International Tables for Crystallography (2006). Vol. C, Section 5.3.3.7, pp. 528–533.

pattern. Formula (5.3.3.34), since $C'A' = R\cos\mu$, can be presented in another form:

$$R = \frac{H^2 - H_p P}{2H_n \cos\mu \cos\beta}, \qquad (5.3.3.35)$$

where two setting angles, μ and β, are taken into account. When the indices are known, both (5.3.3.34) and (5.3.3.35) can be used for the determination or refinement of lattice parameters.

Another analytical method for indexing multiple-diffraction patterns, based on the determination of the Lorentz point, has been described by Kshevetsky, Mikhailyuk, Ostapovich, Polyak, Remenyuk & Fomin (1979).

Formulae (5.3.3.34) and (5.3.3.35) are valid for all crystal systems. In practice, however, the rather complicated method is used mainly for cubic crystals, and a special approach proved to be needed in order to adapt the method to other (rectangular) systems (Kshevetsky, Mikhalchenko, Stetsko & Shelud'ko, 1985). In the case of a cubic lattice, it is convenient to substitute

$$R = a/\lambda \qquad (5.3.3.35a)$$

into (5.3.3.34) and (5.3.3.35) rather than $R = 1/\lambda$ used in the general case, so that the lengths of the reciprocal vectors, being now functions of the indices only, are:

$$P = (h_0^2 + k_0^2 + l_0^2)^{1/2}, \qquad (5.3.3.35b)$$

$$H = (h^2 + k^2 + l^2)^{1/2}, \qquad (5.3.3.35c)$$

$$H_p P = \mathbf{HP} = h_0 h + k_0 k + l_0 l. \qquad (5.3.3.35d)$$

The lengths of the components of $\mathbf{H}$ can be determined from (5.3.3.35*b*,*c*,*d*) taking $H_p = H_p P/P$ and $H_n = (H^2 - H_p^2)^{1/2}$. After introducing the alterations [equation (5.3.3.35*a*) and the resulting equations (5.3.3.35*b*,*c*,*d*)], (5.3.3.35) now describes a simple dependence between the ratio a/λ, the indices, and the setting angles.

The accuracy of the lattice-parameter determination resulting from (5.3.3.35) in the cubic case can be assumed to be:

$$\frac{\Delta a}{a} = \tan\mu\Delta\mu + \tan\beta\Delta\beta; \qquad (5.3.3.36)$$

this thus depends on the values of the setting angles β, μ and their accuracies $\Delta\beta$, $\Delta\mu$. The latter depend on various systematic errors.

Since the differences between the two angular settings at which a given set of planes diffracts are measured rather than their absolute values, the systematic errors due to absorption, specimen displacement, and zero-setting are eliminated. In contrast, errors due to vertical divergence, refraction and the change of wavelength of the incident radiation (when it enters the crystal), alignment, and dynamical effects should be taken into account. In the case described by Post (1975), when a fine focus (effective size 0.4×0.5 mm) and collimation limiting the beam divergence to $2'$ were used, the vertical divergence causing the relative error in d of about 5×10^{-8} could be ignored.

The errors due to the real structure (inhomogeneity, mosaicity and internal stress) were discussed by Kshevetsky *et al.* (1979).

The accuracy possible by this method (from 1 to 4 parts in 10^6) is comparable with that obtained with the Bond (1960) method. The advantages of this method from the point of view of lattice-parameter determination are as follows:

(*a*) a large number of reflections can be measured without realigning or removing the crystal;

(*b*) all the lattice parameters can be determined and not only one, as in the Bond (1960) method;

(*c*) the narrow diffraction profiles can be located with very high accuracy and precision;

(*d*) the arrangement makes it possible to remove some systematic errors;

(*e*) the high accuracy resulting from (*a*)–(*d*), which is comparable with that obtained by means of the Bond (1960) method;

(*f*) the high precision that results from (*a*) and (*c*).

A disadvantage, on the other hand, is the complicated interpretation (indexing) of multiple-diffraction patterns, so that this method is less popular than the Bond (1960) method.

The Post (1975) method has been applied to the accurate lattice-parameter determination of germanium, silicon, and diamond single crystals (Hom, Kiszenick & Post, 1975).

5.3.3.7. *Multiple-crystal – pseudo-non-dispersive techniques*

5.3.3.7.1. *Double-crystal spectrometers*

Detailed information concerning the double-crystal spectrometer, which consists of two crystals successively diffracting the X-rays, can be found in James (1967, pp. 306–318), Compton & Allison (1935), and Azároff (1974). This device, usually used for wavelength determination, may also be applied to lattice-parameter determination, if the wavelength is accurately known. The principle of the device is shown in Fig. 5.3.3.8. The first crystal, the monochromator, diffracts the primary beam in the direction defined by the Bragg law for a given set of planes, so that the resulting beam is narrow and parallel. It can thus be considered to be both a collimator (or an additional collimator, if the primary beam has already been collimated) and a wavelength filter. The final profile $h(\theta)$, obtained as a result of the second diffraction by the specimen when the first crystal remains stationary and the second is rotated, is narrower than that which would be obtained with only one crystal. The final crystal profile $h_C(\theta)$ [*cf.* equation (5.3.1.6)] is due to both crystals, which, if it is assumed that they are cut from the same block, can be described by the autocorrelation function (Hart, 1981):

$$h_C(\theta) = K \int\limits_{-\infty}^{\infty} R(\theta')R(\theta' - \theta)\,\mathrm{d}\theta', \qquad (5.3.3.37)$$

where $R(\theta)$ is an individual reflectivity function of one crystal and K is a coefficient of proportionality. Its half-width is 1.4 times larger than that related to only one crystal. In spite of this, the recorded profile can be as narrow as, for example, $2.6''$ (Godwod, Kowalczyk & Szmid, 1974), since the profile due to the wavelength $h_\lambda(\theta)$, modified by the first crystal, is extremely narrow. Additional advantages of the diffraction profile are: its symmetry, because $h_C(\theta)$ is symmetric as an effect of autocorreletion, and smoothness, as an effect of additional integration. The profile can thus be located with very high accuracy and precision.

When there is a small difference in the two lattice spacings, so that one has a value d and the other $d + \delta d$, if $\delta\lambda/\lambda$ is small enough, it can be assumed that the profile does not alter in shape but in its peak position [*cf.* §5.3.3.4.3.3, paragraph (3)]. If for two identical crystals this were located at θ_0, the peak position

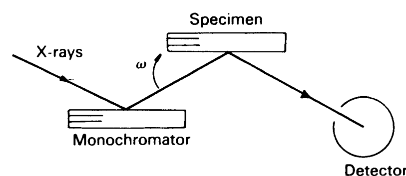

Fig. 5.3.3.8. Schematic representation of the double-crystal spectrometer.

Copyright © 2006 International Union of Crystallography

shifts to $\theta_0 - \tan\theta\delta d/d$. The measurement of this shift rather than the absolute position of the rocking curve is the basis of all the double-crystal methods. An example of the application of a double-crystal spectrometer with photographic recording has been given in §5.3.2.3.5 (Bearden & Henins, 1965).

The basic requirements that should be fulfilled to make the most of the double-crystal spectrometer are: limitation of the primary beam by means of a collimator, parallelism of the two axes [precision as high as 1″ obtained by Godwod, Kowalczyk & Szmid (1974)], and high thermal stability (0.1 K; Godwod, Kowalczyk & Szmid, 1974). Alignment procedure, errors, and corrections valid for the double-crystal spectrometer have been considered by Bearden & Thomsen (1971).

The double-crystal diffractometer, because of the small width of the diffraction profile, is a very suitable tool for local measurements of lattice-parameter differences, for example between an epitaxic layer and its substrate. Hart & Lloyd (1975) carried out such a measurement on a standard single-axis diffractometer (APEX) to which a simple second axis, goniometer head, and detector were added (Fig. 5.3.3.9). The diffracted beam was recorded simultaneously by three detectors. A *symmetric arrangement* with two detectors, D_1 and D_2, with no layer present, makes possible the determination of the absolute value of the lattice parameter of the substrate, as in the Bond (1960) method. The third detector makes it possible to record the double-crystal rocking curve, which usually fully resolves the layer and substrate profiles. The changes in the lattice parameter between the two components can be used for determination of strain (at 1 part in 10^4).

The very important advantage of this method, from the point of view of local measurements, is that single- or double-crystal diffraction can be selected, simultaneously if needed, on exactly the same specimen area. Other examples of strain measurements by means of a double-crystal spectrometer are given by Takano & Maki (1972), who measured lattice strain due to oxygen diffusing into a silicon single crystal; by Fukahara & Takano (1977), who compared experimental rocking curves and theoretical ones computed within the frame of the dynamical theory; and Barla, Herino, Bomchil & Pfister (1984), who examined the elastic properties of silicon.

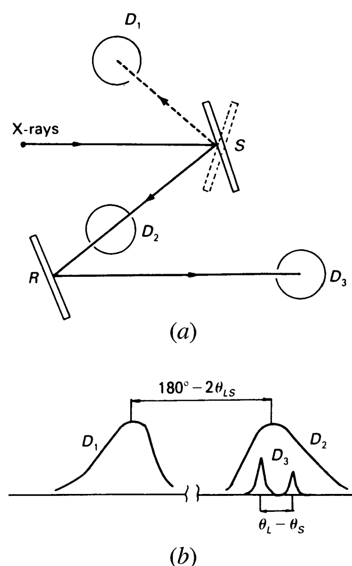

Fig. 5.3.3.9. Schematic representation of the double-crystal arrangement of Hart & Lloyd (1975) for the examination of epitaxic layers. (*a*) Experimental set-up. (*b*) Diffraction profiles recorded by detectors D_1, D_2, and D_3.

The standard double-crystal technique does not allow determination of relatively small strains, *i.e.* ones that affect the lattice parameter by, for example, less than 2–3 parts in 10^5, as in the case of (004) Si reflection and Cu $K\alpha$ radiation. To overcome this difficulty, Zolotoyabko, Sander, Komem & Kantor (1993) propose a new method that combines double-crystal X-ray diffraction with *high-frequency ultrasonic excitation*. Since ultrasound has a wavelength a little less than the X-ray excitation length, it affects the diffraction profile close to the Bragg position and so permits the detection of very small profile broadenings caused by lattice distortions. With this method, lattice distortion as small as 5 parts in 10^6 can be measured.

As has been shown in the case of the device used by Hart & Lloyd (1975), the symmetric arrangement due to Bond (1960) proves to be very useful when the double-crystal spectrometer is to be used for absolute lattice-parameter determination, since such an arrangement combines the high precision and sensitivity of a double-crystal spectrometer with the high absolute accuracy of the Bond method. Other examples of a similar idea are presented by Kurbatov, Zubenko & Umansky (1972), who report measurements of the thermal expansion of silicon; Godwod, Kowalczyk & Szmid (1974), who also discuss the theoretical basis of their arrangement; Ridou, Rousseau & Freund (1977), who examine a phase transition; Sasvári & Zsoldos (1980), and Fewster (1982). The latter two papers are concerned with epitaxic layers. A rapid method is proposed by Sasvári & Zsoldos (1980) for deconvoluting the overlapping peaks due to the layer and the substrate. A particular feature of the arrangement proposed in the first of these papers (Kurbatov, Zubenko & Umansky, 1972) is the use of a germanium-crystal monochromator with anomalous transmission, to obtain a nearly parallel primary beam (the horizontal divergence is 28″ and the vertical 14″).

The error analyses given by Godwod, Kowalczyk & Szmid (1974) and Sasvári & Zsoldos (1980) show that systematic errors due to eccentricity, absorption, and zero position are eliminated experimentally, owing to the symmetric arrangement, as in the Bond (1960) method. In contrast, the errors due to crystal tilt, refraction and the Lorentz–polarization factor [their uncertainties in lattice parameters, as evaluated by Sasvári & Zsoldos (1980), are 10^{-6} Å each], axial divergence (2×10^{-6} Å), angle reading (10^{-4} Å), and instrument correction and calculations (each to 5×10^{-5} Å) should be taken into account. The effect of absorption, discussed by Kurbatov, Zubenko & Umansky (1972), proved to be negligible. The final accuracy achieved for silicon single crystals by Godwod, Kowalczyk & Szmid (1974) is comparable with that obtained by Bond (1960).

A specific group of double-crystal arrangements is formed by those in which *white X-radiation* is used instead of characteristic. Such an arrangement makes possible very large values of the Bragg angle (larger than about 80°), which increases the accuracy, precision, and sensitivity of measurement of the lattice parameters and their change with change of temperature. This task is rather difficult to realize by means of

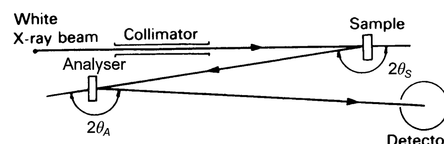

Fig. 5.3.3.10. Schematic representation of the double-crystal arrangement of Okazaki & Kawaminami (1973*a*); white incident X-rays are used.

traditional methods, in which both the wavelengths and the lattice parameters are fixed, and it is difficult to find a suitable combination of their values.

The principle of the method presented by Okazaki & Kawaminami (1973*a*) is shown in Fig. 5.3.3.10. The first crystal (the specimen to be measured) remains fixed during a single measurement, the second (the analyser) is mounted on the goniometer of an X-ray diffractometer and can be operated with either an ω or a θ–2θ scan. As diffraction phenomena appear for both the specimen and the analyser (in general of different materials) whose interplanar spacings are equal to d_s and d_A, respectively, the following relation results from Bragg's law:

$$d_s \sin\theta_s = d_A \sin\theta_A, \qquad (5.3.3.38)$$

where θ_s and θ_A are the respective Bragg angles. Since d_A and θ_s are kept constant, a change in d_s as a function of temperature is determined from a change in θ_A. The relative error $\delta d/d$ resulting from (5.3.3.38) with $\theta_A \approx 90^\circ$ is

$$\frac{\delta d_s}{d_s} = \cot\theta_A\,\delta\theta_A = \tan(\pi/2-\theta_A)\delta\theta_A \approx (\pi/2-\theta_A)\delta\theta_A. \qquad (5.3.3.39)$$

The method initiated by Okazaki & Kawaminami (1973*a*) has been developed by Okazaki & Ohama (1979), who constructed the special diffractometer HADOX (the positions of the specimen and the analyser were interchanged) and discussed systematic errors. Precision as high as 1 part in 10^7 was reported. Examples of the application of such an arrangement for measuring the temperature dependence of lattice parameters were given by Okazaki & Kawaminami (1973*b*) and Ohama, Sakashita & Okazaki (1979). Various versions of the HADOX diffractometer are still reported. By introducing two slits (Soejima, Tomonoga, Onitsuka & Okazaki, 1991) – one to limit the area of the specimen surface to be examined and the other to define the resolution of 2θ – it is possible to combine ω and 2θ scans and obtain a two-dimensional intensity distribution in the plane parallel to the plane of the diffractometer, and to determine the temperature dependence of lattice parameters on a selected area of the specimen (avoiding the effects of the surroundings). The HADOX diffractometer may work with both a rotating-anode high-power X-ray source (examples reported above) and a sealed-tube X-ray source. In the latter case (Irie, Koshiji & Okazaki, 1989), to increase the efficiency of the X-ray tube, the distance between the X-ray source and the first crystal has been shortened by a factor of five. As is implied by (5.3.3.39), one can increase the relative precision of the method by using the analyser angle close to $\pi/2$. This idea has been realized by Okazaki & Soejima (2001), who achieved the relative accuracy of determination of lattice-parameter changes as high as 1 part in 10^9–10^{10} by extending the Bragg angle from 78° (previous versions) to 89.99° and by elimination of systematic errors due to crystal tilt, crystal displacement, temperature effects and radiation damage.

An original method for the measurement of lateral lattice-parameter variation by means of a double-crystal arrangement

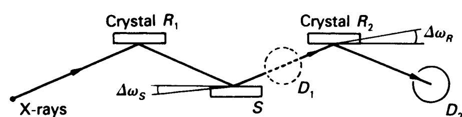

Fig. 5.3.3.11. Schematic representation of the triple-crystal spectrometer developed by Buschert (1965) (after Hart, 1981).

with an oscillating slit was proposed by Korytár (1984). This method permitted simultaneous recording of two rocking curves from two locations on a crystal. Precision of 3 parts in 10^7 was reported. The method has been applied for the measurement of growth striations in silicon.

The main disadvantage of double-crystal spectrometers, in their basic form (Fig. 5.3.3.8), is that they cannot be used for measurements on an absolute scale. Combination of the double-crystal arrangement with the system proposed by Bond (1960) makes it possible to recover the origin of the angular scale and thus such an absolute measurement, but the reported precision is rather moderate.

There are two other ways to overcome this difficulty in pseudo-non-dispersive methods: addition either of a third crystal (more accurately, a third reflection) (§5.3.3.7.2) or of a second source (a second beam) (§5.3.3.7.3). Such arrangements require additional detectors. Combinations of both techniques are also available (§5.3.3.7.4).

5.3.3.7.2. *Triple-crystal spectrometers*

Higher precision than that obtained with the double-crystal arrangements (§5.3.3.7.1) can be achieved by means of triple-crystal diffractometers. Arrangements specially designed for the determination of lattice-parameter changes are described by Buschert (1965) and Skupov & Uspeckaya (1975), and reviewed by Hart (1981).

The principle of the triple-axis spectrometer is shown in Fig. 5.3.3.11. The arrangement consists of one standard crystal S, ultimately replaced by the sample under investigation, and two reference crystals R_1 and R_2. The principle of the measurement is as follows. First, the crystals S, R_1, and R_2 are set to their diffraction (peak) positions using two detectors D_1 and D_2. Then the standard crystal S is replaced by the sample and the new peak position is found by means of D_1 when the sample is turned from its original position to its reflecting position. The angle of rotation of the sample $\Delta\omega_s$ depends on the lattice-parameter difference Δd between the sample and the standard. The relation is given by (Hart, 1981)

$$\Delta\omega_s = -\tan\theta\Delta d/d. \qquad (5.3.3.40)$$

Next, the second reference crystal R_2 is turned through the angle $\Delta\omega_R$ to its diffracting position, the intensity being controlled with the second detector D_2. From the geometry of the arrangement,

$$\Delta\omega_R = 2\Delta\omega_s. \qquad (5.3.3.41)$$

Because the origin of the ω_s scale is lost during the crystal exchange, this second angle of rotation ($\Delta\omega_R$) is used to determine Δd rather than the first one ($\Delta\omega_s$), by using (5.3.3.41) and (5.3.3.40).

The diffraction profiles observed in the second detector, described by Hart (1981),

$$h(\theta)_R = \int\limits_{-\infty}^{\infty} R^2(\theta')R(\theta'-\theta)\,\mathrm{d}\theta, \qquad (5.3.3.42)$$

are not symmetric but can be as narrow as 0.1–1″, so that a precision of 2 parts in 10^8 is possible.

The main experimental problem here is to adjust the tilts of the crystals. The errors resulting both from the crystal tilts and from the vertical divergence were discussed by Skupov & Uspeckaya (1975).

Triple-crystal spectrometers are often applied as lattice-spacing comparators, when very small changes of lattice parameters ($10^{-8} \le |\Delta d|/d \le 10^{-6}$) are to be detected, in

particular for the examination of a correlation between lattice parameter and the dopant or impurity concentration (Baker, Tucker, Moyer & Buschert, 1968). Such an arrangement can also be a very suitable tool in deformation studies, since it allows the separation of the effect of deformation on the Bragg angle from that due to lattice-parameter change (Skupov & Uspeckaya, 1975).

The basis of the accurate lattice-parameter comparison proposed by Bowen & Tanner (1995) is the use of a high-purity silicon standard (*cf.* §5.3.3.9 below) with a well known lattice parameter. To compensate an error that may result from a slight misalignment of crystal planes in relation to the axes of the instrument, the authors recommend a twofold measurement of the diffraction-peak position of the reference crystal (for a given diffraction position and after rotating the specimen holder through 180° about the axis normal to its surface) and a similar twofold measurement of the diffraction-peak position of the sample – after replacing the reference crystal by the sample. The mean positions of the reference crystal and of the sample are used in calculations of the Bragg-angle difference and then of the unknown interplanar spacing. The method uses a standard double-crystal diffractometer fitted with a monochromator (therefore, a third crystal), which provides a well defined wavelength, and with a specimen rotation stage. The measurement is accompanied by a detailed error analysis. The accuracy of absolute lattice-parameter determination as high as a few tens of parts in 10^6, and a much greater relative sensitivity are reported.

By combining a triple-axis spectrometer with the Bond (1960) method, the device can be used for absolute measurements (Pick, Bickmann, Pofahl, Zwoll & Wenzl, 1977). The device described in the latter paper is an automatic triple-crystal diffractometer that permits intensity measurement to be made in any direction in reciprocal space in the diffraction plane with step sizes down to 0.01″ and therefore can be used for very precise measurements [see also §5.3.3.4.3.2, paragraph (5)].

5.3.3.7.3. *Multiple-beam methods*

The other possibility of recovering the crystal-angle scale in differential measurements with a double-crystal spectrometer (*cf.* §§5.3.3.7.1, 5.3.3.7.2) is to obtain reflections from two crystal planes [for example, from (hkl) and $(\bar{h}\bar{k}\bar{l})$ planes] by means of a double-beam arrangement and to measure them simultaneously.

The second X-ray beam may come from an additional X-ray source (Hart, 1969) or may be formed from a single X-ray source by using a beam-splitting crystal (Hart, 1969, second method; Larson, 1974; Cembali, Fabri, Servidori, Zani, Basile, Cavagnero, Bergamin & Zosi, 1992). In particular, two beams with different wavelengths ($K\alpha_1, K\beta_1$) separated with a slit system can be used for this purpose (Kishino, 1973, second technique). The principle of the double-beam method is shown in Fig. 5.3.3.12. The beams are directed at the first crystal (the reference crystal) so that the Bragg condition is simultaneously fulfilled for both beams, and they then diffract from the second crystal (the specimen). As the second crystal is rotated, a double-crystal diffraction profile is recorded first in one detector and then in the other. The angle $\Delta\theta$ of crystal rotation between the two rocking curves is given by (Baker & Hart, 1975):

$$\Delta\theta = (\theta_1 - \theta_2) = \tan\theta\,\Delta d/d. \qquad (5.3.3.43)$$

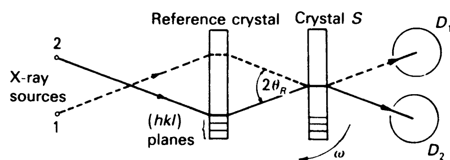

Fig. 5.3.3.12. Schematic representation of the double-beam comparator of Hart (1969).

This formula leads to the lattice-parameter changes Δd.

A double-beam diffractometer can be used for the examination of variations in lattice parameters of about 10 parts in 10^6 within a sample in a given direction. An example was reported by Baker, Hart, Halliwell & Heckingbottom (1976), who used Larson's (1974) arrangement for this task.

The highest reported sensitivity (1 part in 10^9) can be achieved in the double-source double-crystal X-ray spectrometer proposed by Buschert, Meyer, Stuckey Kauffman & Gotwals (1983). The device can be used for the investigation of small concentrations of dopants and defects.

The method can also be applied for the absolute determination of a lattice parameter, if that of the reference crystal is accurately known and the difference between the two parameters is sufficiently small. Baker & Hart (1975), using multiple-beam X-ray diffractometry (Hart, 1969, first technique), determined the d spacing of the 800 reflection in germanium by comparing it with the d spacing of the 355 reflection in silicon. The latter had been previously determined by optical and X-ray interferometry (Deslattes & Henins, 1973; the method is presented in Subsection 5.3.3.8).

In the case of two different wavelengths and diffraction from two different diffraction planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$, the lattice parameter a_0 of a cubic crystal can be determined using the formula (Kishino, 1973)

$$a_0 = \tfrac{1}{2}\{(L\lambda_1)^2 + [(M\lambda_2 - L\lambda_1\cos\theta_{1-2})/\sin\theta_{1-2}]^2\}^{1/2}, \qquad (5.3.3.44)$$

where $L = (h_1^2 + k_1^2 + l_1^2)^{1/2}$, $M = (h_2^2 + k_2^2 + l_2^2)^{1/2}$, and θ_{1-2} is the difference between the two Bragg angles for the specimen crystal, estimated from the measurement of $\Delta\theta = |\theta_{1-2} - \theta'_{1-2}|$ if the difference θ'_{1-2} for the first (reference crystal) is known beforehand. The idea of Kishino was modified by Fukumori, Futagami & Matsunaga (1982) and Fukumori & Futagami (1988), who used the Cu $K\alpha$ doublet instead of $K\alpha_1$ and $K\beta_1$ radiation. Owing to the change, they could use only one detector (Kishino's original method needs two detectors), but a special approach is sometimes needed to resolve two peaks that relate to the components of the doublet. A similar problem of separation of two peaks (recorded by two detectors) is reported by Cembali *et al.* (1992). By introducing a computer simulation of the reflecting curves (using a convolution model), the authors managed to determine the separation with an error of 0.01″ and to achieve a precision of some parts in 10^7. The same precision is reported by Fukumori, Imai, Hasegawa & Akashi (1997), who introduced a precise positioning device and a position-sensitive proportional counter to their instrument.

As in the other multiple-crystal methods, the most important experimental problem is accurate crystal setting. Larson (1974), as a result of detailed analysis, gave the dependence between the angular separation of two peaks and angles characterizing misalignment of the first and second crystals.

5.3.3.7.4. *Combined methods*

The idea of multiple-beam measurement (§5.3.3.7.3) can be applied to other arrangements that combine the features of the double-beam comparator with those of the triple-crystal spectrometer; there are additional advantages in such a system.

The application of the double-beam technique makes it possible to realize a triple-reflection scheme for comparing lattice parameters on the basis of a double-axis spectrometer. The arrangement proposed by Ando, Bailey & Hart (1978), shown in Fig. 5.3.3.13, consists of a sample and a reference crystal, which are made from the same material but differ in purity (or strain, stoichiometry, vacancy concentration, *etc*). The angular difference $\Delta\theta$ in the Bragg angles of the sample and the reference crystal, θ_S and θ_R, respectively,

$$\Delta\theta = \theta_S - \theta_R, \qquad (5.3.3.45a)$$

is measured as the sample angle $\Delta\omega$ between the double-reflected peak D and the triply diffracted peak T:

$$\Delta\theta = \Delta\omega, \qquad (5.3.3.45b)$$

$$\Delta\omega = \omega_D - \omega_T. \qquad (5.3.3.45c)$$

Assuming that $\Delta\theta$ is entirely due to changes Δd in atomic spacings, the authors use the following relation for determination of the latter:

$$\Delta d/d = -\cot\theta\Delta\theta. \qquad (5.3.3.46)$$

The experimental requirements are simple and inexpensive, owing to simple shapes of both the reference crystal and the sample crystal, so that the measurement can be made quickly. By combining the two reference crystals into a single monolithic reference crystal, excellent stability, difficult to achieve with triple-axis arrangements (*cf.* §5.3.3.7.2), is obtained at the same time. The disadvantage of the method is that it covers a smaller range of lattice parameters than the other double-beam methods (Hart, 1969; Larson, 1974) described in §5.3.3.7.3. A new version of the double-crystal triple-reflection scheme (Häusermann & Hart, 1990) allows one to achieve a precision of 1 part in 10^8 in 2 min of measurement time, which includes the data analysis; 30 min are needed to change the sample. Errors due to the crystal tilt and thermal drifts are considered.

Another example of the triple-reflection scheme realized by means of the double-beam technique has been presented by Kovalchuk, Kovev & Pinsker (1975), who realized the triple-crystal arrangement on the basis of a double-crystal spectrometer by parallel mounting of the two crystals to be compared (the sample and the reference crystal) on one common axis. The advantage of this system is that Bragg angles as high as 80° are available. The device can be applied in studies of the real structure of a single crystal.

High-sensitivity ($\Delta d/d$ up to $\pm 3 \times 10^{-8}$) lattice-parameter-comparison measurement over a wide range of temperatures can be performed by means of the triple-crystal (more accurately, triple-axis) X-ray spectrometer realized by Buschert, Pace, Inzaghi & Merlini (1980). The arrangement (Fig. 5.3.3.14) consists of four crystals. The first is used for obtaining a very wide but extremely parallel exit beam, which is incident on both the standard crystal S and an unknown crystal X, placed side by side on a common axis in the cryostat. The reflected beams from S and X are recorded by partially transmitting detectors DA_2 and DB_2, so that the beams reflect from the third crystal and are detected by the counters DA_3 and DB_3. There is a small, sensitive, angle adjustment to rotate the crystal X with respect to the standard S and it is used to bring the peaks of S and X into approximate coincidence. The angular difference in the peak positions on the third axis is used for determination of lattice-parameter changes from (5.3.3.46), so that

$$\Delta\theta = \Delta\theta_3/2 - \Delta\theta_2, \qquad (5.3.3.47)$$

where $\Delta\theta_2$ and $\Delta\theta_3$ are the differences in peak positions at axes (2) and (3), respectively. The device was used, for example, to study the effect of isotope concentration on the lattice parameter of germanium perfect crystals (Buschert, Merlini, Pace, Rodriguez & Grimsditch, 1988). The measured differences in the lattice parameter, of the order of 1 part in 10^5, were compared with those evaluated theoretically, and a very good agreement was obtained.

Another variant of a multiple-beam arrangement, based on a triple-crystal spectrometer, was proposed by Kubena & Holý (1988). The authors compared the distances of lattice planes in a direction perpendicular to the surface of the sample while studying the growth striations. One well collimated and monochromated beam coming from the first crystal was directed into the sample, and then two beams – one transmitted and one diffracted in the sample – diffracted in the reference crystal. Intensities of the diffracted beams were measured by two detectors. The difference of lattice spacings of the sample and the reference crystal was determined from the difference in positions of respective peaks. The accuracy of the lattice-spacing comparison of 2 parts in 10^7 and the precision of 1 part in 10^7 were obtained.

A four-crystal six-reflection diffractometer (Fewster, 1989) was built to study crystals distorted by epitaxy and defects in nearly perfect crystals. Fig. 5.3.3.15 is a schematic diagram of this device. The two-crystal four-reflection Bartels monochromator (Bartels, 1983) defines a narrow reflectivity profile. The analyser selects the angular range diffracted from the sample. The device may be used for recording both near-perfect rocking curves from distorted crystals (when rotations of the sample and the analyser are coupled) and a diffraction-space map for studying the diffuse scattering (when the two rotations are

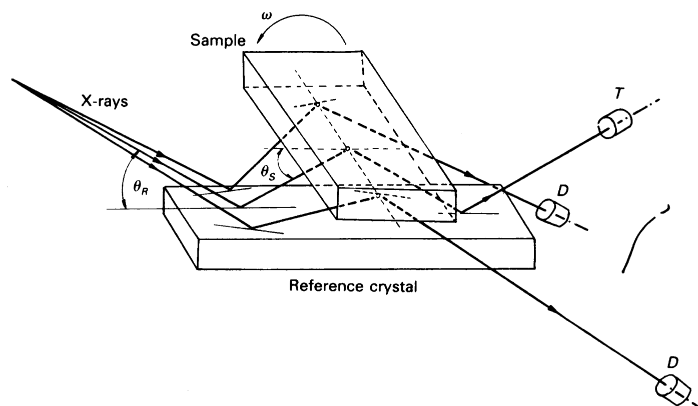

Fig. 5.3.3.13. The double-axis lattice-spacing comparator of Ando, Bailey & Hart (1978); a triple-diffracted beam is used.

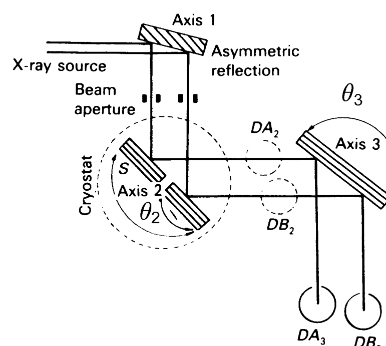

Fig. 5.3.3.14. Schematic representation of the double-beam triple-crystal spectrometer of Buschert *et al.* (1980).

uncoupled). Various applications of such high-sensitivity multiple-crystal X-ray spectrometers for reciprocal-space mapping and imaging (topography), which are outside the scope of the present paper, are reviewed by Fewster (1993, and references therein).

As was shown a few years later by Fewster & Andrew (1995), the device can also be used for absolute lattice-parameter measurements of single-crystal and polycrystalline materials with a relative accuracy of a few parts in 10^6. The authors checked the angular resolution and the sample centring of their instrument, and discussed systematic errors due to refraction, the Lorenz and polarization factor, the diffracting-plane tilt and the peak-position determination.

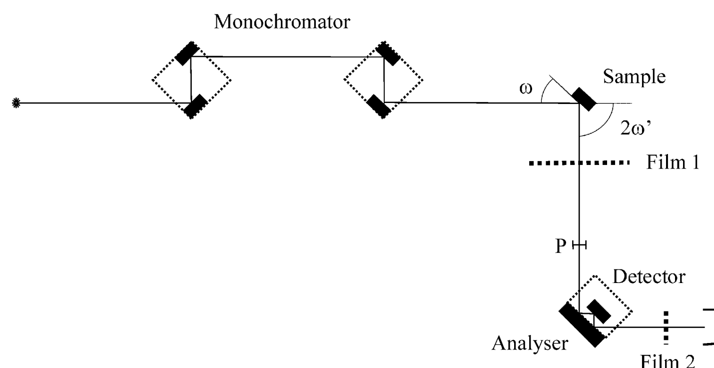

Fig. 5.3.3.15. The geometry of the diffractometer used by Fewster & Andrew (1995). The scattering angle, $2\omega'$, is the fundamental angle for determination of the interplanar spacing and P is the analyser-groove entrance.

5.3.3.8. *Optical and X-ray interferometry – a non-dispersive technique*

The accuracy of an absolute measurement can be improved, in relation to that obtained in traditional methods (*cf.* Subsection 5.3.3.5), either if the wavelength of the radiation used in an experiment is known with better accuracy [*cf.* equation (5.3.1.3)] or if a high-quality standard single crystal is given, whose lattice spacing has been very accurately determined (Baker & Hart, 1975; mentioned in §5.3.3.7.3). The two tasks, *i.e.* very accurate determination of both lattice spacings and wavelengths in metric units, can be realized by use of combined optical and X-ray interferometry. This original concept of absolute-lattice-spacing determination directly in units of a standard light wavelength has been proposed and realized by Deslattes (1969) and Deslattes & Henins (1973).

The principle of the method is presented in Fig. 5.3.3.16. The silicon-crystal X-ray interferometer is a symmetric Laue-case type (Bonse & te Kaat, 1968). The parallel translation device consists of the stationary assembly (*a*) formed by two specially prepared crystals, and a moveable one (*b*), to which belongs the third crystal. One of the two mirrors of a high-resolution Fabry–Perot interferometer is attached to the stationary assembly and the second to the moving assembly. A stabilized He–Ne laser is used as a source of radiation, the wavelength of which has been established relative to visible standards. The first two crystals produce a standing wavefield, which is intercepted by the third crystal, so that displacement of the third crystal parallel to the diffraction vector (as suggested by the large arrow) produces alternate maxima and minima in the diffracted beams, detected by X-ray detector (*c*). Resonant transmission maxima of the optical interferometer are detected simultaneously by the photomultiplier indicated at (*d*). Analysis of the fringes (shown in Fig. 5.3.3.17) is the basis for the calculation of the lattice-spacing-to-optical-wavelength ratio (d/λ), which is given by

$$\frac{2d}{\lambda} = \frac{n}{m}\frac{\cos\alpha}{\cos\beta}, \qquad (5.3.3.48)$$

where n and m are the numbers of optical and X-ray diffraction fringes, respectively, and α and β are the measured angular deviations of the optical and X-ray diffraction vectors from the direction of motion. The measurements are carried out in two steps. First, the lattice parameter of silicon along the [110] crystallographic direction was measured in the metric system, independently of the X-ray wavelength used in the experiment. As the next step, a specimen of known lattice spacing, treated as a reference crystal, was used for the accurate wavelength determination of Cu $K\alpha_1$ and Mo $K\alpha_1$. Accuracy better than 1 part in 10^6 was reported (see Section 4.2.2).

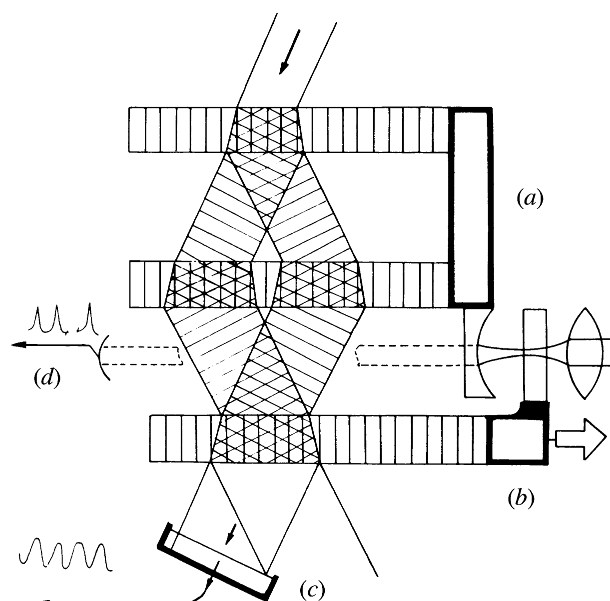

Fig. 5.3.3.16. Optical and X-ray interferometry. Schematic representation of the experimental set-up (after Deslattes & Henins, 1973; Becker *et al.*, 1981).

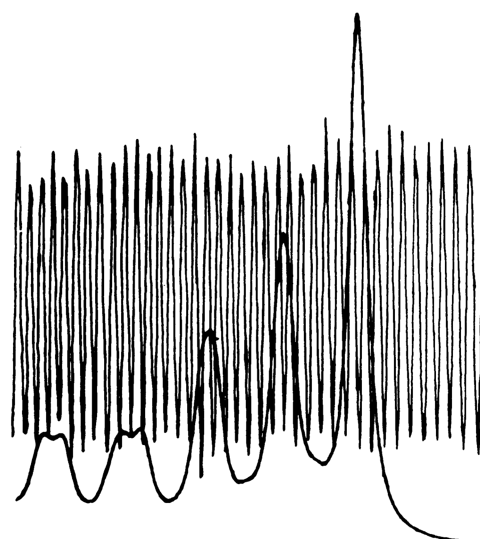

Fig. 5.3.3.17. Portion of a dual-channel recording of X-ray and optical fringes (Deslattes, 1969).

references