1.1. RECIPROCAL SPACE IN CRYSTALLOGRAPHY

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

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

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

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 $h = (-\hbar^2/2m)\nabla^2 + U(\mathbf{r})$, where $U(\mathbf{r})$ is the crystal potential and $\mathbf{U}(\mathbf{r} + \mathbf{r}_L) = U(\mathbf{r})$ 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

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

where

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

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:

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

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

$$\psi(\mathbf{r} + \mathbf{r}_L) = \psi(\mathbf{r}),$$

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.

I wish to thank Professor D. W. J. Cruickshank for bringing to my attention the contribution of M. von Laue (Laue, 1914), who was the first to introduce general reciprocal bases to crystallography.

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