

## 1.4. SYMMETRY IN RECIPROCAL SPACE

ship:  $\mathbf{P}^{-1} = \mathbf{P}^T$  is not satisfied if  $\mathbf{P}$  is referred to some oblique crystal systems, higher than the orthorhombic.

Detailed descriptions of the 32 crystallographic point groups are presented in the crystallographic and other literature; their complete tabulation is given in Part 10 of Volume A (*IT A*, 2005).

## 1.4.2.2. Relationship between structure factors at symmetry-related points of the reciprocal lattice

Of main interest in the context of the present chapter are symmetry relationships that concern the values of a function defined at the points of the reciprocal lattice. Such functions, of crystallographic interest, are Fourier-transform representations of direct-space functions that have the periodicity of the crystal, the structure factor as a Fourier transform of the electron-density function being a representative example (see *e.g.* Lipson & Taylor, 1958). The value of such a function, attached to a reciprocal-lattice point, is called the weight of this point and the set of all such weighted points is often termed the weighted reciprocal lattice. This section deals with a fundamental relationship between functions (weights) associated with reciprocal-lattice points, which are related by point-group symmetry, the weights here considered being the structure factors of Bragg reflections (*cf.* Chapter 1.2).

The electron density, an example of a three-dimensional periodic function with the periodicity of the crystal, can be represented by the Fourier series

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{r}), \quad (1.4.2.1)$$

where  $\mathbf{h}$  is a reciprocal-lattice vector,  $V$  is the volume of the (direct) unit cell,  $F(\mathbf{h})$  is the structure factor at the point  $\mathbf{h}$  and  $\mathbf{r}$  is a position vector of a point in direct space, at which the density is given. The summation in (1.4.2.1) extends over all the reciprocal lattice.

Let  $\mathbf{r}' = \mathbf{P}\mathbf{r} + \mathbf{t}$  be a space-group operation on the crystal, where  $\mathbf{P}$  and  $\mathbf{t}$  are its rotation and translation parts, respectively, and  $\mathbf{P}$  must therefore be a point-group operator. We then have, by definition,  $\rho(\mathbf{r}) = \rho(\mathbf{P}\mathbf{r} + \mathbf{t})$  and the Fourier representation of the electron density, at the equivalent position  $\mathbf{P}\mathbf{r} + \mathbf{t}$ , is given by

$$\begin{aligned} \rho(\mathbf{P}\mathbf{r} + \mathbf{t}) &= \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp[-2\pi i \mathbf{h}^T (\mathbf{P}\mathbf{r} + \mathbf{t})] \\ &= \frac{1}{V} \sum_{\mathbf{h}} [F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t})] \\ &\quad \times \exp[-2\pi i (\mathbf{P}^T \mathbf{h})^T \mathbf{r}], \end{aligned} \quad (1.4.2.2)$$

noting that  $\mathbf{h}^T \mathbf{P} = (\mathbf{P}^T \mathbf{h})^T$ . Since  $\mathbf{P}$  is a point-group operator, the vectors  $\mathbf{P}^T \mathbf{h}$  in (1.4.2.2) must range over all the reciprocal lattice and a comparison of the functional forms of the equivalent expansions (1.4.2.1) and (1.4.2.2) shows that the coefficients of the exponentials  $\exp[-2\pi i (\mathbf{P}^T \mathbf{h})^T \mathbf{r}]$  in (1.4.2.2) must be the structure factors at the points  $\mathbf{P}^T \mathbf{h}$  in the reciprocal lattice. Thus

$$F(\mathbf{P}^T \mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t}), \quad (1.4.2.3)$$

wherefrom it follows that the magnitudes of the structure factors at  $\mathbf{h}$  and  $\mathbf{P}^T \mathbf{h}$  are the same:

$$|F(\mathbf{P}^T \mathbf{h})| = |F(\mathbf{h})|, \quad (1.4.2.4)$$

and their phases are related by

$$\varphi(\mathbf{P}^T \mathbf{h}) = \varphi(\mathbf{h}) - 2\pi \mathbf{h}^T \mathbf{t}. \quad (1.4.2.5)$$

The relationship (1.4.2.3) between structure factors of symmetry-related reflections was first derived by Waser (1955), starting from a representation of the structure factor as a Fourier transform of the electron-density function.

It follows that an application of a point-group transformation to the (weighted) reciprocal lattice leaves the moduli of the structure factors unchanged. The distribution of diffracted intensities obeys, in fact, the same point-group symmetry as that of the crystal. If, however, anomalous dispersion is negligibly small, and the point group of the crystal is noncentrosymmetric, the apparent symmetry of the diffraction pattern will also contain a false centre of symmetry and, of course, all the additional elements generated by the inclusion of this centre. Under these circumstances, the diffraction pattern from a single crystal may belong to one of the eleven centrosymmetric point groups, known as Laue groups (*IT I*, 1952).

According to equation (1.4.2.5), the phases of the structure factors of symmetry-related reflections differ, in the general case, by a phase shift that depends on the translation part of the space-group operation involved. Only when the space group is symmorphic, *i.e.* it contains no translations other than those of the Bravais lattice, will the distribution of the phases obey the point-group symmetry of the crystal. These phase shifts are considered in detail in Section 1.4.4 where their tabulation is presented and the alternative interpretation (Bienenstock & Ewald, 1962) of symmetry in reciprocal space, mentioned in Section 1.4.1, is given.

Equation (1.4.2.3) can be usefully applied to a classification of all the general systematic absences or – as defined in the space-group tables in the main editions of *IT* (1935, 1952, 1983, 1987, 1992, 1995, 2002) – general conditions for possible reflections. These systematic absences are associated with special positions in the reciprocal lattice – special with respect to the point-group operations  $\mathbf{P}$  appearing in the relevant relationships. If, in a given relationship, we have  $\mathbf{P}^T \mathbf{h} = \mathbf{h}$ , equation (1.4.2.3) reduces to

$$F(\mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t}). \quad (1.4.2.6)$$

Of course,  $F(\mathbf{h})$  may then be nonzero only if  $\cos(2\pi \mathbf{h}^T \mathbf{t})$  equals unity, or the scalar product  $\mathbf{h}^T \mathbf{t}$  is an integer. This well known result leads to a ready determination of lattice absences, as well as those produced by screw-axis and glide-plane translations, and is routinely employed in crystallographic computing. An exhaustive classification of the general conditions for possible reflections is given in the space-group tables (*IT*, 1952, 1983). It should be noted that since the axes of rotation and planes of reflection in the reciprocal lattice are parallel to the corresponding elements in the direct lattice (Buerger, 1960), the component of  $\mathbf{t}$  that depends on the location of the corresponding space-group symmetry element in direct space does not contribute to the scalar product  $\mathbf{h}^T \mathbf{t}$  in (1.4.2.6), and it is only the intrinsic part of the translation  $\mathbf{t}$  (*IT A*, 1983) that usually matters.

It may, however, be of interest to note that some screw axes in direct space cannot give rise to any systematic absences. For example, the general Wyckoff position No. (10) in the space group  $Pa\bar{3}$  (No. 205) (*IT A*, 1983) has the coordinates  $\bar{y}, \frac{1}{2} + z, \frac{1}{2} - x$ , and corresponds to the space-group operation

$$(\mathbf{P}, \mathbf{t}) = (\mathbf{P}, \mathbf{t}_i + \mathbf{t}_t) = \left[ \begin{pmatrix} 0 & \bar{1} & 0 \\ 0 & 0 & 1 \\ \bar{1} & 0 & 0 \end{pmatrix}, \begin{pmatrix} -\frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} + \begin{pmatrix} \frac{1}{2} \\ 0 \\ 0 \end{pmatrix} \right], \quad (1.4.2.7)$$

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where  $\mathbf{t}_i$  and  $\mathbf{t}_l$  are the intrinsic and location-dependent components of the translation part  $\mathbf{t}$ , and are parallel and perpendicular, respectively, to the threefold axis of rotation represented by the matrix  $\mathbf{P}$  in (1.4.2.7) (IT A, 1983; Shmueli, 1984). This is clearly a threefold screw axis, parallel to  $[\bar{1}\bar{1}1]$ . The reciprocal-lattice vectors which remain unchanged, when postmultiplied by  $\mathbf{P}$  (or premultiplied by its transpose), have the form:  $\mathbf{h}^T = (h\bar{h}\bar{h})$ ; this is the special position for the present example. We see that (i)  $\mathbf{h}^T \mathbf{t}_l = 0$ , as expected, and (ii)  $\mathbf{h}^T \mathbf{t}_i = -h$ . Since the scalar product  $\mathbf{h}^T \mathbf{t}$  is an integer, there are no values of index  $h$  for which the structure factor  $F(h\bar{h}\bar{h})$  must be absent.

Other approaches to systematically absent reflections include a direct inspection of the structure-factor equation (Lipson & Cochran, 1966), which is of considerable didactical value, and the utilization of transformation properties of direct and reciprocal base vectors and lattice-point coordinates (Buerger, 1942).

Finally, the relationship between the phases of symmetry-related reflections, given by (1.4.2.5), is of fundamental as well as practical importance in the theories and techniques of crystal structure determination which operate in reciprocal space (Part 2 of this volume).

### 1.4.2.3. Symmetry factors for space-group-specific Fourier summations

The weighted reciprocal lattice, with weights taken as the structure factors, is synonymous with the discrete space of the coefficients of a Fourier expansion of the electron density, or the Fourier space ( $F$  space) of the latter. Accordingly, the asymmetric unit of the Fourier space can be defined as the subset of structure factors within which the relationship (1.4.2.3) does not hold – except at special positions in the reciprocal lattice. If the point group of the crystal is of order  $g$ , this is also the order of the corresponding factor-group representation of the space group (IT A, 1983) and there exist  $g$  relationships of the form of (1.4.2.3):

$$F(\mathbf{P}_s^T \mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t}_s). \quad (1.4.2.8)$$

We can thus decompose the summation in (1.4.2.1) into  $g$  sums, each extending over an asymmetric unit of the  $F$  space. It must be kept in mind, however, that some classes of reciprocal-lattice vectors may be common to more than one asymmetric unit, and thus each reciprocal-lattice point will be assigned an occupancy factor, denoted by  $q(\mathbf{h})$ , such that  $q(\mathbf{h}) = 1$  for a general position and  $q(\mathbf{h}) = 1/m(\mathbf{h})$  for a special one, where  $m(\mathbf{h})$  is the multiplicity – or the order of the point group that leaves  $\mathbf{h}$  unchanged. Equation (1.4.2.1) can now be rewritten as

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{s=1}^g \sum_{\mathbf{h}_a} q(\mathbf{h}_a) F(\mathbf{P}_s^T \mathbf{h}_a) \exp[-2\pi i (\mathbf{P}_s^T \mathbf{h}_a)^T \mathbf{r}], \quad (1.4.2.9)$$

where the inner summation in (1.4.2.9) extends over the reference asymmetric unit of the Fourier space, which is associated with the identity operation of the space group. Substituting from (1.4.2.8) for  $F(\mathbf{P}_s^T \mathbf{h}_a)$ , and interchanging the order of the summations in (1.4.2.9), we obtain

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}_a} q(\mathbf{h}_a) F(\mathbf{h}_a) \sum_{s=1}^g \exp[-2\pi i \mathbf{h}_s^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)] \quad (1.4.2.10)$$

$$= \frac{1}{V} \sum_{\mathbf{h}_a} q(\mathbf{h}_a) F(\mathbf{h}_a) [A(\mathbf{h}_a) - iB(\mathbf{h}_a)], \quad (1.4.2.11)$$

where

$$A(\mathbf{h}) = \sum_{s=1}^g \cos[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)] \quad (1.4.2.12)$$

and

$$B(\mathbf{h}) = \sum_{s=1}^g \sin[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)]. \quad (1.4.2.13)$$

The symmetry factors  $A$  and  $B$  are well known as geometric or trigonometric structure factors and a considerable part of Volume I of IT (1952) is dedicated to their tabulation. Their formal association with the structure factor – following from direct-space arguments – is closely related to that shown in equation (1.4.2.11) (see Section 1.4.2.4). Simplified trigonometric expressions for  $A$  and  $B$  are given in Tables A1.4.3.1–A1.4.3.7 in Appendix 1.4.3 for all the two- and three-dimensional crystallographic space groups, and for all the parities of  $hkl$  for which  $A$  and  $B$  assume different functional forms. These expressions are there given for general reflections and can also be used for special ones, provided the occupancy factors  $q(\mathbf{h})$  have been properly accounted for.

Equation (1.4.2.11) is quite general and can, of course, be applied to noncentrosymmetric Fourier summations, without neglect of dispersion. Further simplifications are obtained in the centrosymmetric case, when the space-group origin is chosen at a centre of symmetry, and in the noncentrosymmetric case, when dispersion is neglected. In each of the latter two cases the summation over  $\mathbf{h}_a$  is restricted to reciprocal-lattice vectors that are not related by real or apparent inversion (denoted by  $\mathbf{h}_a > 0$ ), and we obtain

$$\rho(\mathbf{r}) = \frac{2}{V} \sum_{\mathbf{h}_a > 0} q(\mathbf{h}_a) F(\mathbf{h}_a) A(\mathbf{h}_a) \quad (1.4.2.14)$$

and

$$\rho(\mathbf{r}) = \frac{2}{V} \sum_{\mathbf{h}_a > 0} q(\mathbf{h}_a) |F(\mathbf{h}_a)| [A(\mathbf{h}_a) \cos \varphi(\mathbf{h}_a) + B(\mathbf{h}_a) \sin \varphi(\mathbf{h}_a)] \quad (1.4.2.15)$$

for the dispersionless centrosymmetric and noncentrosymmetric cases, respectively.

### 1.4.2.4. Symmetry factors for space-group-specific structure-factor formulae

The explicit dependence of structure-factor summations on the space-group symmetry of the crystal can also be expressed in terms of symmetry factors, in an analogous manner to that described for the electron density in the previous section. It must be pointed out that while the above treatment only presumes that the electron density can be represented by a three-dimensional Fourier series, the present one is restricted by the assumption that the atoms are isotropic with regard to their motion and shape (*cf.* Chapter 1.2).

Under the above assumptions, *i.e.* for isotropically vibrating spherical atoms, the structure factor can be written as

$$F(\mathbf{h}) = \sum_{j=1}^N f_j \exp(2\pi i \mathbf{h}^T \mathbf{r}_j), \quad (1.4.2.16)$$

where  $\mathbf{h}^T = (hkl)$  is the diffraction vector,  $N$  is the number of atoms in the unit cell,  $f_j$  is the atomic scattering factor including