1.1. Reciprocal space in crystallography

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1.1.1. Introduction

The purpose of this chapter is to provide an introduction to several aspects of reciprocal space, which are of general importance in crystallography and which appear in the various chapters and sections to follow. We first summarize the basic definitions and briefly inspect some fundamental aspects of crystallography, while recalling that they can be usefully and simply discussed in terms of the concept of the reciprocal lattice. This introductory section is followed by a summary of the basic relationships between the direct and associated reciprocal lattices. We then introduce the elements of tensor-algebraic formulation of such dual relationships, with emphasis on those that are important in many applications of reciprocal space to crystallographic algorithms. We proceed with a section that demonstrates the role of mutually reciprocal bases in transformations of coordinates and conclude with a brief outline of some important analytical aspects of reciprocal space, most of which are further developed in other parts of this volume.

1.1.2. Reciprocal lattice in crystallography

The notion of mutually reciprocal triads of vectors dates back to the introduction of vector calculus by J. Willard Gibbs in the 1880s (*e.g.* Wilson, 1901). This concept appeared to be useful in the early interpretations of diffraction from single crystals (Ewald, 1913; Laue, 1914) and its first detailed exposition and the recognition of its importance in crystallography can be found in Ewald's (1921) article. The following free translation of Ewald's (1921) introduction, presented in a somewhat different notation, may serve the purpose of this section:

> To the set of $\mathbf{a}_i$, there corresponds in the vector calculus a set of 'reciprocal vectors' $\mathbf{b}_i$, which are defined (by Gibbs) by the following properties:
>
> $$\mathbf{a}_i \cdot \mathbf{b}_k = 0 \quad \text{(for } i \neq k\text{)} \qquad (1.1.2.1)$$
>
> and
>
> $$\mathbf{a}_i \cdot \mathbf{b}_i = 1, \qquad (1.1.2.2)$$
>
> where i and k may each equal 1, 2 or 3. The first equation, (1.1.2.1), says that each vector $\mathbf{b}_k$ is perpendicular to two vectors $\mathbf{a}_i$, as follows from the vanishing scalar products. Equation (1.1.2.2) provides the norm of the vector $\mathbf{b}_i$: the length of this vector must be chosen such that the projection of $\mathbf{b}_i$ on the direction of $\mathbf{a}_i$ has the length $1/a_i$, where a_i is the magnitude of the vector $\mathbf{a}_i$....

The consequences of equations (1.1.2.1) and (1.1.2.2) were elaborated by Ewald (1921) and are very well documented in the subsequent literature, crystallographic as well as other.

As is well known, the reciprocal lattice occupies a rather prominent position in crystallography and there are nearly as many accounts of its importance as there are crystallographic texts. It is not intended to review its applications, in any detail, in the present section; this is done in the remaining chapters and sections of the present volume. It seems desirable, however, to mention by way of an introduction some fundamental geometrical, physical and mathematical aspects of crystallography, and try to give a unified demonstration of the usefulness of mutually reciprocal bases as an interpretive tool.

Let us assume that the coordinates of all the (direct) lattice points are integers. This can only be true for P-type lattices. Consider the equation of a lattice plane in the direct lattice. It can

be shown (*e.g.* Buerger, 1941; also Shmueli, 2007) that this equation is given by

$$hx + ky + lz = n, \qquad (1.1.2.3)$$

where h, k and l, known as Miller indices of the (hkl) lattice plane, are (under the above assumption) relatively prime integers (*i.e.* do not have a common factor other than $+1$ or -1). In this equation, x, y and z are the coordinates of any point lying in the plane and are expressed as fractions of the magnitudes of the basis vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ of the direct lattice, and n is an integer denoting the serial number of the lattice plane within the family of parallel and equidistant (hkl) planes. The interplanar spacing is denoted by d_{hkl}, the value $n = 0$ corresponding to the (hkl) plane passing through the origin.

Let $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$ and $\mathbf{r}_\mathrm{L} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, where u, v, w are any integers, denote the position vectors of the point xyz and a lattice point uvw lying in the plane (1.1.2.3), respectively, and assume that $\mathbf{r}$ and $\mathbf{r}_\mathrm{L}$ are different vectors. If the plane normal is denoted by $\mathbf{N}$, where $\mathbf{N}$ is proportional to the vector product of two in-plane lattice vectors, the vector form of the equation of the lattice plane becomes

$$\mathbf{N} \cdot (\mathbf{r} - \mathbf{r}_\mathrm{L}) = 0 \quad \text{or} \quad \mathbf{N} \cdot \mathbf{r} = \mathbf{N} \cdot \mathbf{r}_\mathrm{L}. \qquad (1.1.2.4)$$

For equations (1.1.2.3) and (1.1.2.4) to be identical, the plane normal $\mathbf{N}$ must satisfy the requirement that $\mathbf{N} \cdot \mathbf{r}_\mathrm{L} = n$, where n is an (unrestricted) integer.

While the Miller indices of lattice planes in P-type lattices must be relatively prime, if the direct lattice is based on a non-primitive unit cell (any centring type) the Miller indices of some lattice planes are no longer relatively prime (*e.g.* Nespolo, 2015).

Let us now consider the basic diffraction relations (*e.g.* Lipson & Cochran, 1966). Suppose a parallel beam of monochromatic radiation, of wavelength λ, falls on a lattice of identical point scatterers. If it is assumed that the scattering is elastic, *i.e.* there is no change of the wavelength during this process, the wavevectors of the incident and scattered radiation have the same magnitude, which can conveniently be taken as $1/\lambda$. A consideration of path and phase differences between the waves outgoing from two point scatterers separated by the lattice vector $\mathbf{r}_\mathrm{L}$ (defined as above) shows that the condition for their maximum constructive interference is given by

$$(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{r}_\mathrm{L} = n, \qquad (1.1.2.5)$$

where $\mathbf{s}_0$ and $\mathbf{s}$ are the wavevectors of the incident and scattered beams, respectively, and n is an arbitrary integer.

Since $\mathbf{r}_\mathrm{L} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, where u, v and w are unrestricted integers, equation (1.1.2.5) is equivalent to the equations of Laue:

$$\mathbf{h} \cdot \mathbf{a} = h, \quad \mathbf{h} \cdot \mathbf{b} = k, \quad \mathbf{h} \cdot \mathbf{c} = l, \qquad (1.1.2.6)$$

where $\mathbf{h} = \mathbf{s} - \mathbf{s}_0$ is the diffraction vector, and h, k and l are integers corresponding to orders of diffraction from the three-dimensional lattice (Lipson & Cochran, 1966). The diffraction vector thus has to satisfy a condition that is analogous to that imposed on the normal to a lattice plane.

The next relevant aspect to be commented on is the Fourier expansion of a function having the periodicity of the crystal lattice. Such functions are *e.g.* the electron density, the density of nuclear matter and the electrostatic potential in the crystal, which are the operative definitions of crystal structure in X-ray, neutron and electron-diffraction methods of crystal structure determination. A Fourier expansion of such a periodic function may be