where the band index j (described below) may change to j'. The Bloch factor stays constant under the operation of q and thus the periodic cell function $u^j_{\mathbf{k}}(\mathbf{r})$ must show this symmetry, namely

$$q u^j_{\mathbf{k}}(\mathbf{r}) = u^{j'}_{\mathbf{k}}(\mathbf{r}) \text{ for } q \in G_{\mathbf{k}}. \qquad (2.2.6.5)$$

For example, a p_x-like orbital may be transformed into a p_y-like orbital if the two are degenerate, as in a tetragonal lattice.

A star of $\mathbf{k}$ determines an irreducible basis, provided that the functions of the star are symmetrized with respect to the irreducible representation of the group of $\mathbf{k}$ vectors, which are called *small representations*. The basis functions for the irreducible representations are given according to Seitz (1937) by

$$\langle s\psi^j_{\mathbf{k}}|, \text{ where } s \in S_{\mathbf{k}},$$

written as a row vector $\langle|$ with $j = 1, \ldots, n$, where n is the dimension of the irreducible representation of $S_{\mathbf{k}}$ with the order $|S_{\mathbf{k}}|$. Such a basis consists of $n|S_{\mathbf{k}}|$ functions and forms an $n|S_{\mathbf{k}}|$-dimensional irreducible representation of the space group. The degeneracies of these representations come from the star of $\mathbf{k}$ (not crucial for band calculations except for determining the weight of the $\mathbf{k}$ vector) and the degeneracy from $G_{\mathbf{k}}$. The latter is essential for characterizing the energy bands and using the compatibility relations (Bouckaert *et al.*, 1930; Bradley & Cracknell, 1972).

2.2.6.2. *Energy bands*

Each irreducible representation of the space group, labelled by $\mathbf{k}$, denotes an energy $E^j(\mathbf{k})$, where $\mathbf{k}$ varies quasi-continuously over the BZ and the superscript j numbers the band states. The quantization of $\mathbf{k}$ according to (2.2.4.13) and (2.2.4.15) can be done in arbitrary fine steps by choosing corresponding periodic boundary conditions (see Section 2.2.4.2). Since $\mathbf{k}$ and $\mathbf{k} + \mathbf{K}$ belong to the same Bloch state, the energy is periodic in reciprocal space:

$$E^j(\mathbf{k}) = E^j(\mathbf{k} + \mathbf{K}). \qquad (2.2.6.6)$$

Therefore it is sufficient to consider $\mathbf{k}$ vectors within the first BZ. For a given $\mathbf{k}$, two bands will not have the same energy unless there is a multidimensional small representation in the group of $\mathbf{k}$ or the bands belong to different irreducible representations and thus can have an accidental degeneracy. Consequently, this can not occur for a general $\mathbf{k}$ vector (without symmetry).

2.2.7. The k vector and the Brillouin zone

2.2.7.1. *Various aspects of the* k *vector*

The $\mathbf{k}$ vector plays a fundamental role in the electronic structure of a solid. In the above, several interpretations have been given for the $\mathbf{k}$ vector that

(*a*) is given in reciprocal space,

(*b*) can be restricted to the first Brillouin zone,

(*c*) is the quantum number for the electronic states in a solid,

(*d*) is quantized due to the periodic boundary conditions,

(*e*) labels the irreducible representation of the lattice translation subgroup T (see Section 2.2.4.3)

(*f*) is related to the momentum [according to (2.2.5.5)] in the free-electron case and

(*g*) is the propagation vector (wavevector) associated with the plane-wave part of the wavefunction (see Fig. 2.2.5.1).

2.2.7.2. *The Brillouin zone (BZ)*

Starting with one of the 14 Bravais lattices, one can define the reciprocal lattice [according to (2.2.2.4)] by the Wigner–Seitz construction as discussed in Section 2.2.2.2. The advantage of using the BZ instead of the parallelepiped spanned by the three unit vectors is its symmetry. Let us take a simple example first,

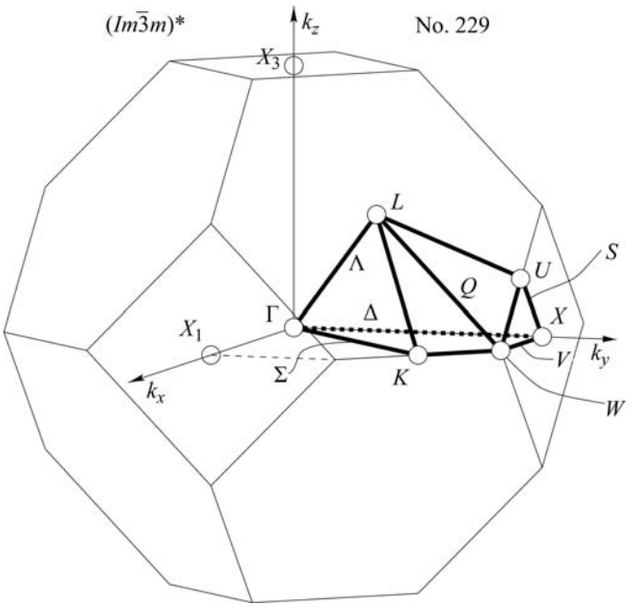

Fig. 2.2.7.1. The Brillouin zone (BZ) and the irreducible wedge of the BZ for the f.c.c. direct lattice. After the corresponding figure from the Bilbao Crystallographic Server (http://www.cryst.ehu.es/cryst/). The IBZ for any space group can be obtained by using the option KVEC and specifying the space group (in this case No. 225).

namely an element (say copper) that crystallizes in the face-centred-cubic (f.c.c.) structure. With (2.2.2.4) we easily find that the reciprocal lattice is body-centred-cubic (bcc) and the corresponding BZ is shown in Fig. 2.2.7.1. In this case, f.c.c. Cu has O_h symmetry with 48 symmetry operations $p \in P$ (point group). The energy eigenvalues within a star of $\mathbf{k}$ (*i.e.* $\mathbf{k} \in S_k$) are the same, and therefore it is sufficient to calculate one member in the star. Consequently, it is enough to consider the irreducible wedge of the BZ (called the IBZ). In the present example, this corresponds to 1/48th of the BZ shown in Fig. 2.2.7.1. To count the number of states in the BZ, one counts each $\mathbf{k}$ point in the IBZ with a proper weight w_k to represent the star of this $\mathbf{k}$ vector.

2.2.7.3. *The symmetry of the Brillouin zone*

The BZ is purely constructed from the reciprocal lattice and thus only follows from the translational symmetry (of the 14 Bravais lattices). However, the energy bands $E^j(\mathbf{k})$, with $\mathbf{k}$ lying within the first BZ, possess a symmetry associated with one of the 230 space groups. Therefore one *can not* simply *use* the *geometrical symmetry* of the BZ to find its irreducible wedge, although this is tempting. Since the effort of computing energy eigenvalues increases with the number of $\mathbf{k}$ points, one wishes to restrict such calculations to the basic domain, but the latter can only be found by considering the space group of the corresponding crystal (including the basis with all atomic positions).

One possible procedure for finding the IBZ is the following. First a uniform grid in reciprocal space is generated by dividing the three unit-cell vectors $\mathbf{b}_i$ by an integer number of times. This is easy to do in the parallelepiped, spanned by the three unit-cell vectors, and yields a (more-or-less) uniform grid of $\mathbf{k}$ points. Now one must go through the complete grid of $\mathbf{k}$ points and extract a list of non-equivalent $\mathbf{k}$ points by applying to each $\mathbf{k}$ point in the grid the point-group operations. If a $\mathbf{k}$ point is found that is already in the list, its weight is increased by 1, otherwise it is added to the list. This procedure can easily be programmed and is often used when $\mathbf{k}$ integrations are needed. The disadvantage of this scheme is that the generated $\mathbf{k}$ points in the IBZ are not necessarily in a connected region of the BZ, since one member of the star of $\mathbf{k}$ is chosen arbitrarily, namely the first that is found by going through the complete list.