

5. DETERMINATION OF LATTICE PARAMETERS

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 epitaxial 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-epitaxial 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 U , *i.e.* a matrix such that

$$A^* = UA_G, \quad (5.3.3.1)$$

where

$$A^* = \begin{bmatrix} a^* \\ b^* \\ c^* \end{bmatrix} \quad (5.3.3.1a)$$

is the reciprocal-axis system with metric

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

and

$$A_G = \begin{bmatrix} a_G \\ b_G \\ c_G \end{bmatrix} \quad (5.3.3.1c)$$

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

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4.1.1; Gabe, 1980), the reciprocal-cell parameters are related to the orientation matrix by the following equation:

$$\mathbf{A}^* \mathbf{A}^{*'} = \mathbf{U} \cdot \mathbf{U}', \quad (5.3.3.2)$$

where $\mathbf{A}^* \mathbf{A}^{*'} = \mathbf{G}^{-1}$ is given by (5.3.3.1b). It is thus possible to calculate the lattice parameters from the terms of the orientation matrix.

The determination of the orientation matrix is usually the first step in measurements performed on the four-circle diffractometer. This task can be accomplished when the preliminary lattice-parameter values are known, and even when they are unknown. In the first case, the setting angles of two reflections, and, in the second, of three reflections, have to be determined. The procedure (Busing & Levy, 1967; Hamilton, 1974) is usually accomplished by the software of the four-circle diffractometer. Least-squares refinement of the lattice and orientation parameters may be performed when the setting angles of several reflections have been observed (Clegg, 1984). Appropriate constraints, resulting from the presence of symmetry elements in the given crystal structure, to be introduced during the refinement, are discussed by Bolotina (1989).

In a particular case, the four-circle diffractometer can be used for lattice-parameter measurements performed in the plane perpendicular to the main goniometer axis (say, the horizontal plane), for which $\chi = 0^\circ$, so that, in practice, only 2θ and ω values are used for lattice-parameter determination (see also §5.3.3.4.1). The equations to be solved can be simplified if only axial reflections are taken into account. In an example described by Luger (1980, Section 4.2.2), the \mathbf{b}^* axis of a monoclinic crystal is oriented in the direction of the main axis. Then each of the two axial lengths, a^* and c^* (see Fig. 5.3.3.1), can be obtained from only one measurement:

$$a^* = \frac{2 \sin \theta}{|h| \lambda}, \quad (5.3.3.3a)$$

$$c^* = \frac{2 \sin \theta}{|l| \lambda}, \quad (5.3.3.3b)$$

whereas φ values of two reflections are used to determine the β^* angle between \mathbf{a}^* and \mathbf{c}^* axes, since

$$\beta^* = \varphi_{h00} - \varphi_{00l}. \quad (5.3.3.3c)$$

This method is more suitable for orthogonal systems than for non-orthogonal ones, because of the difficulties in obtaining the proper orientation in the case of the monoclinic and, particularly, the triclinic system. In the latter case, the crystal has to be set three times.

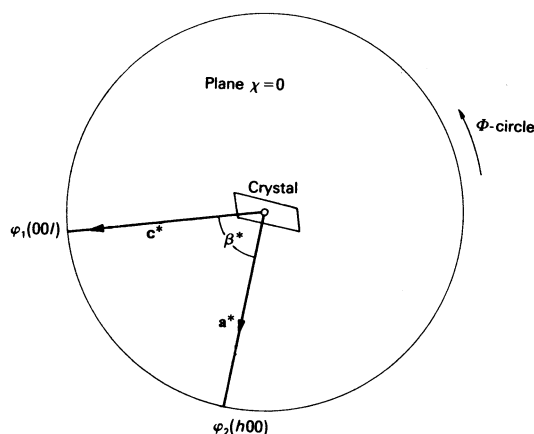


Fig. 5.3.3.1. Determination of reciprocal-lattice angles on the θ circle (after Luger, 1980).

5.3.3.2.2. Two-circle diffractometer

Lattice-parameter determination by the use of the two-circle (inclination) diffractometer, the so-called 'Weissenberg diffractometer', is more troublesome than by means of the four-circle one, because only two rotations [ω (or φ) of the crystal, and 2θ (or γ) of the detector] are motor-driven under computer control, while two inclination angles (μ for the crystal and ν for the detector) must be set by hand.

The problem of application of the popular two-circle (Eulerian-cradle) diffractometer for measurements similar to those presented in §5.3.3.2.1 was discussed by Clegg & Sheldrick (1984). The main idea of their paper was to introduce equations combining setting angles, obtained for selected reflections, with reciprocal-cell parameters, for calculating the latter. The authors started with zero-layer reflections for which, for a crystal mounted about the c axis,

$$\sin \theta = (x^2 + y^2)^{1/2}, \quad (5.3.3.4a)$$

$$\omega = \omega_0 + \theta - \tan^{-1}(y, x), \quad (5.3.3.4b)$$

where

$$x = \lambda(ha^* + kb^* \cos \gamma^*)/2, \quad (5.3.3.4c)$$

$$y = (\lambda kb^* \sin \gamma^*)/2, \quad (5.3.3.4d)$$

and ω_0 is a zero-point correction.

The remaining parameter c had to be determined from the inclination angle μ , measured by hand. The use of zero-layer reflections was advantageous, apart from the simplicity of the formulae (5.3.3.4a,b,c,d), because they were less affected by crystal misalignment than were upper-layer reflections. However, a zero-point correction ω_0 for ω had to be performed. For this purpose, the ω_0 value was treated as an additional parameter in off-line least-squares refinement.

As the next step, the authors introduced equations for a general crystal orientation instead of an aligned crystal (cf. §5.3.3.2.1) and derived equations defining the setting angles for an arbitrary reflection useful for data collection from a randomly oriented crystal if preliminary lattice-parameter values had been assumed. This made possible measurements of reflections on a range of layers; only one crystal mounting was required. The matrix formulae suitable for Eulerian-geometry diffractometers are also given by Kheiker (1973, Chap. 3, Section 9) and Gabe (1980).

In order to perform precise refinement of all six cell parameters, Clegg & Sheldrick (1984) used least squares with empirical weights:

$$W_{hkl} = 1/\sqrt{\omega_{hkl}}, \quad (5.3.3.5)$$

where ω_{hkl} is the width of the hkl reflection. An additional (third) motor to control the μ circle was proposed.

The authors point out that the two-circle diffractometer, owing to its simpler construction in comparison with the four-circle one, is well suited to operations that require additional attachments; for example, for low-temperature operation.

5.3.3.3. Data processing and optimization of the experiment

5.3.3.3.1. Models of the diffraction profile

Every measurement is based on a certain model of its object. By 'model' we understand here* all the 'systematized *a priori*

* Statisticians (Schwarzenbach, Abrahams, Flack, Gonschorek, Hahn, Huml, Marsh, Prince, Robertson, Rollett & Wilson, 1989) define model as 'conjecture about physical reality used to interpret the observations'. Based on their definition, the author proposes its operative interpretation.