

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

1.4. SYMMETRY IN RECIPROCAL SPACE

its temperature factor and depending on the magnitude of \mathbf{h} only, and \mathbf{r}_j is the position vector of the j th atom referred to the origin of the unit cell.

If the crystal belongs to a point group of order m_p and the multiplicity of its Bravais lattice is m_L , there are $g' = m_p \times m_L$ general equivalent positions in the unit cell of the space group (IT A, 1983). We can thus rewrite (1.4.2.16), grouping the contributions of the symmetry-related atoms, as

$$F(\mathbf{h}) = \sum_j f_j \sum_{s=1}^{g'} \exp[2\pi i \mathbf{h}^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)], \quad (1.4.2.17)$$

where \mathbf{P}_s and \mathbf{t}_s are the rotation and translation parts of the s th space-group operation respectively. The inner summation in (1.4.2.17) contains the dependence of the structure factor of reflection \mathbf{h} on the space-group symmetry of the crystal and is known as the (complex) geometric or trigonometric structure factor.

Equation (1.4.2.17) can be rewritten as

$$F(\mathbf{h}) = \sum_j f_j [A_j(\mathbf{h}) + iB_j(\mathbf{h})], \quad (1.4.2.18)$$

where

$$A_j(\mathbf{h}) = \sum_{s=1}^{g'} \cos[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r}_j + \mathbf{t}_s)] \quad (1.4.2.19)$$

and

$$B_j(\mathbf{h}) = \sum_{s=1}^{g'} \sin[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r}_j + \mathbf{t}_s)] \quad (1.4.2.20)$$

are the real and imaginary parts of the trigonometric structure factor. Equations (1.4.2.19) and (1.4.2.20) are *mathematically* identical to equations (1.4.2.11) and (1.4.2.12), respectively, apart from the numerical coefficients which appear in the expressions for A and B , for space groups with centred lattices: while only the order of the point group need be considered in connection with the Fourier expansion of the electron density (see above), the multiplicity of the Bravais lattice must of course appear in (1.4.2.19) and (1.4.2.20).

Analogous functional forms are arrived at by considerations of symmetry in direct and reciprocal spaces. These quantities are therefore convenient representations of crystallographic symmetry in its interaction with the diffraction experiment and have been indispensable in all of the early crystallographic computing related to structure determination. Their applications to modern crystallographic computing have been largely superseded by fast Fourier techniques, in reciprocal space, and by direct use of matrix and vector representations of space-group operators, in direct space, especially in cases of low space-group symmetry. It should be noted, however, that the degree of simplification of the trigonometric structure factors generally increases with increasing symmetry (see, *e.g.*, Section 1.4.3), and the gain of computing efficiency becomes significant when problems involving high symmetries are treated with this 'old-fashioned' tool. Analytic expressions for the trigonometric structure factors are of course indispensable in studies in which the knowledge of the functional form of the structure factor is required [*e.g.* in theories of structure-factor statistics and direct methods of phase determination (see Chapters 2.1 and 2.2)].

Equations (1.4.2.19) and (1.4.2.20) are simple but their expansion and simplification for all the space groups and relevant

hkl subsets can be an extremely tedious undertaking when carried out in the conventional manner. As shown below, this process has been automated by a suitable combination of symbolic and numeric high-level programming procedures.

1.4.3. Structure-factor tables

1.4.3.1. Some general remarks

This section is a revised version of the structure-factor tables contained in Sections 4.5 through 4.7 of Volume I (IT I, 1952). As in the previous edition, it is intended to present a comprehensive list of explicit expressions for the real and the imaginary parts of the trigonometric structure factor, for all the 17 plane groups and the 230 space groups, and for the hkl subsets for which the trigonometric structure factor assumes different functional forms. The tables given here are also confined to the case of general Wyckoff positions (IT I, 1952). However, the expressions are presented in a much more concise symbolic form and are amenable to computation just like the explicit trigonometric expressions in Volume I (IT I, 1952). The present tabulation is based on equations (1.4.2.19) and (1.4.2.20), *i.e.* the numerical coefficients in A and B which appear in Tables A1.4.3.1–A1.4.3.7 in Appendix 1.4.3 are appropriate to space-group-specific structure-factor formulae. The functional form of A and B is, however, the same when applied to Fourier summations (see Section 1.4.2.3).

1.4.3.2. Preparation of the structure-factor tables

The lists of the coordinates of the general equivalent positions, presented in IT A (1983), as well as in earlier editions of the *Tables*, are sufficient for the expansion of the summations in (1.4.2.19) and (1.4.2.20) and the simplification of the resulting expressions can be performed using straightforward algebra and trigonometry (see, *e.g.*, IT I, 1952). As mentioned above, the preparation of the present structure-factor tables has been automated and its stages can be summarized as follows:

- (i) Generation of the coordinates of the general positions, starting from a computer-adapted space-group symbol (Shmueli, 1984).
- (ii) Formation of the scalar products, appearing in (1.4.2.19) and (1.4.2.20), and their separation into components depending on the rotation and translation parts of the space-group operations:

$$\mathbf{h}^T (\mathbf{P}_s, \mathbf{t}_s) \mathbf{r} = \mathbf{h}^T \mathbf{P}_s \mathbf{r} + \mathbf{h}^T \mathbf{t}_s, \quad (1.4.3.1)$$

for the space groups which are not associated with a unique axis; the left-hand side of (1.4.3.1) is separated into contributions of the relevant plane group and unique axis for the remaining space groups.

- (iii) Analysis of the translation-dependent parts of the scalar products and automatic determination of all the parities of hkl for which A and B must be computed and simplified.

(iv) Expansion of equations (1.4.2.19) and (1.4.2.20) and their reduction to trigonometric expressions comparable to those given in the structure-factor tables in Volume I of IT (1952).

(v) Representation of the results in terms of a small number of building blocks, of which the expressions were found to be composed. These representations are described in Section 1.4.3.3.

All the stages outlined above were carried out with suitably designed computer programs, written in numerically and symbolically oriented languages. A brief summary of the underlying algorithms is presented in Appendix 1.4.1. The computer-adapted space-group symbols used in these computations are described in Section A1.4.2.2 and presented in Table A1.4.2.1.