Part IV

Application to Periodic Lattices

9

Space Groups in Real Space

According to the one-electron Hamiltonian for the electronic energy band structure for solids, we write Schrödinger's equation as

$$\mathcal{H}\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})\,, \tag{9.1}$$

where $V(\boldsymbol{r})$ is a periodic potential. The symmetry group of the one-electron Hamiltonian and of the periodic potential in (9.1) is the *space group* of the crystal lattice, which consists of both *translational* symmetry operations and *point group* symmetry operations. Both the translational and point group symmetry operations leave the Hamiltonian invariant, and consequently all these symmetry operators will commute with the Hamiltonian, and provide quantum numbers for labeling the energy eigenvalues and eigenfunctions.

In this chapter we introduce the basic background for space group operations (Sect. 9.1) and show how these operations form space groups (Sect. 9.2). In addition to the point group and translation operations, we consider the compound symmetry operations of glide planes and screw axes (Sect. 9.1.2) and the nonsymmorphic space groups associated with these compound symmetry operations (Sect. 9.2.3). An introduction to a few kinds of 3D space groups is given in Sect. 9.2. However, for pedagogic purposes we discuss all 17 two-dimensional (2D) space groups in some detail in Sect. 9.3 to familiarize the reader with the notation and the symmetry operations occurring in both symmorphic and nonsymmorphic 2D-space groups. A brief introduction to line groups, describing the properties of systems exhibiting translational properties in one dimension, is given in Sect. 9.4. Finally we discuss the determination of the crystal structure and space groups in Sect. 9.5, and the use of standard reference texts, [58, 76] such as the Crystal Structures, by R.W.G. Wyckoff, and the International Tables for X-Ray Crystallography.

9.1 Mathematical Background for Space Groups

9.1.1 Space Groups Symmetry Operations

Definition 18. *The point group and translation symmetry operations which carry the crystal into itself form a group called the space group.*

A common notation for space group operators is

$$\{R_\alpha|\tau\}\ , \tag{9.2}$$

where R_α denotes point group operations such as rotations, reflections, improper rotations and inversions, while τ denotes translation operations. Pure rotations and pure translations are special cases of space group operations:

$\{\varepsilon|0\}$ = identity

$\{\alpha|0\}$ = pure rotations or more generally point group operations

$\{\varepsilon|\tau\}$ = pure translations by vector $\boldsymbol{\tau}$.

We can relate the operator $\{\alpha|\tau\}$ for the space group to a coordinate transformation

$$\{\alpha|\tau\}\boldsymbol{r} = \boldsymbol{r'} = \overleftrightarrow{\alpha}\cdot\boldsymbol{r} + \boldsymbol{\tau}\,, \tag{9.3}$$

where $\overleftrightarrow{\alpha}$ denotes the transformation matrix for rotations and $\boldsymbol{\tau}$ denotes a translational transformation.

Definition 19. *The result for the multiplication of two space group operators is*

$$\{\beta|\tau'\}\{\alpha|\tau\} = \{\beta\alpha|\beta\tau + \tau'\}\ , \tag{9.4}$$

where $\{\alpha|\tau\}$ is the first space group operator and $\{\beta|\tau'\}$ is the second.

Proof. Multiplication of two space group operators proceeds from this identification:

$$\begin{aligned}\{\beta|\boldsymbol{\tau'}\}\{\alpha|\tau\} &= \overleftrightarrow{\beta}\cdot\left[\overleftrightarrow{\alpha}\cdot\boldsymbol{r} + \boldsymbol{\tau}\right] + \boldsymbol{\tau'} \\ &= \overleftrightarrow{\beta}\cdot\overleftrightarrow{\alpha}\cdot\boldsymbol{r} + \overleftrightarrow{\beta}\cdot\boldsymbol{\tau} + \boldsymbol{\tau'} \\ &= \{\beta\alpha|\beta\tau + \tau'\}\ .\end{aligned}$$

Using the results of this definition of the multiplication of two space group operations we can write

$$\{\alpha|\tau\}\,\{\beta|\tau'\} = \overleftrightarrow{\alpha}\cdot\overleftrightarrow{\beta}\cdot\boldsymbol{r} + \overleftrightarrow{\alpha}\cdot\boldsymbol{\tau'} + \boldsymbol{\tau} \tag{9.5}$$

so that commutation of these two space group operators requires that

$$\overleftrightarrow{\alpha} \cdot \overleftrightarrow{\beta} = \overleftrightarrow{\beta} \cdot \overleftrightarrow{\alpha} \quad \text{and} \quad \overleftrightarrow{\beta} \cdot \boldsymbol{\tau} + \boldsymbol{\tau}' = \overleftrightarrow{\alpha} \cdot \boldsymbol{\tau}' + \boldsymbol{\tau} \tag{9.6}$$

which is not generally valid. Thus we conclude that although simple translations commute with each other, general space group operations do not commute. □

Definition 20. *The inverse of* $\{\alpha|\tau\}$ *is given by*

$$\{\alpha|\tau\}^{-1} = \{\alpha^{-1}| - \alpha^{-1}\tau\}\,. \tag{9.7}$$

Proof. Using the proposed definition of $\{\alpha|\tau\}^{-1}$ we carry out the following multiplication of two space group symmetry elements to obtain

$$\{\alpha|\tau\}\{\alpha|\tau\}^{-1} = \{\alpha\alpha^{-1}|\alpha(-\alpha^{-1}\tau) + \tau\} = \{\varepsilon|0\} \tag{9.8}$$

which verifies the definition for $\{\alpha|\tau\}^{-1}$. □

Having specified the identity operation $\{\varepsilon|0\}$, the rules for multiplication, and the rules for specifying the inverse operation, and noting that the associative law applies, we see that the elements $\{\alpha|\tau\}$ *form a space group.*

Definition 21. *The matrix representation for the space group operator is*

$$\{\alpha|\tau\} = \begin{pmatrix} 1 & 0 \\ \boldsymbol{\tau} & \overleftrightarrow{\alpha} \end{pmatrix}, \tag{9.9}$$

where 1 is a number, 0 denotes a row of three zeros, $\boldsymbol{\tau}$ *is a column vector, and* $\overleftrightarrow{\alpha}$ *is a* (3×3) *rotation matrix. Introducing the basis*

$$\begin{pmatrix} 1 \\ \boldsymbol{r} \end{pmatrix},$$

where 1 is a number and $\boldsymbol{r}$ *is a column vector consisting for example of*

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix},$$

the action of the space group operation on the coordinate system then is written as

$$\begin{pmatrix} 1 & 0 \\ \boldsymbol{\tau} & \overleftrightarrow{\alpha} \end{pmatrix} \begin{pmatrix} 1 \\ \boldsymbol{r} \end{pmatrix} = \begin{pmatrix} 1 \\ \boldsymbol{\tau} + \overleftrightarrow{\alpha} \cdot \boldsymbol{r} \end{pmatrix} = \begin{pmatrix} 1 \\ \boldsymbol{r}' \end{pmatrix}. \tag{9.10}$$

Theorem. *The matrix*

$$\begin{pmatrix} 1 & 0 \\ \boldsymbol{\tau} & \overleftrightarrow{\alpha} \end{pmatrix}$$

forms a representation for the space group operator $\{\alpha|\tau\}$.

Proof. To prove that the matrix of (9.9) is a representation for the space group operator $\{\alpha|\tau\}$, we write down the multiplication and inverse transformations. Multiplication of two matrices yields

$$\begin{pmatrix} 1 & 0 \\ \boldsymbol{\tau}' & \overleftrightarrow{\beta} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ \boldsymbol{\tau} & \overleftrightarrow{\alpha} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ \boldsymbol{\tau}' + \overleftrightarrow{\beta} \cdot \boldsymbol{\tau} & \overleftrightarrow{\beta} \cdot \overleftrightarrow{\alpha} \end{pmatrix}, \tag{9.11}$$

which yields another symmetry operation of the space group

$$\{\beta|\tau'\}\{\alpha|\tau\} = \{\beta\alpha|\beta\tau + \tau'\}\,. \tag{9.12}$$

Using (9.11) we can write the product of the matrix representation of $\{\alpha|\tau\}$ with that of its inverse operator $\{\alpha|\tau\}^{-1}$ to obtain

$$\begin{pmatrix} 1 & 0 \\ -\overleftrightarrow{\alpha}^{-1} \cdot \boldsymbol{\tau} & \overleftrightarrow{\alpha}^{-1} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ \boldsymbol{\tau} & \overleftrightarrow{\alpha} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & \varepsilon \end{pmatrix}, \tag{9.13}$$

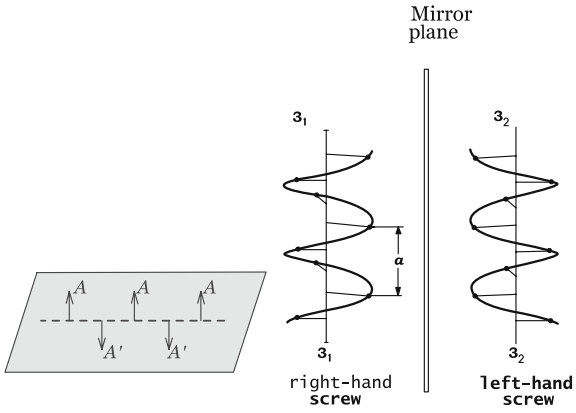
thereby showing that

$$\{\alpha|\tau\}^{-1}\{\alpha|\tau\} = \{\varepsilon|0\}\,. \tag{9.14}$$

□

9.1.2 Compound Space Group Operations

In space groups we may find instead of simple translation operations, compound symmetry operations that combine translations and point group operations. The two types of compound symmetry operations are the glide planes and the screw axes.



(a) Glide plane (b) Screw axis

Fig. 9.1. (**a**) The glide plane operation that takes A into A'. (**b**) Right- and left-hand screw axes (belong to closely related but different space groups)

A *glide plane* consists of a translation parallel to a given plane followed by a reflection in that plane (see Fig. 9.1(a)). There are in fact three different types of glide planes that are identified: the *axial glide* along a symmetry axis ($\boldsymbol{a}$, $\boldsymbol{b}$, or $\boldsymbol{c}$), the *diagonal glide* or *n-glide* in two or three directions (e.g., $(\boldsymbol{a}+\boldsymbol{b})/2$ or $(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})/2$) and finally the *diamond glide* corresponding to $(\boldsymbol{a}+\boldsymbol{b})/4$ or $(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})/4$).

A *screw axis* is a translation along an axis about which a rotation is simultaneously occurring. In Fig. 9.1(b) we show a threefold screw axis, where a is the lattice constant. The tellurium and selenium structures have threefold screw axes similar to those shown in Fig. 9.1b. A summary of the various possible screw axes and the crystallographic notation for each is given in Fig. 9.2. The screw axes shown in Fig. 9.2 are from top to bottom: the first row shows twofold screw axes, followed by a row of threefold and fourfold screw axes and the last two rows show sixfold screw axes. An n-fold screw axis has a trans-

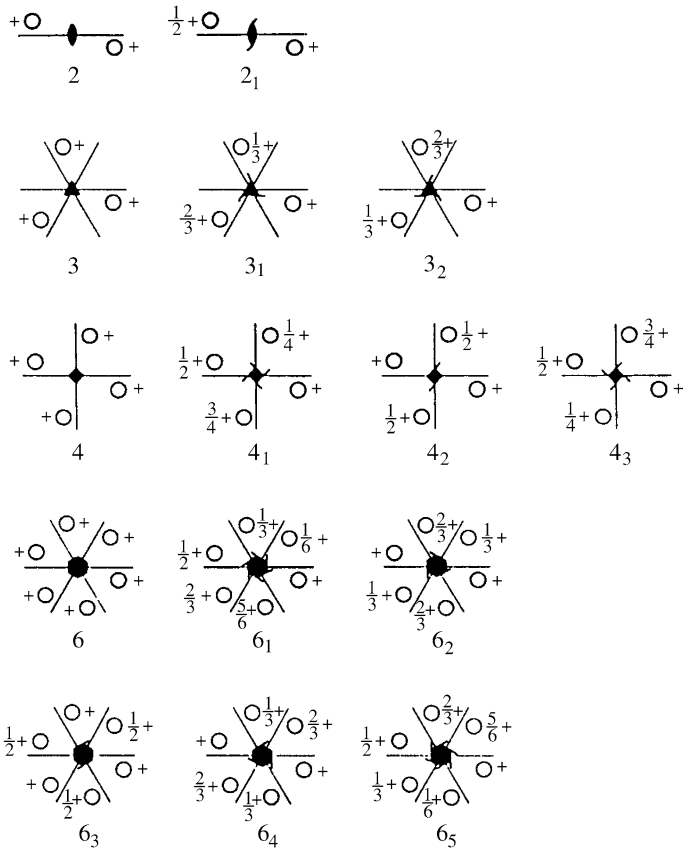


Fig. 9.2. A summary of all possible screw axes, including twofold, threefold, fourfold and sixfold screw axes (see text)

lation of $p\tau_0/n$ where τ_0 is a unit cell translation of the translation group, p is an integer $p = 1, \ldots, n$, and the rotation that goes with the translation is $2\pi p/n$. Thus for the threefold row, the first entry is a 2π or zero rotation every time there is a translation of $\tau_0/3$, while the second entry has a rotation of $2\pi/3$, for each $\tau_0/3$ translation and the last entry has a rotation of $4\pi/3$ or $(-2\pi/3)$, for each $\tau_0/3$ translation.

9.1.3 Translation Subgroup

Theorem. *All the elements of the space group G that are of the form $\{\varepsilon|\tau\}$ constitute the translation group T. Here T is a subgroup of G and defines the Bravais lattice.*

Proof. Symmetry elements of the group T are defined by the translation vectors $\boldsymbol{R}_n$ which leave the Bravais lattice invariant $\boldsymbol{R}_n = \Sigma n_i \boldsymbol{a}_i$, and $\boldsymbol{a}_i$ is the primitive vector of the Bravais lattice. The *translation* group is a *self-conjugate* or invariant or normal subgroup of G since

$$\begin{aligned}\{R_\alpha|\tau\}\{\varepsilon|t\}\{R_\alpha|\tau\}^{-1} &= \{R_\alpha|\tau\}\{\varepsilon|t\}\{R_\alpha^{-1}|-R_\alpha^{-1}\tau\}\\ &= \{R_\alpha|\tau\}\{R_\alpha^{-1}|-R_\alpha^{-1}\tau+t\}\\ &= \{\varepsilon|-R_\alpha R_\alpha^{-1}\tau+R_\alpha t+\tau\}\\ &= \{\varepsilon|R_\alpha t\}\,. \end{aligned} \tag{9.15}$$

But $R_\alpha \boldsymbol{t}$ is just another translation vector in group T and therefore the operation $\{\varepsilon|R_\alpha t\}$ is a symmetry operation of group T, and we have shown that $\{\varepsilon|\tau\}$ forms the translation subgroup of G. □

Although the translation group T is an invariant subgroup of G, we cannot generally say that the space group G is a direct product of a translation group with a point group, as discussed in Sect. 9.1.4. It should be noted that since the individual elements $\{\varepsilon|\tau'\}$ and $\{R_\alpha|\tau\}$ do not commute, as we show below:

$$\begin{aligned}\{\varepsilon|\tau'\}\{R_\alpha|\tau\} &= \{R_\alpha|\tau'+\tau\}\\ \{R_\alpha|\tau\}\{\varepsilon|\tau'\} &= \{R_\alpha|R_\alpha\tau'+\tau\}\,. \end{aligned} \tag{9.16}$$

However, since the translation group is an invariant subgroup of G, it is of interest to study the cosets of the factor group which it defines. A right coset of the translation group considered as a subgroup of G is then

$$C_\alpha = [\{\varepsilon|\tau'\}\{R_\alpha|\tau\}] = [\{R_\alpha|\tau''\}]\,, \tag{9.17}$$

where the bracket in (9.17) denotes all the terms in the coset that can be formed using all possible values of $\boldsymbol{\tau}'$. Although each element $\{R_\alpha|\tau\}$ does not commute with $\{\varepsilon|\tau'\}$ as seen in (9.16), all $\{R_\alpha|\tau''\}$ are contained in the right coset. Using the same argument as used above for the right coset, we can show that C_α is also a left coset of the translation group from which we conclude that T is a self-conjugate (or normal) subgroup of G.

Theorem. *The cosets C_α form a factor group of the space group G.*

Proof. Consider the multiplication rule for the cosets:

$$C_\alpha C_\beta = [\{R_\alpha|\tau_1\}\{R_\beta|\tau_2\}] = [\{R_\alpha R_\beta|R_\alpha\tau_2+\tau_1\}] = [\{R_\gamma|\tau_3\}] = C_\gamma\,, \quad (9.18)$$

where $R_\alpha R_\beta = R_\gamma$ defines the group property in the point group and $\boldsymbol{\tau}_3 = R_\alpha\boldsymbol{\tau}_2+\boldsymbol{\tau}_1$ is a translation of the lattice. Since $\boldsymbol{\tau}_1$ and $\boldsymbol{\tau}_2$ range over all possible translation vectors, the vector $\boldsymbol{\tau}_3$ also spans all possible translations, and C_γ satisfies the multiplication rule. □

The factor group G/T will be very important in applications of group theory to space groups, since it factors out the pure translational properties of the space groups, being isomorphic with the point group which makes up the rotational parts of the operators of the space groups. For a summary of cosets and factor group properties, see Sect. 1.5–1.7.

9.1.4 Symmorphic and Nonsymmorphic Space Groups

The space group G consists of all operations $\{R_\alpha|\tau\}$ which leave a given lattice invariant. We can write the space group operations in the form

$$\{R_\alpha|\tau\} = \{R_\alpha|R_n+\tau_\alpha\} = \{\varepsilon|R_n\}\{R_\alpha|\tau_\alpha\}\,, \quad (9.19)$$

where R_n is a general vector of the Bravais lattice and the vector τ_α (associated with each of the point group operators R_α) is either zero or a translation that is not a primitive translation of the Bravais lattice. The $\{R_\alpha|\tau_\alpha\}$ for which $R_n = 0$ are either simple point group operations, when $\tau_\alpha = 0$, or one of the compound operations (glide plane or screw axis discussed in Sect 9.1.2) when $\tau_\alpha \neq 0$.

Definition 22. *If, with a suitable choice of origin in the direct lattice, we find that all the elements of G are in the form $\{R_\alpha|\tau\} = \{R_\alpha|R_n\} = \{\varepsilon|R_n\}\{R_\alpha|0\}$ ($\tau_\alpha = 0$ for all symmetry operations), then the space group G is called a simple or symmorphic group. If, with any suitable choice of origin in the direct lattice, $\tau_\alpha \neq 0$ for at least one $\{R_\alpha|\tau_\alpha\}$ operation, then G is called a nonsymmorphic group.*

Symmorphic space groups, therefore, contain an entire point group as a subgroup. The point group g is obtained from the space group G by placing $\tau = R_n = 0$ for all $\{R_\alpha|\tau\}$ elements in G. The space group is said to be a *semi-direct* product of the translation and point groups, where *semi* is used since a *direct* product would give $\{R_\alpha|R_n\} \otimes \{\varepsilon|R_{n'}\} = \{R_\alpha|R_n+R_{n'}\}$. We will see in the next chapters that, once the wavevector k of the wavefunctions under study is chosen, we can work the space group problem by considering the rotational aspects, which reduce the work to a point group g_k problem. We then have h symmetry elements rather than $\mathcal{N}h$, where $\mathcal{N} \sim 10^{23}$.

For nonsymmorphic groups, τ_α is not zero for at least one R_α. By multiplying two space group elements of the type $\{R_\alpha|\tau_\alpha\}$ $(R_n = 0)$ we get

$$\{R_\alpha|\boldsymbol{\tau}_\alpha\}\{R_\beta|\boldsymbol{\tau}_\beta\} = \{R_\gamma|\boldsymbol{\tau}_\gamma + R_n\} \tag{9.20}$$

and R_n may or may not be zero. Therefore, the entire set of space group elements $\{R_\alpha|\boldsymbol{\tau}_\alpha\}$ may fail to form a group if the lattice vector $R_n \neq 0$. Furthermore, the entire point group g of the crystal, obtained by setting all translations (including the nonprimitive ones) in G equal to zero is a subgroup of its Bravais lattice point group (called the *holohedral* group, which is defined as the group of the Bravais lattice), but it is not a subgroup of G. In this case, to work with the rotational aspects of the nonsymmorphic space group, a procedure to remove the translational effect is needed. Two alternative procedures are available: (1) One approach is to form the factor group G/T of G with respect to the translation group T (Sect. 9.1.3). The G/T factor group will be isomorphic with the point group which makes up the rotational parts of the operators in the space group. (2) The G/T factor group representation can be obtained by means of the *multiplier algebra*, where all members of a given coset are represented by a single element, and we work with the *multiplier groups* or *multiplier representation*. These concepts will be discussed briefly in Sect. 10.4.

To fully describe a space group G, it is sufficient to list the elements $\{R_\alpha|\boldsymbol{\tau}_\alpha\}$ representing the cosets of G/T and the $\boldsymbol{a}_i$ primitive vectors of the Bravais lattice. It is clear that the applications of group theory to symmorphic space groups are simpler when compared to applications to nonsymmorphic space groups. The operations R_α apply to the translation vectors in accordance with the definition of the space group operations, and the symmetry operations of the factor group G/T for symmorphic space groups are isomorphic with the point group g. Thus irreducible representations of the factor group G/T are also irreducible representations of g and are likewise irreducible representations of G. It can be shown that all irreducible representations of G can be compounded from irreducible representations of g and T, even though G is not a direct product group of g and T [47]. The development of representations for the space groups will be discussed in Chap. 10.

9.2 Bravais Lattices and Space Groups

Now that we have introduced the mathematical background for working with space groups, we can introduce the 14 Bravais lattices which denote the possible crystallographic lattices that can form three-dimensional structures, and the 230 space groups (73 symmorphic and 157 nonsymmorphic) that can be formed by placing different atomic structures in the Bravais lattice sites.

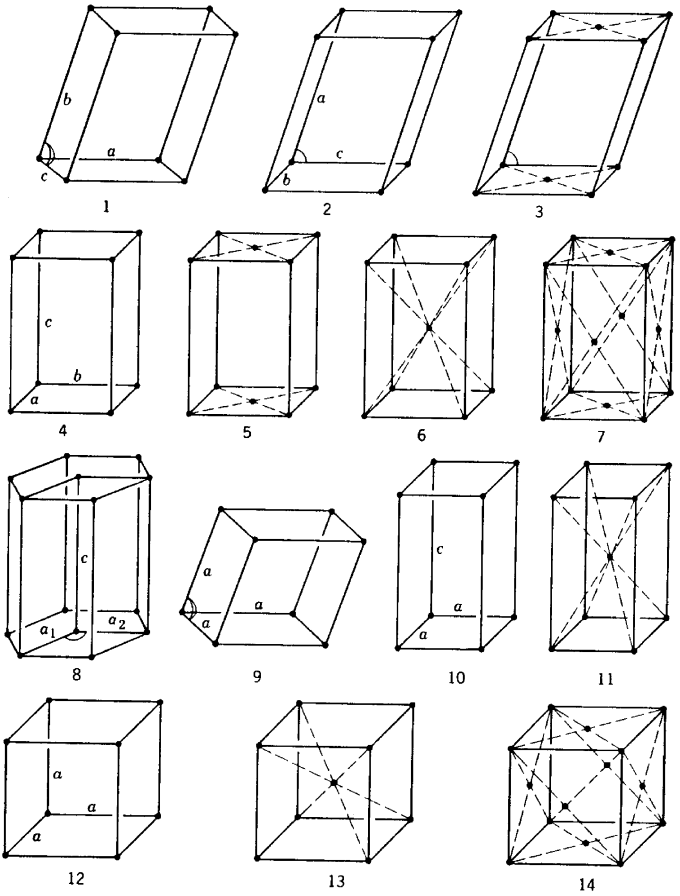


Fig. 9.3. The fourteen Bravais space lattices illustrated by a unit cell of each: (1) triclinic, simple; (2) monoclinic, simple; (3) monoclinic, base centered; (4) orthorhombic, simple; (5) orthorhombic, base centered; (6) orthorhombic, body centered; (7) orthorhombic, face centered; (8) hexagonal; (9) rhombohedral; (10) tetragonal, simple; (11) tetragonal, body centered; (12) cubic, simple; (13) cubic, body centered; and (14) cubic, face centered

The requirements of translational symmetry limit the possible rotation angles of a Bravais lattice and in particular restrict the possible rotation axes to onefold, twofold, threefold, fourfold and sixfold. Fivefold axes or axes greater than six do not occur in crystalline materials because these axes are not compatible with translational symmetry [7][1] as shown in Problem 9.5. When rotational symmetry does occur in crystals, then severe restrictions on the rotation angle are imposed by the simultaneous occurrence of the repetition of the unit cells through rotations and translations. The 14 Bravais lattices

[1]See [47], pp. 14 and 178.

which form 3D space groups are shown in Fig. 9.3. They are also discussed in solid state physics texts [45] and in crystallography texts [58, 68].

9.2.1 Examples of Symmorphic Space Groups

If all the operations of the space group are simply point group operations on to which we add translation operations from the Bravais lattice, we have a simple or *symmorphic* space group. The 73 symmorphic space groups are listed in Table 9.1, and they can be found in the "International Crystallographic Tables". Symbols that are used for 3D space groups (see Table 9.1) include A or B for monoclinic groups, and C, A or B, I, F for orthorhombic groups, and these are defined in Table 9.1. In the case of rectangular lattices,

Table 9.1. The 73 symmorphic space groups

crystal system	Bravais lattice	space group
triclinic	P	$P1$, $P\bar{1}$
monoclinic	P	$P2$, Pm, $P2/m$
	B or A	$B2$, Bm, $B2/m$
orthorhombic	P	$P222$, $Pmm2$, $Pmmm$
	C, A, or B	$C222$, $Cmm2$, $Amm2$[a], $Cmmm$
	I	$I222$, $Imm2$, $Immm$
	F	$F222$, $Fmm2$, $Fmmm$
tetragonal	P	$P4$, $P\bar{4}$, $P4/m$, $P422$, $P4mm$
		$P42m$, $P\bar{4}m2$[a], $P4/mmm$
	I	$I4$, $I\bar{4}$, $I4/m$, $I422$, $I4mm$
		$I\bar{4}2m$, $I\bar{4}m2$[a], $I4/mmm$
cubic	P	$P23$, $Pm3$, $P432$, $P\bar{4}3m$, $Pm3m$
	I	$I23$, $Im3$, $I432$, $I\bar{4}3m$, $Im3m$
	F	$F23$, $Fm3$, $F432$, $F\bar{4}3m$, $Fm3m$
trigonal	P[b]	$P3$, $P\bar{3}$, $P312$, $P321$[a], $P3m1$
		$P31m$[a], $P\bar{3}1m$, $P\bar{3}m1$[a]
(rhombohedral)	R	$R3$, $R\bar{3}$, $R32$, $R3m$, $R\bar{3}m$
hexagonal	P[b]	$P6$, $P\bar{6}$, $P6/m$, $P622$, $P6mm$
		$P\bar{6}m2$, $P\bar{6}m2$[a], $P6/mmm$

[P, I, F (A, B or C) and R, respectively, denote primitive, body centered, face centered, base centered (along the a, b or c crystallographic axis) and rhombohedral Bravais lattices (see Fig. 9.3)]

[a] The seven additional space groups that are generated when the orientations of the point group operations are taken into account with respect to the Bravais unit cell

[b] Primitive hexagonal and trigonal crystal systems have the same hexagonal Bravais lattice

the inequivalent axes are parallel to the sides of the conventional rectangular unit cell. In the case of square lattices, the first set of axes is parallel to the sides and the second set is along the diagonals. In the case of hexagonal lattices, one axis is 30° away from a translation vector.

We now illustrate the idea of symmorphic space groups using an example based on the D_{2d} point group (see character Table A.8) embedded in a tetragonal Bravais lattice (no. 11 in Fig. 9.3). Suppose that we have a molecule with atoms arranged in a D_{2d} point group configuration as shown in Fig. 9.4. We see that the D_{2d} point group has classes E, C_2 rotations about the z-axis, $2S_4$ improper rotations about the z-axis, $2\sigma_d$ passing through the z axis and through the center of each of the dumbbell axes, and $2C_2'$ axes in (110) directions in the median plane. The top view of this molecule is shown in Fig. 9.4(b).

We could put such X_4 molecules into a solid in many ways and still retain the point group symmetry of the molecule. To illustrate how different space

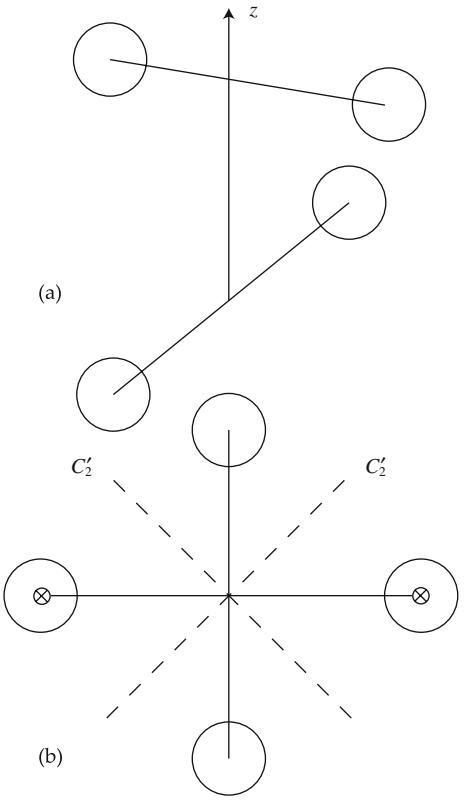


Fig. 9.4. (**a**) Schematic diagram of an X_4 molecule with point group D_{2d} ($\bar{4}2m$) symmetry. (**b**) Top view of a molecule X_4 with D_{2d} symmetry. The symmetry axes are indicated

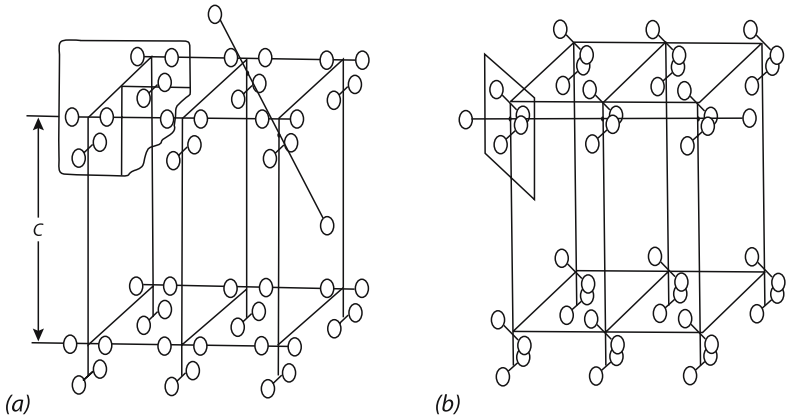


Fig. 9.5. Tetragonal Bravais lattice with two possible orientations of a molecule with D_{2d} symmetry resulting in two different three-dimensional space groups. The maximum symmetry that the tetragonal Bravais lattice can support is $D_{4h} = D_4 \otimes i$ $(4/mmm)$

groups can be produced with a single molecular configuration, we will put the X_4 molecule with D_{2d} symmetry into two different symmorphic space groups, as shown in Fig. 9.5.

We note that with either of the placements of the molecule in Fig. 9.5, *all the point group operations of the molecule are also operations of the space lattice*. However, if the symmetry axes of the molecule do not coincide with the symmetry axes of the lattice in which they are embedded, the combined space group symmetry is lowered. Particular point group operations are appropriate to specific Bravais lattices, but the connection is homomorphic rather than isomorphic. For example, the point group operations T, T_d, T_h, O and O_h leave each of the simple cubic, face-centered cubic and body-centered cubic Bravais lattices invariant. Even though a given Bravais lattice is capable of supporting a high symmetry point group (e.g., the FCC structure), if we have a lower symmetry structure at each of the lattice sites (e.g., the structure in Fig. 9.4), then the point symmetry is lowered to correspond to that structure. On the other hand, the highest point group symmetry that is possible in a crystal lattice is that which has all the symmetry operations of the Bravais lattice, so that the group O_h will be the appropriate point group for an FCC structure with spherical balls at each lattice site (see Problem 9.1).

9.2.2 Cubic Space Groups and the Equivalence Transformation

We now introduce the cubic groups that will be frequently discussed for illustrative purposes in subsequent chapters. The use of the equivalence transformation to obtain the characters $\chi^{\text{a.s.}}$ for this transformation is also discussed. Figure 9.6 illustrates several different kinds of cubic space groups com-

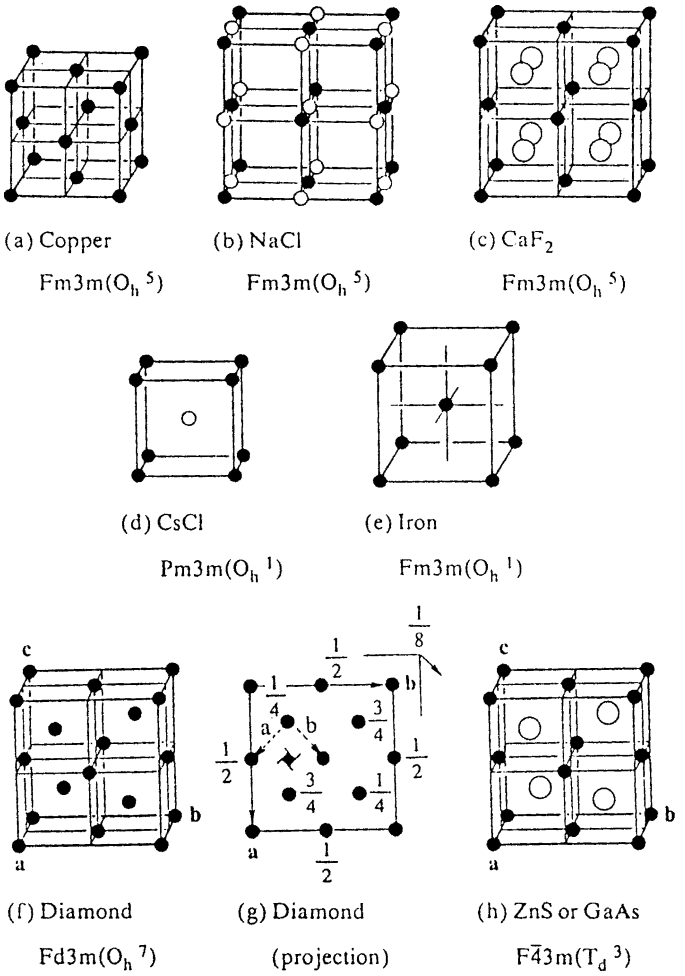


Fig. 9.6. Example of cubic lattices. Here (**a**), (**b**), (**c**) pertain to space group #225; (**d**) pertains to #221 and (**e**) to #229; while (**f**) and (**g**) are for #227; and (**h**) is for #223

monly occurring in solid state physics, including FCC, BCC, diamond and zinc blende structures. The diamond structure is nonsymmorphic and will be discussed in Sect. 9.2.3. First we show that a given space can support several different crystal structures. We illustrate this with Fig. 9.7 which shows three different crystal structures all having the same space group symmetry operations of $O_h^1(Pm3m)$. This space group will support full O_h point symmetry. The different crystal structures are obtained by occupying different sites as listed in the "International Crystallographic Tables" (see Table C.2). The space group is specified in terms of an origin at the center which has the full

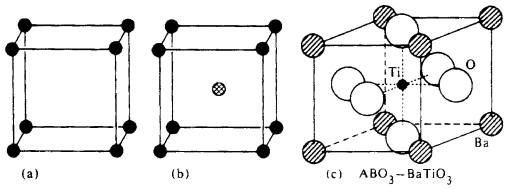


Fig. 9.7. Example of three cubic lattices with the space group #221 O_h^1 ($Pm3m$) (see Table C.2). (**a**) Simple cubic (SC), (**b**) body centered cubic (BCC), and (**c**) perovskite structure

symmetry of the Bravais lattice ($P4/m(\bar{3})2/m$). Inspection of space group 221 yields the structure shown in Fig. 9.7(a) where only site b is occupied, while Fig. 9.7(b) has site occupation of both sites a and b, each having site symmetry $m3m$ (see Table C.2). For the perovskite structure in Fig. 9.7(c) we have occupation of Ba atoms on b sites, Ti atoms on a sites and three oxygens on c sites. We note in Table C.2 that the site symmetry $4/mmm$ is different on the c sites than for the a or b sites which have $m3m$ site symmetries.

Important for many applications of group theory is the number of atoms within the primitive cell (for example for calculation of $\chi^{\text{a.s.}}$). For example, in Fig. 9.7(a) there is one atom per unit cell. This can be obtained from Fig. 9.7(a) by considering that only one eighth of each of the eight atoms shown in the figure is inside the cubic primitive cell. In Fig. 9.7(b) there are two distinct atoms per unit cell but for each $\Gamma^{\text{a.s.}} = \Gamma_1$ to give a total $\Gamma^{\text{a.s.}} = 2\Gamma_1$. In Fig. 9.7(c), there are one Ti, six half O, and eight 1/8 parts of Ba inside the primitive cell, giving altogether five atoms, i.e., one unit of $BaTiO_3$ per unit cell. Here $\Gamma^{\text{a.s.}}$ for each of the Ba and Ti sublattices we have $\Gamma^{\text{a.s.}} = \Gamma_1$ but for the three oxygens $\Gamma^{\text{a.s.}} = \Gamma_1 + \Gamma_{12}$ to give a total of $\Gamma^{\text{a.s.}} = 3\Gamma_1 + \Gamma_{12}$ for the whole $BaTiO_3$ molecule (see Sect. 11.3.2).

Concerning more general cubic groups, the structures for Fig. 9.6(a–c) are all group #225 based on a FCC Bravais lattice, while (d) has the CsCl structure (group #221) as in Fig. 9.7(b) which has two atoms per unit cell. The structure for iron (group #229) is based on the full BCC Bravais lattice where the central atom and the corner atoms are the same. Figures 9.6(f) and (g) are for the nonsymmorphic diamond lattice, discussed in detail in Sect. 9.2.3, which has two atoms/unit cell. The zinc blende structure shown in Fig. 9.6(h) is similar to that of Fig. 9.6(f) except that the atoms on the two sublattices are of a different species and therefore the zinc blende structure has a different symmetry group #203, and this group is a symmorphic group.

9.2.3 Examples of Nonsymmorphic Space Groups

A familiar example of a *non-symmorphic space group* is the *diamond* structure shown in Fig. 9.6(f), where we note that there are two atoms per unit cell

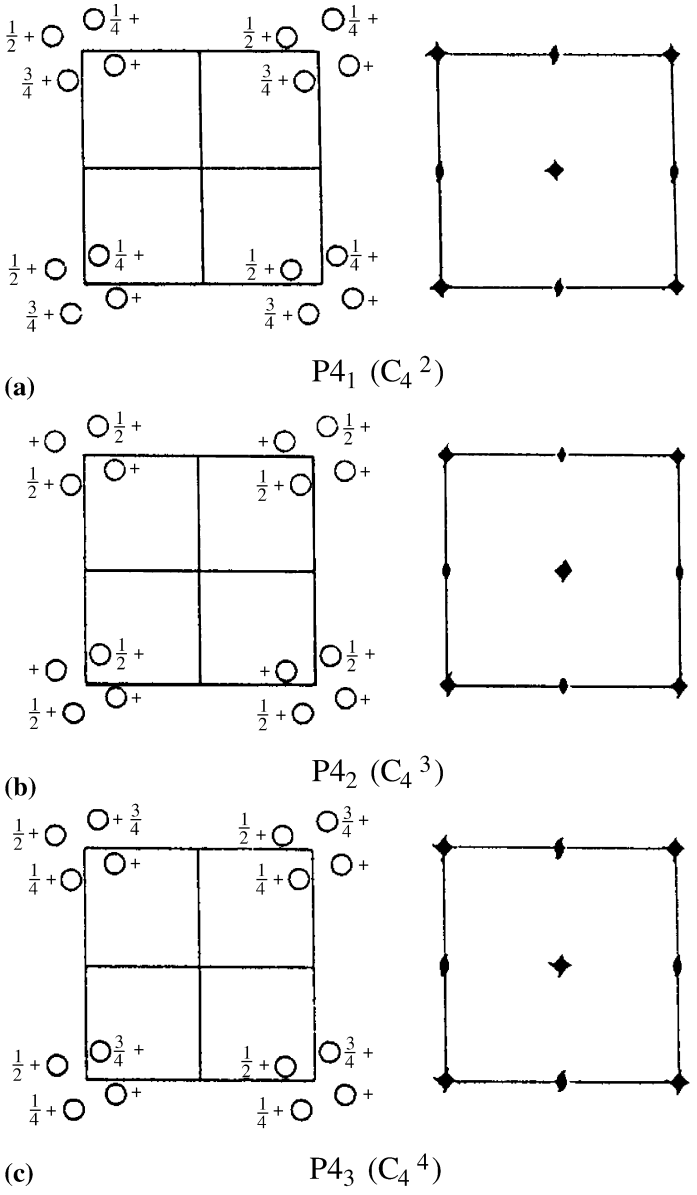


Fig. 9.8. Examples of space groups with screw axes. The three examples are (**a**) $P4_1$ (C_4^2) #76, (**b**) $P4_2$ (C_4^3) #77 and (**c**) $P4_3$ (C_4^4) #78. See Sect. 9.1.2 and Fig. 9.2 for notation

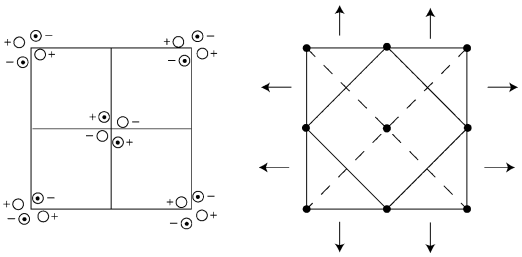


Fig. 9.9. Example of a space group with a screw axis in the plane of the figure: $P\bar{4}2_1m$ (D^3_{2d}) (#113)

(the atoms on the cube corner positions and those in the centered positions). The symmetry operations of T_d represent all the point group operations that take one type of atom into another. In addition, each of the operations of T_d can be compounded with a translation along $(a/4)(111)$ which takes one inequivalent atom into another. Because of these additional symmetry operations, which are not point group operations of T_d, the diamond structure is not a Bravais lattice and is nonsymmorphic. The screw axis pertinent to the diamond structure is shown in Fig. 9.6(g).

Another example of space groups with screw axes is given in Fig. 9.8 for space groups $P4_1$ (C^2_4) #76, $P4_2$ (C^3_4) #77 and $P4_3$ (C^4_4) #78. The space group $P4$ #75 is a symmorphic space group with a similar arrangement of the four atom cluster but without a screw axis. The group numbers #75 to #78 come from the International Tables of X-ray Crystallography [58] (see Appendix C for a few examples of such tables). Each space group in Fig. 9.8 has point group C_4 symmetry, but has a different fourfold screw axis $(4_1, 4_2, 4_3)$. The atom locations are given in the left hand diagrams and the symmetry operations which include screw axes are shown in the right hand diagrams. Some twofold screw axes are also present.

Screw axes may also occur normal to the c-axis, as is shown in Fig. 9.9 for space group $P\bar{4}2_1m$ (D^3_{2d}) #113. Diamond glide planes along $\langle 110 \rangle$ directions also occur for this space group. The D_{2d} operations result in the occurrence of equivalent sites (x, y, z), $(-y, x, -z)$, $(-x, -y, z)$ and $(y, -x, -z)$.

Three-dimensional space groups will be discussed further in the next chapters. The reader is referred to texts such as Burns and Glazer [16] who give a detailed treatment of space group symmetries. In the next section we discuss the 2D space groups in more depth, first because they are simpler, and because they provide an instructive pedagogic introduction to space groups.

9.3 Two-Dimensional Space Groups

In this section we use the 17 two-dimensional space groups to illustrate in some detail the concepts introduced in this chapter from a pedagogic standpoint.

Table 9.2. Summary of the 17 two-dimensional space groups, their properties and notations

point group	lattice type	international[a] table number	notation full	type	notation short
1	oblique	1	$p1$	symmorphic	$p1$
2	$a \neq b, \phi \neq 90^\circ$	2	$p211$	symmorphic	$p2$
m	rectangular	3	$p1m1$	symmorphic	pm
	(p or c)	4	$p1g1$	nonsymmorphic	pg
	$a \neq b, \phi = 90^\circ$	5	$c1m1$	symmorphic	cm
$2mm$	rectangular	6	$p2mm$	symmorphic	pmm
	$a \neq b, \phi = 90^\circ$	7	$p2mg$	nonsymmorphic	pmg
		8	$p2gg$	nonsymmorphic	pgg
		9	$c2mm$	symmorphic	cmm
4	square p	10	$p4$	symmorphic	$p4$
$4mm$	$a = b, \phi = 90^\circ$	11	$p4mm$	symmorphic	$p4m$
		12	$p4gm$	nonsymmorphic	$p4g$
3	hexagonal	13	$p3$	symmorphic	$p3$
$3m$	$a = b, \phi = 120^\circ$	14	$p3m1$	symmorphic	$p3m1$
		15	$p31m$	symmorphic	$p31m$
6		16	$p6$	symmorphic	$p6$
$6mm$		17	$p6mm$	symmorphic	$p6m$

[a] International Tables for X-Ray Crystallography, published by the International Union of Crystallography, Kynoch Press, [58] Birmingham, England (1952). See also G. Burns and A.M. Glazer, [16] "Space Groups for Solid State Scientists", Academic Press, Inc., 2nd Edition 1978

There are five distinct Bravais lattices in two-dimensions. If we consider $\boldsymbol{a}, \boldsymbol{b}$ to be the two primitive translation vectors and ϕ to be the angle between $\boldsymbol{a}$ and $\boldsymbol{b}$, then the five lattice types are summarized in Table 9.2, where the 17 two-dimensional space groups are listed.

If we add two-dimensional objects, e.g., a set of atoms, to each cell of a Bravais lattice, we can change the symmetry of the lattice. If the object, sometimes called a motif, lowers the symmetry to that of another group, then the resulting symmetry space group for the structure is identified with the lower symmetry space group.

We give in this table the symmetries of each of these space groups, classified in terms of the five Bravais lattices in two dimensions. Listings from the "International Tables for X-Ray Crystallography" are given in Tables B.2–B.17 of Appendix B [58].

The notation used to designate the two-dimensional space groups is illustrated by the example $p4gm$ (see Table 9.2). The initial symbol ("p" in this example) indicates that the unit cell is either a primitive (p) unit cell or a cen-

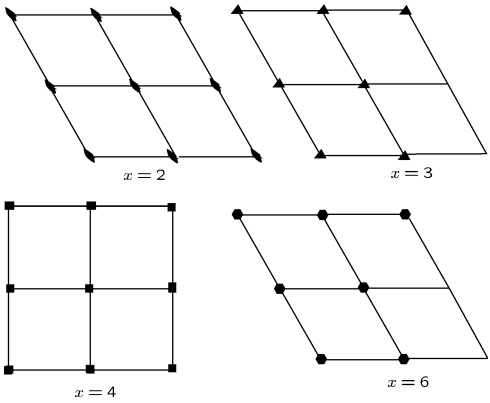


Fig. 9.10. Space group symbols used at lattice points for twofold (an American football), threefold (a triangle), fourfold (a square), and sixfold (a hexagon) rotations ($x = n$ to denote an n-fold rotation)

tered (c) unit cell. The next symbol "4" indicates rotational symmetry about an axis perpendicular to the plane of the two-dimensional crystal. The possible n-fold rotations for a space group are 1, 2, 3, 4, and 6, and the symbols used to denote such axes are shown in Fig. 9.10. The last two symbols in $p4gm$, when present, indicate either additional symmetries for the two inequivalent in-plane axes, or they refer to a glide plane (denoted by "g") through the primary axis, or to a mirror plane denoted by "m" through the primary axis, and "1" indicates that there is no additional symmetry.

In the following sections we discuss the space groups associated with each of the five 2D Bravais lattices.

9.3.1 2D Oblique Space Groups

The symmetries of the two 2 oblique space groups are shown in Tables B.1 and B.2 of Appendix B. The lowest symmetry two-dimensional space group (#1) only has translational symmetry ($p1$) and no additional point group operations. We use the lower case notation $p1$ to denote 2D space groups and $P1$ with a capital letter to denote the corresponding 3D space groups. The diagram for $p1$ shows only one general point (x, y) with translations by lattice vectors (1,0), (0,1), and (1,1). Open circles on the left hand diagram in Table B.1 are used to denote the three open circles obtained from the first open circle by these three translations.

However, by placing a motif with twofold rotational symmetry normal to the plane, the $p211$ space group (#2) is obtained, as shown in the symmetry diagram from the International Tables for X-Ray Crystallography. The twofold axis through the center of the rhombus (indicated by an American-football-shaped symbol on the right of Table B.2) denotes the symmetry operation that takes a general point (x, y) into $(-x, -y)$, shown

as point symmetry type e on the crystallographic table for space group #2($p211$). Points obtained by rotations are indicated by open circles in Table B.2. For the four special points (1/2, 1/2), (1/2, 0), (0, 1/2), (0, 0), labeled d, c, b, a, respectively, the twofold rotation takes the point into itself or into an equivalent point separated by a lattice vector. The site symmetry for these four special points is listed in the table for group $p2$ as having a twofold axis. A general point (such as e) under the action of the twofold axis and translation by (1,0), (0,1), and (1,1) yields the eight open points in the figure for group $p2$, two of which are within the unit cell shown in Table B.2.

These special points d, c, b, a are examples of what is generally called *Wyckoff positions* [76]. The concept of *Wyckoff positions* and their site symmetries is fundamental for the determination and description of crystal structures, since it is important to establish the reference point for the symmetry operations of an overall consistent coordinate system. The group of all symmetry operations that leaves a point P invariant is called the *site-symmetry group*. A point P is called the *point of special position* with respect to the space group G if there is at least one symmetry operation of G, in addition to the identity, that leaves P invariant (otherwise, P is called a *point of general position*). A Wyckoff position consists of all points P for which the site-symmetry groups are conjugate subgroups of G, and each Wyckoff position of a space group is labeled by a letter which is called the *Wyckoff letter*, and the site symmetries are indicated in the International Crystallography Tables [58].

9.3.2 2D Rectangular Space Groups

Primitive lattices. Of the seven rectangular 2D space groups, five are primitive and two are centered (see Table 9.2). We consider these together as is done in the International Tables for X-Ray Crystallography [58]. Of the five primitive rectangular space groups only two are symmorphic, and three are nonsymmorphic. In general, the full rectangular point symmetry is $2mm$ (C_{2v}). The point group $2mm$ has elements E, C_{2z}, σ_x, σ_y: the identity; a twofold axis C_{2z} perpendicular to the plane; and mirror planes parallel to the x and y axes through C_{2z}. The corresponding space group listed as space group #6 is $p2mm$ (see Table B.6). When introducing a lower symmetry motif, the resulting group must be a subgroup of the original group. The lower symmetry rectangular space group $p1m1$ has point group operations (E, σ_x) and is listed as space group #3 (see Table B.4). We note that (E, σ_y) is equivalent to (E, σ_x) by an interchange of axes and each corresponds to point group m (C_{1h}).

The symbol ⊙ containing a comma inside the circle provides a sense of orientation that is preserved under translations. Under a mirror plane operation (see Table B.4), the symbols ⊙ and ◯ are interchanged; the mirror plane is represented on the right by a solid horizontal line. The three kinds of Wyckoff

positions [76] and site symmetries (the general point c and the points a and b on the mirror planes) are also listed in Table B.4 for space group #3.

So far we have dealt with space groups where the point group operations are separable from the translation group operations. Such groups are symmorphic space groups.

In the case of the rectangular primitive lattice, mirror operations can be replaced by glide reflections. The glide planes are denoted by dashed lines (see diagram for space group #4 ($p1g1$) in Table B.4). No distinct screw operations are possible in two-dimensions. A glide reflection symmetry operation is a compound operation consisting of a reflection combined with a fractional unit cell translation, not a primitive unit cell translation. The resulting space group is nonsymmorphic because of the glide plane operation. Replacing m by g in $p1m1$ (space group #3) gives $p1g1$ (space group #4) where the translation $\boldsymbol{\tau}_1/2$ is compounded with the reflection operation; this translation can be followed by comparing the $\odot$ symbols for space groups #3 and #4 (Tables B.3 and B.4).

For the case of space group #6 ($p2mm$), replacing one of the mirror planes by a glide plane gives the nonsymmorphic group $p2mg$ (#7) as shown in Table B.7. When both mirror planes of space group #6 are replaced by glide planes, we get space group #8 ($p2gg$) which has the fractional translation $(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2$, but a mirror plane reflection σ_x or σ_y as shown in Table B.8. The compound mirror plane translation operations can be denoted by $\{\sigma_x|(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2\}$, $\{\sigma_y|(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2\}$.

Centered Rectangular Lattices. The centered rectangular lattice with the full centered rectangular symmetry (see Table B.9) is the space group $c2mm$ (#9) which is a centering of space group #6 ($p2mm$). The lower symmetry centered rectangular subgroup, related to space group #3 ($p1m1$) is space group #5 ($c1m1$) (shown in Table B.5). We note that the centering is equivalent to introducing a $(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2$ translation as indicated in Table B.5 for space group $c1m1$ (#5). All the centered rectangular lattices are considered to be symmorphic even though they have the translation $(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2$ to do the centering operation. As a more interesting example of a centered rectangular space group, let us look at space group #9 which is denoted by $c2mm$ (Table B.9). This space group has two equivalent positions (0,0) and (1/2, 1/2). The symmetry operations include a twofold axis along the z-direction and two sets of intersecting mirror planes. Four of the symmetry operations shown in Table B.9 are connected with the $2mm$ operations, and the other four symmetry operations are related to compounding these point group operations with the simple translation $(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2$ taking $(0, 0)$ to $(1/2, 1/2)$. The table shows that $c2mm$ can be realized through six different kinds of Wyckoff positions and their corresponding site symmetries. It should be noted that the various 2D space group tables provide special relations for the crystallographic h and k Miller indices that are used to distinguish diffraction patterns associated with each of the space groups.

9.3.3 2D Square Space Group

There are three 2D square space groups. The square lattice space with the full $4mm$ point group symmetry is $p4mm$ (space group #11), which is shown in Table B.11. The point group symmetry elements are E, C_{4z}^{+}, C_{4z}^{-}, C_{2z}, σ_y, σ_x, σ_{da}, σ_{db} corresponding to C_{4v}. The only distinct subgroup of C_{4v} is C_4 which has symmetry elements E, C_{4z}^{+}, C_{4z}^{-}, C_{2z}. In this case, the space group is $p4$ (space group #10 in International Tables for X-Ray Crystallography). The fourfold axis is clearly seen on the left hand diagram in Table B.10. The ⊙ points in space group #11 are obtained by adding mirror planes to space group #10. In the diagram on the right we see lattice locations with fourfold and with twofold axes, a feature found in all three 2D square lattices (see Tables B.10–B.12).

By combining the translation $(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2$, where $1/2\boldsymbol{\tau}_1$ and $(1/2)\boldsymbol{\tau}_2$ are translation vectors, with the mirror planes $\sigma_x, \sigma_y, \sigma_{da}, \sigma_{db}$ we obtain the glide reflections $\{\sigma_x|(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2\}$, $\{\sigma_y|(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2\}$, $\{\sigma_{da}|(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2\}$, $\{\sigma_{db}|(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2\}$. These glide reflections are used to form the nonsymmorphic square lattice of space group #12 ($p4gm$). We note there are mirror planes along the square diagonals and also mirror planes through the x- and y-axes. Space group #12 ($p4gm$) is obtained from space group #11 ($p4mm$) by translation of the comma points by $(1/2)\boldsymbol{\tau}_1 + (1/2)\boldsymbol{\tau}_2$, taking the open points into comma points.

9.3.4 2D Hexagonal Space Groups

There are five 2D hexagonal space groups, and all are symmorphic. The —)hexagonal space group #17 with the full hexagonal point group symmetry is $p6mm$. The point group symmetry elements are E, C_6^{+}, C_6^{-}, C_3^{+}, C_3^{-}, C_2, $\sigma_{d1}, \sigma_{d2}, \sigma_{d3}, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$. The diagram for $p6mm$ (#17) is shown in Table B.17.

The four subgroups of C_{6v} are C_6, C_{3v}, C_{3d}, C_3, giving rise, respectively, to space groups $p6$ (#16), $p3m1$ (#14), $p31m$ (#15), and $p3$ (#13), as summarized in Table 9.3. The symmetry diagrams for the five 2D hexagonal space groups are shown in Tables B.13–B.17.

Table 9.3. Summary of the symmetry operations of two-dimensional hexagonal space groups that are subgroups of #17 ($p6mm$)

space group	point group elements
$p3$	E, C_3^{+}, C_3^{-}
$p3m1$	E, C_3^{+}, C_3^{-}, $\sigma_{v1}, \sigma_{v2}, \sigma_{v3}$
$p31m$	E, C_3^{+}, C_3^{-}, $\sigma_{d1}, \sigma_{d2}, \sigma_{d3}$
$p6$	E, C_6^{+}, C_6^{-}, C_3^{+}, C_3^{-}, C_2

9.4 Line Groups

Line groups describe the symmetry of systems exhibiting translational periodicity in one dimension [71]. Examples of quasi-one-dimensional systems, are stereoregular polymers and carbon nanotubes. In addition, some three-dimensional crystals can be highly anisotropic, as for example chain-type crystals which have line groups as subgroups of their space group. Whenever only one direction is relevant for some physical properties of a three-dimensional system, one can expect to derive useful information by applying suitable line group approaches. The advantage of using line groups is their simplicity.

Generally, quasi-1D systems exhibit, besides translational symmetry, point group and compound operations. As explained further below, line groups generally involve a *generalized* translation group Z and an *axial* point group P giving the internal symmetries [22]. By a *generalized* translation group we mean that Z denotes an infinite cyclic group composed of general translational operations along the line axis, that may include screw axes or glide planes. The line group symmetry elements are represented by $\{C_n^r|\alpha\}$, where C_n^r is a rotation of $2\pi r/n$, and n and r are non-negative integers and where $r < n$, and $0 < \alpha < 1$ represent a translation along the line axis by αa, where a is the translational period of the system. For a given choice for r, any multiple of q/n, where q is a divisor of n, may be added to r with no effect on the resulting line group L, so that the minimum value of r is used to avoid nonuniqueness. There are three different types of generalized translation groups:

- Those formed by simple translations, $T = \{E|\alpha\}$ and the translational period is αa;
- Those with the occurrence of a screw axis, $T_n^r = \{C_n^r|\alpha\}$ and in this case the translational period is $n\alpha a$;
- Those with the occurrence of a glide plane, $T_c = \{\sigma_v|\alpha\}$ and in this case the translational period is $2\alpha a$.

The *axial* point groups P are: C_n, S_{2n}, C_{nh}, C_{nv}, D_n, D_{nh} and D_{nd}, where $n = 1, 2, 3, \ldots$ is the order of the principal rotational axis.

The line groups are formed by taking the weak direct product $L = Z \cdot P$. The product between Z and P must be a weak direct product[2] (indicated here by "$\cdot$") because all elements of Z, except for the identity, have a nonzero translational part, while no point group element on P has translations. The intersection between groups Z and P is, therefore, only the identity operation. However, the product $Z \cdot P$ forms a group only if Z and P commute (this is

[2]The general concept of a weak direct product is defined in the following way: A Group G is said to be the weak direct product of its subgroups H and K when (i) the identity element is the only intersection of H and K and (ii) each element of G is the product of one element in H with one element in K. Semi-direct and direct products are special cases of the weak-direct product. When H and K are invariant subgroups, the result is a direct product. When only H is an invariant subgroup, the result is a semidirect product.

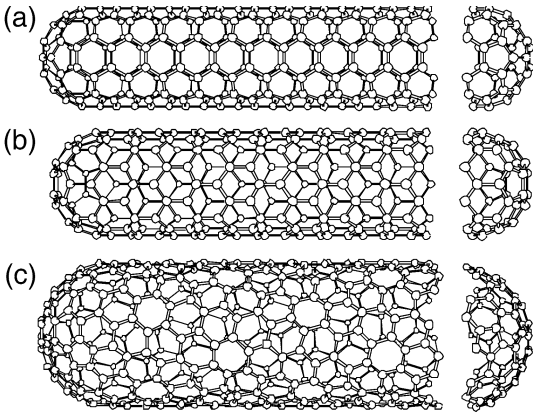


Fig. 9.11. Schematic theoretical model for the three different types of single-wall carbon nanotubes: (**a**) the "armchair" nanotube, (**b**) the "zigzag" nanotube, and (**c**) the "chiral" nanotube [63]

always the case only for $Z = T$). Furthermore, some products with different factors are identical. There are an infinite number of line groups, and they are classified into 13 families [22]. In Problem 9.7 we use carbon nanotubes to exemplify the use of line groups.

Carbon nanotubes can be viewed as a graphene sheet (a single layer from a 3D graphite crystal) rolled up into a cylinder, one atomic layer in thickness. Their physical properties depend on how the graphene sheet is rolled up, and from a symmetry point of view, two types of tubes can be formed, namely the achiral tubes, as shown in Fig. 9.11(a) and (b), or the chiral tubes, illustrated in Fig. 9.11(c). Because of the small diameter of a carbon nanotube ($\sim$10 Å) and the large length-to-diameter ratio ($> 10^4$), a carbon nanotube from a symmetry standpoint is a one-dimensional crystal with a translation vector $\boldsymbol{T}$ along the cylinder axis and a small number of carbon hexagons associated with the circumferential direction. For this reason, this structure is a very appropriate system to study line groups. The relation between carbon atoms on a carbon nanotube and the symmetry operations on the respective line groups is one-to-one, and nanotubes are, therefore, a prototype system for illustrating line groups [23, 24].

9.5 The Determination of Crystal Structure and Space Group

In many research situations, the researcher must first identify the crystal structure and the space group, as summarized below.

9.5.1 Determination of the Crystal Structure

The standard determinations of crystal structures are carried out using diffraction techniques, either X-ray or neutron diffraction. The elastically scattered beams give rise to a series of diffraction peaks which can be indexed according to the points in reciprocal lattice. The results of many such structural determinations for specific materials are listed in the series of books by Wyckoff [76].

We illustrate the use of Wyckoff's books to find the crystal structure of a particular material in Problem 9.6. The information to be extracted from Wyckoff's book concerns the number of allotropic structures of a given chemical species, the Wyckoff positions of the atoms within the unit cell, the site symmetries of the atoms in each of the structures and the space group designations. Such information is also available from websites [58]. Appendix C shows some illustrative crystal structures.

9.5.2 Determination of the Space Group

The International Tables for X-Ray Crystallography [58] helps with the determination of the space group and the symmetry operations of the space group[3] [58]. These volumes deal with space groups in general but do not refer to specific materials, which is the central theme of Wyckoff's books. In some cases Wyckoff's books give the space group designation, and then the listing of the Wyckoff positions needs to match up with the proper Wyckoff positions in the International Tables for X-Ray Crystallography under the appropriate space group. If the space group is not given explicitly in Wyckoff's books [76], then the space group must be found from the Crystallographic information and the Wyckoff positions. The procedure that is used to find the space group is to first find the Wyckoff positions and site symmetries as illustrated in Problems 9.4 and 9.6. Information about space groups is also available from websites [54, 58, 76].

Selected Problems

9.1. (a) For the crystal structure shown in Fig. 9.5(a) list the symmetry elements and identify the space group and give the space group number and symmetry designations for this symmorphic space group (see Table 9.1).
(b) Find the Wyckoff positions for the four atoms per unit cell and find the site symmetries for the structure shown in Fig. 9.5(a).
(c) Find χ^{equiv} for the space group in Fig. 9.5(a) and find the irreducible representations contained in Γ^{equiv}.
(d) Repeat (a), (b) and (c) for the space group in Fig. 9.5(b).

[3] International Tables for X-ray Crystallography.

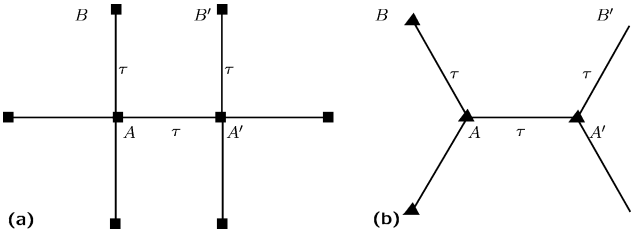


Fig. 9.12. Translation–rotation symmetry for a fourfold axis (**a**), and a threefold axis (**b**)

9.2. (a) List the real space symmetry operations of the nonsymmorphic two-dimensional square space group $p4gm$ (#12).
(b) Explain all the open and filled points, and the solid and dashed lines in the diagram for the 2D space group $p4gm$ (#12). Explain the point symmetry entries for each of the site symmetries a, b, c, d on the table for space group #12 ($p4gm$) in Table B.12 in Appendix B which was taken from the International Crystallography Tables.
(c) Explain the differences in the symmetry operations between the 2D space group #12 and the 2D space group #11. Why does the figure for group #11 have dashed lines? Why is group #12 not classified as a centered space group? Why are there no centered square 2D space groups?

9.3. Show that in the diamond structure, the product of two symmetry operations involving translations τ yields a symmetry element with no translations

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

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

9.4. Consulting Wyckoff's book "Crystal Structures" 2nd edn., Krieger (1981) for the crystal structure of Nb_3Sn, a prototype superconductor with the A–15 (or β–W) structure used for high field superconducting magnet applications:

(a) List the site locations of each atom within the unit cell of Nb_3Sn as obtained from Wyckoff's book or from another source.
(b) Identify the proper space group for Nb_3Sn and give the Wyckoff positions for each atom and its site symmetry.

9.5. To understand why fivefold symmetry does not form a Bravais lattice, consider the interplay of a fourfold or threefold axes and their translations, shown in Fig. 9.12. In general, the only acceptable values of α are those that cause BB' in Fig. 9.12 to be an integer multiple of the original translation, τ (that is we require $BB' = m\tau$, where m is an integer).

(a) By relating BB' to τ and α, show that the only values of α satisfying the restriction $BB' = m\tau$ are 0, $\pi/3$, $\pi/2$, $2\pi/3$ and π.

(b) Show schematically that in the case of fivefold symmetry, BB' gives rise to a new translation τ' in the same direction as τ, but inconsistent with the original lattice vectors coming from A. This inconsistency can also be expressed by stating that BB' violates the initial hypothesis that τ is the shortest translation in the direction BB'.

9.6. This problem provides experience with finding the Wyckoff positions for 3D graphite in the hexagonal crystal structure (see Fig. C.1 in Appendix C) and in the rhombohedral crystal structure (see Fig. C.2)

(a) From the crystal structure model, find the coordinates for the four distinct atoms per unit cell in 3D graphite and give their site symmetries.
(b) Using space group #194 (Table C.3 in Appendix C) find the Wyckoff positions and their symmetries.
(c) Explain the diagrams appearing at the top of Table C.3, especially the notation. Why are space groups #191, #192, and #193 not appropriate for describing the structure for 3D graphite (Fig. C.1)?
(d) Repeat (a) for rhombohedral graphite (Table C.4) with 6 atoms/unit cell in the hexagonal system and two atoms/unit cell in the rhombohedral system (space group #166).

9.7. Consider single wall carbon nanotubes, as presented in Sect. 9.4 and discussed in Appendix E.

(a) Find the space groups with the appropriate symmetries for the semiconducting (6,5) and the metallic (6,6) carbon nanotubes.
(b) The physical properties of carbon nanotubes can be obtained from those– of a graphene sheet by the zone-folding procedure. Using the linear-helical construction (see Appendix E), show how the allowed k vectors of a carbon nanotube can be mapped into the Brillouin zone of two-dimensional graphite, and discuss the conservation of the linear and helical quantum numbers. The diagram on the cover to this book can be very helpful for solving this problem.
(c) Find the appropriate line groups for chiral and achiral carbon nanotubes.