

1. GENERAL RELATIONSHIPS AND TECHNIQUES

phase-shift part of an entry is given only if $(p_n q_n r_n)$ is *not* a vector in the direct lattice, since such a vector would give rise to a trivial phase shift (an integer multiple of 2π).

1.4.4.3. Effect of direct-space transformations

The phase shifts given in Table A1.4.4.1 depend on the translation parts of the space-group operations and these translations are determined, all or in part, by the choice of the space-group origin. It is a fairly easy matter to find the phase shifts that correspond to a given shift of the space-group origin in direct space, directly from Table A1.4.4.1. Moreover, it is also possible to modify the table entries so that a more general transformation, including a change of crystal axes as well as a shift of the space-group origin, can be directly accounted for. We employ here the frequently used concise notation due to Seitz (1935) (see also *IT A*, 1983).

Let the direct-space transformation be given by

$$\mathbf{r}_{\text{new}} = \mathbf{T}\mathbf{r}_{\text{old}} + \mathbf{v}, \quad (1.4.4.3)$$

where \mathbf{T} is a nonsingular 3×3 matrix describing the change of the coordinate system and \mathbf{v} is an origin-shift vector. The components of \mathbf{T} and \mathbf{v} are referred to the old system, and \mathbf{r}_{new} (\mathbf{r}_{old}) is the position vector of a point in the crystal, referred to the new (old) system, respectively. If we denote a space-group operation referred to the new and old systems by $(\mathbf{P}_{\text{new}}, \mathbf{t}_{\text{new}})$ and $(\mathbf{P}_{\text{old}}, \mathbf{t}_{\text{old}})$, respectively, we have

$$(\mathbf{P}_{\text{new}}, \mathbf{t}_{\text{new}}) = (\mathbf{T}, \mathbf{v})(\mathbf{P}_{\text{old}}, \mathbf{t}_{\text{old}})(\mathbf{T}, \mathbf{v})^{-1} \quad (1.4.4.4)$$

$$= (\mathbf{T}\mathbf{P}_{\text{old}}\mathbf{T}^{-1}, \mathbf{v} - \mathbf{T}\mathbf{P}_{\text{old}}\mathbf{T}^{-1}\mathbf{v} + \mathbf{T}\mathbf{t}_{\text{old}}). \quad (1.4.4.5)$$

It follows from (1.4.4.2) and (1.4.4.5) that if the old entry of Table A1.4.4.1 is given by

$$({}^n)\mathbf{h}^T\mathbf{P} : -\mathbf{h}^T\mathbf{t},$$

the transformed entry becomes

$$({}^n)\mathbf{h}^T\mathbf{T}\mathbf{P}\mathbf{T}^{-1} : \mathbf{h}^T\mathbf{T}\mathbf{P}\mathbf{T}^{-1}\mathbf{v} - \mathbf{h}^T\mathbf{v} - \mathbf{h}^T\mathbf{T}\mathbf{t}, \quad (1.4.4.6)$$

and in the important special cases of a pure change of setting ($\mathbf{v} = 0$) or a pure shift of the space-group origin (\mathbf{T} is the unit matrix \mathbf{I}), (1.4.4.6) reduces to

$$({}^n)\mathbf{h}^T\mathbf{T}\mathbf{P}\mathbf{T}^{-1} : -\mathbf{h}^T\mathbf{T}\mathbf{t} \quad (1.4.4.7)$$

or

$$({}^n)\mathbf{h}^T\mathbf{P} : \mathbf{h}^T\mathbf{P}\mathbf{v} - \mathbf{h}^T\mathbf{v} - \mathbf{h}^T\mathbf{t}, \quad (1.4.4.8)$$

respectively. The rotation matrices \mathbf{P} are readily obtained by visual or programmed inspection of the old entries: if, for example, $\mathbf{h}^T\mathbf{P}$ is $kh\bar{l}$, we must have $P_{21} = 1$, $P_{12} = 1$ and $P_{33} = 1$, the remaining P_{ij} 's being equal to zero. Similarly, if $\mathbf{h}^T\mathbf{P}$ is kil , where $i = -h - k$, we have

$$(kil) = (k, -h - k, l) = (hkl) \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The rotation matrices can also be obtained by reference to Part 7 and Tables 11.2.2.1 and 11.2.2.2 in Volume A (*IT A*, 2005).

As an example, consider the phase shifts corresponding to the operation No. (16) of the space group $P4/nmm$ (No. 129) in its two origins given in Volume A (*IT A*, 1983). For an Origin 2-to-Origin 1 transformation we find there $\mathbf{v} = (\frac{1}{4}, -\frac{1}{4}, 0)$ and the old Origin 2 entry in Table A1.4.4.1 is (16) $kh\bar{l}$ (\mathbf{t} is zero). The appropriate entry for the Origin 1 description of this operation should therefore be $\mathbf{h}^T\mathbf{P}\mathbf{v} - \mathbf{h}^T\mathbf{v} = k/4 - h/4 - h/4 + k/4 = -h/2 + k/2$, as given by (1.4.4.8), or $-(h+k)/2$ if a trivial shift of 2π is subtracted. The (new) Origin 1 entry thus becomes: (16) $kh\bar{l} : -110/2$, as listed in Table A1.4.4.1.

1.4.4.4. Symmetry in Fourier space

As shown below, Table A1.4.4.1 can also be regarded as a collection of the general equivalent positions of the symmetry groups of Fourier space, in the sense of the treatment by Bienenstock & Ewald (1962). This interpretation of the table is, however, restricted to the underlying periodic function being real and positive (see the latter reference). The symmetry formalism can be treated with the aid of the original 4×4 matrix notation, but it appears that a concise Seitz-type notation suits better the present introductory interpretation.

The symmetry dependence of the fundamental relationship (1.4.2.5)

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

is given by a table entry of the form: $(n)\mathbf{h}^T\mathbf{P} : -\mathbf{h}^T\mathbf{t}$, where the phase shift is given in units of 2π , and the structure-dependent phase $\varphi(\mathbf{h})$ is omitted. Defining a combination law analogous to Seitz's product of two operators of affine transformation:

$$[\mathbf{a}^T : b](\mathbf{R}, \mathbf{r}) = [\mathbf{a}^T\mathbf{R} : \mathbf{a}^T\mathbf{r} + b], \quad (1.4.4.9)$$

where \mathbf{R} is a 3×3 matrix, \mathbf{a}^T is a row vector, \mathbf{r} is a column vector and b is a scalar, we can write the general form of a table entry as

$$[\mathbf{h}^T : \delta](\mathbf{P}, -\mathbf{t}) = [\mathbf{h}^T\mathbf{P} : -\mathbf{h}^T\mathbf{t} + \delta], \quad (1.4.4.10)$$

where δ is a constant phase shift which we take as zero. The positions $[\mathbf{h}^T : 0]$ and $[\mathbf{h}^T\mathbf{P} : -\mathbf{h}^T\mathbf{t}]$ are now related by the operation $(\mathbf{P}, -\mathbf{t})$ via the combination law (1.4.4.9), which is a shorthand transcription of the 4×4 matrix notation of Bienenstock & Ewald (1962), with the appropriate sign of \mathbf{t} .

Let us evaluate the result of a successive application of two such operators, say $(\mathbf{P}, -\mathbf{t})$ and $(\mathbf{Q}, -\mathbf{v})$ to the reference position $[\mathbf{h}^T : 0]$ in Fourier space:

$$\begin{aligned} [\mathbf{h}^T : 0](\mathbf{P}, -\mathbf{t})(\mathbf{Q}, -\mathbf{v}) &= [\mathbf{h}^T : 0](\mathbf{P}\mathbf{Q}, -\mathbf{P}\mathbf{v} - \mathbf{t}) \\ &= [\mathbf{h}^T\mathbf{P}\mathbf{Q} : -\mathbf{h}^T\mathbf{P}\mathbf{v} - \mathbf{h}^T\mathbf{t}], \end{aligned} \quad (1.4.4.11)$$

and perform an inverse operation:

$$\begin{aligned} [\mathbf{h}^T\mathbf{P} : -\mathbf{h}^T\mathbf{t}](\mathbf{P}, -\mathbf{t})^{-1} &= [\mathbf{h}^T\mathbf{P} : -\mathbf{h}^T\mathbf{t}](\mathbf{P}^{-1}, \mathbf{P}^{-1}\mathbf{t}) \\ &= [\mathbf{h}^T\mathbf{P}\mathbf{P}^{-1} : \mathbf{h}^T\mathbf{P}\mathbf{P}^{-1}\mathbf{t} - \mathbf{h}^T\mathbf{t}] \\ &= [\mathbf{h}^T : 0]. \end{aligned} \quad (1.4.4.12)$$

These equations confirm the validity of the shorthand notation (1.4.4.9) and illustrate the group nature of the operators $(\mathbf{P}, -\mathbf{t})$ in the present context.

1.4. SYMMETRY IN RECIPROCAL SPACE

Table 1.4.4.1. Correspondence between types of centring in direct and reciprocal lattices

Direct lattice		Reciprocal lattice		
Lattice type(s)	Centring translations	Lattice type(s)	Restriction on hkl	Multiple unit cell
P, R		P, R		$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$
A	$0, \frac{1}{2}, \frac{1}{2}$	A	$k + l = 2n$	$\mathbf{a}^*, 2\mathbf{b}^*, 2\mathbf{c}^*$
B	$\frac{1}{2}, 0, \frac{1}{2}$	B	$h + l = 2n$	$2\mathbf{a}^*, \mathbf{b}^*, 2\mathbf{c}^*$
C	$\frac{1}{2}, \frac{1}{2}, 0$	C	$h + k = 2n$	$2\mathbf{a}^*, 2\mathbf{b}^*, \mathbf{c}^*$
I	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	F	$h + k + l = 2n$	$2\mathbf{a}^*, 2\mathbf{b}^*, 2\mathbf{c}^*$
F	$0, \frac{1}{2}, \frac{1}{2}$ $\frac{1}{2}, 0, \frac{1}{2}$ $\frac{1}{2}, \frac{1}{2}, 0$	I	$k + l = 2n$ $h + l = 2n$ $h + k = 2n$	$2\mathbf{a}^*, 2\mathbf{b}^*, 2\mathbf{c}^*$
R_{hex}	$\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$	R_{hex}	$-h + k + l = 3n$	$3\mathbf{a}^*, 3\mathbf{b}^*, 3\mathbf{c}^*$

Following Bienenstock & Ewald, the operators $(\mathbf{P}, -\mathbf{t})$ are symmetry operators that act on the positions $[\mathbf{h}^T : 0]$ in Fourier space, provided they satisfy the following requirements: (i) the application of such an operator leaves the magnitude of the (generally) complex Fourier coefficient unchanged, and (ii) after g successive applications of an operator, where g is the order of its rotation part, the phase remains unchanged up to a shift by an integer multiple of 2π (a trivial phase shift, corresponding to a translation by a lattice vector in direct space).

If our function is the electron density in the crystal, the first requirement is obviously satisfied since $|F(\mathbf{h})| = |F(\mathbf{h}^T \mathbf{P})|$, where F is the structure factor [cf. equation (1.4.2.4)]. In order to make use of the second requirement in deriving permissible symmetry operators on Fourier space, all the relevant transformations, *i.e.* those which have rotation operators of the orders 1, 2, 3, 4 and 6, must be individually examined. A comprehensive example, covering most of the tetragonal system, can be found in Bienenstock & Ewald (1962).

It is of interest to illustrate the above process for a simple particular instance. Consider an operation, the rotation part of which involves a mirror plane, and assume that it is associated with the monoclinic system, in the second setting (unique axis b). We denote the operator by $(\mathbf{m}, -\mathbf{u})$, where $\mathbf{u}^T = (uvw)$, and the permissible values of u , v and w are to be determined. The operation is of order 2, and according to requirement (ii) above we have to evaluate

$$\begin{aligned} [\mathbf{h}^T : 0](\mathbf{m}, -\mathbf{u})^2 &= [\mathbf{h}^T : 0](\mathbf{I}, -\mathbf{m}\mathbf{u} - \mathbf{u}) \\ &= [\mathbf{h}^T : -\mathbf{h}^T(\mathbf{m} + \mathbf{I})\mathbf{u}] \\ &= [hkl : -2(hu + lw)], \end{aligned} \quad (1.4.4.13)$$

where

$$\mathbf{m} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

is the matrix representing the operation of reflection and \mathbf{I} is the unit matrix. For $(\mathbf{m}, -\mathbf{u})$ to be an admissible symmetry operator, the phase-shift part of (1.4.4.13), *i.e.* $-2(hu + lw)$, must be an integer (multiple of 2π). The smallest non-negative values of u and w which satisfy this are the pairs: $u = w = 0$, $u = \frac{1}{2}$ and $w = 0$, $u = 0$ and $w = \frac{1}{2}$, and $u = w = \frac{1}{2}$. We have thus obtained four symmetry operators in Fourier space, which are identical (except for the sign of their translational parts) to those of the direct-space monoclinic mirror and glide-plane operations. The fact that the component v cancels out simply means that an arbitrary component of the phase shift can be added along the b^* axis; this is concurrent with arbitrary direct-space translations

that appear in the characterization of individual types of space-group operations [see *e.g.* Koch & Fischer (2005)].

Each of the 230 space groups, which leaves invariant a (real and non-negative) function with the periodicity of the crystal, thus has its counterpart which determines the symmetry of the Fourier expansion coefficients of this function, with equivalent positions given in Table A1.4.4.1.

1.4.4.5. Relationships between direct and reciprocal Bravais lattices

Centred Bravais lattices in crystal space give rise to systematic absences of certain classes of reflections (*IT I*, 1952; *IT A*, 1983) and the corresponding points in the reciprocal lattice have accordingly zero weights. These absences are periodic in reciprocal space and their 'removal' from the reciprocal lattice results in a lattice which – like the direct one – must belong to one of the fourteen Bravais lattice types. This must be so since the point group of a crystal leaves its lattice – and also the associated reciprocal lattice – unchanged. The magnitudes of the structure factors (the weight functions) are also invariant under the operation of this point group.

The correspondence between the types of centring in direct and reciprocal lattices is given in Table 1.4.4.1.

Notes:

(i) The vectors \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* , appearing in the definition of the multiple unit cell in the reciprocal lattice, define this lattice *prior to the removal* of lattice points with zero weights (absences). All the restrictions on hkl pertain to indexing on \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* .

(ii) The centring type of the reciprocal lattice refers to the multiple unit cell given in the table.

(iii) The centring type denoted by R_{hex} is a representation of the rhombohedral lattice R by a triple hexagonal unit cell, in the obverse setting (*IT I*, 1952), *i.e.* according to the transformation

$$\begin{aligned} \mathbf{a} &= \mathbf{a}_R - \mathbf{b}_R \\ \mathbf{b} &= \mathbf{b}_R - \mathbf{c}_R \\ \mathbf{c} &= \mathbf{a}_R + \mathbf{b}_R + \mathbf{c}_R, \end{aligned} \quad (1.4.4.14)$$

where \mathbf{a}_R , \mathbf{b}_R and \mathbf{c}_R pertain to a primitive unit cell in the rhombohedral lattice R .

The corresponding multiple reciprocal cell, with centring denoted by R_{hex} , contains nine lattice points with coordinates 000, 021, 012, 101, 202, 110, 220, 211 and 122 – indexed on the usual reciprocal to the triple hexagonal unit cell defined by (1.4.4.14). Detailed derivations of these correspondences are given by Buerger (1942), and an elementary proof of the reciprocity of I and F lattices can be found, *e.g.*, in pamphlet No. 4 of the Commission on Crystallographic Teaching (Authier, 1981).