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

$$\boldsymbol{A}^*\boldsymbol{A}^{*\prime} = \boldsymbol{U}\cdot\boldsymbol{U}', \tag{5.3.3.2}$$

where $\boldsymbol{A}^*\boldsymbol{A}^{*\prime} = \boldsymbol{G}^{-1}$ is given by (5.3.3.1*b*). 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 $2\theta$ and $\omega$ 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:

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

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

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

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

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.

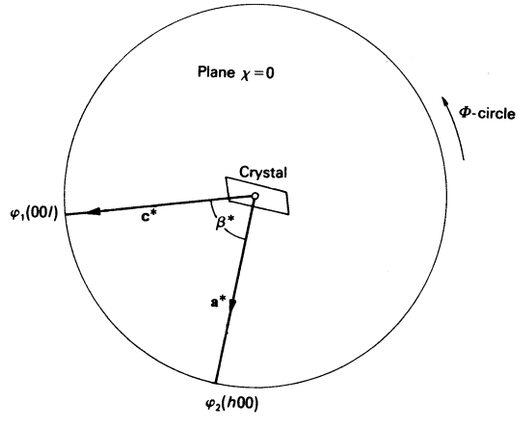


Fig. 5.3.3.1. Determination of reciprocal-lattice angles on the $\theta$ circle (after Luger, 1980).

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 [$\omega$ (or $\varphi$) of the crystal, and $2\theta$ (or $\gamma$) of the detector] are motor-driven under computer control, while two inclination angles ($\mu$ for the crystal and $\nu$ 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,

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

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

where

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

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

and $\omega_0$ is a zero-point correction.

The remaining parameter $c$ had to be determined from the inclination angle $\mu$, measured by hand. The use of zero-layer reflections was advantageous, apart from the simplicity of the formulae (5.3.3.4*a*,*b*,*c*,*d*), because they were less affected by crystal misalignment than were upper-layer reflections. However, a zero-point correction $\omega_0$ for $\omega$ had to be performed. For this purpose, the $\omega_0$ 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:

$$W_{hkl} = 1/\sqrt{\omega_{hkl}}, \tag{5.3.3.5}$$

where $\omega_{hkl}$ is the width of the *hkl* reflection. An additional (third) motor to control the $\mu$ 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.





references