establishment and control of the temperature (Baker, George, Bellamy & Causer, 1968; Łukaszewicz, Kucharczyk, Malinowski & Pietraszko, 1978; Okazaki & Ohama, 1979; Okada, 1982; Soejima, Tomonaga, Onitsuka & Okazaki, 1991), so that the basic instrument should be relatively simple (Glazer, 1972; Berger, 1984; Clegg & Sheldrick, 1984). Since measurements at many temperatures are then performed, the problem is to obtain the desired precision in as short a time as possible by using automatic control (Baker, George, Bellamy & Causer, 1968), special strategy of measurement (Barns, 1972; Urbanowicz, 1981*a*), and special sources of radiation [synchrotron radiation used by Buras *et al*. (1977) and Ando, Hagashi, Usuda, Yasuami & Kawata (1989)]. Analogous problems appear when the effects of other factors such as pressure (Mauer, Hubbard, Piermarini & Block, 1975; d'Amour, Denner, Schulz & Cardona, 1982; Leszczyński, Podlasin & Suski, 1993), or electric field (Kobayashi, Yamada & Nakamura, 1963) are examined.

(iv) To detect *small differences of lattice parameter* between the sample and the standard or between two points of the same specimen, the highest precision is required. To improve resolution in traditional methods, a finely collimated X-ray beam (Kobayashi, Yamada & Nakamura, 1963) and cameras with large radius (Kobayashi, Yamada & Azumi, 1968) are required. Really high precision, which reaches 1 part in 10^9, can be obtained with multiple-crystal (pseudo-non-dispersive) techniques (Hart, 1969; Buschert, Meyer, Stuckey Kauffman & Gotwals, 1983).

In the present review, all the methods are classified with respect to the measurement technique, in particular into photographic and counter-diffractometer techniques. Moreover, the methods will be described in approximately chronological sequence,* *i.e.* from the earliest and simplest rotating-crystal method to the latest more-complex non-dispersive techniques, and at the same time from those of poor accuracy and precision to those attaining the highest precision and/or accuracy. In each of the methods realizing a given technique, first the absolute and then the relative methods will be described.

5.3.2. Photographic methods

5.3.2.1. *Introduction*

Photographic single-crystal techniques used for unit-cell determination can be divided into three main groups:

(1) the Laue method with a well collimated beam of polychromatic X-radiation with a stationary crystal;

(2) methods with a well collimated beam of characteristic radiation and a moving crystal;

(3) methods with a highly divergent X-ray beam of monochromatic radiation (usually combined with white radiation).

In the past, only techniques belonging to groups (2) and (3) were used in absolute lattice-parameter measurements. As recently shown by Carr, Cruickshank & Harding (1992), a single synchrotron-radiation Laue photograph can provide all necessary information for the determination of unit-cell dimensions on an absolute scale (though with low accuracy for the present).

The methods of the second group are popular moving-crystal methods or their modifications especially adapted for lattice-parameter determination. Cameras and other equipment for performing these measurements – with the exception of special designs – are available in every typical X-ray diffraction laboratory. At present, these methods of poor (1 part in 10^2) or moderate (up to 1 part in 10^4) accuracy are suitable only for preliminary measurements.

Less popular and more specific divergent-beam methods (third group) give satisfactory accuracy (1 part in 10^4 or 1 part in 10^5), comparable with that obtained by counter-diffractometer methods, by means of very simple equipment.

In spite of the common use of counter diffractometers, and of the increasing use of imaging plates (and synchrotron radiation), traditional photographic methods of the second and the third groups are still popular and new designs are reported.

5.3.2.2. *The Laue method*

As based on polychromatic radiation, the Laue method is, in principle, useless for accurate lattice-parameter determination. It is true that, from a single Laue diffraction pattern (in transmission), one can determine precisely the axial ratios and interaxial angles (a method based on the gnomonic projection is described by Amorós, Buerger & Amorós, 1975), but the unit cell determined will differ from the true cell by a simple scale factor.

The problem of absolute scaling of the cell is important nowadays, when synchrotron-radiation Laue diffraction patterns are currently being used for collecting X-ray data (from single-crystal systems including proteins, for example). As shown by Cruickshank, Carr & Harding (1992), it is possible to estimate the scale factor using the minimum wavelength present in the incident X-ray beam. A method proposed by the authors (Carr, Cruickshank & Harding, 1992) allows one to determine the unit cell and orientation of an unknown crystal (in a general orientation) from a single Laue pattern. The accuracy of the absolute lattice-parameter determination depends on the accuracy with which the minimum wavelength is known for the experiment and is, at present, about 5% in favourable cases (while the error in axial ratio determination after refinement is typically 0.25%). To increase the accuracy, the authors propose either to record the Laue patterns with an attenuator in the incident beam that has a suitable absorption edge ($\lambda_{\min}$ can become a sharp and accurately known limit) or to locate the bromine-absorption edge, if the X-ray detector contains bromine, as in photographic films and image plates.

5.3.2.3. *Moving-crystal methods*

Moving-crystal methods of lattice-parameter determination apply basic photographic techniques, such as:

(1) the rotating- or oscillating-crystal method;

(2) the Weissenberg method;

(3) the technique of de Jong–Bouman; or

(4) the Buerger precession method.

In the first of these methods, the film remains stationary, while in the others it is moved during the exposure. The principles and detailed descriptions of these techniques have been presented elsewhere (Buerger, 1942; Henry, Lipson & Wooster, 1960; Evans & Lonsdale, 1959; Stout & Jensen, 1968, Chapter 5; Sections 2.2.3, 2.2.4, and 2.2.5 of this volume) and only their use in lattice-parameter measurements will be considered here.

5.3.2.3.1. *Rotating-crystal method*

The rotating-crystal method – the simplest of the moving-crystal methods – determines the identity period I along the axis of rotation (or oscillation), $\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, from the formula

$$I(uvw) = n\lambda/\sin\nu, \qquad (5.3.2.1)$$

* With some exceptions; for example, multiple-diffraction methods introduced by Renninger (1937) are placed after the Bond (1960) method.

in which n is the number of the layer line and ν is the angle between the directions of the primary and diffracted beams.

The angle ν is determined from the measurement of the distance l_n between two lines corresponding to the same layer number n from the equation

$$\tan \nu = l_n/R, \tag{5.3.2.2}$$

where R is the camera radius.

All the lattice parameters may be determined from separate photographs made for rotations of the crystal along different rotation axes, *i.e.* the system axis, plane and spatial diagonals (Evans & Lonsdale, 1959), without indexing the photographs. In practice, however, this method is rarely used alone and is most often applied together with other photographic methods (for example, the Weissenberg method), but it is a useful preliminary stage for other methods. In particular, the length of a unit-cell vector may be directly determined if the rotation axis coincides with this vector.

Advantages of this method are:

(*a*) simple equipment (only rotation of the crystal is required, since the film is stationary);

(*b*) immediate determination of direct-cell parameters (photographs obtained with other cameras afford information about reciprocal-lattice parameters only);

(*c*) indexing of the photographs is unnecessary.

Drawbacks of the method are:

(*a*) poor precision and accuracy of the measurement ($|\delta d|/d \approx 10^{-2}$);

(*b*) small amount of information from a single photograph (one parameter only);

(*c*) necessity of taking several photographs in the case of a lower-symmetry system if this method is the only one used.

5.3.2.3.2. *Moving-film methods*

A two-dimensional picture of a reciprocal cell from one photograph can be obtained by the methods in which rotation of the crystal is accompanied by movement of the film, as in the Weissenberg, the de Jong–Bouman, and the Buerger precession techniques. These methods give greater precision ($|\delta d|/d \approx 10^{-4}$) than the previous one (§5.3.2.3.1).

The advantages of the Weissenberg method in relation to the other two are:

(*a*) a simpler camera;

(*b*) a larger range of reciprocal-lattice points recorded on one photograph (larger range of θ angles, up to 90° for the zero layer).

On the other hand, the disadvantage, in contrast to the de Jong–Bouman and the Buerger precession methods, is that it gives deformed pictures of the reciprocal lattice. This is not a fundamental problem, especially now that computer programs that calculate lattice parameters and draw the lattice are available (Luger, 1980). In lattice-parameter measurements, both the zero-layer Weissenberg photographs and the higher-layer ones are used. The latter can be made both by the normal-beam method and by the preferable equi-inclination method. Photographs in the de Jong–Bouman and precession methods give undeformed pictures of the reciprocal lattice, but afford less information about it than do Weissenberg photographs.

5.3.2.3.3. *Combined methods*

The most effective photographic method of lattice-parameter measurement is a combination of two techniques (Buerger, 1942; Luger, 1980), which makes it possible to obtain a *three-dimensional picture* of the reciprocal lattice; for example: the rotation method with the Weissenberg (lower accuracy); or the precession (or the Weissenberg) method with the de Jong–Bouman (higher accuracy).

A suitable combination of the two methods will determine all the lattice parameters, even for monoclinic and triclinic systems, *from one crystal mounting*. This problem has been discussed and resolved by Buerger (1942, pp. 388–390), Hulme (1966), and Hebert (1978). Wölfel (1971) has constructed a special instrument for this task, being a combination of a de Jong–Bouman and a precession camera.

5.3.2.3.4. *Accurate and precise lattice-parameter determinations*

To measure with a precision and an accuracy better than is possible in routine photographic methods, additional work has to be performed. The first methods allowing precise measurement of lattice parameters were photographic powder methods (Parrish & Wilson, 1959). Special single-crystal methods with photographic recording to realize this task (earlier papers are reviewed by Woolfson, 1970, Chap. 9) combine elements of basic single-crystal methods (presented in §§5.3.2.3.1 and 5.3.2.3.2) with ideas more often met in powder methods (asymmetric film mounting). A similar treatment of some systematic errors (extrapolation) is met in both powder and single-crystal methods.

(i) The relative accuracy $\Delta I/I$ of the identity period I in the rotating-crystal method, estimated by differentiation of formula (5.3.2.1), is given by

$$\Delta I/I = -\cot \nu \Delta \nu. \tag{5.3.2.3}$$

This formula shows that the highest accuracy is obtained for ν tending to 90°. Since reflections with large values of ν are difficult to record in commonly used cameras, a special camera may be used for this task, in which a flat film is placed perpendicular to the rotation axis, or a different one, whose axis coincides with the primary beam (Umansky, 1960). The accuracy achieved with these improvements is still no better than 5 parts in 10^3.

(ii) The asymmetric film mounting proposed by Straumanis & Ieviņš (1940) in the case of powder cameras can also be used in a simple oscillating camera (Farquhar & Lipson, 1946). In particular, this idea can be realized in a precision Debye–Scherrer camera adapted to single-crystal measurements by mounting in it a goniometer head (Popović, 1974). The Straumanis mounting allows the recording of the high-angle reflections close together on the film, thus reducing the effect of film shrinkage and making it possible to measure the effective camera radius.

(iii) Sometimes, to eliminate systematic errors (uncertainty of the camera radius), the separations resulting from the wavelength differences of the $K\alpha_1$ and $K\alpha_2$ doublet are measured rather than the absolute distances on the film (Main & Woolfson, 1963; Alcock & Sheldrick, 1967). The first reference related to the zero-layer normal-beam photograph, the second to higher layer lines (in the equi-inclination method also) and oscillation photographs.

(iv) Systematic errors connected with film shrinkage can also be eliminated by means of the *ratio method*, introduced by Černohorský (1960) for powder samples and adapted by Polcarová & Zůra (1977) for single crystals. In this method, pairs of reflections that differ from one another in wavelength and/or in *hkl* indices are used and the ratio of the two diameters of the diffraction rings corresponding to these reflections is taken into account. The accuracy of the method is about 1 part in 10^4

if systematic errors due to absorption, refraction, Lp factor, temperature, changes of the camera radius, and misalignment of the sample and the goniometer are corrected. The ratio method was generalized by Horváth (1983) to the monoclinic crystal system.

(v) Graphical extrapolation, similar to that used in powder methods (Parrish & Wilson, 1959), can also be used for single crystals (Farquhar & Lipson, 1946; Weisz, Cochran & Cole, 1948), to reduce systematic errors proportional to $\sin\theta$. Least-squares refinement, on the other hand, permits a reduction of the standard deviations of the results (Main & Woolfson, 1963; Clegg, 1981). Mathematical methods of processing the data obtained from oscillation photographs, including 'eigenvalue filtering' and profile fitting (Rossmann, 1979; Reeke, 1984) have been applied to the refinement of unit-cell parameters, crystal orientation, and reflecting-range parameters needed to process oscillation photographs.

(vi) By measuring the *angle between two reflecting crystal positions*, symmetrical in relation to the primary beam [the idea used in the original Bragg spectrometer (Bragg & Bragg, 1915)], one can eliminate some sources of systematic errors. Such a spectrometer with photographic recording was used by Weisz, Cochran & Cole (1948). In spite of the great simplicity of the arrangement, the accuracy obtained was about 1 part in 10^4. The authors indicated the need for introducing counter recording to the method. 12 years later, their idea was realized by Bond (1960) (*cf.* Subsection 5.3.3.4, in particular §5.3.3.4.3).

(vii) The other way of reducing some systematic errors is to introduce a *reference crystal*. Singh & Trigunayat (1988) adapted the idea to the oscillation method. By mounting the specimen crystal and the reference crystal, properly centred and set, on two identical goniometer heads with a screw-type base, they recorded layer lines of the two crystals simultaneously. The identity period I of the crystal was then determined from the formula that results from a combination of (5.3.2.1) and (5.3.2.2) for layer lines of the two crystals (notation of the present Section):

$$I = n\lambda\left[\frac{l_n^2(I_r^2 - m^2\lambda^2)}{l_{m,r}^2 m^2\lambda^2} + 1\right]^{1/2}, \qquad (5.3.2.4)$$

in which l_n and $l_{m,r}$ are the measured distances between nth layer lines of the crystal and between mth layer lines of the specimen, respectively, and I_r is the identity period of the reference crystal. The result is thus independent of the camera radius. When the differences between l_n and $l_{m.r}$ are no greater than a few mm, the error due to film shrinkage is automatically taken care of, and the error due to a parallel shift of the axis of the cylindrical cassette in relation to the axis of rotation is negligible in practice. The other possible misalignments related to the cassette and the collimator can be readily detected beforehand by taking a complete rotation photograph.

Reference crystals are commonly used in multiple-crystal methods reviewed in Subsection 5.3.3.7.

5.3.2.3.5. *Photographic cameras for investigation of small lattice-parameter changes*

Small changes of lattice parameters caused by thermal expansion or other factors can be investigated in *multiple-exposure cameras*.

Bearden & Henins (1965) used the double-crystal spectrometer with photographic detection to examine *imperfections* and *stresses* of large crystals. The technique allowed the detection of angle deviations as small as $0.5''$. A nearly perfect calcite crystal was used as the first crystal (monochromator), the sample was the second. The device distinguished itself with very good sensitivity. The use of the long distance (200 cm) between the focus and the second crystal made possible resolution of the doublet $K\alpha_{1,2}$, and elimination of the $K\alpha_2$ radiation. An additional advantage was that the arrangement was less time-consuming, so that it was suitable for controlling the perfection of growing crystals and useful for choosing adequate samples for the wavelength measurements.

Kobayashi, Yamada & Azumi (1968) have described a special 'strainmeter' for measuring small strains of the lattice. The strain x_i along an axis normal to the i plane results in a change δd_i of the interplanar distance d_i:

$$x_i = \delta d_i/d_i = -\cot\theta_i\delta_i. \qquad (5.3.2.5)$$

The use of a large camera radius $R = 2639$ mm makes it possible to obtain both high sensitivity and high precision (2 parts in 10^6) even in the range of lower Bragg angles ($\theta \simeq 55^\circ$). The device is suitable for the investigation of defects resulting from small strains and may be used in measurements of thermal expansion.

Glazer (1972) described an automatic arrangement, based on the Weissenberg goniometer, for the photographic recording of high-angle Bragg reflections as a function of temperature, pressure, time, *etc*. A careful choice of the oscillation axis and oscillation range makes it possible to obtain a distorted but recognizable phase diagram (Fig. 5.3.2.1) within several hours. The method had been applied by Glazer & Megaw (1973) in studies of the phase transitions of $NaNbO_3$.

Popović, Šljukić & Hanic (1974) used a Weissenberg camera equipped with a thermocouple mounted on the goniometer head for precise measurement of lattice parameters and thermal expansion in the high-temperature range.

5.3.2.4. *The Kossel method and divergent-beam techniques*

5.3.2.4.1. *The principle*

Another group of methods with photographic recording has been developed in parallel with those discussed in Subsection 5.3.2.3. These are the methods in which the crystal remains stationary and the diffraction conditions are fulfilled, simultaneously for more than one set of crystallographic planes, by the use of a highly divergent beam, dispersed from a point source (Fig. 5.3.2.2). The Kossel method (Kossel, 1936, and references therein), the divergent-beam techniques initiated by Lonsdale (1947), and their numerous modifications belong to this group.

The excitation of the characteristic X-rays used in these methods can be performed by X-radiation (Lonsdale, 1947), by electron bombardment (Kossel, 1936; Gielen *et al.*, 1965; Ullrich & Schulze, 1972) or by proton irradiation (Geist & Ascheron, 1984) of a single crystal. The source of emitted X-rays may be located either *in* the sample itself (the Kossel method), *on* the surface of the sample in a layer of target material (the pseudo-Kossel method), or *outside* the sample (the divergent-beam techniques). The divergent X-ray beam diffracts from sets of crystallographic planes. The diffracted rays for each Bragg reflection form a conical surface whose semivertical angle is equal to $90^\circ - \theta$ and whose axis is normal to the Bragg plane (*i.e.* coincides with the reciprocal-lattice vector).

The conical surface of an *hkl* reflection can be described in the form (Morris, 1968; Chang, 1984):

$$x'^2 + y'^2 = z'^2\tan^2\alpha, \qquad (5.3.2.6)$$

where (x', y', z') is an orthogonal coordinate system with its origin at the vertex of the cone and with z' along the axis of the

cone and normal to the plane of interest, and α is the semivertical angle. Since α depends on the Bragg angle, it is possible to combine (5.3.2.6) with the Bragg law [equations (5.3.1.1) or (5.3.1.2)], and so with the lattice parameters. In particular, the dependence can be presented as:

$$\frac{r}{z'} = \frac{1}{\sin\theta} = \frac{2d}{n\lambda}, \qquad (5.3.2.6a)$$

where $r = (x'^2 + y'^2 + z'^2)^{1/2}$.

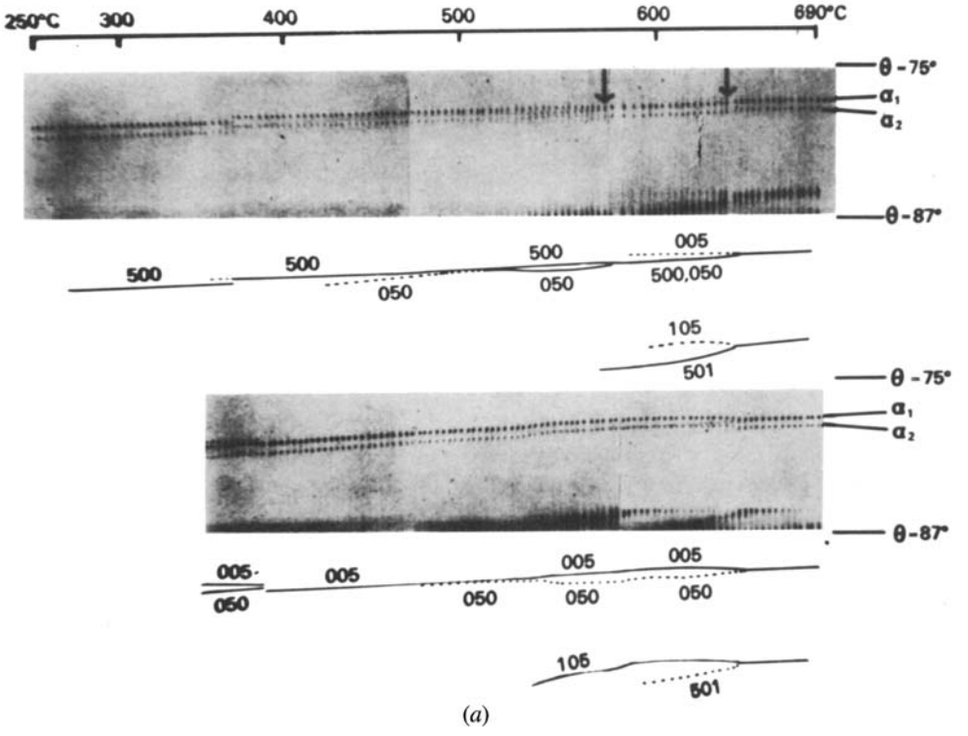
In another convenient coordinate system (x, y, z) common for all the cones, say with z along the direction of the incident beam, (5.3.2.6*a*) will take the form:

$$\frac{r}{c_x x + c_y y + c_z z} = \frac{2d}{n\lambda}, \qquad (5.3.2.6b)$$

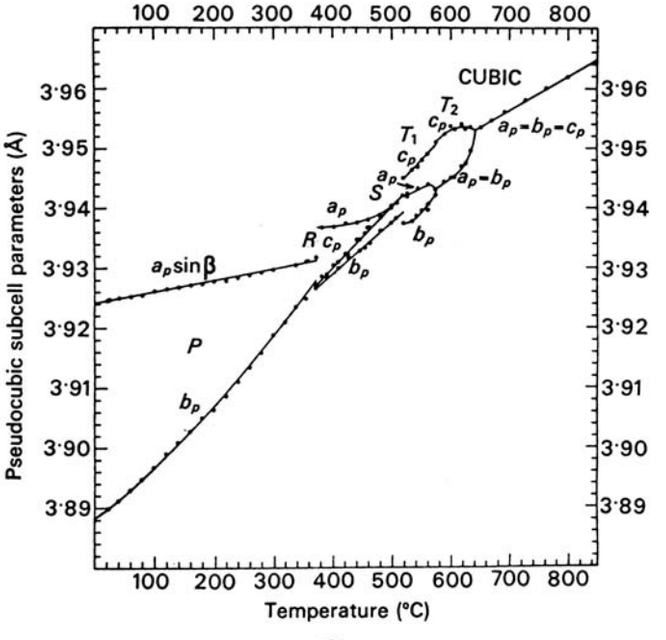
where c_x, c_y, c_z are direction cosines of the angles between the z' axis and the axes x, y and z, respectively. Since the origin of the coordinate system has not been changed,

$$r = (x^2 + y^2 + z^2)^{1/2}. \qquad (5.3.2.6c)$$

The Kossel lines (Fig. 5.3.2.3) are formed at the intersections of the cones with a flat film placed parallel to the specimen surface (Fig. 5.3.2.2). When the film plane is normal to the z axis, and the focus-to-film distance is equal to Z, putting $z = Z$ in



(*a*)



(*b*)

Fig. 5.3.2.1. (*a*) Photographic recording of lattice-parameter changes. (*b*) Corresponding diagram of the variation of lattice parameters in pseudocubic $NaNbO_3$ (Glazer & Megaw, 1973).

(5.3.2.6*b*,*c*) gives the formulae describing the conic section on the film.

A high-precision Kossel camera is described by Reichard (1969) and the generation of pseudo-Kossel patterns by the divergent-beam method has been described by Imura, Weissmann & Slade (1962), Ellis, Nanni, Shrier, Weissmann, Padawer & Hosokawa (1964), and Berg & Hall (1975).

The photographs may be in either the transmission or the back-reflection region (Fig. 5.3.2.2). The second arrangement seems to be (Lutts, 1968) more suitable for lattice-parameter determination, since the background is less intensive and the lines on the photographs have greater contrast. Both possibilities are used in practice. Photographs in the back-reflection region have been reported by Imura, Weissmann & Slade (1962), Ullrich (1967), Newman & Weissmann (1968), Newman & Shrier (1970), and Berg & Hall (1975). Examples of the use of the transmission region are given by Yakowitz (1966*a*), Reichard (1969), and Glass & Weissmann (1969).

The recommended *crystal thickness* t for work in the transmission region, according to Hanneman, Ogilvie & Modrzejewski (1962), is given by:

$$t = 1/0.2\mu_L, \qquad (5.3.2.7)$$

where μ_L is the linear absorption coefficient for $K\alpha$ radiation generated in the crystal. A more detailed study of the effect of sample thickness, as well as operating voltage, on the contrast of Kossel transmission photographs is given by Yakowitz (1966*a*).

The picture geometry does not depend, in principle, on whether the Kossel, pseudo-Kossel, or divergent-beam technique is applied. Imura (1954) has studied in detail the form of the curves of the light or deficiency type, and recorded both in the transmission and in the back-reflection region. The curves on transmission patterns can be considered to be conics; those recorded in the back-reflection region are related to ellipses, but of higher order. In general, the photograph has to be indexed before performing measurement on the film. For this purpose, the pattern may be compared with a calculated pattern (gnomonic, orthogonal, cylindrical, or stereographic projection). For lattice-parameter determination, various features of the photographs may be used, *i.e.* intersections or near-intersections of Kossel lines, their near-tangency, lens-shaped figures, and the whole lines approximated with a function.

5.3.2.4.2. *Review of methods of accurate lattice-parameter determination*

The basis of lattice-parameter determination involves measurements performed on the film. There are various methods covering most of the different geometrical features of the cones and recorded pictures. These were reviewed by Lutts (1968), Yakowitz (1966*b*, 1969) and Tixier & Waché (1970). In each case, the wavelength of the excited radiation has to be known. Often, the resolved $K\alpha_{1,2}$ doublet and/or $K\beta$ radiation is applied rather than a single (but most pronounced) $K\alpha_1$ line. The other data needed (a sufficient number of equations, the solution of which leads to lattice-parameter determination; camera geometry; crystal system; and indices) depend on the method.

Biggin & Dingley (1977) propose a classification of all the methods using a divergent beam based on the information required.

(i) All the kinds of information mentioned above are needed in the earliest method (Kossel, 1936), in which near-tangency of Kossel lines is taken into account.

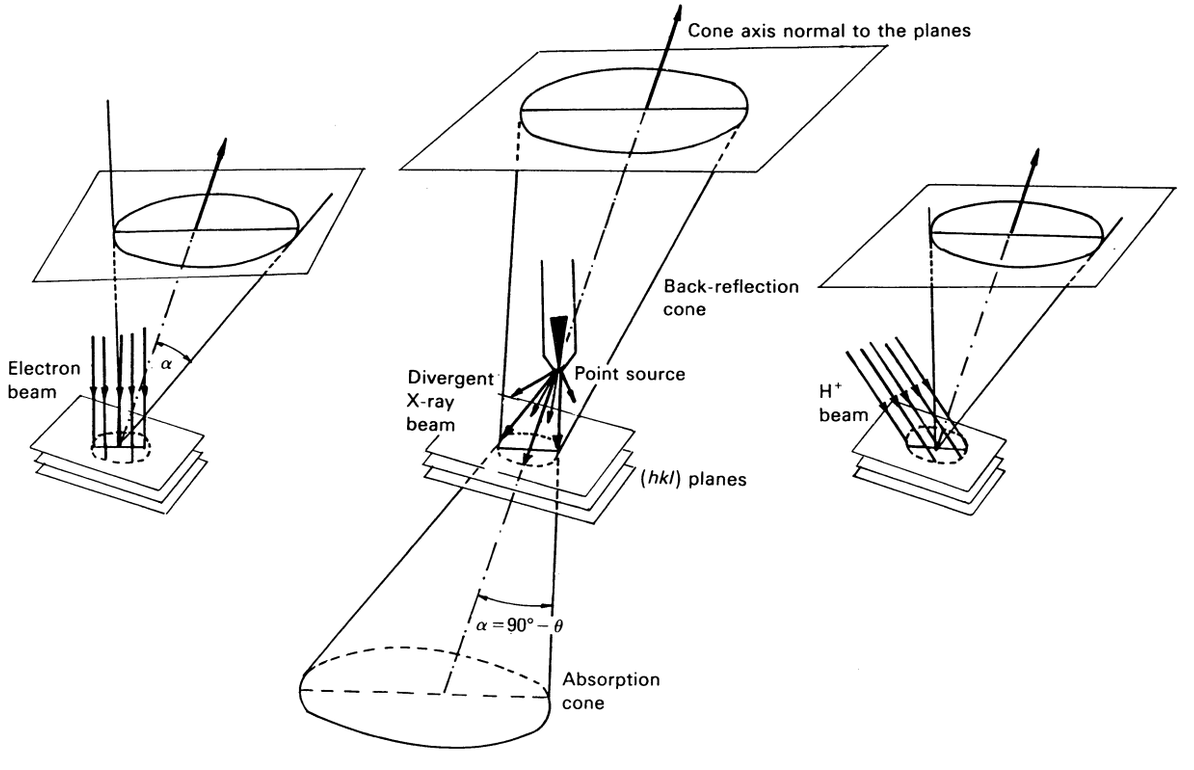
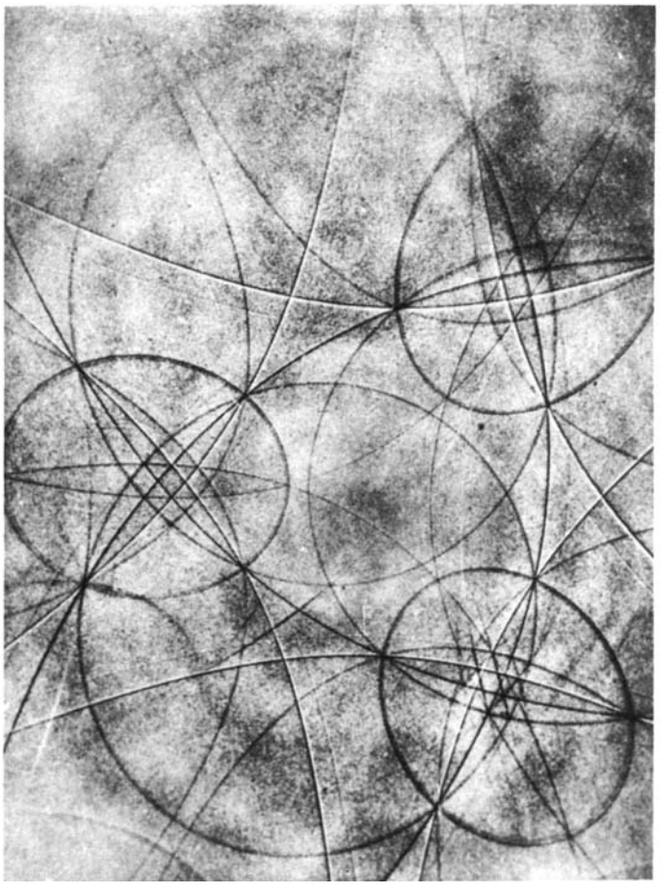
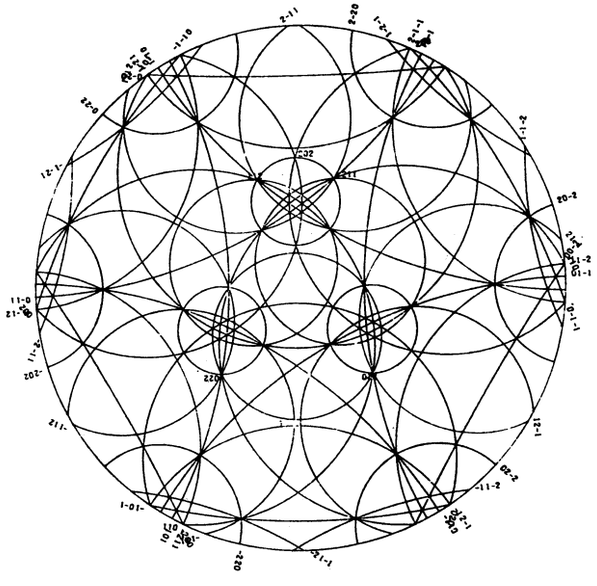


Fig. 5.3.2.2. Schematic representation of the origin of the Kossel lines. (*a*) The Kossel (1936) method. (*b*) The divergent-beam method developed by Lonsdale (1947). (*c*) The proton-induced Kossel effect (Geist & Ascheron, 1984). In (*b*), the divergent X-ray beam is directed onto the sample from a point source while in the remaining cases it is generated within a crystal by (*a*) electrons or (*c*) protons.

(ii) As has been shown in successive papers that appeared from 1947 to the early 1970's, information on camera dimensions can be eliminated if the crystallographic system is known and the photograph is indexed. Some dependence between crystal planes and, as a consequence, between lines on the photograph, is then taken into consideration. This is of great importance, since camera dimensions, in particular the distance from the focus to the centre of the photograph, are difficult to measure accurately and negatively influence the precision and accuracy of the determined lattice parameters.



(*a*)



(*b*)

Fig. 5.3.2.3. (*a*) The Kossel pattern from iron and (*b*) the corresponding stereographic projection (Tixier & Waché, 1970).

The Lonsdale (1947) method is based on triple *intersections* of the Kossel lines resulting from **multiple-diffraction** effects (*cf.* Subsection 5.3.3.6), which are *dependent on the wavelength*, so first the particular wavelength has to be determined by an extrapolation. Two or three lines with known indices produced by different wavelengths ($K\alpha_1$, $K\alpha_2$, and/or $K\beta$) are used for this task (Schwartzenberger, 1959; Mackay, 1966; Isherwood & Wallace, 1971; Spooner & Wilson, 1973). Similar problems arise when near-tangency of two lines is taken into consideration (Kossel, 1936; Mackay, 1966).

With the use of reciprocal-lattice geometry, the equation of the so-called Kossel plane (Isherwood & Wallace, 1971) for a diffracting plane (*hkl*) is given by (Spooner & Wilson, 1973; Chang, 1984):

$$L_1x^* + L_2y^* + L_3z^* = \frac{1}{d}, \qquad (5.3.2.8)$$

where L_1, L_2, and L_3 are direction cosines between the reciprocal vector $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ and the unit-cell vectors $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$, *i.e.*

$$L_1 = \frac{ha^*}{H}, \quad L_2 = \frac{kb^*}{H}, \quad L_3 = \frac{lc^{*\prime}}{H}, \qquad (5.3.2.8a)$$

where $H = |\mathbf{H}| = 1/d$, $a^* = |\mathbf{a}^*|$, $b^* = |\mathbf{b}^*|$, $c^* = |\mathbf{c}^*|$.

In the case of the triple intersection, (5.3.2.8) is satisfied simultaneously by three sets of diffracting planes, the Miller indices of those being $(h_ik_il_i)$, $i = 1, 2, 3$. From the Ewald construction, it follows that the triple point (x_0^*, y_0^*, z_0^*) must lie on the sphere of reflection:

$$x^{*2} + y^{*2} + z^{*2} = \frac{4}{\lambda_0^2}. \qquad (5.3.2.8b)$$

The radius of the sphere, $2/\lambda_0$, is the modulus of the double wavevector defined by Isherwood & Wallace (1971).

For cubic crystals, where $H = (h^2 + k^2 + l^2)^{1/2}/a$, the set of equations to be solved, resulting from (5.3.2.8) and (5.3.2.8*a*), which relates to the triple point, takes the form

$$h_ix_0^* + k_iy_0^* + l_iz_0^* = (h_i^2 + k_i^2 + l_i^2)/a, \qquad (5.3.2.9)$$

where $i = 1, 2, 3$.

First, coordinates x_0^*, y_0^*, z_0^* dependent on a are determined from (5.3.2.9), and next a is calculated from (5.3.2.8*b*). It should be noted that the measurements performed on the film are used here for determination of the wavelength only. As shown (theoretically and experimentally) by Brühl & Rhan (1985) for cubic lattices, positions of the lines on the film that result from the multiple-diffraction phenomenon are insensitive to lattice-parameter changes (caused by thermal expansion, for example), while positions of the primary reflections depend on actual lattice-parameter values. Practical examples of photographic multiple-diffraction methods are given by Lonsdale (1947) (see also Tixier & Waché, 1970; Chang, 1984), Isherwood & Wallace (1966), Isherwood (1968), Isherwood & Wallace (1970), Spooner & Wilson (1973), Brown, Halliwell & Isherwood (1980), and Isherwood, Brown & Halliwell (1981, 1982).

The technique, in which triple intersections of Kossel lines are analysed, can be used both for back-reflection and for transmission. In the second case, the thickness t of the crystal should be such that $\mu_L t \simeq 1$ [*cf.* equation (5.3.2.7)]. However, thicker crystals, for which $\mu_L t \gtrsim 10$, can be examined by anomalous transmission, if the degree of crystal perfection is

high (Glass & Moudy, 1974). A correction for displacement of the conics due to wafer thickness t is necessary in the case when the intersection lies along the normal to the specimen surface. One triple intersection allows the determination of the lattice parameter of a cubic crystal, but for a structure in the orthorhombic system three such intersections would be required.

Two intersecting Kossel lines sometimes form a *lens configuration* (Fig. 5.3.2.4*a*). The use of such a figure, consisting of two lenses (Fig. 5.3.2.4*b*) owing to the resolved doublet of $K\alpha_1$ and $K\alpha_2$ (or $K\beta$) radiation, makes it possible to determine lattice parameters without a knowledge of the distance between the source and the film. Lattice parameters are then calculated from the ratio L_1/L_2 of the distances L_1 and L_2 between pairs of the sections. Heise (1962) used this method for cubic crystals in the simplest case, in which the cone axes are perpendicular to the film (symmetrical method). His idea had been generalized by Gielen *et al.* (1965), who formed a theory of the lens in the case of arbitrarily situated diffracting planes and arbitrary wavelengths, but for cubic crystals only. Lutts (1968) derived suitable formulae for cubic, tetragonal, and hexagonal systems by combining the ratio L_1/L_2 with interplanar spacings and lattice parameters.

Several features of the Kossel pattern may be jointly taken into account for its interpretation and lattice-parameter determination. Hanneman, Ogilvie & Modrzejewski (1962) used the conic sections formed by $K\alpha_1$ and $K\beta$ radiation and the lens figures.

Lang & Pang (1995) observed and analysed fine streaks in the transmitted pseudo-Kossel patterns caused by both the coherent multiple diffraction and the enhanced Borrmann (anomalous) transmission. As they have found, these fine-scale features of a few arcseconds in angular width, which add markers to the broad-line Kossel patterns, may be taken into account in accurate lattice-parameter measurements.

(iii) Determination of lattice parameters by means of techniques utilizing a highly divergent beam becomes much more complicated if there is no information about indices and the *crystal system*. Such a problem arises in the case when the crystal system of the specimen is *unknown* or when the lattice is deformed. Then, a three-dimensional array of intersecting cones with a common vertex should be taken into consideration.

It is difficult to dispense with the data concerning the camera geometry. However, the distance of X-ray source from the film center may be eliminated in calculations when the *multiple-exposure technique* is used. This technique, introduced by Ellis *et al.* (1964) for back-reflection patterns, depends on recording the Kossel lines at variable but controlled distances from the focus to the film (Fig. 5.3.2.5), so that three or more positions of a cone generator can be established and, as a consequence, the cone axis and the semivertical angle are determined. The interpretation of the multiple-exposure pictures is based, in principle, on the coordinates of general points of lines rather than on their special properties.

The basic formula valid for all the methods applying the Kossel idea,

$$\mathbf{P} \cdot \mathbf{N} = \cos\alpha, \qquad (5.3.2.10)$$

where $\mathbf{P}$ is the unit vector defining the cone generator and $\mathbf{N}$ is the axial direction of a cone, can now be fully utilized, since multiple-exposure techniques make possible accurate calculations of direction cosines. Lengthy and complicated calculations resulting from measurements performed on the film may be realized by means of a computer. A suitable program is given by Fischer & Harris (1970). This technique has also been applied and developed by Slade, Weissmann, Nakajima & Hirabayashi (1964), Shrier, Kalman & Weissmann (1966), Newman & Weissmann (1968), Schneider & Weik (1968), Fischer & Harris (1970), Newman & Shrier (1970), Aristov, Shekhtman & Shmytko (1973), and Soares & Pimentel (1983) for both the back-reflection and the transmission region.

As mentioned above, the Kossel lines occurring in the back-reflection region are similar to ellipses; they can be described using an equation of the fourth degree (Newman, 1970). In general, the major axes of such ellipse-shaped figures have been

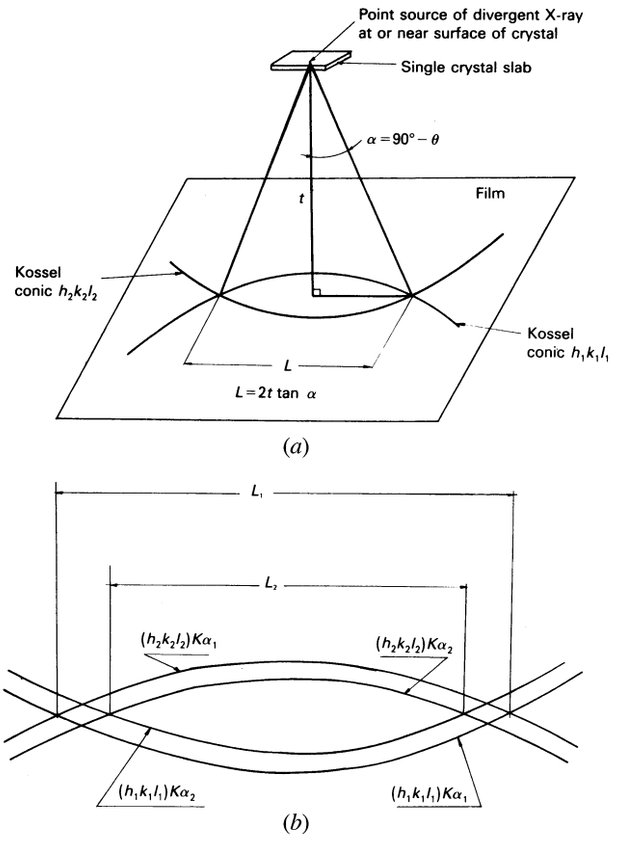


Fig. 5.3.2.4. Lens-shaped figures formed by pairs of intersecting conics. (*a*) Schematic representation of the method of Heise (1962). (*b*) The use of the $K\alpha_{1,2}$ doublet for precise and accurate lattice-parameter determination.

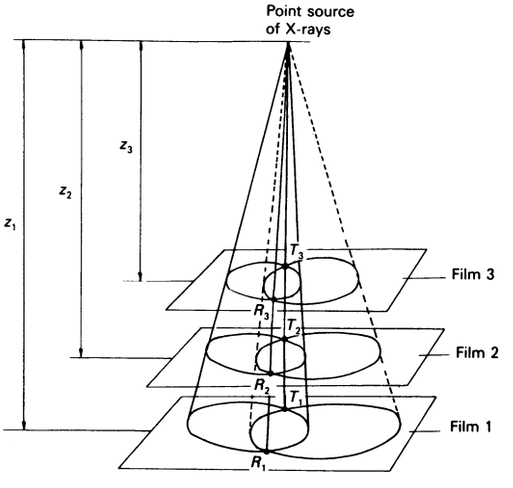


Fig. 5.3.2.5. Schematic representation of the multiple-exposure technique (after Fischer & Harris, 1970).

taken into account in lattice-parameter determination. A novelty introduced by Lider & Rozhansky (1967) was to also use the minor axes in the calculations. The essential feature of their method is the location of the X-ray source in the plane of a flat film.

(iv) The other possibility for gathering the necessary information for the recorded picture is a more detailed study of the form of the Kossel lines. Morris (1968) proposed a method based on the mathematical analysis of a cone, which makes possible the determination of lattice parameters in any crystal system, with a relative accuracy as high as 10 parts in 10^6. The necessary calculations can be made by a computer program. A conic section can usually be expressed by a general equation of the second degree (Bevis, Fearon & Rowlands, 1970; Harris & Kirkham, 1971; Morris, 1968):

$$x^2 + Ay^2 + Bxy + Cx + Dy + E = 0, \qquad (5.3.2.11)$$

which results from a combination and a transformation of (5.3.2.6*b*) and (5.3.2.6*c*). The coefficients A, B, C, D, and E, being functions of the direction cosines and of the ratio $2d/n\lambda$, can be found by the method of least squares. Methods based on *Kossel-line fitting* can be realized both in the single-exposure (Harris & Kirkham, 1971) and in the multiple-exposure technique (Aristov, Shekhtman & Shmytko, 1973; Aristov & Shmytko, 1978).

(v) From theoretical considerations based on the shape of pseudo-Kossel lines (Harris & Kirkham, 1971), it is possible to eliminate the need for information concerning camera geometry if the source and the pattern centre are accurately located. Lattice parameters of an unknown or deformed crystal can thus be determined with no information other than measurements on the film and a knowledge of the *wavelength*.

A general method for locating the X-ray source and the centre of the pattern – which permits the realization of the above idea – has been developed by Biggin & Dingley (1977). Its characteristic feature is the introduction of steel balls between the specimen and the film; these cast sharp shadows on the film by blocking the diffuse radiation. Coordinates of points along the Kossel lines as well as the shadow ellipses recorded on the film are taken into account in calculations.

5.3.2.4.3. *Accuracy and precision*

Although the precision theoretically obtainable by means of the Lonsdale (1947) method is of the order of 1 part in 10^6, this limit is unattainable in practice. The reported values are in the range of about 10^{-4}–10^{-5} Å, depending not only on the method but also on the crystal – its symmetry and perfection. The highest accuracy known by the author was achieved by Lonsdale [(1947), $\pm 5 \times 10^{-5}$ Å, for diamond], Morris [(1968), 2 parts in 10^5] and Aristov & Shmytko [(1978), $|\delta d|/d \sim 3 \times 10^{-5}$, 1–5 $\times 10^{-5}$ rad for angles between crystallographic directions].

Systematic errors due to the methods in which a divergent beam is applied have been discussed by Hanneman, Ogilvie & Modrzejewski (1962), Gielen, Yakowitz, Ganow & Ogilvie (1965), Beu (1967), Lutts (1968), and Aristov & Shmytko (1978). The main sources of systematic error are:

(i) those common to all X-ray methods, resulting from a finite depth of X-ray penetration, wavelength dispersion, refraction (Isherwood & Wallace, 1966; Isherwood, 1968), and from the real structure (substructures and mosaic blocks; and

(ii) those common to methods with photographic recording, resulting from film shrinkage and inaccurate determination of camera dimensions and distances on the film.

The errors of the second group may be to some extent removed if small differences of the length resulting from the resolved $K\alpha_{1,2}$ doublet are measured on the film rather than distances due to only one wavelength, and/or if the camera dimensions can be eliminated from the equations used in the calculations of lattice parameters (see §5.3.2.4.2). A relative misorientation between the specimen and the flat film has been analysed by Lutts (1973).

An error typical for methods realized by means of an electron microscope or an electron-beam probe may result from the thermal effects of the electron beam generating a divergent X-ray beam at the crystal surface. Uncontrolled thermal effects may also occur in the case of the Kossel method, since the sample is situated inside the X-ray tube. In the latter method, the wavelength of the radiation emitted depends on the chemical composition of the sample, since the sample plays the role of the anode of the X-ray tube.

The reported precision of the methods, limited by the finite width of the lines on the photograph, and depending also on the geometrical features taken into account, is 1 part in 10^3 to 1 part in 10^5. The highest [$\sigma(d)/d = 10^{-5}$] is reported by Hanneman, Ogilvie & Modrzejewski (1962), Gielen, Yakowitz, Ganow & Ogilvie (1965), and Lider & Rozhansky (1967). On the other hand, the lowest (1 part in 10^3), obtained by Harris & Kirkham (1971), is attributed to the method in which neither the indexing of the lines nor a knowledge of the crystallographic system or camera geometry is required.

For precision determination of lattice-parameter differences, a 'point' source (*i.e.* as small as possible) is required and the high-order Kossel lines should be used to obtain both well resolved $K\alpha_{1,2}$ doublets and 'thin' figures. The near-intersections of conic sections, applied in Lonsdale's (1947) method, the major axes of lens-shaped figures, used in Heise's (1962) method, and the small spherical polygons formed by several Kossel cones are very sensitive to lattice-parameter changes, so that these figures can be taken into account in the precise measurements reported in §5.3.2.4.4.

5.3.2.4.4. *Applications*

As was mentioned in §5.3.2.4.3, the methods in which a highly divergent beam is used are applied both to the accurate determination of the unit cell and to the precision detection of lattice-parameter changes or differences. It should be added that the Kossel method is especially suitable for small single crystals or fine-grained polycrystals, whereas the other divergent-beam techniques need larger specimens (Lutts, 1968).

Since all the methods are relatively simple (stationary specimen, stationary film, simple construction of the camera) and, on the other hand, are applicable mainly for highly symmetric systems, they proved to be particularly useful in studies of metals and semiconductors. Various applications of the Kossel method and other divergent-beam techniques for this task have been discussed by Ullrich (1967), Ullrich & Schulze (1972), and Geist & Ascheron (1984). The latter paper relates especially to semiconductors.

A task that arises both in metallurgy and in the semiconductor industry is the examination of the real structure – in particular, measurements of strains introduced by variation in temperature, pressure, mechanical stress (elastic strains) or by point defects, deviation from exact stoichiometry, irradiation damage, and phase changes (permanent strains).

Measurements of small changes in interplanar spacings of independent sets of crystal planes enable a stress–strain analysis to be made (Imura, Weissmann & Slade, 1962; Elllis *et al.*,

1964; Slade *et al.*, 1964; Newman & Weissmann, 1968; Berg & Hall, 1975). A special case of strains is an extensional deformation of the lattice in the direction of crystal growth (Isherwood, 1968).

A typical metallurgical problem is the effect of heat treatment on the microstructure of alloys. An example of the application of the Kossel method to the task is given by Shinoda, Isokawa & Umeno (1969), who reported a study of precipitation of α from β in copper–zinc alloys. The lattice parameters and thermal expansion of α-iron and its alloys were examined by Lutts & Gielen (1971). Structure defects resulting from over-pressure experiments and annealing were investigated by Potts & Pearson (1966). Irradiation effects caused by neutrons were the subject of papers of Hanneman, Ogilvie & Modrzejewski (1962), Yakowitz (1972), and Spooner & Wilson (1973); those caused by electron bombardment were reported by Ullrich (1967).

Divergent-beam techniques are considered to be a suitable tool for studying strains in epitaxic layers (Hart, 1981), since corresponding lines of the layer and substrate, observed on one photograph, can be readily identified. Relevant examples are given by Brühl (1978), Chang, Patel, Nannichi & de Prince (1979), and Chang (1979), who examined lattice mismatch in LPE heterojunction systems, and by Brown, Halliwell & Isherwood (1980), and Isherwood, Brown & Halliwell (1981, 1982), who reported characterization of distortions in hetero-epitaxic structures together with a theoretical basis (multiple diffraction) for the method.

Another task of real-structure examination is the determination of angles between crystal blocks. A method has been worked out by Aristov, Shmytko & Shulakov (1974*a*,*b*).

Divergent-beam techniques can also be used in X-ray topographic studies, realized either by means of Kossel-line scanning (Rozhansky, Lider & Lyutzau, 1966) or by line-profile analysis (Glass & Weissmann, 1969).

Schetelich & Geist (1993) used the Kossel method for lattice-parameter determination and a qualitative estimation of the crystal perfection of *quasicrystals* and showed that the fine structure of Kossel lines of quasicrystals is the same as observed for conventional crystals.

Mendelssohn & Milledge (1999) used a Dingley–Kossel camera for quick and simple computer-aided measurements of cell parameters of isotopically distinct samples of LiF over a wide temperature range of 15–375 K.

5.3.3. Methods with counter recording

5.3.3.1. *Introduction*

Although, theoretically, the limit of accuracy in all methods based on the Bragg law [equation (5.3.1.1)] is given by the accuracy of the wavelength measurement ($\delta\lambda/\lambda \sim 10^{-6}$), with photographic recording this limit is not attained. Surprisingly high accuracy may be offered by accurately applied Kossel or divergent-beam techniques. In practice, however, even in this case the accuracy achieved is poorer by an order of magnitude.

The use of Geiger–Müller, proportional, or scintillation counters together with a step-scanning motor makes it possible to record the diffraction profile in a quantitative numerical form convenient for data processing, to locate it with better accuracy and precision and, as a consequence, to obtain better accuracy and precision for the Bragg angle and thus for the lattice parameter. To make the most of this possibility, theoretical papers concerning methods of peak location, estimation of systematic and statistical errors, and optimization of the measurement were developed in parallel with constructional and experimental methods.

Methods of lattice-parameter determination with counter recording form a large and heterogeneous group. As well as measurements on two- or four-circle standard diffractometers, a separate method developed by Bond (1960) and a variety of non-dispersive (X-ray and optical interferometry) and pseudo-non-dispersive methods (two- and three-circle spectrometers, multiple-beam techniques, and combined methods) are included in this group.

5.3.3.2. *Standard diffractometers*

The determination of lattice parameters by the use of a standard diffractometer is based, as in the case of photographic methods, on (5.3.1.1) and (5.3.1.2), and the main task is to measure a sufficient number of reflections (the θ values for various *hkl* indices) for determining and solving the equations and for calculating the unknown parameters. The reflections can be chosen arbitrarily or in a special way (high θ angle, axial or non-axial reflections).

The characteristic feature of measurements performed on a diffractometer is, however, that to satisfy the Ewald condition for a given reflection the crystal and the detector are rotated or, depending on the geometry (equatorial or inclination), shifted round their axes as well. Basic and more detailed information about the geometry of diffractometers is given elsewhere (Arndt & Willis, 1966, Chap. 3; Stout & Jensen, 1968, Section 6.3; Kheiker, 1973, Chap. 4; Luger, 1980, Chap. 4; Section 2.2.6 of this volume). For calculating the *setting angles* for given *hkl* reflections, the lattice parameters (at least preliminary values) have to be known, and conversely, if the setting angles are known, it is possible to calculate or to refine lattice parameters. Therefore, not only the θ values (given by the angle 2θ of rotation of the detector about the goniometer axis) but also the values of the remaining setting angles (*i.e.* ω, φ, and χ of the crystal rotation in equatorial geometry, or μ and φ for the crystal and ν for the detector in inclination geometry) can be used for lattice-parameter determination. This problem can be treated by a matrix analysis.

5.3.3.2.1. *Four-circle diffractometer*

In the case of an automated four-circle (equatorial geometry) diffractometer, the setting angles are calculated by means of the orientation matrix $\boldsymbol{U}$, *i.e.* a matrix such that

$$\boldsymbol{A}^* = \boldsymbol{U}\boldsymbol{A}_G, \tag{5.3.3.1}$$

where

$$\boldsymbol{A}^* = \begin{bmatrix} a^* \\ b^* \\ c^* \end{bmatrix} \tag{5.3.3.1a}$$

is the reciprocal-axis system with metric

$$\boldsymbol{G}^{-1} = \begin{bmatrix} a^{*2} & a^*b^*\cos\gamma^* & a^*c^*\cos\beta^* \\ a^*b^*\cos\gamma^* & b^{*2} & b^*c^*\cos\alpha^* \\ a^*c^*\cos\beta^* & b^*c^*\cos\alpha^* & c^{*2} \end{bmatrix} \tag{5.3.3.1b}$$

and

$$\boldsymbol{A}_G = \begin{bmatrix} a_G \\ b_G \\ c_G \end{bmatrix} \tag{5.3.3.1c}$$

is the crystal-fixed orthonormal system. As can be proved (Busing & Levy, 1967; Hamilton, 1974; Luger, 1980, Section

references