

6. INTERPRETATION OF DIFFRACTED INTENSITIES

$$b_{ij} = F_j \cdot W_i / W_i^2, \quad i < j; \quad b_{ij} = 1, \quad i = j; \\ b_{ij} = 0, \quad i > j, \quad (6.3.3.54)$$

the vector determining the coefficients is

$$C = B^{-1}A, \quad (6.3.3.55)$$

in which the inversion of **B** is straightforward.

In difficult cases, with data affected by errors in addition to absorption, the method described may give physically unreasonable absorption corrections for some reflections. In such cases, it may help to impose the approximate constraints

$$\sum_S w_S^2 H_{mS} / \sum_S w_S^2 = \sum_S w_S^2 I_{mS} / \sum_S w_S^2. \quad (6.3.3.56)$$

If $m = 1, 2, \dots, M$, this reduces to the M constraint equations

$$\sum_{p=1} C_p \left\{ \frac{\sum_S w_S^2 H_{mS} g_{pS}}{\sum_S w_S^2} \right\} = \sum_{p=1} C_p \left\{ \frac{\varepsilon w_m \sum_S w_S^2 H_{mS} g_{pS}}{\sum_S w_S^2} \right\} = 0, \quad (6.3.3.57)$$

where w_m is the square root of the weight for the weighted mean of the equivalent reflections H_m , defined as

$$H_m = \sum_S w_S^2 H_{mS} / \sum_S w_S^2 \quad \text{for each } S, \quad (6.3.3.58)$$

and the multiplier ε controls the strength with which the additional constraints are enforced. With the additional constraint equations, the sum of squares to be minimized, corresponding to (6.3.3.48), becomes

$$\sum_{S,m} w_S^2 (I_{mS} - I_m)^2 + \sum_m \varepsilon^2 w_m^2 (H_m - I_m)^2. \quad (6.3.3.59)$$

A closely related procedure expressing the absorption corrections as Fourier series in polar angles for the incident and diffracted beams is described by Katayama, Sakabe & Sakabe (1972). A similar method minimizing the difference between observed and calculated structure factors is described by Walker & Stuart (1983). Other experimental techniques for

measuring data for empirical absorption corrections that could be analysed by the Fourier-series method are described by Kopfmann & Huber (1968), North, Phillips & Mathews (1968), Flack (1974), Stuart & Walker (1979), Lee & Ruble (1977*a,b*), Schwager, Bartels & Huber (1973), and Santoro & Wlodawer (1980).

6.3.3.6. Measuring crystals for absorption

In general, A depends both on the shape of the crystal and on its orientation with respect to the incident and diffracted beams. To measure the shape of the crystal, a measuring microscope is mounted in the xy plane, and the crystal rotated about the z axis at right angles to that plane. A rotation about the z axis changes the orientation of the crystal x and y coordinates with respect to those (X and Y) for the measuring device. The x axis is directed from crystal to microscope when the angle of rotation about the z axis (φ) is zero. During rotation, each face will at some stage be oriented with its normal $N(S)$ perpendicular to the line of view, *i.e.* in the XY plane for instrument coordinates. If the angle of rotation at that orientation is denoted φ_N , the appearance of a typical face $ABCD$ will be as indicated in Fig. 6.3.3.4.

The equation for the plane is

$$x \sin \varphi_N + y \cos \varphi_N + z \tan \chi = Y$$

or, equivalently,

$$(x \sin \varphi_N + y \cos \varphi_N) \cot \chi + z = Z.$$

For a crystal oriented on an Eulerian cradle, it is necessary to specify the orientation of the crystal, *i.e.* the angles Ω, χ, φ in which the measurements of the diffraction intensities are made. In a reflecting position, the reciprocal-lattice vector **S**, which is normal to the Bragg planes, bisects the angle between the incident and diffracted beams, as shown in Fig. 6.3.3.5.

If the crystal is rotated about the reciprocal-lattice vector **S**, varying the angle ψ , the crystal remains in a reflecting position. That is, there is a degree of freedom in the scattering experiment that enables the same reflection to be observed at different sets of Ω, χ, φ values. The path length varies with ψ , except for spherical crystals. In order to calculate an absorption correction, the value of ψ and its origin must be specified. For a crystal mounted on an Eulerian cradle, the bisecting position, with $\Omega = \theta$, is usually chosen as the origin for ψ .

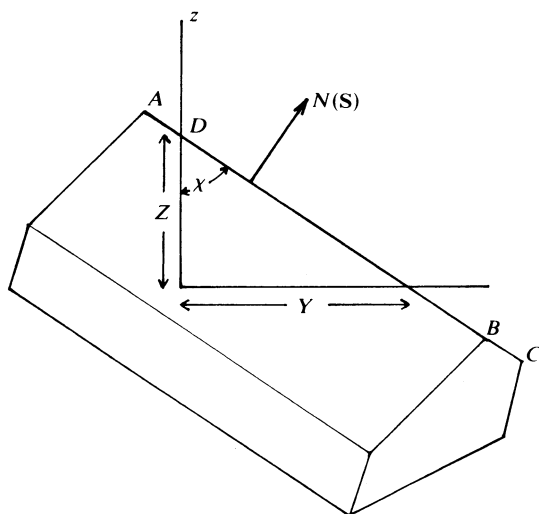


Fig. 6.3.3.4. Crystal oriented with the normal $N(S)$ to the face $ABCD$ in the plane of view.

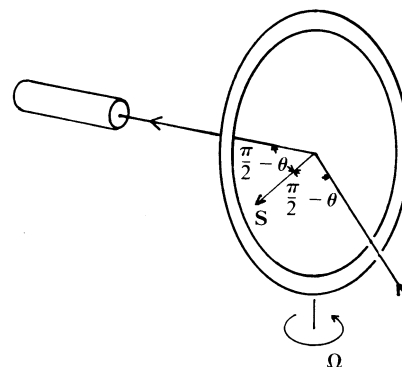


Fig. 6.3.3.5. Geometry of the Eulerian cradle in the bisecting position.