

1. GENERAL RELATIONSHIPS AND TECHNIQUES

$$\mathbf{u}^T(1) = \mathbf{u}^T(2)\{\mathbf{G}(22)[\mathbf{G}(12)]^{-1}\} \quad \mathbf{r} = X^k \mathbf{e}_k, \quad (1.1.5.12)$$

and

$$\mathbf{u}^T(2) = \mathbf{u}^T(1)\{\mathbf{G}(12)[\mathbf{G}(22)]^{-1}\}, \quad (1.1.5.7)$$

and

$$\mathbf{u}^T(1)\mathbf{G}(11) = \mathbf{u}^T(2)\mathbf{G}(21), \quad (1.1.5.8)$$

leading to

$$\mathbf{u}^T(1) = \mathbf{u}^T(2)\{\mathbf{G}(21)[\mathbf{G}(11)]^{-1}\}$$

and

$$\mathbf{u}^T(2) = \mathbf{u}^T(1)\{\mathbf{G}(11)[\mathbf{G}(21)]^{-1}\}. \quad (1.1.5.9)$$

Equations (1.1.5.7) and (1.1.5.9) are symbolic general expressions for the transformation of the coordinates of \mathbf{r} from one representation to the other.

In the general case, therefore, we require the matrices of scalar products of the basis vectors, $\mathbf{G}(12)$ and $\mathbf{G}(22)$ or $\mathbf{G}(11)$ and $\mathbf{G}(21)$ – depending on whether the basis $\mathbf{c}_k(2)$ or $\mathbf{c}_k(1)$, $k = 1, 2, 3$, was chosen to multiply scalarly equations (1.1.5.1) and (1.1.5.2). Note, however, the following simplifications.

(i) If the bases $\mathbf{c}_k(1)$ and $\mathbf{c}_k(2)$ are mutually reciprocal, each of the matrices of mixed scalar products, $\mathbf{G}(12)$ and $\mathbf{G}(21)$, reduces to a unit matrix. In this important special case, the transformation is effected by the matrices of the metric tensors of the bases in question. This can be readily seen from equations (1.1.5.7) and (1.1.5.9), which then reduce to the relationships between the covariant and contravariant components of the same vector [see equations (1.1.4.11) and (1.1.4.12) above].

(ii) If one of the bases, say $\mathbf{c}_k(2)$, is Cartesian, its metric tensor is by definition a unit tensor, and the transformations in (1.1.5.7) reduce to

$$\mathbf{u}^T(1) = \mathbf{u}^T(2)[\mathbf{G}(12)]^{-1}$$

and

$$\mathbf{u}^T(2) = \mathbf{u}^T(1)\mathbf{G}(12). \quad (1.1.5.10)$$

The transformation matrix is now the mixed matrix of the scalar products, whether or not the basis $\mathbf{c}_k(1)$, $k = 1, 2, 3$, is also Cartesian. If, however, both bases are Cartesian, the transformation can also be interpreted as a rigid rotation of the coordinate axes (see Chapter 3.3).

It should be noted that the above transformations do not involve any shift of the origin. Transformations involving such shifts, notably the symmetry transformations of the space group, are treated rather extensively in Volume A of *International Tables for Crystallography* (2005) [see e.g. Part 5 there (Arnold, 2005)].

1.1.5.2. Example

This example deals with the construction of a Cartesian system in a crystal with given basis vectors of its direct lattice. We shall also require that the Cartesian system bear a clear relationship to at least one direction in each of the direct and reciprocal lattices of the crystal; this may be useful in interpreting a physical property which has been measured along a given lattice vector or which is associated with a given lattice plane. For a better consistency of notation, the Cartesian components will be denoted as contravariant.

The appropriate version of equations (1.1.5.1) and (1.1.5.2) is now

$$\mathbf{r} = x^i \mathbf{a}_i \quad (1.1.5.11)$$

and

where the Cartesian basis vectors are: $\mathbf{e}_1 = \mathbf{r}_L/|\mathbf{r}_L|$, $\mathbf{e}_2 = \mathbf{r}^*/|\mathbf{r}^*|$ and $\mathbf{e}_3 = \mathbf{e}_1 \times \mathbf{e}_2$, and the vectors \mathbf{r}_L and \mathbf{r}^* are given by

$$\mathbf{r}_L = u^i \mathbf{a}_i \quad \text{and} \quad \mathbf{r}^* = h_k \mathbf{a}^k,$$

where u^i and h_k , $i, k = 1, 2, 3$, are arbitrary integers. The vectors \mathbf{r}_L and \mathbf{r}^* must of course be chosen to be mutually perpendicular, $\mathbf{r}_L \cdot \mathbf{r}^* = u^i h_i = 0$. The $X^1(X)$ axis of the Cartesian system thus coincides with a direct-lattice vector, and the $X^2(Y)$ axis is parallel to a vector in the reciprocal lattice.

Since the basis in (1.1.5.12) is a Cartesian one, the required transformations are given by equations (1.1.5.10) as

$$x^i = X^k (T^{-1})_k^i \quad \text{and} \quad X^i = x^k T_k^i, \quad (1.1.5.13)$$

where $T_k^i = \mathbf{a}_k \cdot \mathbf{e}_i$, $k, i = 1, 2, 3$, form the matrix of the scalar products. If we make use of the relationships between covariant and contravariant basis vectors, and the tensor formulation of the vector product, given in Section 1.1.4 above (see also Chapter 3.1), we obtain

$$\begin{aligned} T_k^1 &= \frac{1}{|\mathbf{r}_L|} g_{ki} u^i \\ T_k^2 &= \frac{1}{|\mathbf{r}^*|} h_k \\ T_k^3 &= \frac{V}{|\mathbf{r}_L||\mathbf{r}^*|} e_{kip} u^i g^{pj} h_j. \end{aligned} \quad (1.1.5.14)$$

Note that the other convenient choice, $\mathbf{e}_1 \propto \mathbf{r}^*$ and $\mathbf{e}_2 \propto \mathbf{r}_L$, interchanges the first two columns of the matrix \mathbf{T} in (1.1.5.14) and leads to a change of the signs of the elements in the third column. This can be done by writing e_{kpi} instead of e_{kip} , while leaving the rest of T_k^3 unchanged.

1.1.6. Some analytical aspects of the reciprocal space

1.1.6.1. Continuous Fourier transform

Of great interest in crystallographic analyses are Fourier transforms and these are closely associated with the dual bases examined in this chapter. Thus, e.g., the inverse Fourier transform of the electron-density function of the crystal

$$F(\mathbf{h}) = \int_{\text{cell}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d^3 \mathbf{r}, \quad (1.1.6.1)$$

where $\rho(\mathbf{r})$ is the electron-density function at the point \mathbf{r} and the integration extends over the volume of a unit cell, is the fundamental model of the contribution of the distribution of crystalline matter to the intensity of the scattered radiation. For the conventional Bragg scattering, the function given by (1.1.6.1), and known as the *structure factor*, may assume nonzero values *only* if \mathbf{h} can be represented as a reciprocal-lattice vector. Chapter 1.2 is devoted to a discussion of the structure factor of the Bragg reflection, while Chapters 4.1, 4.2 and 4.3 discuss circumstances under which the scattering need not be confined to the points of the reciprocal lattice only, and may be represented by reciprocal-space vectors with non-integral components.

1.1.6.2. Discrete Fourier transform

The electron density $\rho(\mathbf{r})$ in (1.1.6.1) is one of the most common examples of a function which has the periodicity of the crystal. Thus, for an ideal (infinite) crystal the electron density $\rho(\mathbf{r})$ can be written as

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + u\mathbf{a} + v\mathbf{b} + w\mathbf{c}), \quad (1.1.6.2)$$

and, as such, it can be represented by a three-dimensional Fourier series of the form

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$$\rho(\mathbf{r}) = \sum_{\mathbf{g}} C(\mathbf{g}) \exp(-2\pi i \mathbf{g} \cdot \mathbf{r}), \quad (1.1.6.3) \quad \psi(\mathbf{r} + \mathbf{r}_L) = \psi(\mathbf{r}),$$

where the periodicity requirement (1.1.6.2) enables one to represent all the \mathbf{g} vectors in (1.1.6.3) as vectors in the reciprocal lattice (see also Section 1.1.2 above). If we insert the series (1.1.6.3) in the integrand of (1.1.6.1), interchange the order of summation and integration and make use of the fact that an integral of a periodic function taken over the entire period must vanish unless the integrand is a constant, equation (1.1.6.3) reduces to the conventional form

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (1.1.6.4)$$

where V is the volume of the unit cell in the direct lattice and the summation ranges over all the reciprocal lattice.

Fourier transforms, discrete as well as continuous, are among the most important mathematical tools of crystallography. The discussion of their mathematical principles, the modern algorithms for their computation and their numerous applications in crystallography form the subject matter of Chapter 1.3. Many more examples of applications of Fourier methods in crystallography are scattered throughout this volume and the crystallographic literature in general.

1.1.6.3. Bloch's theorem

It is in order to mention briefly the important role of reciprocal space and the reciprocal lattice in the field of the theory of solids. At the basis of these applications is the periodicity of the crystal structure and the effect it has on the dynamics (*cf.* Chapter 4.1) and electronic structure of the crystal. One of the earliest, and still most important, theorems of solid-state physics is due to Bloch (1928) and deals with the representation of the wavefunction of an electron which moves in a periodic potential. Bloch's theorem states that:

The eigenstates ψ of the one-electron Hamiltonian $\mathcal{H} = (-\hbar^2/2m)\nabla^2 + U(\mathbf{r})$, where $U(\mathbf{r})$ is the crystal potential and $U(\mathbf{r} + \mathbf{r}_L) = U(\mathbf{r})$ for all \mathbf{r}_L in the Bravais lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice.

Thus

$$\psi(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u(\mathbf{r}), \quad (1.1.6.5)$$

where

$$u(\mathbf{r} + \mathbf{r}_L) = u(\mathbf{r}) \quad (1.1.6.6)$$

and \mathbf{k} is the wavevector. The proof of Bloch's theorem can be found in most modern texts on solid-state physics (*e.g.* Ashcroft & Mermin, 1975). If we combine (1.1.6.5) with (1.1.6.6), an alternative form of the Bloch theorem results:

$$\psi(\mathbf{r} + \mathbf{r}_L) = \exp(i\mathbf{k} \cdot \mathbf{r}_L)\psi(\mathbf{r}). \quad (1.1.6.7)$$

In the important case where the wavefunction ψ is itself periodic, *i.e.*

we must have $\exp(i\mathbf{k} \cdot \mathbf{r}_L) = 1$. Of course, this can be so only if the wavevector \mathbf{k} equals 2π times a vector in the reciprocal lattice. It is also seen from equation (1.1.6.7) that the wavevector appearing in the phase factor can be reduced to a unit cell in the reciprocal lattice (the basis vectors of which contain the 2π factor), or to the equivalent polyhedron known as the *Brillouin zone* (*e.g.* Ziman, 1969). This periodicity in reciprocal space is of prime importance in the theory of solids. Some Brillouin zones are discussed in detail in Chapter 1.5.

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