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Peter Y. Yu
Manuel Cardona

Fundamentals of Semiconductors

Physics and Materials Properties

Fourth Edition

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Series Editors

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Boston University
Center for Polymer Studies
Department of Physics
590 Commonwealth Avenue, Room 204B
Boston, MA 02215, USA
E-mail: hes@bu.edu

Professor William T. Rhodes
Georgia Institute of Technology
School of Electrical and Computer Engineering
Atlanta, GA 30332-0250, USA
E-mail: bill.rhodes@ece.gatech.edu

Peter Y. Yu
Manuel Cardona

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Professor Dr. Peter Y. Yu
University of California
Department of Physics
Berkeley, CA 94720-7300, USA
E-mail: pyyu@lbl.gov

Professor Dr., Dres. h.c. Manuel Cardona
Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1, 70569 Stuttgart, Germany
E-mail: cardona@cardix.mpi-stuttgart.mpg.de

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1. Introduction

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In textbooks on solid-state physics, a **semiconductor** is usually defined rather loosely as a material with electrical resistivity lying in the range of $10^{-2} - 10^{9}\ \Omega\,\text{cm}$.[1] Alternatively, it can be defined as a material whose **energy gap** (to be defined more precisely in Chap. 2) for electronic excitations lies between zero and about 4 electron volts (eV). Materials with zero bandgap are metals or semimetals, while those with an energy gap larger than 3 eV are more frequently known as insulators. There are exceptions to these definitions. For example, terms such as semiconducting diamond (whose energy gap is about 6 eV) and semi-insulating GaAs (with a 1.5 eV energy gap) are frequently used. GaN, which is receiving a lot of attention as optoelectronic material in the blue region, has a gap of 3.5 eV.

The best-known semiconductor is undoubtedly **silicon** (Si). However, there are many semiconductors besides silicon. In fact, many minerals found in nature, such as zinc-blende (ZnS) cuprite (Cu_2O) and galena (PbS), to name just a few, are semiconductors. Including the semiconductors synthesized in laboratories, the family of semiconductors forms one of the most versatile class of materials known to man.

Semiconductors occur in many different chemical compositions with a large variety of crystal structures. They can be elemental semiconductors, such as Si, carbon in the form of C_{60} or nanotubes and selenium (Se) or binary compounds such as gallium arsenide (GaAs). Many organic compounds, e. g. polyacetylene $(CH)_n$, are semiconductors. Some semiconductors exhibit magnetic ($Cd_{1-x}Mn_xTe$) or ferroelectric (SbSI) behavior. Others become superconductors when doped with sufficient carriers (GeTe and $SrTiO_3$). Many of the recently discovered high-T_c superconductors have nonmetallic phases which are semiconductors. For example, La_2CuO_4 is a semiconductor (gap $\simeq 2$ eV) but becomes a superconductor when alloyed with Sr to form $(La_{1-x}Sr_x)_2CuO_4$.

[1] Ω cm is a "hybrid" SI and cgs resistivity unit commonly used in science and engineering. The SI unit for resistivity should be Ω m

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1.1 A Survey of Semiconductors

The following is a brief survey of several types of the better-known semiconductors.

1.1.1 Elemental Semiconductors

The best-known semiconductor is of course the element Si. Together with germanium (Ge), it is the prototype of a large class of semiconductors with similar crystal structures. The crystal structure of Si and Ge is the same as that of diamond and α-tin (a zero-gap semiconductor also known as "gray" tin). In this structure each atom is surrounded by four nearest neighbor atoms (each atom is said to be **four-fold coordinated**), forming a tetrahedron. These **tetrahedrally bonded** semiconductors form the mainstay of the electronics industry and the cornerstone of modern technology. Most of this book will be devoted to the study of the properties of these tetrahedrally bonded semiconductors. Some elements from the groups V and VI of the periodical table, such as phosphorus (P), sulfur (S), selenium (Se) and tellurium (Te), are also semiconductors. The atoms in these crystals can be three-fold (P), two-fold (S, Se, Te) or four-fold coordinated. As a result, these elements can exist in several different crystal structures and they are also good glass-formers. For example, Se has been grown with monoclinic and trigonal crystal structures or as a glass (which can also be considered to be a polymer).

1.1.2 Binary Compounds

Compounds formed from elements of the groups III and V of the periodic table (such as GaAs) have properties very similar to their group IV counterparts. In going from the group IV elements to the III–V compounds, the bonding becomes partly ionic due to transfer of electronic charge from the group III atom to the group V atom. The ionicity causes significant changes in the semiconductor properties. It increases the Coulomb interaction between the ions and also the energy of the fundamental gap in the electronic band structure. The ionicity becomes even larger and more important in the II–VI compounds such as ZnS. As a result, most of the II–VI compound semiconductors have bandgaps larger than 1 eV. The exceptions are compounds containing the heavy element mercury (Hg). Mercury telluride (HgTe) is actually a zero-bandgap semiconductor (or a semimetal) similar to gray tin. While the large bandgap II–VI compound semiconductors have potential applications for displays and lasers, the smaller bandgap II–VI semiconductors are important materials for the fabrication of infrared detectors. The I–VII compounds (e. g., CuCl) tend to have even larger bandgaps ($>$3 eV) as a result of their higher

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ionicity. Many of them are regarded as insulators rather than semiconductors. Also, the increase in the cohesive energy of the crystal due to the Coulomb interaction between the ions favors the rock-salt structure containing six-fold coordinated atoms rather than tetrahedral bonds. Binary compounds formed from group IV and VI elements, such as lead sulfide (PbS), PbTe and tin sulfide (SnS), are also semiconductors. The large ionicity of these compounds also favors six-fold coordinated ions. They are similar to the mercury chalcogenides in that they have very small bandgaps in spite of their large ionicity. These small bandgap IV–VI semiconductors are also important as infrared detectors. GaN, a large bandgap III–V compound, and the mixed crystals $Ga_{1-x}In_xN$ are being used for blue light emitting diodes and lasers [1.1].

1.1.3 Oxides

Although most oxides are good insulators, some, such as CuO and Cu_2O, are well-known semiconductors. Since cuprous oxide (Cu_2O) occurs as a mineral (cuprite), it is a classic semiconductor whose properties have been studied extensively. In general, oxide semiconductors are not well understood with regard to their growth processes, so they have limited potential for applications at present. One exception is the II–VI compound zinc oxide (ZnO), which has found application as a transducer and as an ingredient of adhesive tapes and sticking plasters. However, this situation has changed with the discovery of superconductivity in many oxides of copper.

The first member of these so-called high-T_c superconductors, discovered by Müller and Bednorz[2], is based on the semiconductor lanthanum copper oxide (La_2CuO_4), which has a bandgap of about 2 eV. Carriers in the form of holes are introduced into La_2CuO_4 when trivalent lanthanum (La) is replaced by divalent barium (Ba) or strontium (Sr) or when an excess of oxygen is present. When sufficient carriers are present the semiconductor transforms into a superconducting metal. So far the highest superconducting transition temperature at ambient pressure ($T_c \simeq 135$ K) found in this family of materials belongs to $HgBaCa_2Cu_3O_{8+\delta}$. $HgBaCa_2Cu_3O_{8+\delta}$ reaches a $T_c \simeq 164$ K under high pressure [1.2]. At the time this third edition went into print this record had not yet been broken.

1.1.4 Layered Semiconductors

Semiconducting compounds such as lead iodide (PbI_2), molybdenum disulfide (MoS_2) and gallium selenide (GaSe) are characterized by their layered crystal structures. The bonding within the layers is typically covalent and much stronger than the van der Waals forces between the layers. These layered semiconductors have been of interest because the behavior of electrons in the layers is quasi-two-dimensional. Also, the interaction between layers can be mod-

[2] For this discovery, Bednorz and Müller received the Physics Nobel Prize in 1987.

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ified by incorporating foreign atoms between the layers in a process known as intercalation.

1.1.5 Organic Semiconductors

Many organic compounds such as polyacetylene $[(CH_2)_n]$ and polydiacetylene are semiconductors. Although organic semiconductors are not yet used in any electronic devices, they hold great promise for future applications. The advantage of organic over inorganic semiconductors is that they can be easily tailored to the applications. For example, compounds containing conjugate bonds such as –C=C–C= have large optical nonlinearities and therefore may have important applications in opto-electronics. The bandgaps of these compounds can be changed more easily than those of inorganic semiconductors to suit the application by changing their chemical formulas. Recently new forms of carbon, such as C_{60} (fullerene), have been found to be semiconductors. One form of carbon consists of sheets of graphite rolled into a tube of some nanometers in diameter known as *nanotubes* [1.3,4]. These carbon nanotubes and their "cousin", BN nanotubes, hold great promise as nanoscale electronic circuit elements. They can be metals or semiconductors depending on their pitch.

1.1.6 Magnetic Semiconductors

Many compounds containing magnetic ions such as europium (Eu) and manganese (Mn), have interesting semiconducting and magnetic properties. Examples of these magnetic semiconductors include EuS and alloys such as $Cd_{1-x}Mn_xTe$. Depending on the amount of the magnetic ion in these alloys, the latter compounds exhibit different magnetic properties such as ferromagnetism and antiferromagnetism. The magnetic alloy semiconductors containing lower concentrations of magnetic ions are known as dilute magnetic semiconductors. These alloys have recently attracted much attention because of their potential applications. Their Faraday rotations can be up to six orders of magnitude larger than those of nonmagnetic semiconductors. As a result, these materials can be used as optical modulators, based on their large magneto-optical effects. The perovskites of the type $Mn_{0.7}Ca_{0.3}O_3$ undergo metal–semiconductor transitions which depend strongly on magnetic field, giving rise to the phenomenon of **collossal magneto-resistance** (CMR) [1.5].

1.1.7 Other Miscellaneous Semiconductors

There are many semiconductors that do not fall into the above categories. For example, SbSI is a semiconductor that exhibits ferroelectricity at low temperatures. Compounds with the general formula I–III–VI_2 and II–IV–V_2 (such as $AgGaS_2$, interesting for its nonlinear optical properties, $CuInSe_2$, useful for solar cells, and $ZnSiP_2$) crystallize in the chalcopyrite structure. The bonding in these compounds is also tetrahedral and they can be considered as analogs

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of the group III–V and II–VI semiconductors with the zinc-blende structure. Compounds formed from the group V and VI elements with formulas such as As_2Se_3 are semiconductors in both the crystalline and glassy states. Many of these semiconductors have interesting properties but they have not yet received much attention due to their limited applications. Their existence shows that the field of semiconductor physics still has plenty of room for growth and expansion.

1.2 Growth Techniques

One reason why semiconductors have become the choice material for the electronics industry is the existence of highly sophisticated growth techniques. Their industrial applications have, in turn, led to an increased sophistication of these techniques. For example, Ge single crystals are nowadays amongst the purest elemental materials available as a result of years of perfecting their growth techniques (see Appendix by E.E. Haller in p. 555). It is now possible to prepare almost isotopically pure Ge crystals (natural Ge contains five different isotopes). Nearly perfect single crystals of Si can be grown in the form of ingots over twelve inches (30 cm) in diameter. Isotopically pure ^{28}Si crystals have been shown to have considerably higher thermal conductivity than their natural Si counterparts [1.6]. **Dislocation** densities in these crystals can be as low as 1000 cm^{-3}, while impurity concentrations can be less than one part per trillion (10^{12}).

More recent developments in crystal growth techniques have made semiconductors even more versatile. Techniques such as Molecular Beam Epitaxy (MBE) and Metal-Organic Chemical Vapor Deposition (MOCVD) allow crystals to be deposited on a substrate one monolayer at a time with great precision. These techniques have made it possible to synthesize artificial crystal structures known as **superlattices** and **quantum wells** (Chap. 9). A recent advance in fabricating low-dimensional nanostructures takes advantage of either alignment of atoms with the substrate or strain between substrate and epilayer to induce the structure to *self-organize* into superlattices or quantum dots. Although a detailed discussion of all the growth techniques is beyond the scope of this book, a short survey of the most common techniques will provide background information necessary for every semiconductor physicist. The references given for this chapter provide further background material for the interested reader.

1.2.1 Czochralski Method

The Czochralski method is the most important method for growing **bulk** crystals of semiconductors, including Si. The method involves melting the raw ma-

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2. Electronic Band Structures

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The property which distinguishes semiconductors from other materials concerns the behavior of their electrons, in particular the existence of gaps in their electronic excitation spectra. The microscopic behavior of electrons in a solid is most conveniently specified in terms of the electronic band structure. The purpose of this chapter is to study the band structure of the most common semiconductors, namely, Si, Ge, and related III–V compounds. We will begin with a quick introduction to the quantum mechanics of electrons in a crystalline solid.

The properties of electrons in a solid containing 10^{23} atoms/cm^3 are very complicated. To simplify the formidable task of solving the wave equations for the electrons, it is necessary to utilize the translational and rotational symmetries of the solid. **Group theory** is the tool that facilitates this task. However, not everyone working with semiconductors has a training in group theory, so in this chapter we will discuss some basic concepts and notations of group theory. Our approach is to introduce the ideas and results of group theory when applied to semiconductors without presenting the rigorous proofs. We will put particular emphasis on notations that are often found in books and research articles on semiconductors. In a sense, band structure diagrams are like maps and the group theory notations are like symbols on the map. Once the meaning of these symbols is understood, the band structure diagrams can be used to find the way in exploring the electronic properties of semiconductors.

We will also examine several popular methods of band structure computation for semiconductors. All band structure computation techniques involve approximations which tend to emphasize some aspects of the electronic prop-

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We should remember that each eigenstate can only accommodate up to two electrons of opposite spin (**Pauli's exclusion principle**).

The calculation of the electronic energies E_n involves two steps. The first step is the determination of the one-electron potential $V(\boldsymbol{r})$. Later in this chapter we will discuss the various ways to calculate or determine $V(\boldsymbol{r})$. In one method $V(\boldsymbol{r})$ can be calculated from *first principles* with the atomic numbers and positions as the only input parameters. In simpler, so-called semi-empirical approaches, the potential is expressed in terms of parameters which are determined by fitting experimental results. After the potential is known, it takes still a complicated calculation to solve (2.4). It is often convenient to utilize the symmetry of the crystal to simplify this calculation. Here by "symmetry" we mean geometrical transformations which leave the crystal unchanged.

2.2 Translational Symmetry and Brillouin Zones

The most important symmetry of a crystal is its invariance under specific translations. In addition to such **translational symmetry** most crystals possess some **rotational** and **reflection** symmetries. It turns out that most semiconductors have high degrees of rotational symmetry which are very useful in reducing the complexity of calculating their energy band structures. In this and the next sections we will study the use of symmetry to simplify the classification of electronic states. Readers familiar with the application of group theory to solids can omit these two sections.

When a particle moves in a periodic potential its wavefunctions can be expressed in a form known as **Bloch functions**. To understand what Bloch functions are, we will assume that (2.4) is one-dimensional and $V(x)$ is a periodic function with the translational period equal to R. We will define a **translation operator** T_R as an operator whose effect on any function $f(x)$ is given by

$$T_R f(x) = f(x + R). \tag{2.5}$$

Next we introduce a function $\Phi_k(x)$ defined by

$$\Phi_k(x) = \exp(\mathrm{i}kx)u_k(x), \tag{2.6}$$

where $u_k(x)$ is a periodic function with the same periodicity as V, that is, $u_k(x + nR) = u_k(x)$ for all integers n. When $\Phi_k(x)$ so defined is multiplied by $\exp[-\mathrm{i}\omega t]$, it represents a plane wave whose amplitude is modulated by the periodic function $u_k(x)$. $\Phi_k(x)$ is known as a Bloch function. By definition, when x changes to $x + R$, $\Phi_k(x)$ must change in the following way

$$T_R\Phi_k(x) = \Phi_k(x + R) = \exp(\mathrm{i}kR)\Phi_k(x). \tag{2.7}$$

It follows from (2.7) that $\Phi_k(x)$ is an eigenfunction of T_R with the eigenvalue $\exp(\mathrm{i}kR)$. Since the Hamiltonian $\mathcal{H}_{1e}$ is invariant under translation by R, $\mathcal{H}_{1e}$ commutes with T_R. Thus it follows from quantum mechanics that the

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eigenfunctions of $\mathcal{H}_{1e}$ can be expressed also as eigenfunctions of T_R. We therefore conclude that an eigenfunction $\Phi(x)$ of $\mathcal{H}_{1e}$ can be expressed as a sum of Bloch functions:

$$\Phi(x) = \sum_k A_k \Phi_k(x) = \sum_k A_k \exp(\mathrm{i}kx) u_k(x), \tag{2.8}$$

where the A_k are constants. Thus the one-electron wavefunctions can be indexed by constants k, which are the **wave vectors** of the plane waves forming the "backbone" of the Bloch function. A plot of the electron energies in (2.4) versus k is known as the **electronic band structure** of the crystal.

The band structure plot in which k is allowed to vary over all possible values is known as the **extended zone scheme**. From (2.6) we see that the choice of k in indexing a wave function is not unique. Both k and $k + (2n\pi/R)$, where n is any integer, will satisfy (2.6). This is a consequence of the translation symmetry of the crystal. Thus another way of choosing k is to replace k by $k' = k - (2n\pi/R)$, where n is an integer chosen to limit k' to the interval $[-\pi/R, \pi/R]$. The region of k-space defined by $[-\pi/R, \pi/R]$ is known as the **first Brillouin zone**. A more general definition of Brillouin zones in three dimensions will be given later and can also be found in standard textbooks [2.2]. The band structure plot resulting from restricting the wave vector k to the first Brillouin zone is known as the **reduced zone scheme**. In this scheme the wave functions are indexed by an integer n (known as the **band index**) and a wave vector k restricted to the first Brillouin zone.

In Fig. 2.1 the band structure of a "nearly free" electron (i. e., $V \to 0$) moving in a one-dimensional lattice with lattice constant a is shown in both schemes for comparison. Band structures are plotted more compactly in the reduced zone scheme. In addition, when electrons make a transition from one state to another under the influence of a translationally invariant operator, k is conserved in the process within the reduced zone scheme (the proof of this

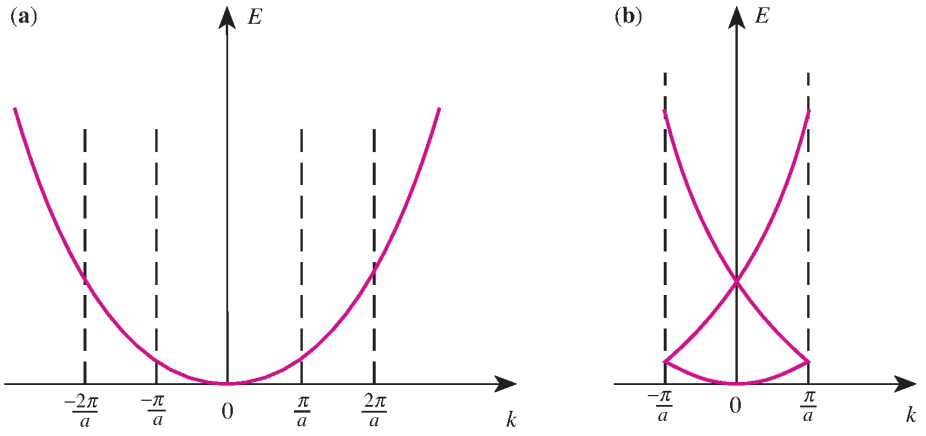


Fig. 2.1. The band structure of a free particle shown in (**a**) the extended zone scheme and (**b**) the reduced zone scheme

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statement will be presented when matrix elements of operators in crystals are discussed, Sect. 2.3), whereas in the extended zone scheme k is conserved only to a multiple of (i. e. *modulo*) $2\pi/R$. Hence, the reduced zone scheme is almost invariably used in the literature.

The above results, obtained in one dimension, can be easily generalized to three dimensions. The translational symmetries of the crystal are now expressed in terms of a set of **primitive lattice vectors**: $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$. We can imagine that a crystal is formed by taking a minimal set of atoms (known as a **basis set**) and then translating this set by multiples of the primitive lattice vectors and their linear combinations. In this book we will be mostly concerned with the diamond and zinc-blende crystal structures, which are shown in Fig. 2.2a. In both crystal structures the basis set consists of two atoms. The ba-

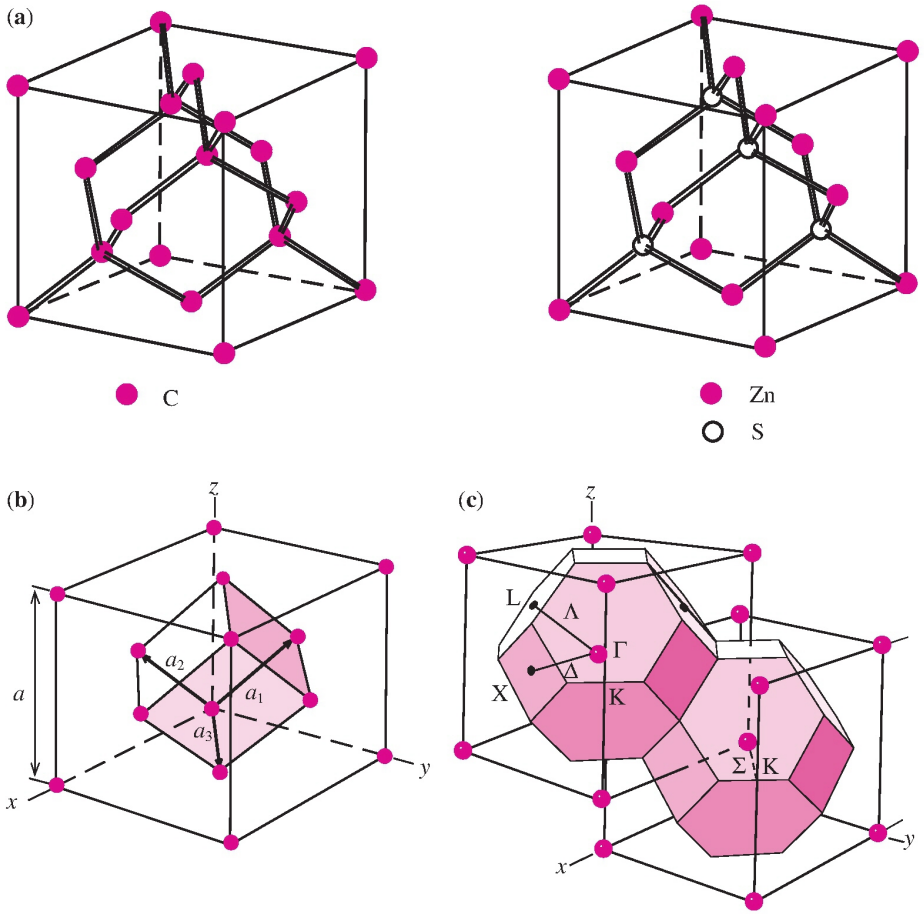


Fig. 2.2. (**a**) The crystal structure of diamond and zinc-blende (ZnS). (**b**) the fcc lattice showing a set of primitive lattice vectors. (**c**) The reciprocal lattice of the fcc lattice shown with the first Brillouin zone. Special high-symmetry points are denoted by Γ, X, and L, while high-symmetry lines joining some of these points are labeled as Λ and Δ

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sis set in diamond consists of two carbon atoms while in zinc-blende the two atoms are zinc and sulfur. The lattice of points formed by translating a point by multiples of the primitive lattice vectors and their linear combinations is known as the **direct lattice**. Such lattices for the diamond and zinc-blende structures, which are basically the same, are said to be **face-centered cubic** (fcc) see Fig. 2.2b with a set of primitive lattice vectors. In general, the choice of primitive lattice vectors for a given direct lattice is not unique. The primitive lattice vectors shown in Fig. 2.2b are

$$\boldsymbol{a}_1 = (0, a/2, a/2),$$
$$\boldsymbol{a}_2 = (a/2, 0, a/2),$$

and

$$\boldsymbol{a}_3 = (a/2, a/2, 0),$$

where a is the length of the side of the smallest cube in the fcc lattice. This smallest cube in the direct lattice is also known as the unit cube or the **crystallographic unit cell**.

For a given direct lattice we can define a **reciprocal lattice** in terms of three **primitive reciprocal lattice vectors**: $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, and $\boldsymbol{b}_3$, which are related to the direct lattice vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$ by

$$\boldsymbol{b}_i = 2\pi \frac{(\boldsymbol{a}_j \times \boldsymbol{a}_k)}{(\boldsymbol{a}_1 \times \boldsymbol{a}_2) \cdot \boldsymbol{a}_3}, \tag{2.9}$$

where i, j, and k represent a cyclic permutation of the three indices 1, 2, and 3 and $(\boldsymbol{a}_1 \times \boldsymbol{a}_2) \cdot \boldsymbol{a}_3$ is the volume of the primitive cell. The set of points generated by translating a point by multiples of the reciprocal lattice vectors is known as the reciprocal lattice. The reason for defining a reciprocal lattice in this way is to represent the wave vector $\boldsymbol{k}$ as a point in **reciprocal lattice space**. The first Brillouin zone in three dimensions can be defined as the smallest polyhedron confined by planes perpendicularly bisecting the reciprocal lattice vectors. It is easy to see that the region $[-\pi/R, \pi/R]$ fits the definition of the first Brillouin zone in one dimension.

Since the reciprocal lattice vectors are obtained from the direct lattice vectors via (2.9), the symmetry of the Brillouin zone is determined by the symmetry of the crystal lattice. The reciprocal lattice corresponding to a fcc lattice is shown in Fig. 2.2c. These reciprocal lattice points are said to form a **body-centered cubic** (bcc) lattice. The primitive reciprocal lattice vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, and $\boldsymbol{b}_3$ as calculated from (2.9) are

$$\boldsymbol{b}_1 = (2\pi/a)\ (-1, 1, 1),$$

$$\boldsymbol{b}_2 = (2\pi/a)\ (1, -1, 1),$$

and

$$\boldsymbol{b}_3 = (2\pi/a)\ (1, 1, -1).$$

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[Incidentally, note that all the reciprocal lattice vectors of the fcc lattice have the form $(2\pi/a)(i,j,k)$, where i, j, and k have to be either all odd or all even]. The first Brillouin zone of the fcc structure is also indicated in Fig. 2.2c. The symmetry of this Brillouin zone can be best visualized by constructing a model out of cardboard. A template for this purpose can be found in Fig. 2.27.

In Fig. 2.2c we have labeled some of the high-symmetry points of this Brillouin zone using letters such as X and Γ. We will conform to the convention of denoting high symmetry points and lines *inside* the Brillouin zone by **Greek** letters and points on the *surfaces* of the Brillouin zone by **Roman** letters. The **center** of the Brillouin zone is always denoted by Γ. The three high-symmetry directions [100], [110], and [111] in the Brillouin zone of the fcc lattice are denoted by:

[100] direction : $\dot{\Gamma}\overline{\qquad\Delta\qquad}\dot{X}$

[111] direction : $\dot{\Gamma}\overline{\qquad\Lambda\qquad}\dot{L}$

[110] direction : $\dot{\Gamma}\overline{\qquad\Sigma\qquad}\dot{K}$

The Brillouin zone of the fcc lattice is highly symmetrical. A careful examination of this Brillouin zone shows that it is unchanged by various rotations, such as a 90° rotation about axes parallel to the edges of the body-centered cube in Fig. 2.2c. In addition it is invariant under reflection through certain planes containing the center of the cube. These operations are known as **symmetry operations** of the Brillouin zone. The symmetry of the Brillouin zone results from the symmetry of the direct lattice and hence it is related to the symmetry of the crystal. This symmetry has at least two important consequences for the electron band structure. First, if two wave vectors $\boldsymbol{k}$ and $\boldsymbol{k}'$ in the Brillouin zone can be transformed into each other under a symmetry operation of the Brillouin zone, then the electronic energies at these wave vectors must be identical. Points and axes in reciprocal lattice space which transform into each other under symmetry operations are said to be **equivalent**. For example, in the Brillouin zone shown in Fig. 2.2c there are eight hexagonal faces containing the point labeled L in the center. These eight faces including the L points are equivalent and can be transformed into one another through rotations by 90°. Therefore it is necessary to calculate the energies of the electron at only one of the eight equivalent hexagonal faces containing the L point. The second and perhaps more important consequence of the crystal symmetry is that wave functions can be expressed in a form such that they have definite transformation properties under symmetry operations of the crystal. Such wave functions are said to be symmetrized. A well-known example of **symmetrized wave functions** is provided by the standard wave functions of electrons in atoms, which are usually symmetrized according to their transformation properties under rotations and are classified as s, p, d, f, etc. For example, an s wave function is unchanged by any rotation. The p wave functions are triply degenerate and transform under rotation like the three components of a vector. The d wave functions transform like the five components of a symmetric and traceless second-rank tensor. By classifying the wave functions in this way, some

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