2. INSTRUMENTATION AND SAMPLE PREPARATION

The plane given by X_L and Y_L is the diffractometer plane. The axis Z_L is perpendicular to the diffractometer plane. The axes X_L, Y_L and Z_L form a right-handed rectangular coordinate system with the origin at the instrument centre. The incident X-ray beam propagates along the X_L axis, which is also the rotation axis of all diffraction cones. The apex angles of the cones are determined by the 2θ values given by the Bragg equation. The apex angles are twice the 2θ values for forward reflection ($2\theta \leq 90°$) and twice the value of $180° - 2\theta$ for backward reflection ($2\theta > 90°$). For clarity, only one diffraction cone of forward reflection is displayed. The γ angle is the azimuthal angle from the origin at the six o'clock direction with a right-handed rotation axis along the opposite direction of incident beam ($-X_L$ direction). A given γ value defines a half plane with the X_L axis as the edge; this will be referred to as the γ plane hereafter. The diffractometer plane consists of two γ planes at $\gamma = 90°$ and $\gamma = 270°$. Therefore many equations developed for 2D-XRD should also apply to conventional XRD if the γ angle is given as a constant of $90°$ or $270°$. A pair of γ and 2θ values represents the direction of a diffracted beam. The γ angle takes a value of 0 to $360°$ for a complete diffraction ring with a constant 2θ value. The γ and 2θ angles form a spherical coordinate system which covers all the directions from the origin of sample (instrument centre). The γ–2θ system is fixed in the laboratory system X_L, Y_L, Z_L, which is independent of the sample orientation and detector position in the goniometer. 2θ and γ are referred to as the diffraction-space parameters. In the laboratory coordinate system $\mathbf{X}_L$, $\mathbf{Y}_L$, $\mathbf{Z}_L$, the surface of a diffraction cone can be mathematically expressed as

$$y_L^2 + z_L^2 = x_L^2 \tan^2 2\theta, \qquad (2.5.1)$$

with $x_L \geq 0$ or $2\theta \leq 90°$ for forward-diffraction cones and $x_L < 0$ or $2\theta > 90°$ for backward-diffraction cones.

Figure 2.5.3
The diffraction cone and the corresponding diffraction-vector cone.

2.5.2.1.2. *Diffraction-vector cones in laboratory coordinates*

Fig. 2.5.3(*b*) shows the diffraction-vector cone corresponding to the diffraction cone in the laboratory coordinate system. *C* is the centre of the Ewald sphere. The diffraction condition can be given by the Laue equation as

$$\frac{\mathbf{s} - \mathbf{s}_0}{\lambda} = \mathbf{H}_{hkl}, \qquad (2.5.2)$$

where $\mathbf{s}_0$ is the unit vector representing the incident beam, $\mathbf{s}$ is the unit vector representing the diffracted beam and $\mathbf{H}_{hkl}$ is the reciprocal-lattice vector. Its magnitude is given as

$$\left| \frac{\mathbf{s} - \mathbf{s}_0}{\lambda} \right| = \frac{2 \sin \theta}{\lambda} = \left| \mathbf{H}_{hkl} \right| = \frac{1}{d_{hkl}}, \qquad (2.5.3)$$
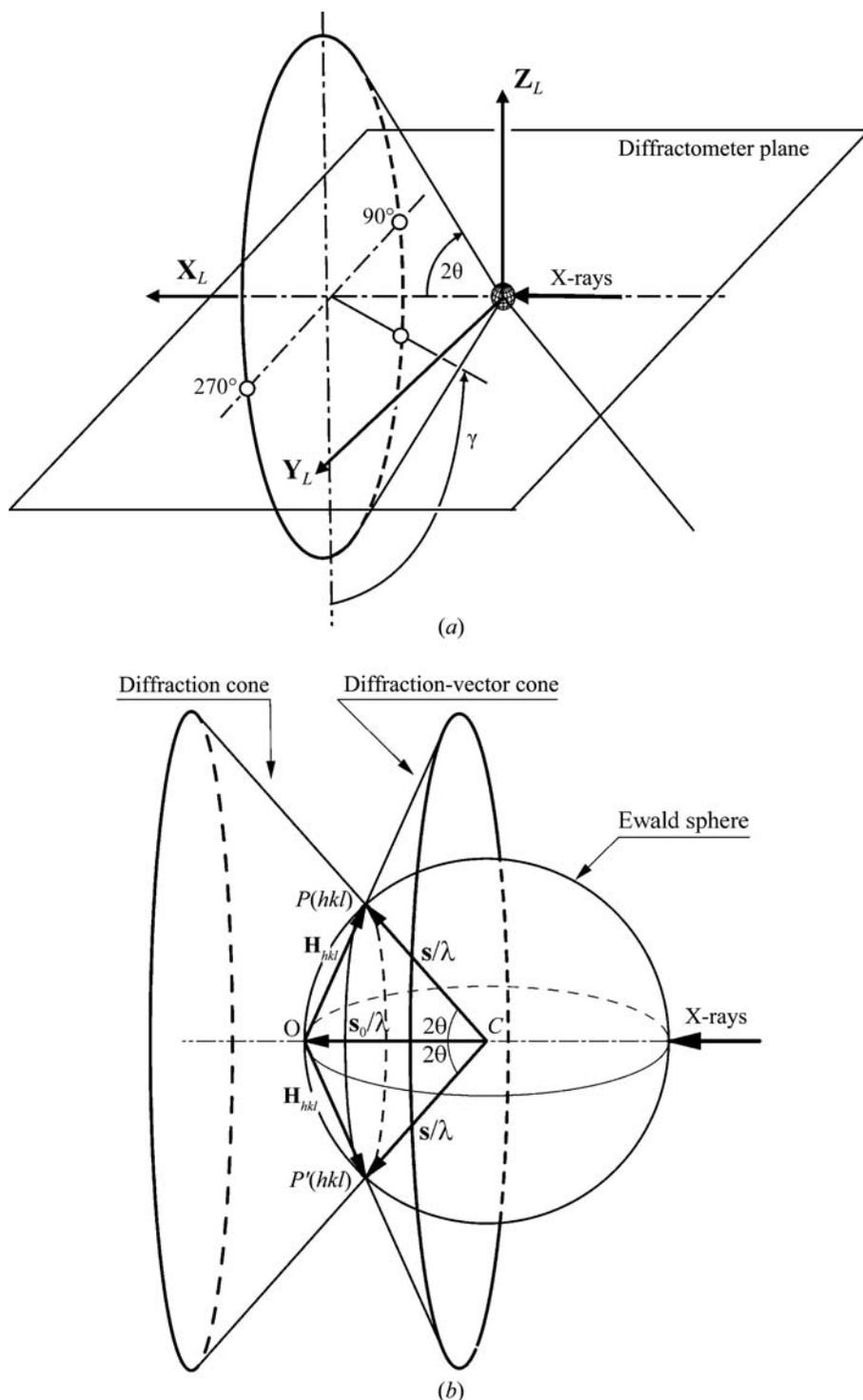
in which d_{hkl} is the *d*-spacing of the crystal planes (*hkl*). It can be easily seen that it is the Bragg law in a different form. Therefore, equation (2.5.2) is the Bragg law in vector form. In the Bragg condition, the vectors $\mathbf{s}_0/\lambda$ and $\mathbf{s}/\lambda$ make angles θ with the diffracting planes (*hkl*) and $\mathbf{H}_{hkl}$ is normal to the (*hkl*) crystal plane. In order to analyse all the X-rays measured by a 2D detector, we extend the concept to all scattered X-rays from a sample regardless of the Bragg condition. Therefore, the index (*hkl*) can be removed from the above expression. $\mathbf{H}$ is then a vector which takes the direction bisecting the incident beam and the scattered beam, and has dimensions of inverse length given by $2 \sin \theta/\lambda$. Here 2θ is the scattering angle from the incident beam. The vector $\mathbf{H}$ is referred to as the scattering vector or, alternatively, the diffraction vector. When the Bragg condition is

satisfied, the diffraction vector is normal to the diffracting lattice planes and its magnitude is reciprocal to the d-spacing of the lattice planes. In this case, the diffraction vector is equivalent to the reciprocal-lattice vector. Each pixel in a 2D detector measures scattered X-rays in a given direction with respect to the incident beam. We can calculate a diffraction vector for any pixel, even if the pixel is not measuring Bragg scattering. Use of the term 'diffracted beam' hereafter in this chapter does not necessarily imply that it arises from Bragg scattering.

For two-dimensional diffraction, the incident beam can be expressed by the vector $\mathbf{s}_0/\lambda$, but the diffracted beam is no longer in a single direction, but follows the diffraction cone. Since the direction of a diffraction vector is a bisector of the angle between the incident and diffracted beams corresponding to each diffraction cone, the trace of the diffraction vectors forms a cone. This cone is referred to as the diffraction-vector cone. The angle between the diffraction vector and the incident X-ray beam is $90° + \theta$ and the apex angle of a vector cone is $90° - \theta$. It is apparent that diffraction-vector cones can only exists on the $-X_L$ side of the diffraction space.

For two-dimensional diffraction, the diffraction vector is a function of both the γ and 2θ angles, and is given in laboratory coordinates as

$$\mathbf{H} = \frac{\mathbf{s} - \mathbf{s}_0}{\lambda} = \frac{1}{\lambda} \begin{bmatrix} \cos 2\theta - 1 \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix}. \tag{2.5.4}$$

The direction of the diffraction vector can be represented by its unit vector, given by

$$\mathbf{h}_L = \frac{\mathbf{H}}{|\mathbf{H}|} = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin \theta \\ -\cos \theta \sin \gamma \\ -\cos \theta \cos \gamma \end{bmatrix}, \tag{2.5.5}$$

where $\mathbf{h}_L$ is a unit vector expressed in laboratory coordinates and the three components in the square brackets are the projections of the unit vector on the three axes of the laboratory coordinates, respectively. If γ takes all values from 0 to 360° at a given Bragg angle 2θ, the trace of the diffraction vector forms a diffraction-vector cone. Since the possible values of θ lie within the range 0 to 90°, h_x takes only negative values.
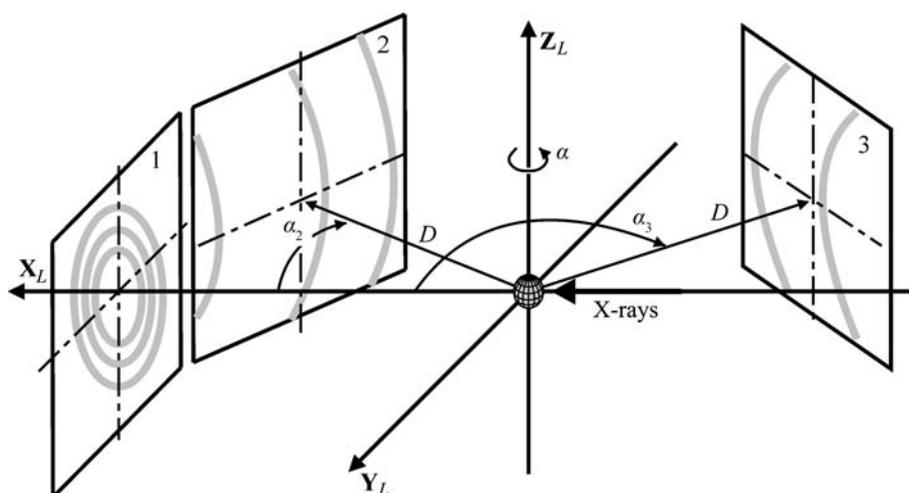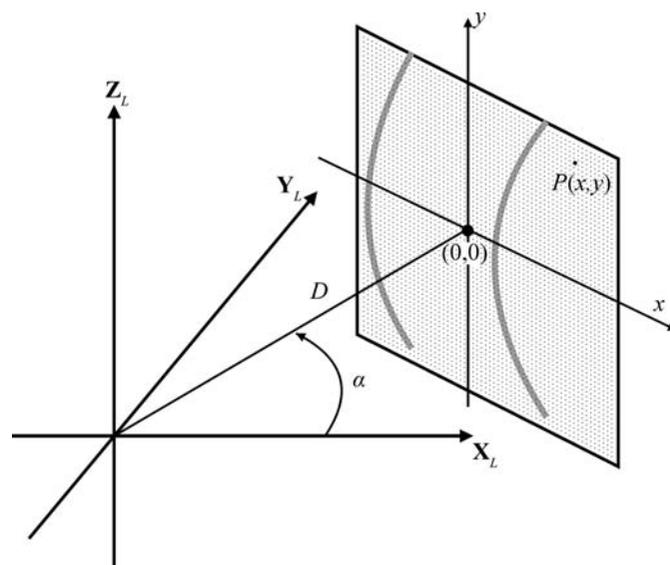

Figure 2.5.5
Relationship between a pixel P and detector position in the laboratory coordinates.

2.5.2.2. Detector space and pixel position

A typical 2D detector has a limited detection surface, and the detection surface can be spherical, cylindrical or flat. Spherical or cylindrical detectors are normally designed for a fixed sample-to-detector distance, while a flat detector has the flexibility to be used at different sample-to-detector distances so as to choose either high resolution at a large distance or large angular coverage at a short distance.

2.5.2.2.1. Detector position in the laboratory system

The position of a flat detector is defined by the sample-to-detector distance D and the detector swing angle α. D and α are referred to as the detector-space parameters. D is the perpendicular distance from the goniometer centre to the detection plane and α is a right-handed rotation angle about the Z_L axis. Detectors at different positions in the laboratory coordinates X_L, Y_L, Z_L are shown in Fig. 2.5.4. The centre of detector 1 is right on the positive side of the X_L axis (on-axis), $\alpha = 0$. Both detectors 2 and 3 are rotated away from the X_L axis with negative swing angles ($\alpha_2 < 0$ and $\alpha_3 < 0$). The detection surface of a flat 2D detector can be considered as a plane, which intersects the diffraction cone to form a conic section. Depending on the swing angle α and the 2θ angle, the conic section can appear as a circle, an ellipse, a parabola or a hyperbola.

2.5.2.2.2. Pixel position in diffraction space for a flat detector

The values of 2θ and γ can be calculated for each pixel in the frame. The calculation is based on the detector-space parameters and the pixel position in the detector. Fig. 2.5.5 shows the relationship of a pixel $P(x, y)$ to the laboratory coordinates X_L, Y_L, Z_L. The position of a pixel in the detector is defined by the (x, y) coordinates, where the detector centre is defined as $x = y = 0$. The diffraction-space coordinates $(2\theta, \gamma)$ for a pixel at $P(x, y)$ are given by

Figure 2.5.4
Detector positions in the laboratory-system coordinates.