1.6. Methods of space-group determination

U. Shmueli, H. D. Flack and J. C. H. Spence

1.6.1. Overview

This chapter describes and discusses several methods of symmetry determination of single-domain crystals. A detailed presentation of symmetry determination from diffraction data is given in Section 1.6.2.1, followed by a brief discussion of intensity statistics, ideal as well as non-ideal, with an application of the latter to real intensity data from a $P\bar{1}$ crystal structure in Section 1.6.2.2. Several methods of retrieving symmetry information from a solved crystal structure are then discussed (Section 1.6.2.3). This is followed by a discussion of chemical and physical restrictions on space-group symmetry (Section 1.6.2.4), including some aids in symmetry determination, and by a brief section on pitfalls in space-group determination (Section 1.6.2.5).

The following two sections deal with reflection conditions. Section 1.6.3 presents the theoretical background of conditions for possible general reflections and their corresponding derivation. A brief discussion of special reflection conditions is included. Section 1.6.4 presents an extensive tabulation of general reflection conditions and possible space groups.

Other methods of space-group determination are presented in Section 1.6.5. Section 1.6.5.1 deals with an account of methods of space-group determination based on resonant (also termed 'anomalous') scattering. Section 1.6.5.2 is a brief description of approaches to space-group determination in macromolecular crystallography. Section 1.6.5.3 deals with corresponding approaches in powder-diffraction methods.

The chapter concludes with a description and illustration of symmetry determination based on electron-diffraction methods (Section 1.6.6), and principally focuses on convergent-beam electron diffraction.

This chapter deals only with single crystals. A supplement (Flack, 2015) deals with twinned crystals and those displaying a specialized metric.

1.6.2. Symmetry determination from single-crystal studies

By U. Shmueli and H. D. Flack

1.6.2.1. Symmetry information from the diffraction pattern

The extraction of symmetry information from the diffraction pattern takes place in three stages.

In the first stage, the unit-cell dimensions are determined and analyzed in order to establish to which Bravais lattice the crystal belongs. A conventional choice of lattice basis (coordinate system) may then be chosen. The determination of the Bravais lattice[1] of the crystal is achieved by the process of cell reduction, in which the lattice is first described by a basis leading to a primitive unit cell, and then linear combinations of the unit-cell vectors are taken to reduce the metric tensor (and the cell dimensions) to a standard form. From the relationships amongst the elements of the metric tensor, one obtains the Bravais lattice, together with a conventional choice of the unit cell, with the aid of standard tables. A detailed description of cell reduction is given in Chapter 3.1 of this volume and in Part 9 of earlier editions (*e.g.* Burzlaff *et al.*, 2002). An alternative approach (Le Page, 1982) seeks the Bravais lattice directly from the cell dimensions by searching for all the twofold axes present. All these operations are automated in software. Regardless of the technique employed, at the end of the process one obtains an indication of the Bravais lattice and a unit cell in a conventional setting for the crystal system, primitive or centred as appropriate. These are usually good indications which, however, must be confirmed by an examination of the distribution of diffracted intensities as outlined below.

In the second stage, it is the point-group symmetry of the intensities of the Bragg reflections which is determined. We recall that the average reduced intensity of a pair of Friedel opposites (hkl and $\overline{hkl}$) is given by

$$|F_{\mathrm{av}}(\mathbf{h})|^2 = \tfrac{1}{2}[|F(\mathbf{h})|^2 + |F(\bar{\mathbf{h}})|^2]$$
$$= \sum_{i,j}[(f_i + f'_i)(f_j + f'_j) + f''_i f''_j]\cos[2\pi\mathbf{h}(\mathbf{r}_i - \mathbf{r}_j)] \equiv A(\mathbf{h}),$$

$$(1.6.2.1)$$

where the atomic scattering factor of atom j, taking into account resonant scattering, is given by

$$\mathbf{f}_j = f_j + f'_j + if''_j,$$

the wavelength-dependent components f'_j and f''_j being the real and imaginary parts, respectively, of the contribution of atom j to the resonant scattering, $\mathbf{h}$ contains in the (row) matrix (1×3) the diffraction orders (hkl) and $\mathbf{r}_j$ contains in the (column) matrix (3×1) the coordinates (x_j, y_j, z_j) of atom j. The components of the $\mathbf{f}_j$ are assumed to contain implicitly the displacement parameters. Equation (1.6.2.1) can be found *e.g.* in Okaya & Pepinsky (1955), Rossmann & Arnold (2001) and Flack & Shmueli (2007). It follows from (1.6.2.1) that

$$|F_{\mathrm{av}}(\mathbf{h})|^2 = |F_{\mathrm{av}}(\bar{\mathbf{h}})|^2 \text{ or } A(\mathbf{h}) = A(\bar{\mathbf{h}}),$$

regardless of the contribution of resonant scattering. Hence the averaging introduces a centre of symmetry in the (averaged) diffraction pattern.[2] In fact, working with the average of Friedel opposites, one may determine the Laue group of the diffraction pattern by comparing the intensities of reflections which should be symmetry equivalent under each of the Laue groups. These are the 11 centrosymmetric point groups: $\bar{1}$, $2/m$, mmm, $4/m$, $4/mmm$, $\bar{3}$, $\bar{3}m$, $6/m$, $6/mmm$, $m\bar{3}$ and $m\bar{3}m$. For example, the reflections of which the intensities are to be compared for the Laue group $\bar{3}$ are: hkl, kil, ihl, $\overline{hkl}$, $\overline{kil}$ and $\overline{ihl}$, where $i = -h - k$. An extensive listing of the indices of symmetry-related reflections in all the point groups, including of course the Laue groups, is

---

[1] The Bravais lattice symbol consists of two characters. The first is the first letter of the name of a crystal family and the second is the centring mode of a conventional unit cell. For details see Tables 3.1.2.1 and 3.1.2.2.

[2] We must mention the well known Friedel's law, which states that $|F(\mathbf{h})|^2 = |F(\bar{\mathbf{h}})|^2$ and which is only a reasonable approximation for noncentrosymmetric crystals if resonant scattering is negligibly small. This law holds well for centrosymmetric crystals, independently of the resonant-scattering contribution.

references