

1

Band Structure of Semiconductors

1.1 Crystals, Lattices, and Cells

A crystal is composed of a periodic repetition of identical groups of atoms: A group is called *basis*. The corresponding crystal lattice is obtained by replacing each group of atoms by a representative point, as shown in Fig. 1.1. A crystal can also be called *lattice with a basis*. When the basis is composed of a single atom, the corresponding lattice is called monoatomic. In a *Bravais lattice*, the position \mathbf{R} of all points in the lattice can be written as :

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \quad (1.1)$$

where \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are three noncoplanar translation vectors called the *primitive vectors*, and n_1 , n_2 , and n_3 are arbitrary (positive or negative) integers. We note that for a given Bravais lattice, the choice of the primitive vectors is not unique. The Bravais lattice looks exactly the same when viewed from any lattice point. Not only the arrangement of points but also the orientation must be exactly the same from every point in a Bravais lattice. No rotations are needed to reach each lattice point. Therefore, two points in the lattice, whose position vectors are given by \mathbf{r} and $\mathbf{r}' = \mathbf{r} + \mathbf{R}$, are completely equivalent environmentally. For example, the two-dimensional honeycomb lattice as shown in Fig. 1.2 is not a Bravais lattice. Indeed, the lattice looks the same when it is viewed from points A and C, but not when it is viewed from point B: In this case, the lattice appears rotated by 180° . We note that, for example, graphene consists of a single layer of carbon atoms arranged in a two-dimensional honeycomb structure.

A lattice can be constructed by infinite repetitions, by translations, of a single cell without any overlapping. This cell can be primitive or nonprimitive (or conventional). Primitive and conventional cells are not uniquely determined, as clearly illustrated in Fig. 1.3. The primitive cell has the minimum possible volume, given by

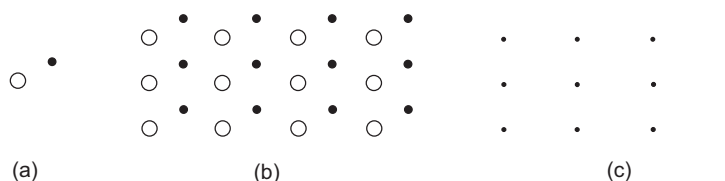


Figure 1.1

(a) Basis composed of two different atoms, (b) bidimensional crystal, and (c) corresponding lattice.

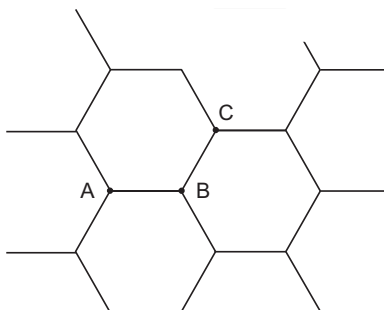


Figure 1.2 A two-dimensional honeycomb lattice is not a Bravais lattice.

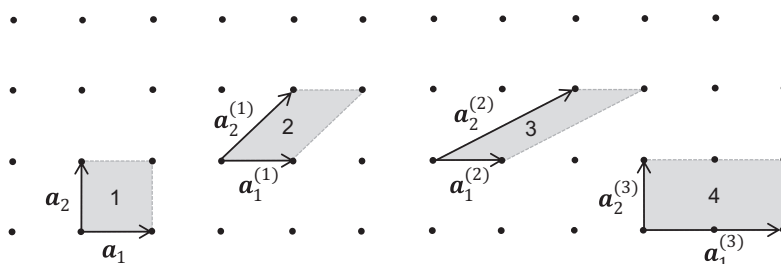


Figure 1.3 Two-dimensional lattice: cells 1, 2, and 3 are primitive cells. Cell 4 is not primitive.

$$V_u = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3), \tag{1.2}$$

and contains exactly one lattice point. Therefore, in Fig. 1.3, which refers to a two-dimensional case, the cells 1–3 are all primitive cells: They have the same area and contain $4 \cdot \frac{1}{4} = 1$ lattice point. The primitive cell contains the minimum possible number of atoms, and there is always a lattice point per primitive cell. Cell 4 is not primitive: Its area is twice the area of the primitive cell and contains $4 \cdot \frac{1}{4} + 2 \cdot \frac{1}{2} = 2$ lattice points. Not all points in the lattice are linear combinations of $\mathbf{a}_1^{(3)}$ and $\mathbf{a}_2^{(3)}$ with integral coefficients ($\mathbf{a}_1^{(3)}$ and $\mathbf{a}_2^{(3)}$ are not the primitive vectors). In some cases, it is more convenient to consider conventional unit cells, with larger volumes (integer multiple of that of the primitive cell) but characterized by the same symmetry of the lattice.

Without entering into any detail about group theory, we can say that all the possible lattice structures are determined by the symmetry group that describes their properties. A lattice structure can be transformed into itself not only by the translations described by Eq. 1.1, which define the translational group, but also by many other symmetry operations. The symmetry operations transforming a lattice into itself keeping at least one point fixed form a group called the *point group*. In the case of three-dimensional structures, the point symmetry gives rise to 14 types of lattices, which can be classified depending on the relationships between the amplitudes of the vectors \mathbf{a}_i and the angles α , β , and γ between them.

Table 1.1 The 14 lattice systems in three dimensions (the last column shows the amplitudes a_i and the angles between vectors \mathbf{a}_i of the unit cell).

System	Number of lattices	Amplitudes a_i and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

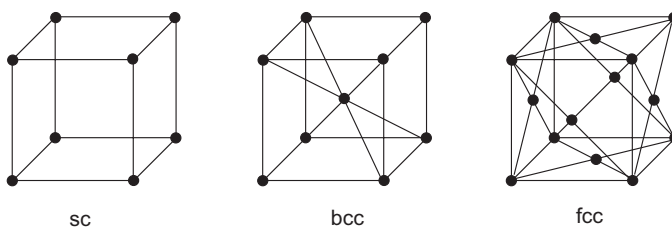


Figure 1.4 Cubic lattices: (sc) simple cubic, (bcc) body-centered cubic, and (fcc) face-centered cubic.

As reported in Table 1.1, the 14 types of lattices can be grouped in one triclinic, two monoclinic, four orthorhombic, two tetragonal, three cubic, one trigonal, and one hexagonal lattices.

Many semiconductors are characterized by a cubic lattice or by an hexagonal lattice. There are three types of cubic lattices: simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc), whose unit cells are shown in Fig. 1.4. Note that only the sc is a primitive cell, with volume a^3 and one lattice point per cell ($8 \times \frac{1}{8}$). The bcc lattice can be obtained from the sc by placing a lattice point at the center of the cube. The conventional cell is the cube with edge a . It has two lattice points per unit cell ($8 \times \frac{1}{8} + 1$). In terms of the cube edge a , a set of primitive vectors can be written as:

$$\begin{aligned}
 \mathbf{a}_1 &= \frac{a}{2}(\mathbf{u}_x + \mathbf{u}_y - \mathbf{u}_z) \\
 \mathbf{a}_2 &= \frac{a}{2}(-\mathbf{u}_x + \mathbf{u}_y + \mathbf{u}_z) \\
 \mathbf{a}_3 &= \frac{a}{2}(\mathbf{u}_x - \mathbf{u}_y + \mathbf{u}_z),
 \end{aligned}
 \tag{1.3}$$

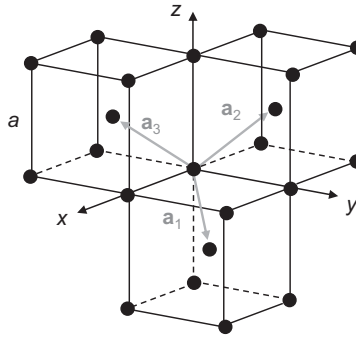


Figure 1.5 Set of primitive vectors for a body-centered cubic lattice.

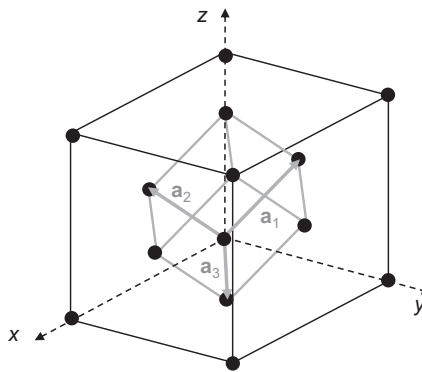


Figure 1.6 Primitive vectors and primitive cell of the face-centered cubic lattice.

where \mathbf{u}_x , \mathbf{u}_y , and \mathbf{u}_z are the unit vectors of the x , y , and z axes, as shown in Fig. 1.5. The corresponding primitive cell, with volume $a^3/2$, contains by definition only one lattice point. This primitive cell does not have an obvious relation with the point symmetry (cubic) of the lattice. For this reason, it is useful to consider a unit cell larger than the primitive cell and with the same symmetry of the crystal. For a bcc lattice, the unit cell is a cube with edge a , with a volume which is twice the volume of the primitive cell. The bcc lattice can also be considered as an sc lattice with a two-point basis $0, (a/2)(\mathbf{u}_x + \mathbf{u}_y + \mathbf{u}_z)$.

The fcc Bravais lattice can be obtained from the sc lattice by adding a point in the center of each face. The fcc structure has lattice points on the faces of the cube, so that they are shared between two cells: The total number of lattice points in the cell is $4 (8 \times \frac{1}{8} + 6 \times \frac{1}{2})$. A particular set of primitive vectors is (see Fig. 1.6):

$$\begin{aligned} \mathbf{a}_1 &= \frac{a}{2}(\mathbf{u}_y + \mathbf{u}_z) \\ \mathbf{a}_2 &= \frac{a}{2}(\mathbf{u}_z + \mathbf{u}_x) \\ \mathbf{a}_3 &= \frac{a}{2}(\mathbf{u}_x + \mathbf{u}_y). \end{aligned} \tag{1.4}$$

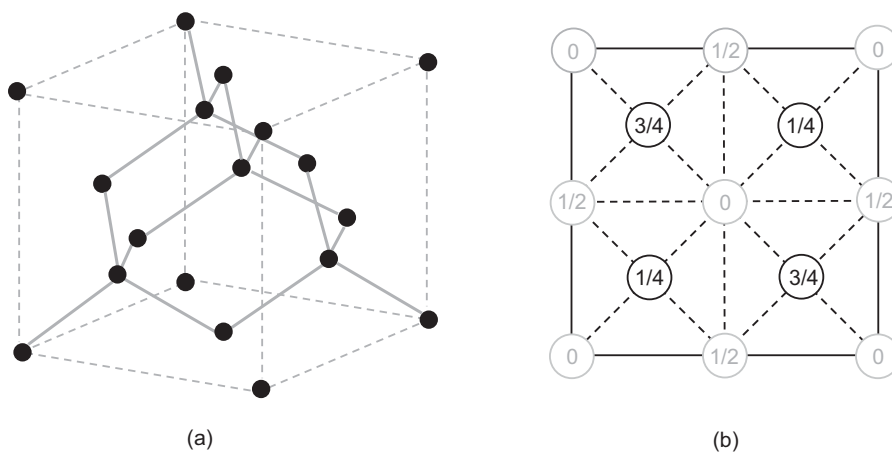


Figure 1.7

(a) Crystal structure of diamond; the solid lines show the tetrahedral bond geometry; (b) atomic position in the cubic cell projected on a cube face. The fractions correspond to the height above the cube face in the unit of the cube edge a ; the black and gray circles correspond to the two interpenetrating fcc lattices, which generate the diamond structure.

The primitive cell has a volume of $a^3/4$ and contains one lattice point. Also in this case, the unit cell is generally assumed as a cube of edge a , with a volume which is four times the volume of a primitive cell. The fcc can be described as an sc lattice with a four-point basis $0, (a/2)(\mathbf{u}_x + \mathbf{u}_y), (a/2)(\mathbf{u}_y + \mathbf{u}_z), (a/2)(\mathbf{u}_z + \mathbf{u}_x)$. We recall that the numbers giving the size of the unit cell (e.g., the number a in the case of a cubic crystal) are called the lattice constants.

Many important semiconductors, for example, silicon and germanium, have a *diamond structure*, which is the lattice formed by the carbon atoms in a diamond crystal. This structure consists of identical atoms that occupy the lattice points of two interpenetrating fcc lattices, which are displaced from each other along the body diagonal of the cubic cell by one quarter the length of the diagonal, as shown in Fig. 1.7. It can be seen as an fcc lattice with a two-point basis $0, (a/4)(\mathbf{u}_x + \mathbf{u}_y + \mathbf{u}_z)$. The four nearest neighbors of each point are on the vertices of a regular tetrahedron. Note that the diamond lattice is not a Bravais lattice, since it does not look exactly the same when it is viewed from the two nearest-neighbor points. Since the unit cell of an fcc structure contains four lattice points, the unit cell of the diamond structure contains eight lattice points. In this case, it is not possible to choose a primitive cell in such a way that the basis of diamond contains only one atom. When the atoms that occupy one of the two fcc structures are different from the atoms occupying the other, the structure is called the *zinc-blende* structure. Several semiconductors are characterized by this structure, such as GaAs, AlAs, and many others.

Largely used semiconductors, such as GaN, AlN, BN, and SiC, have a hexagonal close-packet (hcp) structure (wurtzite structure) as shown in Fig. 1.8. Also, the hcp lattice is not a Bravais lattice. This lattice can be seen as two interpenetrating simple hexagonal Bravais lattices, displaced vertically by $c/2$ in the direction of the common c -axis and displaced

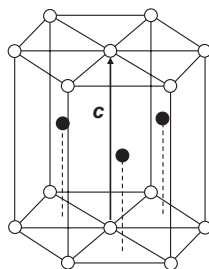


Figure 1.8 Atomic position in the hcp lattice.

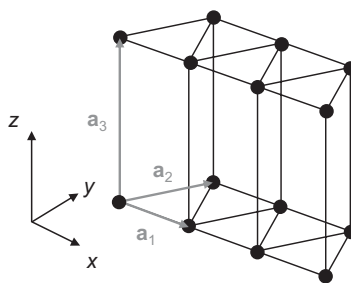


Figure 1.9 Simple hexagonal Bravais lattice.

in the horizontal plane in such a way that the points of one simple hexagonal lattice are placed above the centers of the triangles formed by the points of the other simple hexagonal lattice. Figure 1.9 shows a simple hexagonal Bravais lattice, which is obtained by stacking two-dimensional triangular Bravais lattices – one exactly above the other along a direction perpendicular to each two-dimensional lattice. This stacking direction is usually called the crystallographic c -axis. The primitive vectors can be written as:

$$\begin{aligned}
 \mathbf{a}_1 &= a\mathbf{u}_x \\
 \mathbf{a}_2 &= \frac{a}{2}\mathbf{u}_x + \frac{\sqrt{3}}{2}a\mathbf{u}_y \\
 \mathbf{a}_3 &= c\mathbf{u}_z.
 \end{aligned} \tag{1.5}$$

1.1.1 The Wigner–Seitz Cell

The primitive cell can also be chosen in such a way that it presents the full symmetry of the Bravais lattice. This can be achieved by considering the Wigner–Seitz cell. The mathematical definition is as follows: The Wigner–Seitz cell around a given lattice point is the spatial region that is closer to that particular lattice point than to any other lattice points. It can also be demonstrated that the Wigner–Seitz cell is a primitive cell. While for any given lattice there is an infinite number of possible primitive cells, there is only one Wigner–Seitz cell. The above definition does not refer to any particular choice of primitive

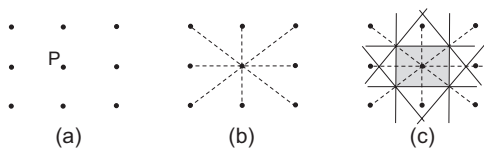


Figure 1.10 Construction of the Wigner–Seitz cell of a two-dimensional rectangular lattice.

vectors; for this reason, the Wigner–Seitz cell is as symmetrical as the Bravais lattice. The procedure for the construction of a Wigner–Seitz cell can be illustrated in the simple case of a two-dimensional rectangular lattice, as shown in Fig. 1.10(a). To determine the Wigner–Seitz cell about the lattice point P , we have first to draw the lines from P to all of its nearest neighbors (Fig. 1.10(b)) and then the bisectors to each of these lines (Fig. 1.10(c)). The Wigner–Seitz cell is the innermost region bounded by the perpendicular bisectors, as shown by the shaded region in Fig. 1.10(c). The same procedure can be applied in the case of a generic three-dimensional lattice.

1.2 The Reciprocal Lattice

In order to develop an analytic study of a crystalline solid, it is often useful to introduce the concept of a reciprocal lattice, which basically represents the Fourier transform of the Bravais lattice. The reciprocal lattice of the reciprocal lattice is the direct lattice. The reciprocal lattice provides a simple and useful basis for analyzing processes characterized by a “wave nature” in crystals, like the behavior of electrons and lattice vibrations, or the geometry of X-ray and electron diffraction patterns. Assuming a Bravais lattice defined by the primitive translation vectors $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, the reciprocal lattice can be defined by introducing its primitive translation vectors $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ in analogy with the lattice in a real space. The axis vectors of the reciprocal space can be written as:

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{V_u} \mathbf{a}_2 \times \mathbf{a}_3 \\ \mathbf{b}_2 &= \frac{2\pi}{V_u} \mathbf{a}_3 \times \mathbf{a}_1 \\ \mathbf{b}_3 &= \frac{2\pi}{V_u} \mathbf{a}_1 \times \mathbf{a}_2, \end{aligned} \quad (1.6)$$

where V_u is the volume of the unit cell given by:

$$V_u = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3). \quad (1.7)$$

The reciprocal lattice can be mapped by using the general translation vector \mathbf{G} given by:

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3, \quad (1.8)$$

where m_1 , m_2 , and m_3 are integers. Vector \mathbf{G} is called the reciprocal lattice vector. Note that each vector given by Eq. 1.6 is orthogonal to two-axis vectors of the crystal lattice, so that:

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}, \quad (1.9)$$

where δ_{ij} is the Kronecker delta symbol: $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$, for $i = j$. Moreover,

$$\mathbf{G} \cdot \mathbf{R} = 2\pi(n_1m_1 + n_2m_2 + n_3m_3) = 2\pi\ell, \quad \ell = 0, \pm 1, \pm 2, \dots, \quad (1.10)$$

so that:

$$\exp(i\mathbf{G} \cdot \mathbf{R}) = 1. \quad (1.11)$$

Any function $f(\mathbf{r})$ with the periodicity of the crystal lattice, that is, $f(\mathbf{r} + \mathbf{R}) = f(\mathbf{r})$, can be expanded as:

$$f(\mathbf{r}) = \sum_{\mathbf{G}} f_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (1.12)$$

where:

$$f_{\mathbf{G}} = \frac{1}{V_u} \int_{cell} f(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} d\mathbf{r}. \quad (1.13)$$

While vectors in the direct lattice have the dimension of length, the vectors in the reciprocal lattice have the dimension of $[\text{length}]^{-1}$. The reciprocal space is therefore the most convenient space for the wave vector \mathbf{k} . Since each point in the reciprocal space can be reached by the translation vector \mathbf{G} , it is evident that we can restrict our analysis to a unit cell defined by the vector \mathbf{b}_i . The Wigner–Seitz cell of the reciprocal lattice is called the *first Brillouin zone*. There are also the second, third, etc. Brillouin zones, at an increasing distance from the origin, all with the same volume. These higher order Brillouin zones can be translated into the first zone by adding suitable translation vector \mathbf{G} . A Wigner–Seitz cell in the reciprocal space can be constructed following the same procedure used in the real space. For example, in the simple case of a linear lattice, we have a single primitive vector in the direct space: $\mathbf{a}_1 = a\mathbf{u}_x$. From Eq. 1.9, it is obvious that the primitive vector in the reciprocal space is:

$$\mathbf{b}_1 = \frac{2\pi}{a}\mathbf{u}_x. \quad (1.14)$$

The corresponding translation vector is given by:

$$\mathbf{G} = m\frac{2\pi}{a}\mathbf{u}_x, \quad m = \pm 1, \pm 2, \dots \quad (1.15)$$

Following the rules for the construction of the first Brillouin zone, we have that this region extends from $k = -\pi/a$ to $k = \pi/a$.

Following the same procedure, it is possible to construct the first Brillouin zone for three-dimensional structures. For a sc lattice, where:

$$\mathbf{a}_1 = a\mathbf{u}_x, \quad \mathbf{a}_2 = a\mathbf{u}_y, \quad \mathbf{a}_3 = a\mathbf{u}_z, \quad (1.16)$$

by using Eq. 1.6, where $V_u = a^3$:

$$\mathbf{b}_1 = \frac{2\pi}{a}\mathbf{u}_x, \quad \mathbf{b}_2 = \frac{2\pi}{a}\mathbf{u}_y, \quad \mathbf{b}_3 = \frac{2\pi}{a}\mathbf{u}_z. \quad (1.17)$$

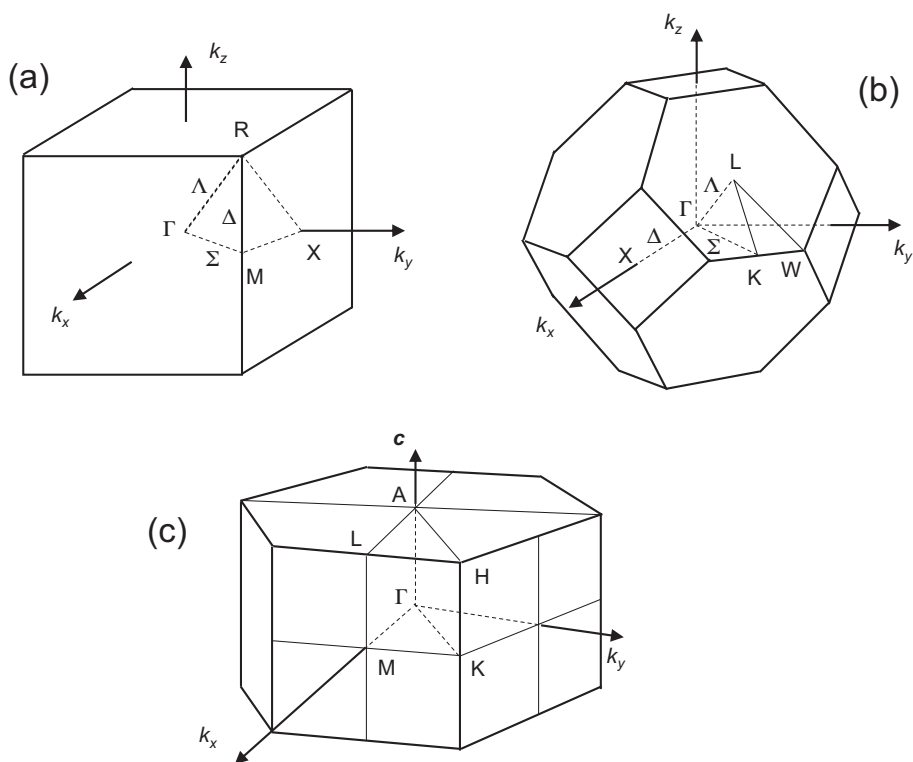


Figure 1.11 First Brillouin zone for (a) the sc lattice, (b) the fcc lattice, which forms the underlying Bravais lattice for the diamond and zinc-blende structures, and (c) the hexagonal wurtzite structure. Reported are the names of points and directions of high symmetry.

Therefore, the reciprocal lattice of an sc lattice with cubic primitive cell of edge a is an sc lattice with a cubic primitive cell of edge $2\pi/a$, and the first Brillouin zone is defined as follows:

$$-\frac{\pi}{a} \leq k_i \leq \frac{\pi}{a}, \quad i = x, y, z. \quad (1.18)$$

This is shown in Fig. 1.11(a). The center of the first Brillouin zone is always called the Γ -point. A typical convention is to call high-symmetry points and directions inside the Brillouin zone by Greek letters and high-symmetry points on the surfaces of the Brillouin zone by roman letters. For example, in the case of the fcc structure (see Fig. 1.11(b)), the three high-symmetry directions $[100]$, $[110]$, and $[111]$ are denoted by:

$$\begin{aligned} [100] \text{ direction: } & \overline{\Gamma} \overline{\Delta} \overline{X} \\ [111] \text{ direction: } & \overline{\Gamma} \overline{\Lambda} \overline{L} \\ [110] \text{ direction: } & \overline{\Gamma} \overline{\Sigma} \overline{K}. \end{aligned}$$

The X -point at $(2\pi/a)(1,0,0)$ identifies the zone edge along the six equivalent $[100]$ directions. The L -point is at $(\pi/a)(1,1,1)$, and it is at the zone edge along the eight equivalent $[111]$ directions.

1.3 Electrons in a Periodic Crystal

After this brief overview of introductory concepts of solid-state physics, we will study the interactions of electrons with a periodic structure. We will consider bulk semiconductors, that is, semiconductors with spatial dimensions much larger than the de Broglie wavelength ($\lambda_B = h/p$, where p is the particle momentum) of the electrons involved in the interaction. In order to study the electronic and optical properties of the crystal, we have first to calculate the electronic wavefunctions and their energies inside the crystal. The system is described by the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_0} \nabla^2 + U(\mathbf{r}) \right] \psi(\mathbf{r}) = \mathcal{E} \psi(\mathbf{r}), \quad (1.19)$$

where $U(\mathbf{r})$ is a periodic potential due to the atoms periodically placed in the crystal lattice and to all interaction potentials between electrons. As a consequence of the crystal structure, $U(\mathbf{r})$ has the same periodicity of the lattice:

$$U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}), \quad (1.20)$$

where \mathbf{R} is a translation vector of the crystal, given by Eq. 1.1. We recall that in vacuum, where $U(\mathbf{r}) = 0$, the stationary wavefunctions of the free electrons in a volume V are given by:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}},$$

delocalized over all the space with uniform probability density, \mathbf{k} is the wavevector. The electron momentum and energy are given by the following expressions:

$$\mathbf{p} = \hbar\mathbf{k}, \quad \mathcal{E} = \frac{\hbar^2 k^2}{2m_0}, \quad (1.21)$$

where m_0 is the free electron mass. It is possible to demonstrate that the solutions of the Schrödinger equation for a periodic potential are *Bloch–Floquet* (or simply Bloch) *functions* so that (*Bloch’s theorem*):

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (1.22)$$

where $u_{n\mathbf{k}}(\mathbf{r})$ has the same periodicity of the crystal:

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}), \quad (1.23)$$

\mathbf{k} is the wave vector, and n refers to the band (as will be discussed in this chapter). The Bloch functions are the product of a plane wave and a function $u_{n\mathbf{k}}(\mathbf{r})$, with the lattice periodicity. It is evident that the Bloch wavefunction is not periodic; indeed,

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \psi_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{R}}, \quad (1.24)$$

while the electron probability density is periodic:

$$|\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})|^2 = |\psi_{n\mathbf{k}}(\mathbf{r})|^2. \quad (1.25)$$