

1. GENERAL RELATIONSHIPS AND TECHNIQUES

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 $[\bar{1}\bar{1}\bar{1}]$. 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