

1.1. RECIPROCAL SPACE IN CRYSTALLOGRAPHY

coefficients, which are related to the experimental data. Numerous examples of such expansions appear throughout this volume.

The permissible wavevectors in the above expansion are restricted by the periodicity of the function $G(\mathbf{r})$. Since, by definition, $G(\mathbf{r}) = G(\mathbf{r} + \mathbf{r}_L)$, where \mathbf{r}_L is a direct-lattice vector, the right-hand side of (1.1.2.7) must remain unchanged when \mathbf{r} is replaced by $\mathbf{r} + \mathbf{r}_L$. This, however, can be true only if the scalar product $\mathbf{g} \cdot \mathbf{r}_L$ is an integer.

Each of the above three aspects of crystallography may lead, independently, to a useful introduction of the reciprocal vectors, and there are many examples of this in the literature. It is interesting, however, to consider the representation of the equation

$$\mathbf{v} \cdot \mathbf{r}_L = n, \quad (1.1.2.8)$$

which is common to all three, in its most convenient form. Obviously, the vector \mathbf{v} which stands for the plane normal, the diffraction vector, and the wavevector in a Fourier expansion, may still be referred to any permissible basis and so may \mathbf{r}_L , by an appropriate transformation.

Let $\mathbf{v} = U\mathbf{A} + V\mathbf{B} + W\mathbf{C}$, where \mathbf{A} , \mathbf{B} and \mathbf{C} are linearly independent vectors. Equation (1.1.2.8) can then be written as

$$(U\mathbf{A} + V\mathbf{B} + W\mathbf{C}) \cdot (u\mathbf{a} + v\mathbf{b} + w\mathbf{c}) = n, \quad (1.1.2.9)$$

or, in matrix notation,

$$(UVW) \begin{pmatrix} \mathbf{A} \\ \mathbf{B} \\ \mathbf{C} \end{pmatrix} \cdot (\mathbf{abc}) \begin{pmatrix} u \\ v \\ w \end{pmatrix} = n, \quad (1.1.2.10)$$

or

$$(UVW) \begin{pmatrix} \mathbf{A} \cdot \mathbf{a} & \mathbf{A} \cdot \mathbf{b} & \mathbf{A} \cdot \mathbf{c} \\ \mathbf{B} \cdot \mathbf{a} & \mathbf{B} \cdot \mathbf{b} & \mathbf{B} \cdot \mathbf{c} \\ \mathbf{C} \cdot \mathbf{a} & \mathbf{C} \cdot \mathbf{b} & \mathbf{C} \cdot \mathbf{c} \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix} = n. \quad (1.1.2.11)$$

The simplest representation of equation (1.1.2.8) results when the matrix of scalar products in (1.1.2.11) reduces to a unit matrix. This can be achieved (i) by choosing the basis vectors \mathbf{ABC} to be orthonormal to the basis vectors \mathbf{abc} , while requiring that the components of \mathbf{r}_L be integers, or (ii) by requiring that the bases \mathbf{ABC} and \mathbf{abc} coincide with the same orthonormal basis, *i.e.* expressing both \mathbf{v} and \mathbf{r}_L , in (1.1.2.8), in the same Cartesian system. If we choose the first alternative, it is seen that:

(1) The components of the vector \mathbf{v} , and hence those of \mathbf{N} , \mathbf{h} and \mathbf{g} , are of necessity integers, since u , v and w are already integral. The components of \mathbf{v} include Miller indices; in the case of the lattice plane, they coincide with the orders of diffraction from a three-dimensional lattice of scatterers, and correspond to the summation indices in the triple Fourier series (1.1.2.7).

(2) The basis vectors \mathbf{A} , \mathbf{B} and \mathbf{C} are reciprocal to \mathbf{a} , \mathbf{b} and \mathbf{c} , as can be seen by comparing the scalar products in (1.1.2.11) with those in (1.1.2.1) and (1.1.2.2). In fact, the bases \mathbf{ABC} and \mathbf{abc} are mutually reciprocal. Since there are no restrictions on the integers U , V and W , the vector \mathbf{v} belongs to a lattice which, on account of its basis, is called the reciprocal lattice.

It follows that, at least in the present case, algebraic simplicity goes together with ease of interpretation, which certainly accounts for much of the importance of the reciprocal lattice in crystallography. The second alternative of reducing the matrix in (1.1.2.11) to a unit matrix, a transformation of (1.1.2.8) to a Cartesian system, leads to non-integral components of the vectors, which makes any interpretation of \mathbf{v} or \mathbf{r}_L much less transparent. However, transformations to Cartesian systems are often very useful in crystallographic computing and will be discussed below (see also Chapters 2.3 and 3.3 in this volume).

We shall, in what follows, abandon all the temporary notation used above and write the reciprocal-lattice vector as

$$\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (1.1.2.12)$$

or

$$\mathbf{h} = h_1\mathbf{a}^1 + h_2\mathbf{a}^2 + h_3\mathbf{a}^3 = \sum_{i=1}^3 h_i\mathbf{a}^i, \quad (1.1.2.13)$$

and denote the direct-lattice vectors by $\mathbf{r}_L = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, as above, or by

$$\mathbf{r}_L = u^1\mathbf{a}_1 + u^2\mathbf{a}_2 + u^3\mathbf{a}_3 = \sum_{i=1}^3 u^i\mathbf{a}_i. \quad (1.1.2.14)$$

The representations (1.1.2.13) and (1.1.2.14) are used in the tensor-algebraic formulation of the relationships between mutually reciprocal bases (see Section 1.1.4 below).

1.1.3. Fundamental relationships

We now present a brief derivation and a summary of the most important relationships between the direct and the reciprocal bases. The usual conventions of vector algebra are observed and the results are presented in the conventional crystallographic notation. Equations (1.1.2.1) and (1.1.2.2) now become

$$\mathbf{a} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{c}^* = \mathbf{b} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{c}^* = \mathbf{c} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{b}^* = 0 \quad (1.1.3.1)$$

and

$$\mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = \mathbf{c} \cdot \mathbf{c}^* = 1, \quad (1.1.3.2)$$

respectively, and the relationships are obtained as follows.

1.1.3.1. Basis vectors

It is seen from (1.1.3.1) that \mathbf{a}^* must be proportional to the vector product of \mathbf{b} and \mathbf{c} ,

$$\mathbf{a}^* = K(\mathbf{b} \times \mathbf{c}),$$

and, since $\mathbf{a} \cdot \mathbf{a}^* = 1$, the proportionality constant K equals $1/[\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})]$. The mixed product $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$ can be interpreted as the positive volume of the unit cell in the direct lattice only if \mathbf{a} , \mathbf{b} and \mathbf{c} form a *right-handed* set. If the above condition is fulfilled, we obtain

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V}, \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V}, \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V} \quad (1.1.3.3)$$

and analogously

$$\mathbf{a} = \frac{\mathbf{b}^* \times \mathbf{c}^*}{V^*}, \quad \mathbf{b} = \frac{\mathbf{c}^* \times \mathbf{a}^*}{V^*}, \quad \mathbf{c} = \frac{\mathbf{a}^* \times \mathbf{b}^*}{V^*}, \quad (1.1.3.4)$$

where V and V^* are the volumes of the unit cells in the associated direct and reciprocal lattices, respectively. Use has been made of the fact that the mixed product, say $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$, remains unchanged under cyclic rearrangement of the vectors that appear in it.

1.1.3.2. Volumes

The reciprocal relationship of V and V^* follows readily. We have from equations (1.1.3.2), (1.1.3.3) and (1.1.3.4)

$$\mathbf{c} \cdot \mathbf{c}^* = \frac{(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{a}^* \times \mathbf{b}^*)}{VV^*} = 1.$$

If we make use of the vector identity

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$$(\mathbf{A} \times \mathbf{B}) \cdot (\mathbf{C} \times \mathbf{D}) = (\mathbf{A} \cdot \mathbf{C})(\mathbf{B} \cdot \mathbf{D}) - (\mathbf{A} \cdot \mathbf{D})(\mathbf{B} \cdot \mathbf{C}), \quad (1.1.3.5)$$

and equations (1.1.3.1) and (1.1.3.2), it is seen that $V^* = 1/V$.

1.1.3.3. Angular relationships

The relationships of the angles α, β, γ between the pairs of vectors (\mathbf{b}, \mathbf{c}) , (\mathbf{c}, \mathbf{a}) and (\mathbf{a}, \mathbf{b}) , respectively, and the angles $\alpha^*, \beta^*, \gamma^*$ between the corresponding pairs of reciprocal basis vectors, can be obtained by simple vector algebra. For example, we have from (1.1.3.3):

(i) $\mathbf{b}^* \cdot \mathbf{c}^* = b^* c^* \cos \alpha^*$, with

$$b^* = \frac{ca \sin \beta}{V} \quad \text{and} \quad c^* = \frac{ab \sin \gamma}{V}$$

and (ii)

$$\mathbf{b}^* \cdot \mathbf{c}^* = \frac{(\mathbf{c} \times \mathbf{a}) \cdot (\mathbf{a} \times \mathbf{b})}{V^2}.$$

If we make use of the identity (1.1.3.5), and compare the two expressions for $\mathbf{b}^* \cdot \mathbf{c}^*$, we readily obtain

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}. \quad (1.1.3.6)$$

Similarly,

$$\cos \beta^* = \frac{\cos \gamma \cos \alpha - \cos \beta}{\sin \gamma \sin \alpha} \quad (1.1.3.7)$$

and

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta}. \quad (1.1.3.8)$$

The expressions for the cosines of the direct angles in terms of those of the reciprocal ones are analogous to (1.1.3.6)–(1.1.3.8). For example,

$$\cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}.$$

1.1.3.4. Matrices of metric tensors

Various computational and algebraic aspects of mutually reciprocal bases are most conveniently expressed in terms of the metric tensors of these bases. The tensors will be treated in some detail in the next section, and only the definitions of their matrices are given and interpreted below.

Consider the length of the vector $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$. This is given by

$$|\mathbf{r}| = [(x\mathbf{a} + y\mathbf{b} + z\mathbf{c}) \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c})]^{1/2} \quad (1.1.3.9)$$

and can be written in matrix form as

$$|\mathbf{r}| = [\mathbf{x}^T \mathbf{G} \mathbf{x}]^{1/2}, \quad (1.1.3.10)$$

where

$$\mathbf{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad \mathbf{x}^T = (xyz)$$

and

$$\mathbf{G} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix} \quad (1.1.3.11)$$

$$= \begin{pmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ba \cos \gamma & b^2 & bc \cos \alpha \\ ca \cos \beta & cb \cos \alpha & c^2 \end{pmatrix}. \quad (1.1.3.12)$$

This is the matrix of the metric tensor of the direct basis, or briefly the direct metric. The corresponding reciprocal metric is given by

$$\mathbf{G}^* = \begin{pmatrix} \mathbf{a}^* \cdot \mathbf{a}^* & \mathbf{a}^* \cdot \mathbf{b}^* & \mathbf{a}^* \cdot \mathbf{c}^* \\ \mathbf{b}^* \cdot \mathbf{a}^* & \mathbf{b}^* \cdot \mathbf{b}^* & \mathbf{b}^* \cdot \mathbf{c}^* \\ \mathbf{c}^* \cdot \mathbf{a}^* & \mathbf{c}^* \cdot \mathbf{b}^* & \mathbf{c}^* \cdot \mathbf{c}^* \end{pmatrix} \quad (1.1.3.13)$$

$$= \begin{pmatrix} a^{*2} & a^* b^* \cos \gamma^* & a^* c^* \cos \beta^* \\ b^* a^* \cos \gamma^* & b^{*2} & b^* c^* \cos \alpha^* \\ c^* a^* \cos \beta^* & c^* b^* \cos \alpha^* & c^{*2} \end{pmatrix}. \quad (1.1.3.14)$$

The matrices \mathbf{G} and \mathbf{G}^* are of fundamental importance in crystallographic computations and transformations of basis vectors and coordinates from direct to reciprocal space and *vice versa*. Examples of applications are presented in Part 3 of this volume and in the remaining sections of this chapter.

It can be shown (*e.g.* Buerger, 1941) that the determinants of \mathbf{G} and \mathbf{G}^* equal the squared volumes of the direct and reciprocal unit cells, respectively. Thus,

$$\det(\mathbf{G}) = [\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})]^2 = V^2 \quad (1.1.3.15)$$

and

$$\det(\mathbf{G}^*) = [\mathbf{a}^* \cdot (\mathbf{b}^* \times \mathbf{c}^*)]^2 = V^{*2}, \quad (1.1.3.16)$$

and a direct expansion of the determinants, from (1.1.3.12) and (1.1.3.14), leads to

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2} \quad (1.1.3.17)$$

and

$$V^* = a^* b^* c^* (1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*)^{1/2}. \quad (1.1.3.18)$$

The following algorithm has been found useful in computational applications of the above relationships to calculations in reciprocal space (*e.g.* data reduction) and in direct space (*e.g.* crystal geometry).

(1) Input the direct unit-cell parameters and construct the matrix of the metric tensor [*cf.* equation (1.1.3.12)].

(2) Compute the determinant of the matrix \mathbf{G} and find the inverse matrix, \mathbf{G}^{-1} ; this inverse matrix is just \mathbf{G}^* , the matrix of the metric tensor of the reciprocal basis (see also Section 1.1.4 below).

(3) Use the elements of \mathbf{G}^* , and equation (1.1.3.14), to obtain the parameters of the reciprocal unit cell.

The direct and reciprocal sets of unit-cell parameters, as well as the corresponding metric tensors, are now available for further calculations.

Explicit relations between direct- and reciprocal-lattice parameters, valid for the various crystal systems, are given in most textbooks on crystallography [see also Chapter 1.1 of Volume C (Koch, 1999)].