

5. DETERMINATION OF LATTICE PARAMETERS

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:

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

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

$$\begin{aligned} \frac{\delta d_s}{d_s} &= \cot \theta_A \delta \theta_A = \tan(\pi/2 - \theta_A) \delta \theta_A \\ &\approx (\pi/2 - \theta_A) \delta \theta_A. \end{aligned} \quad (5.3.3.39)$$

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

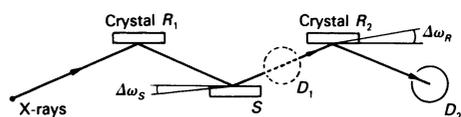


Fig. 5.3.3.11. Schematic representation of the triple-crystal spectrometer developed by Buschert (1965) (after Hart, 1981).

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 & Uspekaya (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)

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

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,

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

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),

$$h(\theta)_R = \int_{-\infty}^{\infty} R^2(\theta') R(\theta' - \theta) d\theta', \quad (5.3.3.42)$$

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 & Uspekaya (1975).

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

5.3. X-RAY DIFFRACTION METHODS: SINGLE CRYSTAL

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 10⁶, 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

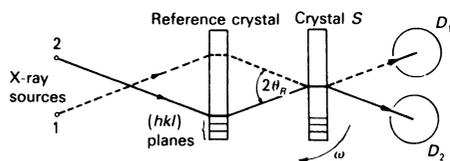


Fig. 5.3.3.12. Schematic representation of the double-beam comparator of Hart (1969).

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):

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

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 10⁶ 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 10⁹) 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)

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

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 10⁷. 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.