative units, which makes its wavelength λ_M extremely well defined. This standard wavelength value, which lies a little outside of scope of the present review (X-ray methods), was next used for the lattice-parameter determination of sapphire single crystals with a relative accuracy of about 0.5 parts in 10^6 (Shvyd'ko *et al.*, 2002). Fig. 5.3.3.20 is a diagram of the measurement arrangement.

5.3.4. Final remarks

Let us review the most important problems concerning accurate and precise lattice-parameter determination.

The first, commonly known, requirement for obtaining the highest accuracy and precision is the use of high-Bragg-angle reflections. The tendency to obtain, record, and use in calculation such reflections can be met in rotating-crystal cameras in which Straumanis mounting is applied (Farquhar &

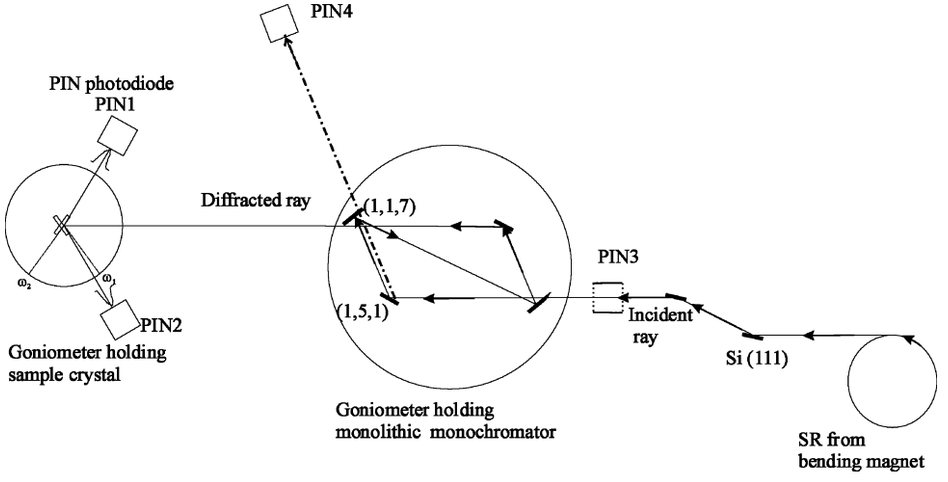

Fig. 5.3.3.18. Synchrotron radiation, SR, from the bending magnet incident on the Si(111) double-crystal monochromator and, after four reflections from the monolithic monochromator (0.1410 nm), impinges on sample Si(444). Two diffractions are recorded at the photodiode detectors, PIN1 and PIN2. The ω_1 and ω_2 values of the crystal positions are recorded using a Heiden height encoder.

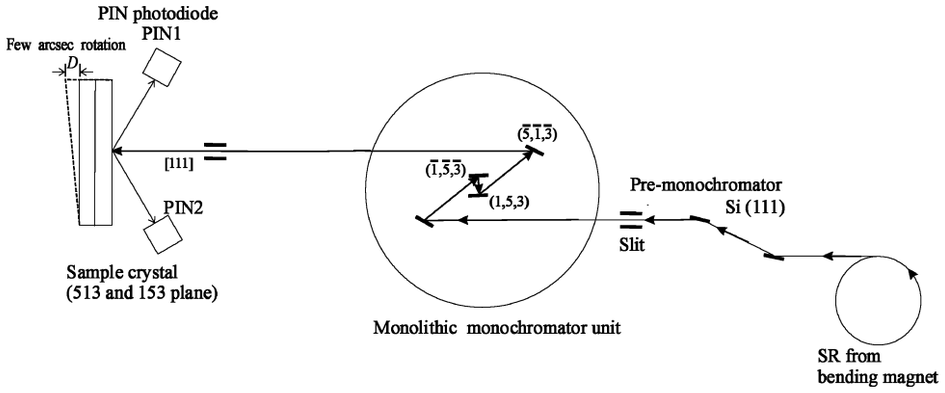

Fig. 5.3.3.19. Synchrotron radiation, SR, from the bending magnet incident on the Si(111) double-crystal monochromator and, after four reflections from the monolithic monochromator (0.1612 nm), impinges on sample Si(153). Two diffractions are recorded at the photodiode detectors, PIN1 and PIN2. The differences between the two peaks' D values are recorded using a Heiden height encoder.

Lipson, 1946; Popović, 1974), in the Weissenberg method (the use of zero-layer photographs), in multiple-exposure cameras (Glazer, 1972; Popović, Šljukić & Hanic, 1974), in standard and special diffractometers (Kobayashi, Yamada & Nakamura, 1963), in double-crystal arrangements with white X-radiation (Okazaki & Kawaminami, 1973*a*,*b*; Okazaki & Ohama, 1979; Ohama, Sakashita & Okazaki, 1979; Okazaki & Soejima, 2001), and in the triple-reflection scheme realized by means of the double-beam technique, proposed by Kovalchuk, Kovev & Pinsker (1975).

Increasing the θ value, in the case of photographic cameras or counter diffractometers, not only reduces the value of $\cot\theta$ in the formulae describing accuracy and precision, but also decreases several systematic errors proportional to $\cos\theta$, $\cos^2\theta$, $\cot\theta$ or $\cot^2\theta$ (Kheiker & Zevin, 1963; Wilson, 1963, 1980). To find the minimum total systematic error, which would occur for $\theta = 90^\circ$ (not attainable in practice), extrapolation of the results is used (Farquhar & Lipson, 1946; Weisz, Cochran & Cole, 1948; Smakula & Kalnajs, 1955; Kobayashi, Yamada & Azumi, 1968; Pierron & McNeely, 1969).

The problem of the choice of suitable reflections for the measurement, calculation, and reduction of systematic errors could be generalized. Not only are such reflections for which θ values are close to 90° desired but also those for which ν tends to 90° in rotating-crystal cameras (Umansky, 1960), high-order Kossel lines in divergent-beam techniques, axial or non-axial reflections in counter-diffractometer methods, *etc*. Zero-layer reflections in Weissenberg photographs or in two-circle

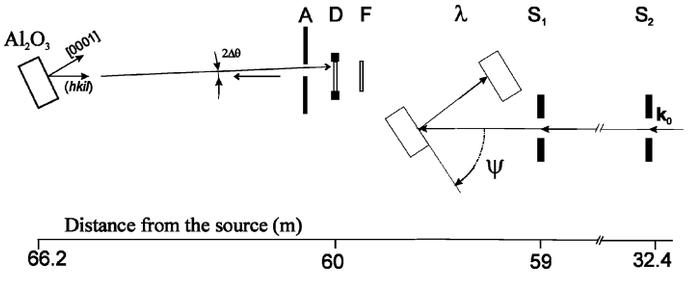

Fig. 5.3.3.20. Experimental set-up for measuring lattice parameters. X-rays after a high-heat-load monochromator (not shown) pass through the vertical slits S_1 and S_2 at a distance of 26.6 m. λ is a 'λ-meter'; F is a ^{57}Fe foil used as a source of the Mössbauer radiation of high brightness; D is a semi-transparent avalanche photodiode with 0.7 ns time resolution; Al_2O_3 is a sapphire single crystal in a furnace on a four-circle goniometer.

('Weissenberg') diffractometers are preferable to upper-layer ones, because they are less affected by crystal misalignment (Clegg & Sheldrick, 1984) and a larger range of reciprocal-lattice points can be recorded (Luger, 1980); they are not sufficient, however, for the determination of all the lattice parameters in the less-symmetric crystal systems.

Use of the orientation matrix makes possible accurate crystal setting for an arbitrary reflection and identification of recorded reflections not only in the case of the automated four-circle diffractometer or the two-circle diffractometer but also in photographic methods.

For obtaining high accuracy of lattice-parameter determination, systematic errors depending on the radiation, the crystal, and the technique should be known, evaluated, and reduced or corrected. As a rule, those systematic errors whose part in the total systematic error is the most important should be removed first. Looking at the development of the X-ray diffraction techniques, the following remarks can be made.

As far as the photographic methods are concerned, the errors due to the means of recording (film shrinkage, uncertainty of measurement of distances on the film) and camera construction (radius in the moving-crystal methods and the source-to-film distance in divergent-beam techniques) play a major role. They can be reduced to some extent by using the Straumanis mounting or the ratio method, or the resolved doublet $K\alpha_{1,2}$. Various methods have been introduced for reducing the error due to the source-to-film distance in divergent-beam techniques.

In counter-diffractometer methods, which give more accurate determinations of the Bragg angles and intensities, several instrumental and physical factors should be taken into account (Kheiker & Zevin, 1963; Wilson, 1963, 1980; Berger, 1984, 1986*a*; Härtwig & Grosswig, 1989). The effects of some can be diminished by the use of Soller slits (Berger, 1984) and the effects of most can be reduced by the Bond (1960) geometry, in its basic form or in its various modifications (Kheiker, 1973; Mauer *et al.*, 1975; Hubbard & Mauer, 1976; Wołcyrz, Pietraszko & Łukaszewicz, 1980; Kudo, 1982; Lisoivan, 1982; Grosswig *et al.*, 1985), in particular in combination with double- or triple-crystal spectrometers (Kurbatov, Zubenko & Umansky, 1972; Godwod, Kowalczyk & Szmid, 1974; Hart & Lloyd, 1975; Sasvári & Zsoldos, 1980; Fewster, 1982; Pick *et al.*, 1977; Obaidur, 2002). Another arrangement giving a partial reduction of systematic errors is that proposed by Renninger (1937) and developed by Post (1975) and Kshevetsky *et al.* (1979, 1985), in which multiple-diffraction phenomena are applied. In most one- or double-crystal asymmetric spectro-

meters, the uncertainty of the origin of the angular (ω) scale is the important problem, which can be resolved by introducing either the Bond (1960) symmetrical arrangement (combinations mentioned above) or an additional instrumental axis (or axes) for obtaining a multiple-crystal arrangement (Buschert, 1965; Skupov & Uspeckaya, 1975; Hart, 1981), or a second beam, used in multiple-beam methods (Hart, 1969; Kishino, 1973; Larson, 1974; Baker & Hart, 1975; Buschert *et al.*, 1983) or in various combined methods (Ando, Bailey & Hart, 1978; Kovalchuk, Kovev & Pinsker, 1975; Buschert *et al.*, 1980; Fewster, 1989; Shvyd'ko *et al.*, 2000; Obaidur, 2002).

The other important problem in single-crystal methods, in the case when high accuracy is desired, is the misalignment of the crystal(s) and some elements of the device. The errors due to the misalignment can be reduced to some extent experimentally, if a respective dependence is known (Baker, George, Bellamy & Causer, 1968; Burke & Tomkeieff, 1968, 1969; Bowen & Tanner, 1995), or by calculation of the exact correction (Burke & Tomkeieff, 1968, 1969; Gruber & Black, 1970; Filscher & Unangst, 1980; Larson, 1974) if the inclinations of the beam(s) and the crystal(s) can be determined (Halliwell, 1970; Nemiroff, 1982).

Along with an increase in the accuracy of the θ-angle determination, the error due to the wavelength determination becomes more important and a correction for the refraction should be introduced [the problem has been more intensively argued by Hart (1981, Section 2.3)]. Among others, measurement performed in the case of the Kossel method and divergent-beam techniques can be strongly affected by uncertainty of the wavelength, especially when the exact value of the wavelength is to be determined from the experiment. The combination of X-ray and optical interferometry (Deslattes, 1969; Deslattes & Henins, 1973; Becker *et al.*, 1981), the use of new lattice-parameter standards (Hölzer *et al.*, 1997), and new X-ray or γ-ray sources and wavelength standards (Shvyd'ko *et al.*, 2000; Obaidur, 2002) gives new possibilities for very accurate lattice-spacing measurements, up to the sub-parts in 10^6 range.

The accuracy of the method can be evaluated theoretically taking into account and estimating the errors that have not yet been eliminated. In the case of some θ-dependent errors, the maximum-likelihood method proves useful for this task (Beu, Musil & Whitney, 1962). Sometimes computer simulation is used to estimate some errors difficult to express in an analytical form (Hubbard & Mauer, 1976; Urbanowicz, 1981*b*; Berger, 1986*a*; Härtwig & Grosswig, 1989). A more objective test of the accuracy would be an inter-laboratory comparison, like that reported by Parrish (1960) many years ago. Usually, the authors introducing new methods, techniques or devices try to compare the results of their lattice-parameter determination with those obtained by other experimenters (Batchelder & Simmons, 1965, p. 2868; Hubbard, Swanson & Mauer, 1975, p. 46; Hubbard & Mauer, 1976, p. 2; Łukaszewicz *et al.*, 1976, p. 70; 1978, p. 566; Lisoivan, 1982, p. 94; Grosswig, Härtwig, Alter & Christoph, 1983, p. 506; Chang, 1984, p. 254; Härtwig, Bąk-Misiuk, Berger, Brühl, Okada, Grosswig, Wokulska & Wolf, 1994; Fewster & Andrew, 1995, p. 455; Herbstein, 2000).

In view of the new achievements in high-accuracy absolute lattice-parameter measurements, such as the results reviewed in §§5.3.3.8 and 5.3.3.9, and the accurate error analysis [Härtwig & Grosswig (1989); §5.3.3.4.3.2, point (7)], Härtwig, with his co-workers, initiated and organized an interlaboratory comparison of various 'traditional' methods and techniques, including the Bond method (*cf.* §5.3.3.4.3), the 'Soller-slit' method (§5.3.3.4.2) and the photographic multiple-diffraction (*Umweganregung*) method (§5.3.2.4.2). In all measurements performed, a common silicon standard (WASO 9, mentioned above) of accurately known lattice parameter was used as the specimen, so it was possible to check independently the validity of all corrections introduced for systematic errors. As shown by Härtwig, Bąk-Misiuk, Berger, Brühl, Okada, Grosswig, Wokulska & Wolf (1994), the agreement of their independent results was not worse than 3 parts in 10^6. The quantity defines the present-day possibilities of accurate 'dispersive' methods.

Herbstein (2000) concluded, 'there has been little improvement in claimed precision over the past 40–60 years', but his analysis relates to widely used 'dispersive' methods [including the Bond (1960) method] rather than to present-day high-precision comparison methods, which are also used for absolute measurements.

For obtaining high precision, a monochromatic and well collimated X-ray beam is desired. The first requirement can be fulfilled by using a filter or monochromator, the second can be satisfied by introducing a point source and a choice of collimation parameters, and both can be accomplished by introducing one or more additional crystals. It is not necessary for a well collimated beam to be very narrow if local measurements in selected small areas of the specimen are not the object of the experiment. The use of a large, parallel X-ray beam may be advantageous in some comparative measurements (Buschert, Pace, Inzaghi & Merlini, 1980).

Very high accuracy and high-precision measurements are, however, expensive; they need additional instrumental axes and detectors, and sometimes additional sources. Relatively simple divergent-beam techniques (photographic recording, stationary crystal) require fine X-ray sources (an electron microscope or an electron-beam probe) if high precision is to be attained.

Some authors have managed to reduce the cost of the experiment using simpler equipment. An example may be the triple-reflection scheme realized by the use of a double-axis spectrometer proposed by Ando, Bailey & Hart (1978) and Häusermann & Hart (1990). An additional advantage of the device is excellent stability.

Apart from the magnificent development of measuring techniques, an increasing role of mathematics is noticeable in contemporary papers. Matrix algebra is used for description of the crystal orientation in relation to the instrumental axes. Mathematical interpretation of the results is a very important part of the measurement, in particular in multiple-diffraction methods, both divergent-beam photographic and collimated-beam counter diffractometric. Syntheses of diffraction profiles are easily done with the aid of a computer. Algebraic and geometrical considerations make it possible to calculate proper corrections for systematic errors. Statistical methods give a tool for estimating and increasing the precision, in particular by means of least-squares refinement, and also for testing the hypothesis of 'no remaining systematic errors'. Commonly used computers are useful in numerous calculations and in controlling automatic devices.

references