10

Space Groups in Reciprocal Space and Representations

When moving from molecules to crystals, the physical properties will be described by dispersion relations in reciprocal space, rather than by energy levels. One of the most important applications of group theory to solid state physics relates to the symmetries and degeneracies of the dispersion relations, especially at high symmetry points in the Brillouin zone. As discussed for the Bravais lattices in Sect. 9.2, the number of possible types of Brillouin zones is limited. The reciprocal space for Bravais lattices is discussed in Sect. 10.1 and this topic is also discussed in solid state physics courses [6, 45].

The classification of the symmetry properties in reciprocal space involves the *group of the wave vector*, which is the subject of this chapter. The group of the wave vector is important because it is the way in which both the *point group symmetry* and the *translational symmetry* of the crystal lattice are incorporated into the formalism that describes the dispersion relations of elementary excitations in a solid. Suppose that we have a symmetry operator $\hat{P}_{\{R_\alpha|\tau\}}$ based on the space group element $\{R_\alpha|\tau\}$ that leaves the periodic potential $V(\boldsymbol{r})$ invariant,

$$\hat{P}_{\{R_\alpha|\tau\}} V(\boldsymbol{r}) = V(\boldsymbol{r})\,. \tag{10.1}$$

The invariance relation of (10.1) has important implications on the form of the wave function $\psi(\boldsymbol{r})$. In particular if we consider only the translation operator $\hat{P}_{\{\varepsilon|\tau\}}$ based on the translation group elements $\{\varepsilon|\tau\}$, we have the result

$$\hat{P}_{\{\varepsilon|\tau\}} \psi(\boldsymbol{r}) = \psi(\boldsymbol{r} + \boldsymbol{\tau})\,. \tag{10.2}$$

Within this framework, we can prove *Bloch's theorem* in Sect. 10.2.2, and then we go on in Sect. 10.3 to determine the symmetry of the wave vector. We then discuss representations for symmorphic and nonsymmorphic space groups and illustrate the group of the wave vector. In Sect. 10.6 we consider the group of the wave vector in some detail for the simple cubic lattice and then we make a few comments to extend these results for the simple cubic lattice to the face centered and body centered cubic structures. The compatibility relations

leading to the formation of branches in the dispersion relations are discussed (Sect. 10.7), illustrated by the same three cubic space groups as in Sect. 10.6. Finally, the group of the wave vector is considered for the nonsymmorphic diamond lattice in Sect. 10.8.

10.1 Reciprocal Space

Definition 23. *The set of all wave vectors* $\boldsymbol{K}_m$ *that yield plane waves with the periodicity of a given Bravais lattice defines its reciprocal lattice, and the* $\boldsymbol{K}_m$ *are called reciprocal lattice vectors.*

The relation

$$\mathrm{e}^{\mathrm{i}\boldsymbol{K}_m\cdot(\boldsymbol{r}+\boldsymbol{R}_n)} = \mathrm{e}^{\mathrm{i}\boldsymbol{K}_m\cdot\boldsymbol{r}} \tag{10.3}$$

holds for any $\boldsymbol{r}$*, and for all* $\boldsymbol{R}_n$ *and* $\boldsymbol{K}_m$ *defining the Bravais lattice in real space and reciprocal space, respectively, where the reciprocal lattice is characterized by the set of wavevectors* $\boldsymbol{K}_m$ *satisfying*

$$\mathrm{e}^{\mathrm{i}\boldsymbol{K}_m\cdot\boldsymbol{R}_n} = 1\,. \tag{10.4}$$

Considering $\boldsymbol{R}_n = \sum n_i\boldsymbol{a}_i$ and $\boldsymbol{K}_m = \sum m_j\boldsymbol{b}_j$ $(i,j = 1,2,3)$, where $\boldsymbol{a}_i$ and $\boldsymbol{b}_j$ are, respectively, the primitive translation vector and the primitive reciprocal lattice vector for the unit cells of a space lattice, then

$$\boldsymbol{b}_j\cdot\boldsymbol{a}_i = 2\pi\delta_{ij} \tag{10.5}$$

defines the orthonormality relation satisfying (10.4).

The more general *ortho*-normality relation for a general lattice vector $\boldsymbol{R}_n$ and a general reciprocal lattice vector $\boldsymbol{K}_m$ will be given by

$$\boldsymbol{R}_n\cdot\boldsymbol{K}_m = 2\pi N_{nm} = 2\pi N_1\,, \tag{10.6}$$

where $N_{nm} = N_1$ is an integer depending on n, m.

Table 10.1. Summary of the real and reciprocal lattice vectors for the five two-dimensional Bravais lattices (see Sect. 9.3)

	translation vectors		reciprocal lattice vectors	
type	$\boldsymbol{a}_1$	$\boldsymbol{a}_2$	$\boldsymbol{b}_1$	$\boldsymbol{b}_2$
oblique, p	$(a_1,\,0)$	$a_2(\cos\theta,\sin\theta)$	$(2\pi/a_1)(1,-\cot\theta)$	$(2\pi/a_2)(0,\csc\theta)$
rectangular, p	$(a_1,\,0)$	$(0,\,a_2)$	$(2\pi/a_1)(1,0)$	$(2\pi/a_2)(0,1)$
rectangular, c	$(a_1/2, a_2/2)$	$(-a_1/2, a_2/2)$	$2\pi(1/a_1, 1/a_2)$	$2\pi(-1/a_1, 1/a_2)$
square, p	$(a,0)$	$(0,a)$	$(2\pi/a)(1,0)$	$(2\pi/a)(0,1)$
hexagonal, p	$(0,-a)$	$a(\sqrt{3}/2, 1/2)$	$(2\pi/a)(1/\sqrt{3},-1)$	$(2\pi/a)(2/\sqrt{3},0)$

To illustrate the primitive translation vectors of the unit cells in real and reciprocal space for the Bravais lattices, we list in Table 10.1 the primitive translation vectors and the corresponding reciprocal lattice vectors for the five two-dimensional Bravais lattices based on (10.5). The vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ for these 2D lattices are expressed in terms of unit vectors along appropriate directions of the five Bravais lattices, and a and b are lattice constants. For three-dimensional space groups, there are three unit vectors $\boldsymbol{a}_i$, and three unit vectors $\boldsymbol{b}_j$ in k-space, using the space group notation. The Brillouin zones for several three-dimensional space groups can be found in Appendix C and in the literature [50].

10.2 Translation Subgroup

For the translation subgroup T which is a subgroup of the space group G, consider the translation operator $\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}$ based on the translation group elements $\{\varepsilon|\boldsymbol{\tau}\}$, yielding the result

$$\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}+\boldsymbol{\tau})\,, \tag{10.7}$$

but since the translation operations all commute with one another, the translations form an Abelian group.

Definition 24. *Since the translation operation $\boldsymbol{\tau}$ can be written in terms of translations over the unit vectors $\boldsymbol{a}_i$*

$$\boldsymbol{\tau} = \sum_{i=1}^{3} n_i \boldsymbol{a}_i\,,$$

we can think of the translation operators in each of the $\boldsymbol{a}_i$ directions as commuting operators:

$$\{\varepsilon|\boldsymbol{\tau}\} = \{\varepsilon|\boldsymbol{\tau}_1\}\{\varepsilon|\boldsymbol{\tau}_2\}\{\varepsilon|\boldsymbol{\tau}_3\}\,, \tag{10.8}$$

where $\boldsymbol{\tau}_i = n_i\boldsymbol{a}_i$. The real space lattice vectors produced by the translation operator are denoted in Sect. 10.1 by $\boldsymbol{R}_n$.

10.2.1 Representations for the Translation Group

The commutativity of the $\{\varepsilon|\boldsymbol{\tau}_i\}$ operations in (10.8) gives three commuting subgroups. It is convenient to use periodic boundary conditions and to relate the periodic boundary conditions to cyclic subgroups (see Sect. 1.3), so that $\{\varepsilon|\boldsymbol{\tau}_1\}^{\mathcal{N}_1} = \{\varepsilon|\boldsymbol{\tau}_2\}^{\mathcal{N}_2} = \{\varepsilon|\boldsymbol{\tau}_3\}^{\mathcal{N}_3} = \{\varepsilon|0\}$, and $\mathcal{N}_i$ is the number of unit cells along $\boldsymbol{\tau}_i$. In a cyclic subgroup, all symmetry elements commute with one another, and therefore the subgroup is Abelian and has only one-dimensional irreducible matrix representations. Furthermore, the number of irreducible representations of the cyclic subgroup is equal to the number of elements h

in the group, and each element is in a class by itself. Since $\{\varepsilon|\boldsymbol{\tau}_i\}^{\mathcal{N}_i} = \{\varepsilon|0\}$, the irreducible representation for the cyclic group can be written as a set of matrices which are phase factors or characters of the form $\exp(\mathrm{i}k_i n_i a_i)$, and are the $\mathcal{N}_i$ roots of unity. Here $k_i = 2\pi m_i/L_i$ (where m_i is an integer and L_i is the length of the crystal in direction $\boldsymbol{a}_i$) defines the irreducible representation, and there are $\mathcal{N}_1\mathcal{N}_2\mathcal{N}_3 \sim 10^{23}$ of such irreducible representations. In this context, the wave vector k serves as a quantum number for the translation operator.

10.2.2 Bloch's Theorem and the Basis Functions of the Translational Group

Theorem. *If an eigenfunction ψ_k transforms under the translation group according to the irreducible representation labeled by k, then $\psi_k(\boldsymbol{r})$ obeys the relation*

$$\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\psi_k(\boldsymbol{r}) = \psi_k(\boldsymbol{r}+\boldsymbol{\tau}) = \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{\tau}}\psi_k(\boldsymbol{r}) \tag{10.9}$$

and $\psi_k(\boldsymbol{r})$ can be written in the form

$$\psi_k(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}u_k(\boldsymbol{r})\,, \tag{10.10}$$

where $u_k(\boldsymbol{r}+\boldsymbol{\tau}) = u_k(\boldsymbol{r})$ has the full translational symmetry of the crystal.

Proof. Since the translation group is Abelian, all the elements of the group commute and all the irreducible representations are one-dimensional. The requirement of the *periodic boundary condition* can be written as

$$\{\varepsilon|\boldsymbol{\tau}_1 + NL_1\} = \{\varepsilon|\boldsymbol{\tau}_1\}\,, \tag{10.11}$$

where N is an integer and L_1 is the length of the crystal along basis vector $\boldsymbol{a}_1$. This results in the one-dimensional matrix representation for the translation operator $\boldsymbol{\tau}_i = n_i\boldsymbol{a}_i$

$$D^{k_1}(n_1a_1) = \mathrm{e}^{ik_1n_1a_1} = \mathrm{e}^{ik_1\boldsymbol{\tau}_1} \tag{10.12}$$

since

$$\hat{P}_R\psi_k(\boldsymbol{r}) = D^k(R)\psi_k(\boldsymbol{r})\,, \tag{10.13}$$

where R denotes a symmetry element $k_1 = 2\pi m_1/L_1$ corresponds to the m_1th irreducible representation and $m_1 = 1, 2, \ldots, (L_1/a_1)$. For each m_1, there is a unique k_1, so that each irreducible representation is labeled by either m_1 or k_1, as indicated above.

We now extend these arguments to three dimensions. For a general translation

$$\boldsymbol{\tau} = \sum_{i=1}^{3} n_i\boldsymbol{a}_i\,, \tag{10.14}$$

the matrix representation or character for the $(m_1m_2m_3)$th irreducible representation is

$$D^{k_1}(n_1a_1)D^{k_2}(n_2a_2)D^{k_3}(n_3a_3) = \mathrm{e}^{\mathrm{i}k_1n_1a_1}\mathrm{e}^{\mathrm{i}k_2n_2a_2}\mathrm{e}^{\mathrm{i}k_3n_3a_3} = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}}\,, \quad (10.15)$$

since

$$\{\varepsilon|\boldsymbol{\tau}\} = \{\varepsilon|\boldsymbol{\tau}_1\}\{\varepsilon|\boldsymbol{\tau}_2\}\{\varepsilon|\boldsymbol{\tau}_3\}\,. \quad (10.16)$$

Thus our basic formula $\hat{P}_R\psi_j = \sum_\alpha \psi_\alpha D(R)_{\alpha j}$ yields

$$\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\psi(\boldsymbol{r}) = \psi(\boldsymbol{r})\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}} = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}}\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}+\boldsymbol{\tau})\,, \quad (10.17)$$

since the representations are all one-dimensional. This result is Bloch's theorem where we often write $\boldsymbol{\tau} = \boldsymbol{R}_n$ in terms of the lattice vector $\boldsymbol{R}_n$. This derivation shows that the phase factor $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}}$ is the eigenvalue of the translation operator $\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}$. □

Because of Bloch's theorem, the wave function $\psi(\boldsymbol{r})$ can be written in the form

$$\psi_k(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}u_k(\boldsymbol{r})\,, \quad (10.18)$$

where $u_k(\boldsymbol{r})$ exhibits the full translational symmetry of the crystal. This result follows from:

$$\psi_k(\boldsymbol{r}+\boldsymbol{R}_n) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}+\boldsymbol{R}_n)}u_k(\boldsymbol{r}+\boldsymbol{R}_n) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n}\left[\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}u_k(\boldsymbol{r})\right]\,, \quad (10.19)$$

where the first equality in (10.19) is obtained simply by substitution in (10.18) and the second equality follows from Bloch's theorem. In these terms, Bloch's theorem is simply a statement of the translational symmetry of a crystal.

The Bloch functions are the basis functions for the translation group T. The wave vector $\boldsymbol{k}$ has a special significance as the *quantum number of translation* and provides a label for the irreducible representations of the translation group. If the crystal has a length L_i on a side so that n_0 different lattice translations can be made for each direction $\boldsymbol{a}_i$, then the number of $\boldsymbol{k}$ vectors must be limited to

$$k_x, k_y, k_z = 0, \pm\frac{2\pi}{n_0a}, \pm\frac{4\pi}{n_0a}, \ldots, \pm\frac{\pi}{a} \quad (10.20)$$

in order to insure that the number of irreducible representations is equal to the number of classes. Since the translation group is Abelian, every group element is in a class by itself, so that the *number of irreducible representations must equal the number of possible translations*. Since the number of translation operators for bulk crystals is very large ($\sim 10^{23}$), the quantum numbers for translations are discrete, but very closely spaced, and form a quasi-continuum of points in reciprocal space. For nanostructures, the number of translation operations can be quite small (less than 100) and some unusual quantum size effects can then be observed.

We note that all of these $\boldsymbol{k}$-vectors are contained within the first Brillouin zone. Thus, if we consider a vector in the extended Brillouin zone $\boldsymbol{k}+\boldsymbol{K}_{\boldsymbol{m}}$, where $\boldsymbol{K}_{\boldsymbol{m}}$ is a reciprocal lattice vector, the appropriate phase factor in Bloch's theorem is

$$\mathrm{e}^{\mathrm{i}(\boldsymbol{k}+\boldsymbol{K}_{\boldsymbol{m}})\cdot\boldsymbol{R}_n} = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n}\,, \quad (10.21)$$

since $\boldsymbol{K}_{\boldsymbol{m}}\cdot\boldsymbol{R}_n = 2\pi N$ where N is an integer.

10.3 Symmetry of k Vectors and the Group of the Wave Vector

When we choose a given eigenstate $\psi_k(\boldsymbol{r})$ of the crystal potential, except for eigenstates at the Γ point ($k = 0$), the basis function will exhibit a modulation described by the wavevector k, and this modulation will decrease the crystal symmetry. In this case, we work with the *group of the wave vector*, that is a subgroup of the space group G. To introduce this concept, we consider in Sect. 10.3.1 the action of a point group symmetry operator on a lattice vector and on a reciprocal lattice vector. Next we discuss the group of the wave vector and the *star of a wave vector*, including an example of these concepts in terms of the two-dimensional square lattice (Sect. 10.3.2). Finally in Sect. 10.3.3 we consider the effect of translations and point group operations on Bloch functions, thereby clarifying the degeneracies introduced by the point group symmetries of crystal lattices.

10.3.1 Point Group Operation in r-space and k-space

The effect of a symmetry operator $\hat{P}_\alpha$ on a lattice vector $\boldsymbol{R}_n$ and on a reciprocal lattice vector $\boldsymbol{K}_m$ subject to the orthogonality relation (10.6) is considered in this section.

Let $\hat{P}_\alpha$ denote a symmetry operator of the point group of the crystal, then $\hat{P}_\alpha \boldsymbol{R}_n$ leaves the crystal invariant. If $\boldsymbol{R}_n$ is a translation operator, then $\hat{P}_\alpha \boldsymbol{R}_n$ is also a translation operator (lattice vector), since the full symmetry of the lattice is preserved. Likewise $\hat{P}_\alpha \boldsymbol{K}_m$ is a translation operator in reciprocal space. Since $\hat{P}_\alpha \boldsymbol{R}_n$ is a lattice vector, we can write

$$(\hat{P}_\alpha \boldsymbol{R}_n) \cdot \boldsymbol{K}_m = 2\pi N_2 \,, \tag{10.22}$$

where N_2 is an integer, not necessarily the same integer as N_1 in (10.6). Since α^{-1} is also a symmetry operator of the group, we have

$$(\hat{P}_\alpha^{-1} \boldsymbol{R}_n) \cdot \boldsymbol{K}_m = 2\pi N_3 \,, \tag{10.23}$$

and again N_3 is not necessarily the same integer as N_1 or N_2. Furthermore, any scalar product (being a constant) must be invariant under any point symmetry operator. Thus if we perform the same symmetry operation on each member of the scalar product in (10.23), then the scalar product remains invariant

$$\hat{P}_\alpha(\hat{P}_\alpha^{-1} \boldsymbol{R}_n) \cdot (\hat{P}_\alpha \boldsymbol{K}_m) = 2\pi N_3 = \boldsymbol{R}_n \cdot (\hat{P}_\alpha \boldsymbol{K}_m) \,. \tag{10.24}$$

Equations (10.22)–(10.24) lead to several results: If $\hat{P}_\alpha$ is a symmetry operator of a point group of a crystal, and $\boldsymbol{R}_n$ and $\boldsymbol{K}_m$ are, respectively, lattice and reciprocal lattice vectors, then $\hat{P}_\alpha^{-1} \boldsymbol{R}_n$ and $\hat{P}_\alpha \boldsymbol{K}_m$ also are, respectively, a lattice vector and a reciprocal lattice vector. Thus the *effect of an operator $\hat{P}_\alpha$ on a direct lattice vector $\boldsymbol{R}_n$ is equivalent to the effect of operator $\hat{P}_\alpha^{-1}$ on the corresponding reciprocal lattice vector $\boldsymbol{K}_m$*.

10.3.2 The Group of the Wave Vector $G_{\boldsymbol{k}}$ and the Star of $\boldsymbol{k}$

Definition 25. *The group of the wave vector is formed by the set of space group operations which transform* $\boldsymbol{k}$ *into itself, or into an equivalent* $\boldsymbol{k} = \boldsymbol{k} + \boldsymbol{K}_m$ *vector, where* $\boldsymbol{K}_m$ *is a vector of the reciprocal lattice.*

The addition of $\boldsymbol{K}_m$ does not change the energy of the system since $e^{i\boldsymbol{k}\cdot\boldsymbol{R}_n} = e^{i(\boldsymbol{k}+\boldsymbol{K}_m)\cdot\boldsymbol{R}_n}$, i.e., both k and $(k + K_m)$ belong to the same translational irreducible representation (see Sect. 10.2.2). Clearly, all the symmetry operations of the space group take the point $\boldsymbol{k} = 0$ into itself so that the space group itself forms the group of the wave vector at $\boldsymbol{k} = 0$. Furthermore, the group of the wave vector for nonzone center $\boldsymbol{k}$-vectors ($\boldsymbol{k} \neq 0$) remains a subgroup of the space group for $\boldsymbol{k} = 0$.

Let us now consider the action of the point group operations on a general vector $\boldsymbol{k}$ in reciprocal space, not necessarily a reciprocal lattice vector. The set of wave vectors $\boldsymbol{k}'$ which are obtained by carrying out all the point group operations on $\boldsymbol{k}$ is called the *star of* $\boldsymbol{k}$. If $\boldsymbol{k}$ *is a general point in the Brillouin zone*, there will be only one symmetry element, namely the identity, which takes $\boldsymbol{k}$ into itself and in this case the wave functions describing electron states only see the translational symmetry $\{\varepsilon|\boldsymbol{\tau}\}$ of the space group. On the other hand, if the $\boldsymbol{k}$-vector under consideration lies on a symmetry axis or is at a high symmetry point in the Brillouin zone, then perhaps several of the point group operations will transform $\boldsymbol{k}$ into itself or into an equivalent $\boldsymbol{k}$-vector $\boldsymbol{k} + \boldsymbol{K}_m$.

An informative example for the formation of the group of the wave vector for various $\boldsymbol{k}$-vectors is provided by the two-dimensional square lattice. Here the point group is D_4 and the symmetry operations are E, $C_2 = 2C_4^2$, $2C_4$, $2C_2'$, $2C_2''$ (diagonals). The various $\boldsymbol{k}$-vectors in the star of $\boldsymbol{k}$ are indicated in the diagrams in Fig. 10.1 for the two-dimensional square lattice. The group elements for the group of the wave vector in each case are indicated within the parenthesis. The top three diagrams are for $\boldsymbol{k}$-vectors to interior points within the first Brillouin zone and the lower set of three diagrams are for $\boldsymbol{k}$-vectors to the Brillouin zone boundary. Thus the star of $\boldsymbol{k}$ shown in Fig. 10.1 is formed by consideration of $\hat{P}_\alpha\boldsymbol{k}$ for all operators $\hat{P}_\alpha$ for the point group. The group of the wave vector is formed by those $\hat{P}_\alpha$ for which $\hat{P}_\alpha\boldsymbol{k} = \boldsymbol{k} + \boldsymbol{K}_m$, where $\boldsymbol{K}_m$ is a reciprocal lattice vector (including $\boldsymbol{K}_m = 0$). The concepts presented in Fig. 10.1, are reinforced in Problem 10.2 for the hexagonal lattice with point group D_6.

10.3.3 Effect of Translations and Point Group Operations on Bloch Functions

We will now consider the effect of the symmetry operations on $\boldsymbol{k}$ with regard to the eigenfunctions of Schrödinger's equation. We already know from

Bloch's theorem that the action of any pure translation operator $\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}$ on wave function $\psi_k(r)$ (where $\boldsymbol{\tau} = \boldsymbol{R}_n$) yields a wave function $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n}\psi_k(\boldsymbol{r})$

$$\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\psi_k(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}}\psi_k(\boldsymbol{r})\,. \tag{10.25}$$

There will be as many wave functions of this functional form as there are translation vectors, each corresponding to the energy $E(\boldsymbol{k})$. These Bloch functions provide basis functions for irreducible representations for the group of the wave vector. If $\boldsymbol{k}$ is a general point in the Brillouin zone, then the star of $\boldsymbol{k}$ contains wave vectors which are all equivalent to $\boldsymbol{k}$ from a physical standpoint. The space group for a general wave vector $\boldsymbol{k}$ will however contain only the symmetry elements $\{\varepsilon|\boldsymbol{R}_n\}$, since in this case all the $\boldsymbol{k}$-vectors are distinct. For a wave vector with higher symmetry, where the operations $\hat{P}_\beta\boldsymbol{k} = \boldsymbol{k}+\boldsymbol{K}_m$ transform $\boldsymbol{k}$ into an equivalent wave vector, the space group of the wave vector contains the symmetry element $\{\beta|\boldsymbol{R}_n\}$ and the energy at equivalent $\boldsymbol{k}$ points must be equal. If the point group of the wave vector contains irreducible representations that have more than one dimension, then a degeneracy in the energy bands will occur. Thus bands tend to "stick together" along high symmetry axes and at high symmetry points.

The effect of a point group operation on this eigenfunction is

$$\hat{P}_{\{R_\alpha|0\}}\psi_k(\boldsymbol{r}) = \hat{P}_{\{R_\alpha|0\}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}u_k(\boldsymbol{r})\,, \tag{10.26}$$

in which we have written the eigenfunction in the Bloch form. Since the effect of a point group operation on a function is equivalent to preserving the form of the function and rotating the coordinate system in the opposite sense, to maintain invariance of scalar products we require

$$\boldsymbol{k}\cdot R_\alpha^{-1}\boldsymbol{r} = R_\alpha\boldsymbol{k}\cdot\boldsymbol{r}\,. \tag{10.27}$$

If we now define $u_{R_\alpha k}(\boldsymbol{r}) \equiv u_k(R_\alpha^{-1}\boldsymbol{r})$ for the periodic part of the Bloch function and denote the transformed wave vector by $\boldsymbol{k}' \equiv R_\alpha\boldsymbol{k}$, then we have

$$\hat{P}_{\{R_\alpha|0\}}\psi_k(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}R_\alpha\boldsymbol{k}\cdot\boldsymbol{r}}u_{R_\alpha k}(\boldsymbol{r}) \equiv \psi_{R_\alpha k}(\boldsymbol{r})\,, \tag{10.28}$$

which we will now show to be of the Bloch form by operating with the translation operator on $\psi_{R_\alpha k}(\boldsymbol{r})$

$$\begin{aligned}\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\psi_{R_\alpha k}(\boldsymbol{r}) &= \hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}[\mathrm{e}^{\mathrm{i}R_\alpha\boldsymbol{k}\cdot\boldsymbol{r}}u_k(R_\alpha^{-1}\boldsymbol{r})] \\ &= \mathrm{e}^{\mathrm{i}R_\alpha\boldsymbol{k}\cdot(\boldsymbol{r}+\boldsymbol{\tau})}u_k(R_\alpha^{-1}\boldsymbol{r}+R_\alpha^{-1}\boldsymbol{\tau})\,.\end{aligned} \tag{10.29}$$

Because of the periodicity of $u_k(\boldsymbol{r})$ we have

$$u_{R_\alpha k}(\boldsymbol{r}+\boldsymbol{\tau}) = u_k(R_\alpha^{-1}\boldsymbol{r}+R_\alpha^{-1}\boldsymbol{\tau}) = u_k(R_\alpha^{-1}\boldsymbol{r}) \equiv u_{R_\alpha k}(\boldsymbol{r})\,, \tag{10.30}$$

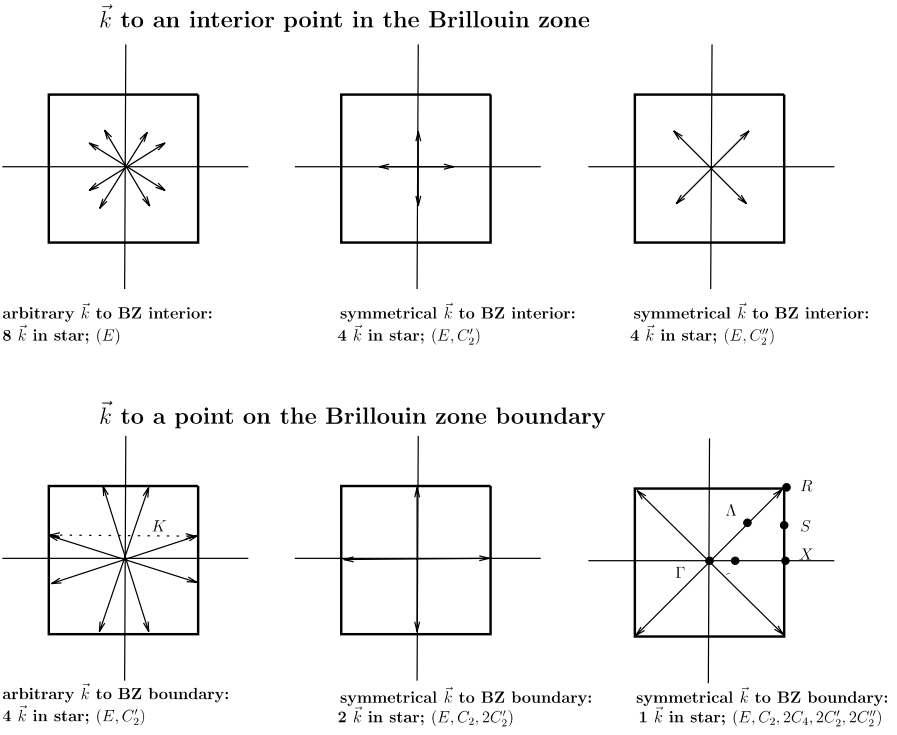

Fig. 10.1. Illustration of the star of $\boldsymbol{k}$ for various wave vectors in the Brillouin zone of a simple 2D square lattice. The *top three diagrams* are for $\boldsymbol{k}$-vectors to an interior point in the Brillouin zone, while the *bottom three diagrams* are for wave vectors extending to the Brillouin zone boundary. In each case the point group elements for the group of the wave vector are given in parentheses

and noting the orthonormality relation (10.6) for the plane wave factor, we get

$$\hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\psi_{R_\alpha k}(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}R_\alpha \boldsymbol{k}\cdot\boldsymbol{\tau}}\psi_{R_\alpha k}(\boldsymbol{r})\,, \tag{10.31}$$

where $u_{R_\alpha k}(\boldsymbol{r})$ is periodic in the direct lattice. The *eigenfunctions* $\psi_{R_\alpha k}(\boldsymbol{r})$ thus forms *basis functions* for the $R_\alpha k$th *irreducible representation* of the translation group T. As we saw in Sect. 10.3.2, the set of distinct wave vectors in $\boldsymbol{k}$-space which can be generated by operating on one $\boldsymbol{k}$ vector by all the symmetry elements of the point group g is called the "star of $\boldsymbol{k}$" (see Fig. 10.1).

Considering the above arguments on symmorphic groups for simplicity, where the point group g is isomorphic to G/T and $\{R_\alpha|\boldsymbol{\tau}\} = \{\varepsilon|\boldsymbol{\tau}\}\hat{P}_{\{R_\alpha|0\}}$, we have

$$\begin{aligned}\hat{P}_{\{R_\alpha|\boldsymbol{\tau}\}}\psi_k(\boldsymbol{r}) &= \hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\hat{P}_{\{R_\alpha|0\}}\psi_k(\boldsymbol{r}) \\ &= \hat{P}_{\{\varepsilon|\boldsymbol{\tau}\}}\psi_{R_\alpha k}(\boldsymbol{r}) \\ &= \mathrm{e}^{\mathrm{i}R_\alpha \boldsymbol{k}\cdot\boldsymbol{\tau}}\psi_{R_\alpha k}(\boldsymbol{r})\,. \end{aligned} \tag{10.32}$$

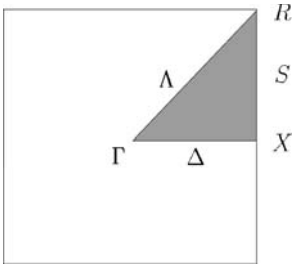

Fig. 10.2. The shaded triangle $\Gamma\Lambda RSX\Delta\Gamma$ which constitutes 1/8 of the Brillouin zone for the 2D square lattice and contains the basic wave vectors and high symmetry points

Similarly we obtain

$$\hat{P}_{\{R_\beta|\tau'\}}\psi_{R_\alpha k}(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}R_\beta R_\alpha \boldsymbol{k}\cdot\boldsymbol{\tau}'}\psi_{R_\beta R_\alpha k}(\boldsymbol{r})\,. \tag{10.33}$$

Thus the set of eigenfunctions $\{\psi_{R_\alpha k}(\boldsymbol{r})\}$ obtained by taking the star of $\boldsymbol{k}$ spans the invariant subspace of the point group g since the product operation $R_\beta R_\alpha$ is contained in g. If h is the order of the group g, there are h functions in the set $\{\psi_{R_\alpha k}(\boldsymbol{r})\}$. All of these representations are completely specified by $\boldsymbol{k}$, but they are equally well specified by any of the $\boldsymbol{k}$ vectors in the star of $\boldsymbol{k}$. Although all the functions in the set $\{\psi_{R_\alpha k}(\boldsymbol{r})\}$ correspond to the same energy, we do *not* say that the functions $\psi_k(\boldsymbol{r})$ and $\psi_{R_\alpha k}(\boldsymbol{r})$ are degenerate. Instead we write $\{\psi_k(\boldsymbol{r})\}$ for all the functions in the set $\{\psi_{R_\alpha k}(\boldsymbol{r})\}$ and consider the extra point group symmetry to yield the relation $E(\boldsymbol{k}) = E(R_\alpha \boldsymbol{k})$ for all R_α. In this way, we guarantee that the energy $E(\boldsymbol{k})$ will show the full point group symmetry of the reciprocal lattice. Thus for the two-dimensional square lattice, it is only necessary to calculate $E(\boldsymbol{k})$ explicitly for k points in 1/8 of the Brillouin zone contained within the sector $\Gamma\Lambda RSX\Delta\Gamma$ (see Fig. 10.2). These statements are generally valid for nonsymmorphic groups as well.

We use the term "degeneracy" to describe states with exactly the same energy *and* the same wave vector. Such degeneracies do in fact occur because of symmetry restrictions at special high symmetry points in the Brillouin zone and such degeneracies are called *"essential" degeneracies*. "Essential" degeneracies occur only at high symmetry or special $\boldsymbol{k}$ points, while accidental ("nonessential") degeneracies occur at arbitrary $\boldsymbol{k}$ points. "Special" high symmetry points in the Brillouin zone are those for which

$$R_\alpha \boldsymbol{k} = \boldsymbol{k} + \boldsymbol{K}_m\,, \tag{10.34}$$

where $\boldsymbol{K}_m$ is the reciprocal lattice vector including $\boldsymbol{K}_m = 0$. In the cases where the symmetry operation yields $R_\alpha \boldsymbol{k} = \boldsymbol{k} + \boldsymbol{K}_m$, then the eigenfunctions have essential degeneracies because we now can have degenerate eigenfunctions with the same energy eigenvalue at the same $\boldsymbol{k}$ vector. These essential band degeneracies are lifted as we move away from the high symmetry points

to a general point in the Brillouin zone. The rules governing the lifting of these degeneracies are called *compatibility relations*, discussed in Sect. 10.7.

10.4 Space Group Representations

We start by saying that tables for the group of the wave vector for each unique $\boldsymbol{k}$ vector for each of the 230 space groups have been established and are available in different references, as reviewed in Sect. 10.9. For each wavevector $\boldsymbol{k}$, the spacial group representations are constructed from the analysis of the group of wavevector and of the star of $\boldsymbol{k}$, and the use of the *multiplier algebra*, that we briefly discuss below. The representations will be square matrices with dimension $(\ell q) \times (\ell q)$, i.e., $\ell \times \ell$ blocks of $q \times q$ matrices, where ℓ is the number of $\boldsymbol{k}$ vectors in the star, and q is defined by the representations in the group of the wavevector. Each line (or column) in the matrix will have only one $q \times q$ nonzero entry and the remaining entries are filled with null $q \times q$ matrices. The $\ell \times \ell$ block arrangement describes the symmetries relating the different vectors in the star of $\boldsymbol{k}$, and the nonzero $q \times q$ matrix describes the symmetry with respect to the specific $\boldsymbol{k}$ and its group of the wavevector.

The rotational aspects of the group of the wave vector are described by the $q \times q$ matrices related to the factor group G_k/T_k. The T_k group can be represented by a linear combination of the three lattice vectors, and the symmetry elements usually shown in the character tables are related to a $\{R_\alpha|\boldsymbol{\tau}_\alpha\}/T_k$ coset. The subgroups of the group of the wave vector $\boldsymbol{k}$ occurring at points in the Brillouin zone with fewer symmetry operations are called the *small representations*, in contrast to the full point group symmetry for $k = 0$ which is called the *large representation*. The Bloch functions with wavevectors $\boldsymbol{k}$ form the basis, and each symmetry element is a coset formed by several elements, but is represented by a typical element, a "representative coset."

10.4.1 Symmorphic Group Representations

The representation theory for symmorphic groups is relatively simple. Since there are no compound operations, the factor group G_k/T_k is symmorphic to the point group g_k.

Small Representation. The small representations for the group of the wave vector of $\boldsymbol{k}$ are given by

$$D_k^{\Gamma_i}(\{R_\alpha|\boldsymbol{R}_n\}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n} D^{\Gamma_i}(R_\alpha)\,, \tag{10.35}$$

where $\{R_\alpha|\boldsymbol{R}_n\}$ belongs to G_k, and $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n}$ comes from T, with $\boldsymbol{R}_n$ being a lattice vector or a primitive translation, and Γ_i is an irreducible representation coming from one of the 32 crystallographic point groups (see Chap. 3), whose character tables are given in Appendix A. Here $D^{\Gamma_i}(R_\alpha)$ refers only to the point group.

Characters for Small Representation. The characters for the irreducible representations are given by

$$\chi_k^{\Gamma_i}(\{R_\alpha|\boldsymbol{R}_n\}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n}\chi^{\Gamma_i}(R_\alpha)\,. \tag{10.36}$$

where $\chi^{\Gamma i}(R_\alpha)$ only refers to the point group.

Large Representation. For the Γ point we have $k = 0$ and $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n} = 1$. Also, if we consider the factor group of G_k with respect to the translations, then also $\boldsymbol{R}_n = 0$ and again $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n} = 1$. In both cases, both representations and characters are identical to those from the point groups.

10.4.2 Nonsymmorphic Group Representations and the Multiplier Algebra

As for the symmorphic groups, we denote the group of the wave vector $\boldsymbol{k}$ by G_k. For symmetry operations $\{R|\boldsymbol{\tau}\}$ that involve translations $\boldsymbol{\tau}$ smaller than the smallest Bravais lattice vector, the translations introduce a phase factor $\exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}]$. However, as discussed in Sect. 9.1.4, the entire set of space group elements $\{R_\alpha|\boldsymbol{\tau}_\alpha\}$ may fail to form a group, and the point group g of the crystal is not a subgroup of G. In this case, to work with the rotational aspects of the nonsymmorphic space group, procedures to remove the translational effect are needed. Furthermore, the factor group G_k/T_k contain cosets formed only by pure translations, giving rise to *irrelevant representations*. The *relevant representations*, describing the rotational aspects of the group of the wavevector, can be directly obtained by using the *multiplier algebra*.

Multiplier Groups. If the representations are written in terms of a Bloch wave basis, the translational group is diagonalized and the multiplier groups are defined by

$$\{R_\alpha|\boldsymbol{\tau}_\alpha\}\{R_\beta|\boldsymbol{\tau}_\beta\} = \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{\tau}_\alpha + R_\alpha\boldsymbol{\tau}_\beta - \boldsymbol{\tau}_{\alpha\beta}]}\{R_\alpha R_\beta|\boldsymbol{\tau}_{\alpha\beta}\}\,, \tag{10.37}$$

where the $[\boldsymbol{\tau}_\alpha + R_\alpha\boldsymbol{\tau}_\beta - \boldsymbol{\tau}_{\alpha\beta}]$ represents a lattice vector translation resulting from the product of the elements in the group of the wave vector. Any element $\{R_\gamma|\boldsymbol{\tau}_\gamma + R_n\}$ thus generated can be represented by a single element

$$M(\gamma) = \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{\tau}_\gamma + R_n]}\{R_\gamma|\boldsymbol{\tau}_\gamma + R_n\} \tag{10.38}$$

in the multiplier group, obeying the algebra

$$M(\alpha)M(\alpha') = \mathrm{e}^{\mathrm{i}\boldsymbol{K}_\alpha\cdot\boldsymbol{\tau}_{\alpha'}}M(\alpha\alpha')\,, \tag{10.39}$$

the exponential factor being 1 except for points at the Brillouin zone boundary, where $R_\alpha\boldsymbol{k} = \boldsymbol{k} + \boldsymbol{K}_\alpha$, and $\boldsymbol{K}_\alpha$ is a reciprocal lattice translation. The factor group G_k/T_k will, therefore, be isomorphic to a point group from which the rotational aspects of the group of the wave vector can be treated.

Small and Large Representations. In general the representations are obtained from the irreducible representations of the multiplier group. From (10.38) and (10.39) it can be shown that the small representations are obtained from ordinary point group representations when the point group operation leaves $\boldsymbol{k}$ invariant, since in that case $\boldsymbol{K}_\alpha = 0$ in (10.39). The same applies to the large representation, where $\boldsymbol{K}_\alpha = 0$ always. Note that the multiplier algebra also applies to symmorphic groups. In this case $\boldsymbol{\tau}_\alpha = \boldsymbol{\tau}_{\alpha'} = \boldsymbol{\tau}_\beta = 0$ in (10.38) and (10.39), and the representations are also obtained from ordinary point group representations, as discussed above.

Characters for Small and Large Representations. At the zone center, the characters for the group of the wave vector are the same as the isomorphic point group, because the phase factor $\exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}]$ reduces to unity when $k = 0$. For each symmetry axis leading away from $\boldsymbol{k} = 0$, the character tables for those $\boldsymbol{k}$ points can be obtained by selecting the

appropriate point group character table and by multiplying the character for the symmetry operations that contain a translation $\boldsymbol{\tau}$ by a phase factor $\exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}]$.

More detailed discussions of the space group representations and *multiplier groups* are available elsewhere [50, 53].

10.5 Characters for the Equivalence Representation

We now discuss the computation of the characters $\chi^{\text{equiv.}}$ for the equivalence representation in space groups, and its decomposition into the irreducible representations of the group. For a specific wavevector $\boldsymbol{k}$, the general formulation for $\chi_k^{\text{equiv.}}$ related to a specific class of symmetry space group operators $\{R_\alpha|\boldsymbol{R}_n + \boldsymbol{\tau}_\alpha\}$ is given by

$$\chi^{\text{equiv.}}(\{R_\alpha|\boldsymbol{R}_n + \boldsymbol{\tau}_\alpha\}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_n+\boldsymbol{\tau}_\alpha)} \sum_j \delta_{\{R_\alpha|\boldsymbol{R}_n+\boldsymbol{\tau}_\alpha\}\boldsymbol{r}_j,\boldsymbol{r}_j} \mathrm{e}^{\mathrm{i}\boldsymbol{K}_m\cdot\boldsymbol{r}_j}\,, \quad (10.40)$$

where the first exponential factor is related to the phase factor for translation $\boldsymbol{R}_n + \boldsymbol{\tau}_\alpha$. The delta function basically gives 1 for atoms remaining in their position under the space group symmetry operation $\{R_\alpha|R_n + \boldsymbol{\tau}_\alpha\}$ or is 0 otherwise. For space groups, however, equivalent atoms on different unit cells must be considered as equivalent. Here $\boldsymbol{r}_j$ is the position in the jth atom with respect to the origin of the point group, and $\delta_{\{R_\alpha|\boldsymbol{R}_n+\boldsymbol{\tau}_\alpha\}\boldsymbol{r}_j,\boldsymbol{r}_j} = 1$ if $\{R_\alpha|\boldsymbol{R}_n + \boldsymbol{\tau}_\alpha\}\boldsymbol{r}_j$ and $\boldsymbol{r}_j$ refer to equivalent atomic positions, occurring when $(R_\alpha\boldsymbol{r}_j = \boldsymbol{r}_j + R_n)$. It is clear that the delta function is always zero when $\boldsymbol{\tau}_\alpha \neq 0$.

The decomposition of the equivalence transformation into the irreducible representations of the space group is made by using the procedure discussed in Sect. 3.4. The first exponential factor in (10.40) turns out not to be important

for this decomposition process, since $\chi^{\text{equiv.}}$ will then be multiplied by $[\chi^{(\Gamma_i)}]^*$ (see (3.20)), which carries the complex conjugate of the exponential factor.

Equation (10.40) gives the general rule for the equivalence transformation in crystalline structures. The last exponential term in (10.40) appears for specific $\boldsymbol{k}$ points at the zone boundary, for which $R_\alpha^{-1}\boldsymbol{k} = \boldsymbol{k} + \boldsymbol{K}_m$ where $\boldsymbol{K}_m$ is a reciprocal lattice vector. At most of the k points, including the Γ point, $R_\alpha^{-1}\boldsymbol{k} = \boldsymbol{k}$ and $\boldsymbol{K}_m = 0$ so that $\mathrm{e}^{\mathrm{i}\boldsymbol{K}_m \cdot \boldsymbol{r}_j} = 1$, and we just work with the general concept of $\chi^{\text{a.s.}} = 0$ or 1.

10.6 Common Cubic Lattices: Symmorphic Space Groups

In this section we limit our discussion to symmorphic space groups, where the group of the wave vector for arbitrary $\boldsymbol{k}$ is a subgroup of the group of the wave vector $\boldsymbol{k} = 0$, which displays the full point group symmetry of the crystal (see Sect. 10.4.1). This situation applies to all crystal lattices, whether they are cubic, hexagonal, etc. We discuss here the group of the wave vector for the three-dimensional simple cubic lattice $Pm3m$ (O_h^1) #221 (see Fig. 10.3) in

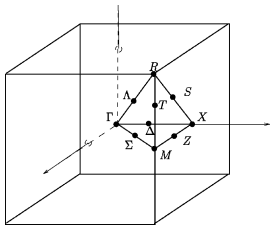

Fig. 10.3. The Brillouin zone for the simple cubic lattice (space group #221) showing the high symmetry points and axes

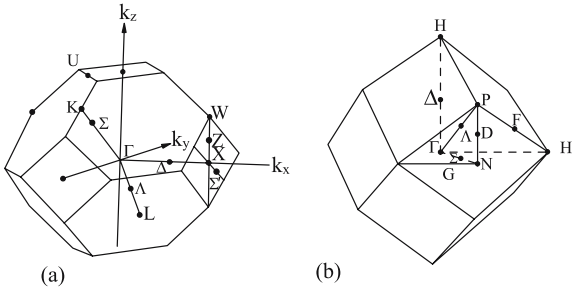

Fig. 10.4. Brillouin zones for the (**a**) face-centered (space group #225) and (**b**) body-centered (space group #229) cubic lattices showing the points and lines of high symmetry in (**a**). The point Z on the line between X and W is also called V in the literature and point Q is between L and W

some detail, and we refer also to the group of the wave vector for the B.C.C. (space group $Im3m$ (O_h^9) #229) and for the F.C.C. (space group $Fm3m$ (O_h^5) #225) structures (see Fig. 10.4).

Figure 10.3 shows the Brillouin zone for the simple cubic lattice. The high symmetry points and axes in these figures are labeled using the standard notation found in the crystallography literature, the group theory literature, and in the solid state physics literature.

10.6.1 The Γ Point

The symmetry operations of the group of the wave vector at the Γ point ($k = 0$) are the symmetry operations of the O_h group indicated in Fig. 3.4 compounded with full inversion symmetry, $O_h = O \otimes i$. The character table for O_h along with the basis functions for all the irreducible representations is given in Table 10.2. The form of the basis functions is helpful in identifying s (Γ_1), p (Γ_{15}) and d ($\Gamma_{12}, \Gamma'_{25}$) electronic states of the O_h cubic crystal where the symmetries of the corresponding irreducible representations are shown.

The notation used in Table 10.2 is that traditionally used in the solid state physics literature [1] and dates back to the 1930s. Here Γ_1 and Γ_2 denote

Table 10.2. Character table for the cubic group O_h corresponding to the group of the wave vector at $k = 0$ for the three cubic space groups #221 (SC), #225 (FCC), and #229 (BCC)†

repr.	basis functions	E	$3C_4^2$	$6C_4$	$6C_2'$	$8C_3$	i	$3iC_4^2$	$6iC_4$	$6iC_2'$	$8iC_3$
$\Gamma_1(\Gamma_1^+)$	1	1	1	1	1	1	1	1	1	1	1
Γ_2 (Γ_2^+)	$x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)$	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12} (Γ_{12}^+)	x^2-y^2 $2z^2-x^2-y^2$	2	2	0	0	−1	2	2	0	0	−1
$\Gamma_{15}(\Gamma_{15}^-)$	x, y, z	3	−1	1	−1	0	−3	1	−1	1	0
$\Gamma_{25}(\Gamma_{25}^-)$	$z(x^2-y^2)\ldots$	3	−1	−1	1	0	−3	1	1	−1	0
Γ_1' (Γ_1^-)	$xyz[x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)]$	1	1	1	1	1	−1	−1	−1	−1	−1
$\Gamma_2'(\Gamma_2^-)$	xyz	1	1	−1	−1	1	−1	−1	1	1	−1
Γ_{12}' (Γ_{12}^-)	$xyz(x^2-y^2)\ldots$	2	2	0	0	−1	−2	−2	0	0	1
Γ_{15}' (Γ_{15}^+)	$xy(x^2-y^2)\ldots$	3	−1	1	−1	0	3	−1	1	−1	0
Γ_{25}' (Γ_{25}^+)	xy, yz, zx	3	−1	−1	1	0	3	−1	−1	1	0

† The basis functions for Γ_{25}^- are $z(x^2-y^2)$, $x(y^2-z^2)$, $y(z^2-x^2)$, for Γ_{12}^- are $xyz(x^2-y^2)$, $xyz(3z^2-r^2)$ and for Γ_{15}^+ are $xy(x^2-y^2)$, $yz(y^2-z^2)$, $zx(z^2-x^2)$

Table 10.3. Character table C_{4v} for the group of the wave vector at a Δ point[a]

representation	basis functions	E	C_4^2	$2C_4$	$2iC_4^2$	$2iC_2'$
Δ_1	$1, x, 2x^2 - y^2 - z^2$	1	1	1	1	1
Δ_2	$y^2 - z^2$	1	1	−1	1	−1
Δ_2'	yz	1	1	−1	−1	1
Δ_1'	$yz(y^2 - z^2)$	1	1	1	−1	−1
Δ_5	$y, z; xy, xz$	2	−2	0	0	0

[a] $\Delta = \frac{2\pi}{a}(x, 0, 0)$ (SC, FCC, BCC); $T = \frac{2\pi}{a}(1, 1, z)$ (SC)

1D irreducible representations, Γ_{12} denotes the 2D irreducible representation, while Γ_{15} and Γ_{25} denote the two 3D irreducible representations and the notations used are historical.[1] In this notation, Γ_{15} and Γ_{25} are odd while Γ_{15}' and Γ_{25}' are even under inversion (as can be seen from the basis functions in Table 10.2). To get around this apparent nonuniformity of notation with regard to even and odd functions, we often use $\Gamma_i^{\pm}$ (e.g., $\Gamma_{15}^{\pm}$) to emphasize the parity (even or odd property) of a wavefunction for the cubic groups. We notice that to obtain basis functions for all the irreducible representations of the group O_h in Table 10.2 we need to include up to sixth-order polynomials.

10.6.2 Points with $k \neq 0$

In Table C.6 in Appendix C we see that the special point R in Fig. 10.3 for the simple cubic lattice that also has full O_h symmetry. Special care must be given to operations taking k into $k + K_m$, since they also add exponential factors to the computation of χ^{equiv}, for example, as discussed in Sect. 10.5.

We next consider the group of the wave vector at lower symmetry points. First we consider the group of the wave vector for a point along the Δ axis (see Fig. 10.3) which has fewer symmetry operations than the group of the wave vector at $\boldsymbol{k} = 0$. The group of the wave vector at Δ is an example of a *small representation*. The symmetry operations for a point along the Δ axis for the simple cubic lattice are those of a square, rather than those of a cube and are the symmetry operations of point group C_{4v}. Group C_{4v} is a subgroup of the full cubic group O_h. The multiplication table for the elements of the point group C_{4v} which is appropriate for a reciprocal lattice point Δ along the $\hat{x}$ axis is given in Table C.9. Multiplication tables like this can be compiled for all the groups of the wave vectors for all high symmetry points in the Brillouin zone for all the space groups.

The character table (including basis functions) for the group of the wave vector for Δ, where $\boldsymbol{\Delta} = (\Delta, 0, 0)$ is along $\hat{x}$, is given in Table 10.3 and Table C.8. Since the Δ point occurs in space groups #221 (SC), #225 (FCC)

[1] The numbers contained in the subscripts denote how the Γ point levels split in the Δ axis direction, as discussed in Sect. 10.7.

Table 10.4. Character table for the group of the wave vector Λ

character table for the Λ axis			
$\Lambda = C_{3v}$	E	$2C_3$	$3iC_2$
Λ_1	1	1	1
Λ_2	1	1	-1
Λ_3	2	-1	0

and #229 (BCC), the character table and basis functions in Table 10.3 are applicable for all these space groups. In Table 10.3 for the Δ point, the C_4 rotation operation is along $\hat{x}$, the $2iC_4^2$ are along $\hat{y}, \hat{z}$, and the $2iC_2'$ are along $\{011\}$. The basis functions in the character table can be found from inspection by taking linear combinations of (x^ℓ, y^m, z^n) following the discussion in Chap. 4. The process of going from higher to the lower symmetry defines the *compatibility relations* (Sect. 10.7) between irreducible representations of O_h and those of C_{4v} showing the path from the higher group O_h to the lower symmetry C_{4v}. The basis functions for the lower symmetry groups (such as the group of Δ) are related to those of O_h by considering the basis functions of the point group O_h as reducible representations of the subgroup Δ, and decomposing these reducible representations into irreducible representations of the group Δ. For example Γ_{25}' (or using Γ_{25}^+ to show its parity) of point group O_h is a reducible representation of C_{4v}, and reduction of Γ_{25}' (or Γ_{25}^+) into irreducible representations of C_{4v} yields the compatibility relation (see Sect. 10.7)

$$[\Gamma_{25}']_{O_h} \equiv \left[\Gamma_{25}^+\right]_{O_h} \rightarrow [\Delta_{2'} + \Delta_5]_{C_{4v}} \ ,$$

showing the origin of the Γ_{25}' notation. We note that yz is the longitudinal partner for $\boldsymbol{\Delta} = (\Delta, 0, 0)$ and corresponds to the irreducible representation Δ_2', while xy, xz are the transverse partners corresponding to Δ_5. What is different here from the discussion in Sect. 5.3 is that the dispersion relations also go from lower to higher symmetry. For example, the Δ point goes into the X point for space groups # 221 and # 225 and into the H point for # 229 (BCC) all having more symmetry operations than at the Δ point. We also note that the group of the wave vector for point T for the simple cubic lattice (see Fig. 10.3) also has C_{4v} symmetry (see Tables C.6 and C.8). In considering the group of the wave vector for point T, remember that any reciprocal lattice point separated by a reciprocal lattice vector from T is an equally good T point. The character Table 10.3 also serves for the T-point, but the symmetry operations and basis functions would need proper modification. Character tables for all the high symmetry points for $\boldsymbol{k}$ vectors in the simple cubic lattice are discussed in this section. For example, the symmetry group for a wave vector along the (111) axis or Λ axis is C_{3v} (see Fig. 10.3), which is given in Table 10.4. For a Λ point along the (111) direction, the $2C_3$ are

along {111}, and the $3iC_2$ are along $(1\bar{1}0)$, $(10\bar{1})$, and $(0\bar{1}1)$ directions. For the Λ point we can do threefold rotations in both $\pm$ senses about ΓR for group #221, about ΓL for #225 and about ΓP for #229 (see Fig. 10.4). Whereas the Λ point follows the same point group C_{3v}, the end points R, L, and P for the three space groups have different point group symmetries. We can also do 180° rotations about twofold axes ΓM followed by inversion (see Fig. 10.3). By $\Gamma M'$ we mean the wave vector to the center of an adjacent cube edge, and we here note that a rotation by π about $\Gamma M'$ in group #221 followed by inversion does not leave Λ invariant. Only three of the "$\Gamma M'$" axes are symmetry operations of the group; the other three such axes (like ΓM in the diagram) are not symmetry operations. Therefore instead of the symmetry operations $6iC_2$ which hold for the Γ and R points, the class $3iC_2$ for the group of the Λ point only has three symmetry elements. Table C.10 in Appendix C gives the basis functions for each irreducible representation of the group of the wave vector at a Λ point and shows that point F for the BCC structure also has C_{3v} symmetry, but the symmetry operations and basis functions need to be appropriately modified.

The final high symmetry point along one of the three main symmetry axes is the Σ point along the {110} axes. The group of the wave vector for the Σ point is C_{2v} and the character table is shown in Table C.11 in Appendix C. This character table applies to the Σ point for the simple cubic, FCC and BCC lattices (see Fig. 10.4). All the irreducible representations are one-dimensional. Table C.6 identifies high symmetry points in other space groups which have high symmetry points with C_{2v} symmetry. Table C.11 in Appendix C also shows that the group of the wave vector for high symmetry points Z and S for the simple cubic lattice, points U, Z, and K for the FCC lattice, and points G and D for the BCC lattice all belong to group C_{2v}.

Table 10.5. Character tables for the group of the wave vector (group D_{4h}) for points M and X for space group #221

M	E	$2C_4^2$	$C_{4\perp}^2$	$2C_{4\perp}$	$2C_2$	i	$2iC_4^2$	$iC_{4\perp}^2$	$2iC_{4\perp}$	$2iC_2$
X	E	$2C_{4\perp}^2$	$C_{4\parallel}^2$	$2C_{4\parallel}$	$2C_2$	i	$2iC_{4\perp}^2$	$iC_{4\parallel}^2$	$2iC_{4\parallel}$	$2iC_2$
M_1, X_1	1	1	1	1	1	1	1	1	1	1
M_2, X_2	1	1	1	−1	−1	1	1	1	−1	−1
M_3, X_3	1	−1	1	−1	1	1	−1	1	−1	1
M_4, X_4	1	−1	1	1	−1	1	−1	1	1	−1
M_1', X_1'	1	1	1	1	1	−1	−1	−1	−1	−1
M_2', X_2'	1	1	1	−1	−1	−1	−1	−1	1	1
M_3', X_3'	1	−1	1	−1	1	−1	1	−1	1	−1
M_4', X_4'	1	−1	1	1	−1	−1	1	−1	−1	1
M_5, X_5	2	0	−2	0	0	2	0	−2	0	0
M_5', X_5'	2	0	−2	0	0	−2	0	2	0	0

It can also happen that two high symmetry points such as M and X for the simple cubic lattice belong to the same point group D_{4h}, but the symmetry operations for the two groups of the wave vector can refer to different axes of rotation, as shown in Table 10.5. The notation $C_{4\|}^2$ in Table 10.5 refers to a twofold axis ΓX, while $2C_{4\perp}^2$ refers to the two twofold axes $\perp$ to ΓX. These are in different classes because in one case X is left invariant, while in the other case X goes into an equivalent X point separated by a reciprocal lattice vector. To put it in more physical terms, if the X point would not exactly be on the zone boundary but were instead at a Δ point arbitrarily close, the $C_{4\|}^2$ operation would still hold, while the $2C_{4\perp}^2$ operations would not. When we list multiple high symmetry points with a given character table in Appendix C, we do not generally distinguish between the symmetry operations for the individual classes (compare for example Table 10.5 and Table C.15). Character tables for all the high symmetry points in the Brillouin zone for the simple cubic lattice (#221) (see Fig. 10.3) and for the FCC and BCC lattices (see Fig. 10.4) are given in Appendix C, since we use these groups frequently for illustrative purposes in this book.

10.7 Compatibility Relations

As stated above, compatibility relations relate the basis functions (wave functions) in going from one wave vector to another belonging to a different symmetry group. Such a situation, for example, occurs when going from $k = 0$ (Γ point with full O_h symmetry) to an interior k point such as a Δ point with C_{4v} symmetry and then in going from the Δ point to the X point with D_{4h} symmetry.

To study these compatibility relations, let us follow some particular energy band around the Brillouin zone and see how its symmetry type and hence how its degeneracy changes. The problem of connectivity (connecting energy bands as we move from one $\boldsymbol{k}$ point to a neighboring $\boldsymbol{k}$ point with a different group of the wave vector) is exactly the same type of problem as that occurring in crystal field splittings (Sect. 5.3) as we go from a high symmetry crystal field to a perturbed crystal field of lower symmetry.

As an illustration of compatibility relations, consider a simple cubic lattice as we move along a (111) direction from $\Gamma \rightarrow \Lambda \rightarrow R$ from the center of the Brillouin zone to the zone corner (see Fig. 10.3). At the Γ point ($\boldsymbol{k} = 0$) we have the full point group symmetry O_h. As we now go from a higher point group symmetry O_h at Γ to a $\boldsymbol{k}$ vector along Λ, we go to a point group of lower symmetry C_{3v}. Since there are no three-dimensional representations in C_{3v}, we know that the degeneracy of the threefold degenerate levels in O_h symmetry, i.e., $\Gamma_{15}^-, \Gamma_{25}^-, \Gamma_{15}^+, \Gamma_{25}^+$ levels, will be at least partially lifted. We proceed as before to write down the character table for the Λ point, and below it we will write down the representations of the Γ point group, which we now treat as reducible representations of the Λ point group. We then reduce out

Table 10.6. Compatibility relations along Λ in the simple cubic BZ

Λ	E	$2C_3$	$3iC_2$	irreducible representations
Λ_1	1	1	1	
Λ_2	1	1	−1	
Λ_3	2	−1	0	
Γ_1 (Γ_1^+)	1	1	1	Λ_1
Γ_2 (Γ_2^+)	1	1	−1	Λ_2
Γ_{12} (Γ_{12}^+)	2	−1	0	Λ_3
Γ'_{15} (Γ_{15}^+)	3	0	−1	$\Lambda_2 + \Lambda_3$
Γ'_{25} (Γ_{25}^+)	3	0	1	$\Lambda_1 + \Lambda_3$
Γ'_1 (Γ_1^-)	1	1	−1	Λ_2
Γ'_2 (Γ_2^-)	1	1	1	Λ_1
Γ'_{12} (Γ_{12}^-)	2	−1	0	Λ_3
Γ_{15} (Γ_{15}^-)	3	0	1	$\Lambda_1 + \Lambda_3$
Γ_{25} (Γ_{25}^-)	3	0	−1	$\Lambda_2 + \Lambda_3$

the irreducible representations of the Λ point symmetry group. This process is indicated in Table 10.6, below where we list the ten irreducible representations of O_h and indicate the irreducible representations of C_{3v} therein contained. This procedure gives a set of compatibility conditions. In a similar way, the compatibility relations for a simple cubic lattice along the Δ and Σ axes follow the progression from Γ to Δ to X and also from Γ to Σ to M as can be seen from Fig. 10.3. In going from $\Delta \to X$ we go from C_{4v} symmetry to D_{4h} symmetry, since at the Brillouin zone boundary, translation by a reciprocal lattice vector introduces additional symmetries associated with a mirror plane. Similarly, in going from $\Sigma \to M$ we get four equivalent M points so that the symmetry group goes from C_{2v} to D_{4h}. Compatibility relations for the simple cubic lattice are summarized in Table 10.7 for illustrative purposes.

Tables of compatibility relations for all space groups are compiled in the literature, e.g. Miller and Love's book [54] (see Sect. 10.9).

As an example of using these compatibility relations, let us consider what happens as we move away from the Γ point $\boldsymbol{k} = 0$ on a threefold level, such as Γ'_{25} (or Γ_{25}^+) in Table 10.7. There are many possibilities, as indicated below:

$$\Gamma'_{25} \to \Delta_{2'} + \Delta_5 \to X_3 + X_5\,, \tag{10.41}$$

$$\Gamma'_{25} \to \Lambda_1 + \Lambda_3 \to R_{15}\,, \tag{10.42}$$

$$\Gamma'_{25} \to \Sigma_1 + \Sigma_2 + \Sigma_3 \to M_1 + M_5\,. \tag{10.43}$$

Suppose that we want to find a set of compatible symmetries in going around a circuit using the Brillouin zone shown in Fig. 10.3.

$$\Gamma \to \Sigma \to M \to Z \to X \to \Delta \to \Gamma\,. \tag{10.44}$$

Table 10.7. Compatibility relations for the high symmetry points in the simple cubic lattice

compatibility relations between Γ and Δ, Λ, Σ

	Γ_1^+	Γ_2^+	Γ_{12}^+	Γ_{15}^-	Γ_{25}^+	Γ_1^-	Γ_2^-	Γ_{12}^-	Γ_{15}^+	Γ_{25}^-
(100)	Δ_1	Δ_2	$\Delta_1\Delta_2$	$\Delta_1\Delta_5$	$\Delta_{2'}\Delta_5$	$\Delta_{1'}$	$\Delta_{2'}$	$\Delta_{1'}\Delta_{2'}$	$\Delta_{1'}\Delta_5$	$\Delta_2\Delta_5$
(111)	Λ_1	Λ_2	Λ_3	$\Lambda_1\Lambda_3$	$\Lambda_1\Lambda_3$	Λ_2	Λ_1	Λ_3	$\Lambda_2\Lambda_3$	$\Lambda_2\Lambda_3$
(110)	Σ_1	Σ_4	$\Sigma_1\Sigma_4$	$\Sigma_1\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_3$	Σ_2	Σ_3	$\Sigma_2\Sigma_3$	$\Sigma_2\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_4$

compatibility relations between X and Δ, Z, S

X_1	X_2	X_3	X_4	X_5	$X_{1'}$	$X_{2'}$	$X_{3'}$	$X_{4'}$	$X_{5'}$
Δ_1	Δ_2	$\Delta_{2'}$	$\Delta_{1'}$	Δ_5	$\Delta_{1'}$	$\Delta_{2'}$	Δ_2	Δ_1	Δ_5
Z_1	Z_1	Z_4	Z_4	Z_3Z_2	Z_2	Z_2	Z_3	Z_3	Z_1Z_4
S_1	S_4	S_1	S_4	S_2S_3	S_2	S_3	S_2	S_3	S_1S_4

compatibility relations between M and Σ, Z, T

M_1	M_2	M_3	M_4	$M_{1'}$	$M_{2'}$	$M_{3'}$	$M_{4'}$	M_5	$M_{5'}$
Σ_1	Σ_4	Σ_1	Σ_4	Σ_2	Σ_3	Σ_2	Σ_3	$\Sigma_2\Sigma_3$	$\Sigma_1\Sigma_4$
Z_1	Z_1	Z_3	Z_3	Z_2	Z_2	Z_4	Z_4	Z_2Z_4	Z_1Z_3
T_1	T_2	$T_{2'}$	$T_{1'}$	$T_{1'}$	$T_{2'}$	T_2	T_1	T_5	T_5

Then we must verify that when we arrive back at Γ we have the same symmetry type as we started with. A set of such compatible symmetries designates a whole band.

To go around one of these circuits, basis functions prove very useful and the tight binding wave functions are often used to keep track of the symmetry. We know that s-functions transform like the identity representation so that a possible circuit would be $\Gamma_1 \to \Lambda_1 \to R_1 \to S_1 \to X_1 \to \Delta_1 \to \Gamma_1$ (see Fig. 10.3). If we have p-functions, the basis functions are (x, y, z) and we can join up representations corresponding to these basis functions. Likewise for the five d-functions in cubic symmetry, we have three that transform as (xy, xz, yz) with Γ_{25}^+ symmetry and two that transform as $(x^2 + \omega y^2 + \omega^2 z^2)$ and $(x^2 + \omega^2 y^2 + \omega z^2)$ corresponding to Γ_{12}^+ symmetry, where $\omega = \exp(2\pi\mathrm{i}/3)$.

As an example of how compatibility relations are used in the *labeling* of energy bands, we show the energy dispersion relation $E(\boldsymbol{k})$ in Fig. 10.5 for the high symmetry directions $\boldsymbol{k}_{100}$ and $\boldsymbol{k}_{111}$ for the simple cubic structure. For the band with lower energy, we have the compatibility relations $\Gamma_1 \to \Delta_1 \to X_1$ and $\Gamma_1 \to \Lambda_1 \to R_1$. For the upper band, we see a splitting of a p-band as we move away from $k = 0$, and a consistent set of compatibility relations is

$$\Gamma_{25}^+ \to \Delta_{2'} + \Delta_5\,, \quad \Delta_{2'} \to X_2 \quad \text{and} \quad \Delta_5 \to X_5$$
$$\Gamma_{25}^+ \to \Lambda_1 + \Lambda_3\,, \quad \Lambda_1 \to R_1^+ \quad \text{and} \quad \Lambda_3 \to R_{12}^+\,.$$

In applying the compatibility relations as we approach the R point from the Λ direction, we note that the R point has the same group of the wave vector as $\boldsymbol{k} = 0$ and the same subscript notation can be used to label the R point, namely R_1, R_2, R_{12}, R_{15} and R_{25}.

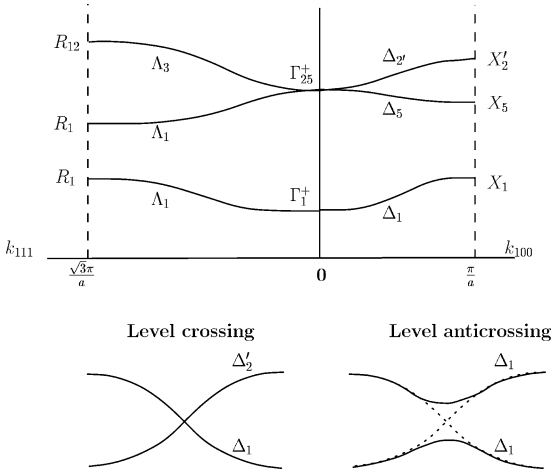

Fig. 10.5. Schematic diagram of energy bands illustrating compatibility relations. The diagrams below show both level crossings between bands of the same symmetries and level anticrossings between bands of different symmetries where interactions occur

When levels of different symmetry approach one another, they can simply cross as indicated in Fig. 10.5 for the Δ_1 and Δ_2' levels, and this is simply referred to as a level crossing, where the two bands retain their original symmetry after the crossing. However, when two levels of the same symmetry approach one another, there is an interaction between them and this case is also illustrated in Fig. 10.5 for two energy levels of Δ_1 symmetry. The effect in this case is called *level anticrossing* because the levels do not actual cross in this case, though their wave functions become admixed in an appropriate linear combination.

10.8 The Diamond Structure: Nonsymmorphic Space Group

In this section we extend our discussion to nonsymmorphic space groups, where the symmetry operations can be a combination of point group and translation operations. In this case, to work with the rotational aspects of the nonsymmorphic space group, procedures to remove the translational effect are needed, and they are discussed in Sect. 10.4.

To illustrate the symmetry of a nonsymmorphic space group we use the diamond lattice (space group #227, O_h^7) which is shown in Fig. 10.6 as a specific example. Not only C, but also Si and Ge crystallize in the diamond structure, that is described by a nonsymmorphic space group with two atoms/primitive unit cell. Figure 10.6 is equivalent to Fig. 9.6(f), except that Fig. 10.6 explicitly shows the two distinct atoms per unit cell, indicated as light atoms and

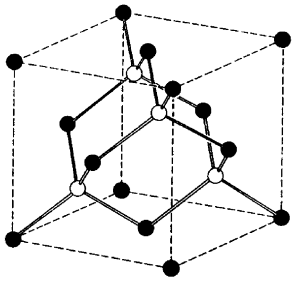

Fig. 10.6. The zinc blende structure with T_d symmetry illustrating the two dissimilar lattice sites. With identical atoms at the two sites, the diamond structure results. The space group for the diamond lattice is $Fd3m$ or #227 (O_h^7). The space group for the zinc blende structure is #216 [$F\bar{4}3m$]

dark atoms. We will take the "primitive unit cell" for the diamond structure to be the FCC primitive unit cell formed by the four dark atoms in Fig. 10.6 surrounding one light atom (see Fig. 9.6(b) for the NaCl structure which consists of inter-penetrating FCC structures for Na and for Cl). The dark atoms in Fig. 10.6 are on sites for one FCC lattice, and the light inequivalent atoms of the same species are on another FCC lattice displaced from the first FCC lattice by $a(1/4, 1/4, 1/4)$, as shown in Fig. 10.6. A screw axis indicated in Fig. 9.6(g) takes the dark atoms on the first sublattice in Fig. 10.6 into the light atoms on the second sublattice and vice versa.

10.8.1 Factor Group and the Γ Point

The factor group G/T for diamond is isomorphic to the point group O_h. The set of operations $\hat{P}_R$ that are relevant for the diamond structure are, therefore, the 48 operations of the O_h point group. Each of the 24 symmetry operators $\hat{P}_R$ of group T_d will leave each distinct atom on the same sublattice. However, the operations in O_h that are not in T_d when combined with a translation $\boldsymbol{\tau}_d = a/4(111)$ for the diamond structure take each atom on one sublattice into the other sublattice. This space group is nonsymmorphic because half of the symmetry operations of the group of the wave vector at $\boldsymbol{k} = 0$ contain translations $\boldsymbol{\tau}_d = a/4(111)$. The 48 symmetry operations and ten classes for the diamond structure at $\boldsymbol{k} = 0$ are given in Table 10.8, showing 24 operations of the form $\{R_\alpha|\varepsilon\}$ and 24 operations of the form $\{R_{\alpha'}|\boldsymbol{\tau}_d\}$. At the Γ point $k = 0$, we have $\exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}] = 1$ so that the phase factor does not matter, and the group of the wave vector is given by the O_h group, compare Tables 10.2 and C.17.

In computing the characters χ^{equiv} for the equivalence transformation Γ^{equiv}, we take into account the two kinds of lattice sites, one on each of the two FCC sublattices. Thus an atom is considered "to go into itself" if it remains on its own sublattice and "*not* to go into itself" if it switches sublattices under a symmetry operation $\hat{P}_R$. Using this criterion, the results for

Table 10.8. Classes and characters for the equivalence transformation for the diamond lattice

	$\{E\|0\}$	$8\{C_3\|0\}$	$3\{C_2\|0\}$	$6\{C_2'\|\boldsymbol{\tau}_d\}$	$6\{C_4\|\boldsymbol{\tau}_d\}$
Γ^{equiv}	2	2	2	0	0
	$\{i\|\boldsymbol{\tau}_d\}$	$8\{iC_3\|\boldsymbol{\tau}_d\}$	$3\{iC_2\|\boldsymbol{\tau}_d\}$	$6\{iC_2'\|0\}$	$6\{iC_4\|0\}$
Γ^{equiv}	0	0	0	2	2

χ^{equiv} for the diamond structure are given in Table 10.8. Note that, although we can count eight C atoms inside the full cubic unit cell, $\chi^{\text{equiv}}(E) = 2$ for the identity operation. One must keep in mind that the primitive unit cell has only 2 atoms/cell while the full cubic unit cell is four times larger. We emphasize that χ^{equiv} must be computed on the basis of the number of atoms in the *primitive* unit cell.

Decomposition of Γ^{equiv} in Table 10.8 into irreducible representations of O_h (see Table 10.2) leads to $\Gamma^{\text{equiv}} = \Gamma_1 + \Gamma_2'$ or $\Gamma_1^+ + \Gamma_2^-$. Here Γ_1^+ is even under inversion and Γ_2^- is odd under inversion, using the usual notation for irreducible representations for solids. We also note that the operation $\{i|\boldsymbol{\tau}_d\}$ interchanges sublattices $1 \leftrightarrow 2$. We make use of this result for Γ^{equiv} in subsequent chapters in discussing the electronic energy band structure and phonon dispersion relations of solids crystallizing in the diamond structure. The character table for the group of the wave vector for the Γ point for the diamond structure is given in Table C.17, utilizing the classes given in Table 10.8 and utilizing the character table for the O_h group in Table 10.2.

10.8.2 Points with $k \neq 0$

We next consider the group of the wave vector for the high symmetry points with $k \neq 0$ in the Brillouin zone for the diamond structure, and we use the FCC Brillouin zone in Fig. 10.4(a) to delineate those high symmetry points.

At the Δ point, which is an interior point in the Brillouin zone, the five classes for group C_{4v} for the Δ point for the symmorphic FCC group in Table 10.3, go into $\{E|0\}$, $\{C_4^2|0\}$, $2\{C_4|\boldsymbol{\tau}_d\}$, $2\{iC_4^2|\boldsymbol{\tau}_d\}$, $\{2iC_2'|0\}$ for the diamond lattice. The characters for the classes with a translation $\boldsymbol{\tau}_d$ will include phase factors $T_\Delta = \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}_d]$ for all k points along the Δ axis where $\boldsymbol{k}\cdot\boldsymbol{\tau}_d = (2\pi/a)(\kappa,0,0)\cdot(a/4)(1,1,1) = \pi\kappa/2$, and where $\kappa \to 0$ as $k \to 0$, and $\kappa \to 1$ as k approaches the X point. Thus κ denotes the fractional length of the k vector along the Δ axis. The corresponding character table then is derived from Table 10.3 by multiplying the characters in classes $2\{C_4|\boldsymbol{\tau}_d\}$ and $2\{iC_4^2|\boldsymbol{\tau}_d\}$ by the phase factor T_Δ to yield Table 10.9.

For interior k points along the Σ direction, the phase factor $\exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}_d]$ enters in a similar way and here the classes and characters for the irreducible

Table 10.9. Character table C_{4v} for the group of the wave-vector at a Δ point for the nonsymmorphic diamond structure[a]

representation	$\{E\|0\}$	$\{C_4^2\|0\}$	$2\{C_4\|\boldsymbol{\tau}_d\}$	$2\{iC_4^2\|\boldsymbol{\tau}_d\}$	$2\{iC_2'\|0\}$
Δ_1	1	1	$1 \cdot T_\Delta$	$1 \cdot T_\Delta$	1
Δ_2	1	1	$-1 \cdot T_\Delta$	$1 \cdot T_\Delta$	-1
$\Delta_{2'}$	1	1	$-1 \cdot T_\Delta$	$-1 \cdot T_\Delta$	1
$\Delta_{1'}$	1	1	$1 \cdot T_\Delta$	$-1 \cdot T_\Delta$	-1
Δ_5	2	-2	0	0	0

[a] $\Delta = 2\pi/a(\kappa, 0, 0)$ (diamond). Phase factor $T_\Delta = \exp[\mathrm{i}\frac{\pi}{2}\kappa]$

Table 10.10. Character table C_{2v} for the group of the wave-vector at a Σ point for the nonsymmorphic diamond lattice[a]

representation	$\{E\|0\}$	$\{C_{2'}\|\boldsymbol{\tau}_d\}$	$2\{iC_4^2\|\boldsymbol{\tau}_d\}$	$\{iC_2'\|0\}$
Σ_1	1	$1 \cdot T_\Sigma$	$1 \cdot T_\Sigma$	1
Σ_2	1	$1 \cdot T_\Sigma$	$-1 \cdot T_\Sigma$	-1
Σ_3	1	$-1 \cdot T_\Sigma$	$-1 \cdot T_\Sigma$	1
Σ_4	1	$-1 \cdot T_\Sigma$	$1 \cdot T_\Sigma$	-1

[a] $\Sigma = 2\pi/a(\kappa, \kappa, 0)$(diamond). Phase factor $T_\Sigma = \exp[\mathrm{i}\pi\kappa]$

Table 10.11. Character table C_{3v} for the group of the wave-vector at a Λ point for the nonsymmorphic diamond structure[a]

representation	$\{E\|0\}$	$2\{C_3\|0\}$	$3\{iC_2'\|0\}$
Λ_1	1	1	1
Λ_2	1	1	-1
Λ_3	2	-1	0

[a] $\Lambda = 2\pi/a\ (\kappa, \kappa, \kappa)$ (diamond)

representations for the group of the wave vector are given in Table 10.10, where the phase factor T_Σ is $\exp[\mathrm{i}\pi\kappa]$. As $\kappa \to 0$ the Σ point approaches the Γ point (group O_h) and as $\kappa \to 3/4$ the K point (see Fig. 10.4(a)) is reached. The corresponding compatibility relations are found by relating Table 10.10 to Table C.17 in the limit $\kappa \to 0$ and to a modified form of Table 10.10 in the limit $\kappa \to 3/4$.

Along the Λ direction the symmetry operations do not involve the translation $\boldsymbol{\tau}_d$ and therefore no phase factors appear in the character table for the group of the wave vector along the Λ axis (Table 10.11), nor do phase factors enter the character table for the end points of the Λ axis either at the Γ point (0,0,0) or at the L point $(\pi/a)(1, 1, 1)$ which has symmetry D_{3d} (see Table C.18).

Table 10.12. Character table for the group of the wave-vector at a X point for the nonsymmorphic diamond structure[a]

representation	$\{E\|0\}$	$\{C_{2'}\|0\}$	$2\{C_2\|\boldsymbol{\tau}_d\}$	$2\{iC_{2'}\|0\}$
X_1	2	2	0	2
X_2	2	2	0	-2
X_3	2	-2	-2	0
X_4	2	-2	2	0

[a] $X = (2\pi/a)(1,0,0)$

The point X at $\boldsymbol{k} = (2\pi/a)(1,0,0)$ is a special point. The primitive translations can be written as

$$\boldsymbol{a}_1 = (a/2)(1,1,0)\,, \quad \boldsymbol{a}_2 = (a/2)(0,1,1)\,, \quad \boldsymbol{a}_3 = (a/2)(1,0,1)\,. \tag{10.45}$$

The translation group T_k is formed by elements $\{\varepsilon|\boldsymbol{R}_n\}$, where $\boldsymbol{R}_n = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$, and where n_1, n_2, n_2 are integers. Using the Bloch wave functions as a basis, the phase factors are represented by $\mathrm{e}^{\mathrm{i}\boldsymbol{K}_X\cdot\boldsymbol{R}_n} = (-1)^{(n_2+n_3)}$ considering the X point at the zone boundary along the Δ-axis.

The factor group G_X/T_X has 14 classes. However, Table 10.12 shows only four classes and four relevant irreducible representations. Six of the 14 classes corresponding to translations have only 0 entries for all the characters, and the remaining four classes can be obtained from Table 10.12 by adding a τ_d translation and multiplying the characters by -1. Because of the irrelevant representations, the compatibility relations between high symmetry points in nonsymmorphic groups are sometimes not evident. For example, $\Delta_1 + \Delta_2'$ go into X_1 and Δ_5 goes into X_4. This is easily seen for the first $\{E|0\}$, second $\{C_4^2|0\}$ and fifth $\{2iC_2'|0\}$ classes in Table 10.9, while the two remaining classes in the Δ group, namely $\{2C_4|\tau_d\}$ and $\{2iC_4^2|\tau_d\}$, go into two classes of the X point that are not listed in Table 10.12 and have all entries for their characters equals zero.

In summary, for some of the high symmetry points of the diamond structure, the group of the wave vector is found in a similar way as for a symmorphic FCC structure, while for other high symmetry points (e.g., along the Δ and Σ axes) the group of the wave vector behaves differently. The high symmetry points where phase factors are introduced are $\Delta, \Sigma, W, S(Z)$ and those without phase factors are Γ, Λ, L, Q. The point X is a special point at which the structure factor vanishes and there is no Bragg reflection, nor are there phase factors, but the behavior of the X point in the diamond structure is different from that of the X point in the FCC structure which is a true Bragg reflection point. The group of the wave vector for all the high symmetry points on the square face, for example W and $S(Z)$, of the Brillouin zone for the diamond structure are also twofold degenerate. This degeneracy reflects the fact that the structure factor for the Bragg reflection for that whole face is

identically zero and hence there is no physical reason for the electronic or phonon dispersion curves to be split by that particular wave vector.

10.9 Finding Character Tables for all Groups of the Wave Vectors

Fortunately, tables for the group of the wave vector for each unique $\boldsymbol{k}$ vector for each of the 230 space groups have been established and are available in various references [49, 54]. These listings contain character tables for all groups of the wave vectors for every space group. These references do not refer to specific materials – they only refer to the space group which describes specific materials.

Appendix C gives the character tables for the group of the wave vector for all the high symmetry points for the simple cubic lattice space group #221. Familiarity with the use of character tables for the group of the wave vector can be gained through the problems at the end of this chapter (Sect. 10.9).

Selected Problems

10.1. Sketch the primitive translation vectors for the unit cells in r-space and k-space for the five 2D Bravais lattices given in Table 10.1. What is the angle between $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$?

10.2. (a) Construct the star and group of the wave vector for a simple 2D hexagonal space group (#17), as discussed in Sect. 10.3.2. Show how the group of the wave vector for $\boldsymbol{k} = \boldsymbol{b}_2/2$ is a subgroup of the group of the wavevector at $k = 0$.
(b) Now construct the star and group of the wave vector for the 2D hexagonal space group #14 and contrast your results with those in (a).

10.3. The Brillouin zone and the high symmetry points of the tetragonal structure shown in Fig. 10.7 on the right applies to the space group of the structure shown on the left. See Problem 9.1 for the real space symmetry of this 3D structure.

(a) Find the star of the wave vector for this space group.
(b) Find the group of the wave vector for the Γ point ($k = 0$).
(c) Now find the group of the wave vector along the Δ, Λ and Σ directions and give the compatibility relations relating the irreducible representations at $k = 0$ to those along these high symmetry axes when we move away from the Γ point.

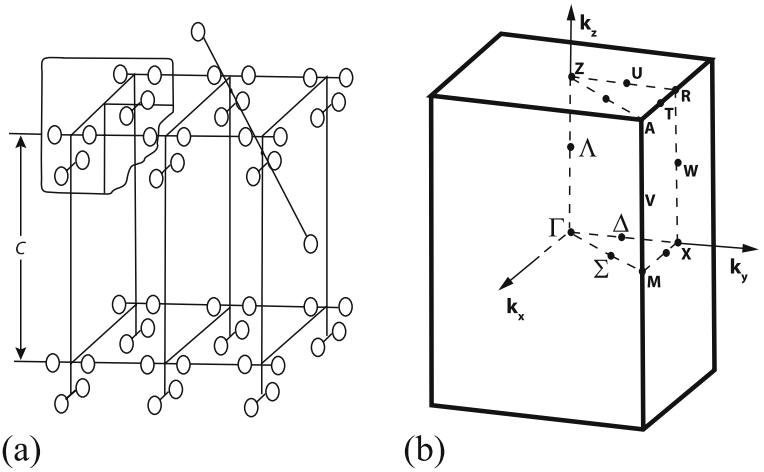

Fig. 10.7. (**a**) 3D crystal structure composed of a tetragonal Bravais lattice with a molecule with D_{2d} symmetry. (**b**) The tetragonal Brillouin zone with the high symmetry points

10.4. (a) Show that for the diamond structure (Sect. 10.8) the product of two symmetry operations involving translations $\boldsymbol{\tau}$ yields a symmetry element with no translations

$$\{\alpha|\boldsymbol{\tau}\}\{\beta|\boldsymbol{\tau}\} = \{\gamma|0\}\,,$$

where $\boldsymbol{\tau} = (1,1,1)a/4$. What is the physical significance of this result?

(b) What is the result of the product of the two symmetry elements $\{\alpha|\boldsymbol{\tau}\}\{\beta|0\}$? Is this product the same as $\{\beta|0\}\{\alpha|\boldsymbol{\tau}\}$? If not what is the difference?

(c) What are the symmetry operations and the group of the wave vector for the diamond structure at the L point? at the K point? at the W point?

(d) Find the characters χ^{equiv} for one symmetry operation in each class of the diamond structure, space group #227.

10.5. (a) List the real space symmetry operations of the nonsymmorphic two-dimensional square space group $p4gm$ (#12).

(b) Explain the symmetry diagrams and the point symmetry notations for space group #12 ($p4gm$) in Table B.12 (Appendix B) which was taken from the International Crystallography Tables.

(c) Find the group of the wave vector for the high symmetry points in the space group $p4gm$ and compare your results with those for the symmorphic group $p4mm$ [Table B.11 (Appendix B)].

(d) What is the difference between the 2D space group #11 ($p4mm$) and the 3D group $P4mm$? What would be the difference in the equivalence transformation Γ^{equiv} for the two cases (you can instead give the characters χ^{equiv} for this transformation)?

10.6. The electronic energy band structure of graphite near the Fermi level has become especially interesting after the discovery of single wall carbon nanotubes in 1993. (The crystal structure of 3D graphite is shown in Fig. C.1 in Appendix C and problem 9.6 relates to the space group crystal structures.)

(a) Find Γ^{equiv} at the Γ-point for the four atoms in the unit cell of graphite (see Fig. C.1 in Appendix C). Give the Γ point irreducible representations contained in Γ^{equiv}.
(b) Explain the symmetry operations for the group of the wave vector at $k = 0$ for group #194 that combine point group operations with translations. Compare your results to Table C.24 in Appendix C.

10.7. This problem makes use of carbon nanotubes (see Problem 9.7) to discuss space groups and line groups. Appendix E provides information of use to solve this problem (see also reference [8]).

(a) Find the lattice vectors in reciprocal space and describe the one-dimensional Brillouin zone of carbon nanotubes. Compare your results to Appendix E.
(b) Find the factor groups G_k/T for the group of the wave vectors at the Γ point ($k = 0$) for chiral and achiral carbon nanotubes, and the character tables for the isomorphic point groups. Then apply your result explicitly to a metallic (6,6) and a semiconducting (6,5) nanotube.
(c) Find the line groups for chiral and achiral carbon nanotubes and their respective character tables. By factoring out the effect of translations from line groups, find the resulting point groups (called isogonal point groups), with the same order of the principal rotation axis, where rotations include a screw-axis. Also give explicit results for the (6,6) and (6,5) nanotubes.
(d) Repeat (a), (b) and (c) for $k \neq 0$.
(e) Discuss the different dimensionalities for the irreducible representations in space groups compared with line groups, for both $k = 0$ and $k \neq 0$.

10.8. Consider the carbon nanotubes presented in Sect. 9.4 and discussed in Appendix E.

(a) Show that the Γ^{equiv} for zigzag SWNTs at $k = 0$ is

$$\Gamma^{\text{equiv}}_{zigzag} = A_{1g} + B_{2g} + A_{2u} + B_{1u} + \sum_{j=1}^{n-1} (E_{jg} + E_{ju}) \,, \tag{10.46}$$

(b) Find the compatibility relations along the one-dimensional Brillouin zone for both chiral and achiral carbon nanotubes.