███████ **CHAPTER 1**

Structure of Crystals

1.1 Introduction

The physical properties of solid-state materials are determined by three principal factors:

1. The properties of constituent atoms (masses, atomic numbers, electron configurations, ionization energies, etc.)
2. The local interactions of atoms with each other in the solid state (i.e., the nature of the bonding and the resulting nearest-neighbor configurations of atoms)
3. The arrangement of atoms in space to form a three-dimensional solid

Many important properties of solids, including their response to electric and magnetic fields, also involve the correlated motions of electrons and their spins. These properties include superconductivity and magnetism, among others, and require additional information for their analysis.

The nearest-neighbor (NN) configurations of atoms mentioned above are referred to here as *local atomic bonding units*. Their structure determines the *short-range order* (SRO) of the solid and the arrangement of the atoms in space constitutes the *long-range order* (LRO). If the LRO in the solid is perfect (i.e., if the arrangement in space of the atoms is perfectly *periodic*), the solid is said to be a *perfect crystal* or, simply, a *crystal*. Most solid-state materials are actually far from being structurally perfect and possess deviations from both SRO and LRO. The lack of structural order and its effect on the properties of the solid are important themes throughout this book.

To illustrate the significance of the three factors listed above, some examples of solid-state materials whose properties differ due to one or more of these factors are given next. First, consider the two crystalline forms of pure carbon: diamond, an insulator, and graphite, a semimetal. The distinctive physical properties and characteristic LRO of diamond and graphite differ significantly, due to the differences in SRO present in the two crystals: tetrahedral (fourfold) local coordination of C atoms for diamond and trigonal (threefold) local coordination of C atoms for graphite. In contrast, crystals of metallic Al and insulating Ar share the same types of SRO and LRO but nevertheless, have very different physical properties, due to the different outer-electron configurations of Al and Ar atoms. Solids comprised of the same atoms and having different LROs but essentially the same SRO are the crystalline and amorphous forms of Si and SiO_2.

As distinguished from the properties of more disordered forms of solids such as glasses and other amorphous materials, the properties of crystals depend on both the local atomic bonding and the fact that in crystals, the local configurations of atoms are

arranged periodically in space. These two fundamental aspects of the structure of crystals — short-range local chemical bonding and long-range periodic array of atoms — are introduced and discussed in this chapter.

The three-dimensional lattice and its unit cell are introduced and defined in a formal way. Together, they serve as the geometric frame of reference for the discussion of crystals. The concept of *crystal structure* and its relationships to the periodic lattice and to local atomic bonding units are then presented and illustrated using well-known crystals as examples. The various forms of chemical bonding that occur between the atoms (or ions) within local atomic bonding units are discussed in Chapter 2 and examples are given of crystals possessing each type of bonding. A summary of some important properties and parameters of atoms which influence their behavior in solid-state materials are also presented in Chapter 2. Additional interesting and important examples of bonding in solids and the resulting crystal structures are presented in later chapters, where specific classes of solid-state materials are discussed in more detail.

INTRODUCTION TO LATTICES

A *lattice* is simply a periodic set of points in space, in principle infinite in extent but which for our purposes can often be limited to the volume enclosed by the crystal. The focus here is on three-dimensional lattices. Two-dimensional lattices are important in discussions of crystal surfaces and are introduced in Chapter 19. A convenient way to define a lattice is in terms of the set of *translation vectors* **R** which can be used to generate the lattice points.

1.2   Translation Vectors

As a concrete example of a three-dimensional lattice, consider one of the simplest possible cases, the *simple cubic* (SC) lattice shown in Fig. 1.1. Starting with an arbitrary lattice point as the origin $(0,0,0)$ of the coordinate system, all other possible points of the SC lattice are generated by using the translation vectors **R**, which originate at $(0,0,0)$ and terminate at the lattice points $(x, y, z) = (n_1 a, n_2 a, n_3 a)$. Here a is the
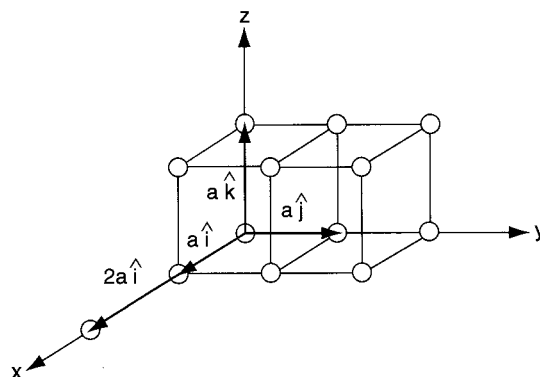
Figure 1.1. Simple cubic lattice and two unit cells. Note that the vector $2a\hat{i}$ is not a primitive translation vector of this lattice.

lattice constant, the distance between NN adjacent points of the SC lattice. The values of n_1, n_2, and n_3 allowed are the set of all integers. In terms of the unit vectors $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$ along the x, y, and z Cartesian axes, the translation vectors $\mathbf{R}$ for the SC lattice can be written as

$$\mathbf{R} = n_1 a\hat{\mathbf{i}} + n_2 a\hat{\mathbf{j}} + n_3 a\hat{\mathbf{k}}. \tag{1.1}$$

For the simple cubic lattice the three vectors $a\hat{\mathbf{i}}$, $a\hat{\mathbf{j}}$, and $a\hat{\mathbf{k}}$ shown in Fig. 1.1 are the *fundamental* or *primitive translation vectors* of the lattice since all points of the lattice can be generated using the vectors $\mathbf{R}$ defined in Eq. (1.1). These primitive translation vectors $a\hat{\mathbf{i}}$, $a\hat{\mathbf{j}}$, and $a\hat{\mathbf{k}}$ serve to define the lattice. Note that the vector $2a\hat{\mathbf{i}}$ shown in Fig. 1.1 is not a primitive translation vector for the SC lattice since only every other lattice point along the x-axis can be reached using the vector $2a\hat{\mathbf{i}}$.

The definition of a lattice is now extended to the most general case, defined by the translation vectors

$$\begin{aligned} \mathbf{R} &= n_1 a\hat{\mathbf{u}}_1 + n_2 b\hat{\mathbf{u}}_2 + n_3 c\hat{\mathbf{u}}_3 \\ &= n_1 \mathbf{u}_1 + n_2 \mathbf{u}_2 + n_3 \mathbf{u}_3, \end{aligned} \tag{1.2}$$

where, in general, $a \neq b \neq c$.[†] The three nonorthogonal unit vectors $\hat{\mathbf{u}}_1$, $\hat{\mathbf{u}}_2$, and $\hat{\mathbf{u}}_3$ are defined as shown in Fig. 1.2, with $\alpha \neq \beta \neq \gamma \neq 90°$.[‡] This most general three-dimensional lattice with primitive translation vectors $\mathbf{u}_1 = a\hat{\mathbf{u}}_1$, $\mathbf{u}_2 = b\hat{\mathbf{u}}_2$, and $\mathbf{u}_3 = c\hat{\mathbf{u}}_3$, is known as the *triclinic lattice*.

The property of the lattice that follows from its definition in terms of the translation vectors $\mathbf{R}$ is known as *translational symmetry*. This is the symmetry that all lattices possess. As a result of translational symmetry, the lattice appears identical when viewed from any lattice point. More generally, any two points in a lattice, defined by the vectors $\mathbf{r}$ and $\mathbf{r}'$, are identical (i.e., have identical surroundings), if they can be connected by a translation vector $\mathbf{R}$ (e.g., if $\mathbf{r}' = \mathbf{r} + \mathbf{R}$). As a result, in a perfect crystal, all the properties of the crystal are identical at points $\mathbf{r}$ and $\mathbf{r}'$ (except, of course, for those
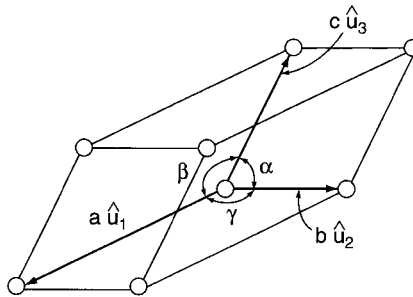
Figure 1.2. Triclinic lattice and unit cell. This is the general lattice in three dimensions, with $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$.

[†] The notation $a \neq b \neq c$ means that these three lengths are all different from each other (i.e., that $a \neq b$, $a \neq c$, and $b \neq c$).

[‡] The notation $\alpha \neq \beta \neq \gamma \neq 90°$ means that these three angles are all different from each other (and from $90°$).

points in a finite perfect crystal that lie near its surface). If the lattice also appears the same from every lattice point after being rotated about a certain axis through an angle of $360/n$ degrees, the lattice also has an axis of n-fold *rotational symmetry* in addition to its translational symmetry.

The full symmetry of a given crystal structure has importance for the physical properties of a crystal since it is expected that any macroscopic physical property has, at the least, the symmetry of the point group of the space group that the crystal possesses. The 32 possible crystallographic point groups are described in Chapter 15. For a more complete discussion of these symmetries and of the 230 possible space groups, see the books by Ashcroft and Mermin (1976), Burns (1985), and Burns and Glazer (1990), or books on crystallography.

1.3 Unit Cells

The cube of edge length a and volume a^3 is the conventional *unit cell* of the SC lattice and can be used to generate the entire lattice. This is done by moving (i.e., by translating) the unit cell through space using the translation vectors $\mathbf{R}$ so that the entire volume occupied by the SC lattice is covered just once.

Lattice points lie at the eight corners of the cubic unit cell, and each lattice point is shared by the eight unit cells, which touch at their single common corner. When lattice points lie only at the corners of the unit cell, as for the SC unit cell shown, the unit cell is then a *primitive unit cell*. This primitive unit cell, which need not in general be cubic, is the smallest volume that can be used to generate the lattice. This definition of a primitive unit cell is not unique since other primitive unit cells can be defined, including one with a lattice point at its center. This is the *Wigner–Seitz cell* described in Chapter 3. Often, a larger unit cell which is not primitive is chosen as the conventional unit cell for a particular lattice. Examples of and reasons for this use are given later.

The volume V of a unit cell defined by the three primitive translation vectors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$ is given by $V = |\mathbf{u}_1 \cdot (\mathbf{u}_2 \times \mathbf{u}_3)| = |a\hat{\mathbf{u}}_1 \cdot (b\hat{\mathbf{u}}_2 \times c\hat{\mathbf{u}}_3)|$.

1.4 Bravais Lattices

Bravais in 1845 showed on the basis of symmetry arguments that there exist only 14 distinct lattice types in three dimensions, two of which have already been mentioned: the simplest, SC, and the most general, triclinic. The 14 *Bravais lattices*, together with their conventional unit cells shown in Fig. 1.3, are usually divided into seven systems. These seven systems are characterized by the special relationships given in Table 1.1, which involve the lengths of the sides a, b, and c and the angles α, β, and γ. These seven lattice systems are discussed next.

Cubic. There are three cubic Bravais lattices: *simple cubic* (SC), *body-centered cubic* (BCC), and *face-centered cubic* (FCC). The BCC lattice is obtained by placing an additional lattice point at the center of the cubic unit cell; the FCC lattice is obtained by placing additional lattice points at the centers of the six faces of the cubic unit cell. The conventional cubic unit cells chosen for these three lattices are shown in Fig. 1.3 and illustrate their essential symmetries, as listed in Table 1.1. The BCC and FCC lattices, however, have smaller, noncubic primitive unit cells which can also be used
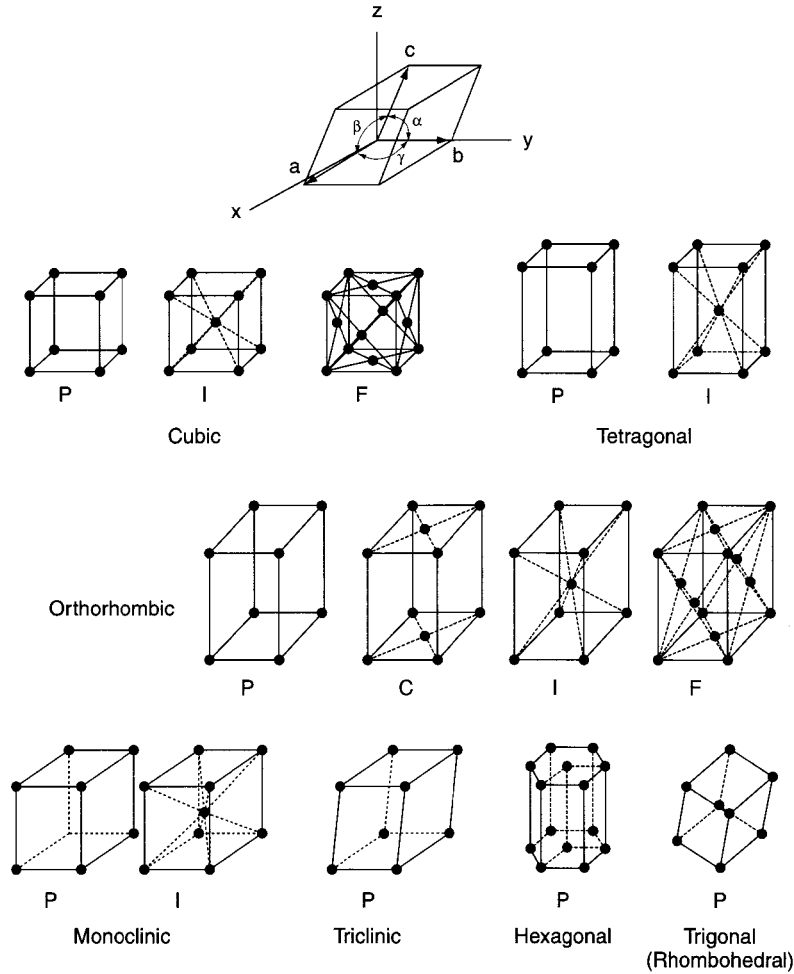
Figure 1.3. The 14 Bravais lattices in three dimensions. See Table 1.1 for the relationships between the sides a, b, and c and between the angles α, β, and γ. P, primitive; I, body-centered; F, face-centered; C, base-centered.

to generate these lattices. The primitive units cells for BCC and FCC are shown in Figs. 1.4 and 1.5, respectively. The corresponding primitive translation vectors are also given. Note that these primitive unit cells for BCC and FCC have lattice points only at their corners. It can readily be shown that the conventional BCC and FCC cubic unit cells are two and four times greater in volume, respectively, than the corresponding primitive unit cells.

The BCC and FCC lattices are quite important since the majority of solid-state materials have crystal structures based on these two lattices. Also, many elements crystallize with atoms or ions located at the lattice points of the BCC or FCC lattices.

Tetragonal. There are only two tetragonal Bravais lattices, *simple tetragonal* (ST) and *body-centered tetragonal* (BCT). These correspond to SC and BCC lattices that

**TABLE 1.1 Bravais Lattices: 14 Distinct Lattice Types in Three Dimensions**

System (Essential Symmetry)	Number of Members	Lattices	Special Relationships
Cubic (four three-fold axes)	3	Simple, body-centered, face-centered	$a = b = c,\ \alpha = \beta = \gamma = 90°$
Tetragonal (one four-fold axis)	2	Simple, body-centered	$a = b \neq c,\ \alpha = \beta = \gamma = 90°$
Orthorhombic (three orthogonal two-fold axes)	4	Simple, body-centered, face-centered, base-centered	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$
Monoclinic (one two-fold axis)	2	Simple, body-centered	$a \neq b \neq c,\ \alpha = \beta = 90° \neq \gamma$
Triclinic (none)	1	Simple	$a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$
Trigonal or rhombohedral (one three-fold axis)	1	Simple	$a = b = c,\ \alpha = \beta = \gamma < 120°$ and $\neq 90°$
Hexagonal (one six-fold axis)	1	Simple	$a = b \neq c,\ \alpha = \beta = 90°,\ \gamma = 120°$
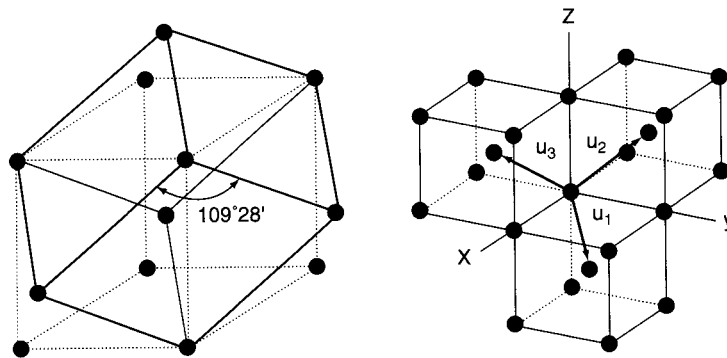
Figure 1.4. Trigonal primitive unit cell and a set of primitive translation vectors u_1, u_2, and u_3 for the body-centered cubic (BCC) lattice. Also shown is the conventional cubic unit cell. Note that $u_1 = a(\hat{i} + \hat{j} - \hat{k})/2 = \sqrt{3}\,a\hat{u}_1/2$, $u_2 = a(-\hat{i} + \hat{j} + \hat{k})/2 = \sqrt{3}\,a\hat{u}_2/2$, $\hat{u}_3 = a(\hat{i} - \hat{j} + \hat{k})/2 = \sqrt{3}\,a\hat{u}_3/2$. (After C. Kittel, *Introduction to Solid State Physics*, 7th ed., copyright 1996 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

have been either elongated or compressed along one axis, so that, for example, $a = b \neq c$ with $\alpha = \beta = \gamma = 90°$. This special axis is often referred to as the c-axis of the tetragonal lattice. The face-centered tetragonal lattice can be shown to be equivalent to the BCT lattice and therefore is not a distinct Bravais lattice.

Orthorhombic. There are four *orthorhombic* Bravais lattices with $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$: *simple*, *body-centered*, *face-centered*, and *base-centered*.
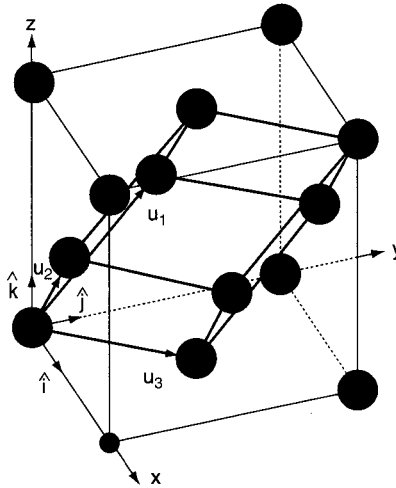
Figure 1.5. Trigonal primitive unit cell and primitive translation vectors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$ for the face-centered cubic (FCC) lattice. Also shown is the conventional cubic unit cell. Note that $\mathbf{u}_1 = a(\hat{\mathbf{j}} + \hat{\mathbf{k}})/2 = \sqrt{2}\,a\hat{\mathbf{u}}_1/2$, $\mathbf{u}_2 = a(\hat{\mathbf{i}} + \hat{\mathbf{k}})/2 = \sqrt{2}\,a\hat{\mathbf{u}}_2/2$, $\mathbf{u}_3 = a(\hat{\mathbf{i}} + \hat{\mathbf{j}})/2 = \sqrt{2}\,a\hat{\mathbf{u}}_3/2$.

Monoclinic. There are two monoclinic Bravais lattices: *simple monoclinic* and *body-centered monoclinic*. These are ordinarily formed using three primitive translation vectors of unequal length $(a \neq b \neq c)$, one of which is perpendicular to the plane of the other two, with $\alpha = \beta = 90° \neq \gamma$.

Triclinic. There is a single *triclinic* Bravais lattice, with $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$. This is the Bravais lattice with minimum symmetry. As mentioned earlier, the triclinic lattice can be considered to be the most general Bravais lattice.

Trigonal (rhombohedral). There is also a single *trigonal* Bravais lattice, generated from the SC lattice by stretching one of the body diagonals of the cubic unit cell. The trigonal lattice therefore has $a = b = c$ and $\alpha = \beta = \gamma < 120°, \neq 90°$. For the special case with $\alpha = \beta = \gamma = 60°$, the trigonal lattice actually has the same symmetry as the FCC lattice. As seen in Fig. 1.5, the FCC primitive unit cell is, in fact, a trigonal cell with angles of 60°.

Hexagonal. The single hexagonal Bravais lattice is *simple hexagonal* and has a conventional hexagonal unit cell (Fig. 1.6), which contains three primitive hexagonal unit cells. The primitive unit cell has $a = b \neq c$, $\alpha = \beta = 90°$, and $\gamma = 120°$. The hexagonal lattice has a six-fold symmetry axis, whereas the trigonal lattice has only a three-fold symmetry axis.

Some additional properties of lattices are discussed next. Still others will become apparent when specific crystal structures based on these lattices are described later in this chapter.

1.5   Lattice Axes, Planes, and Directions

To be able to discuss effectively the properties of lattices and crystal structures, it is necessary to provide ways to specify some important geometrical properties of lattices:
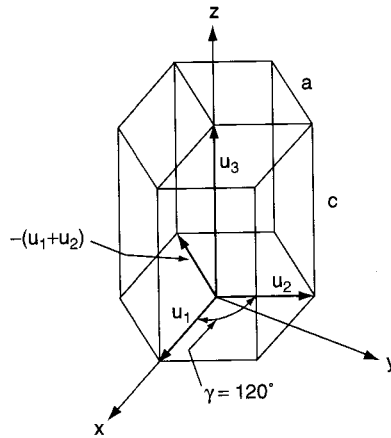
Figure 1.6. Primitive unit cell and primitive translation vectors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$ for the hexagonal lattice. Also shown is the conventional hexagonal unit cell. $\mathbf{u}_1 = a\hat{\mathbf{u}}_1 = a\hat{\mathbf{i}}$, $\mathbf{u}_2 = a\hat{\mathbf{u}}_2 = a(\cos 120°\hat{\mathbf{i}} + \sin 120°\hat{\mathbf{j}}) = a(-\hat{\mathbf{i}} + \sqrt{3}\hat{\mathbf{j}})/2$, $\mathbf{u}_3 = c\hat{\mathbf{u}}_3 = c\hat{\mathbf{k}}$.

the axes of the lattice coordinate system, planes containing lattice points, and directions in the lattice.

Axes of the Lattice. In the same way that different unit cells can be chosen for a given lattice, it is also true that different lattice coordinate systems and sets of lattice axes can be chosen. In general, the axes of a lattice are taken to lie along the edges of its unit cell. For example, when a conventional cubic unit cell is chosen, the axes are chosen to be the x, y, and z axes. The understandable convenience of the use of orthogonal axes makes the choice of the conventional cubic unit cells for the BCC and FCC lattices quite natural.

Lattice Planes. It is important to have a simple way of specifying or labeling planes in a lattice since the corresponding planes of atoms in a crystal are important, for example, in a discussion of diffraction effects. The labeling procedure universally used for this purpose employs the *Miller indices*. The specification of the Miller indices for a set of parallel lattice planes is essentially a two-step process:

1. The three points or intercepts where one of the set of lattice planes in question intersects the lattice axes are located. This is illustrated in Fig. 1.7 for the case of a cubic lattice. The plane shown intersects the three orthogonal axes at $x = 3a$, $y = 2a$, and $z = 3a$. Only the three numerical factors (i.e., 3, 2, 3) are kept.
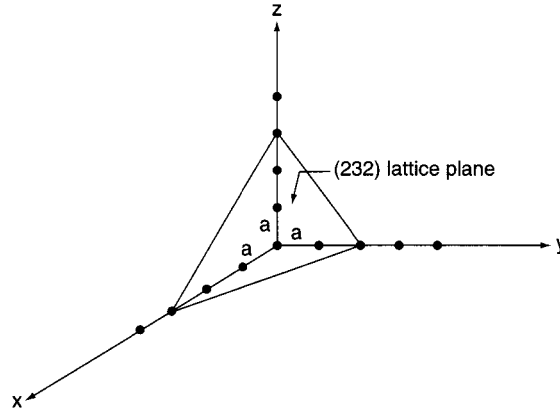
2. The reciprocals of these three numbers are taken:

$$3, 2, 3 \rightarrow \tfrac{1}{3}, \tfrac{1}{2}, \tfrac{1}{3}.$$

The reciprocals are transformed to the three corresponding smallest integers:

$$\tfrac{1}{3}, \tfrac{1}{2}, \tfrac{1}{3}, \rightarrow \tfrac{2}{6}, \tfrac{3}{6}, \tfrac{2}{6}, \rightarrow 2, 3, 2.$$

The resulting set of integers (2,3,2), or simply (232), are the Miller indices (hkl) of the lattice plane shown in Fig. 1.7.

Figure 1.7. Miller indices of lattice planes. The intercepts of the lattice plane shown are at $x = 3a$, $y = 2a$, and $z = 3a$. The Miller indices (hkl) of this plane are (232), obtained as described in the text.
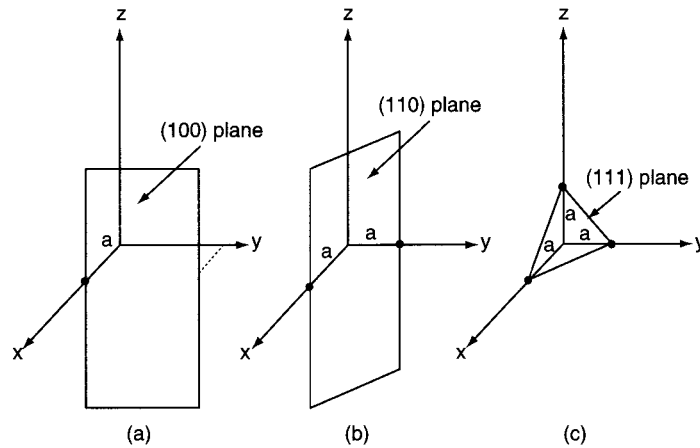
Figure 1.8. Important planes of a cubic lattice. The intercepts for these planes are at (a) $(a, \infty, \infty) \rightarrow (hkl) = (100)$, ($b$) $(a, a, \infty) \rightarrow (hkl) = (110)$, and ($c$) $(a, a, a) \rightarrow (hkl) = (111)$.

The following important points concerning Miller indices are worth noting:

1. The Miller indices of an arbitrary lattice plane are specified by three integers, taken in the general case to be h, k, and l. Actually, (hkl) refers not to a single plane but to the entire set of identical planes in the lattice that are parallel to the given (hkl) plane. For cubic lattices the perpendicular distance between adjacent parallel lattice planes is given by $d = a/\sqrt{h^2 + k^2 + l^2}$.

2. When a lattice plane is parallel to one of the axes of the lattice, the corresponding intercept is taken to be at infinity. The corresponding Miller index is therefore zero. Some examples are given in Fig. 1.8.

3. A lattice plane with a negative intercept has a corresponding negative Miller index. This is indicated with a bar over the index in question [e.g., $(\bar{h}\,\bar{k}\,\bar{l})$].

4. The notation $\{hkl\}$ is used when referring to a set of related lattice planes. For example, the $\{100\}$ set of planes refers to the six faces of a cube, given by (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$. Similarly, the eight faces of a regular octahedron correspond to the $\{111\}$ set of planes (see Fig. 1.13).

5. In general, the important lattice planes in a crystal are those with low Miller indices [e.g., (100), (110), and (111)], since these are the planes that will have the highest concentrations of atoms (per unit area).

6. Specification of the Miller indices for lattice planes in hexagonal lattices involves the intercepts of the plane with four axes instead of three. Three of these are the nonorthogonal axes that lie in the xy-plane, separated from each other by $120°$. These three axes are in the $\mathbf{u}_1$, $\mathbf{u}_2$, and $-(\mathbf{u}_1 + \mathbf{u}_2)$ directions shown in Fig. 1.6. The fourth axis is the c axis (i.e., the usual z-axis), which is orthogonal to the other three. Once the four intercepts are determined, the procedure for finding the indices $(hkil)$ proceeds as outlined earlier. The six faces of the conventional hexagonal unit cell are therefore the $(10\bar{1}0)$, $(01\bar{1}0)$, $(1\bar{1}00)$, $(\bar{1}010)$, $(0\bar{1}10)$, and $(1\bar{1}00)$, planes (i.e., the $\{1\bar{1}00\}$ set of planes). The top and bottom planes of the unit cell are (0001) planes. Note that the index i corresponds to the $-(\mathbf{u}_1 + \mathbf{u}_2)$ direction and is equal to $-(h + k)$.

Directions in the Lattice. The direction from the origin of the lattice to the point reached by the translation vector $\mathbf{R} = n_1 a \hat{\mathbf{u}}_1 + n_2 b \hat{\mathbf{u}}_2 + n_3 c \hat{\mathbf{u}}_3$ is referred to as the $[n_1, n_2, n_3]$ direction or simply $[n_1 n_2 n_3]$. The smallest set of integers n_1, n_2, and n_3 corresponding to a given direction are the direction indices for that direction. In cubic crystals the direction perpendicular to the set of (hkl) planes is the $[hkl]$ direction. For example, the $[100]$ direction (i.e., the $+x$ axis), is perpendicular to the (100) plane, as illustrated in Fig. W1.1 at our Web site.[†] A set of lattice directions related by symmetry is indicated by $\langle n_1 n_2 n_3 \rangle$. For example, the lattice axes correspond to the $\langle 100 \rangle$ set of directions. Note that directions in hexagonal lattices are given by $[hkil]$, where, again, $i = -(h + k)$.

LOCAL ATOMIC BONDING UNITS AND CRYSTAL STRUCTURES

When the same atom or group of atoms is associated with each point of one of the lattices described earlier, a specific *crystal structure* results. In this section some important examples of the wide variety of existing crystal structures are introduced and discussed. Additional examples of crystal structures are given in Chapters 11 to 18, where the following classes of solid-state materials are described: semiconductors, metals and alloys, ceramics, polymers, dielectrics and ferroelectrics, superconductors, magnetic materials, and optical materials.

The first questions to ask about any crystal structure deal with what its lattice is and how the atoms are arranged relative to each lattice point. One approach to answering such questions is based on the equation

$$\text{crystal structure} = \text{lattice} + \text{basis}, \tag{1.3}$$

[†] Supplementary material for this textbook is included on the Web at the resource site (ftp://ftp.wiley.com/public/sci_tech_med/materials). Cross-references to elements of the Web material are prefixed by "W."

which is often used as the operational definition of a crystal structure. Here the term *basis* refers to the set of atoms that lie within or are associated with the unit cell chosen for the structure. Although Eq. (1.3) is technically correct and in fact provides all the information that is ordinarily needed for most purposes (e.g., for the calculation of the scattering of waves from a crystal presented in Chapter 3), this approach often is not particularly helpful in addressing the important question of why the atoms form a particular crystal structure in the first place. Missing from this approach is any information about the local bonding between the atoms which determines the structure and hence the physical properties of the crystal.

To emphasize the role that local bonding plays in determining crystal structure, the following expression is used to supplement the information provided by Eq. (1.3):

$$\text{crystal structure} = \text{local atomic bonding units} + \text{lattice}. \qquad (1.4)$$

Here the term *local atomic bonding unit* refers to one of the smallest groupings or configurations of atoms, which serves to demonstrate some important aspects of the bonding in the crystal.

1.6   Local Atomic Bonding Units

Local atomic bonding units consist in general of a central atom (or molecule) and its NN atoms (or molecules). The central atom can either be neutral, as in the rare gas solid Ar, or can have a net charge, either positive or negative, as in the ionic solid NaCl (Na^+Cl^-). The important bonding units in most solid-state materials contain from as many as 12 NNs to as few as 2 NNs to the central atom. Bonding units with central atoms that have 12, 8, 6, 4, 3, and 2 identical NNs are described in this section.

The notations $A-A_n$ and $A-B_n$ are used to identify local bonding units, with A indicating the central atom and A_n or B_n the n NN atoms. Here n is the *coordination number* ($n = CN$). The bonding units described here are idealized in the sense that the NN A or B atoms are all assumed to be the same distance from and bonded with equal strength to the central A atom. In many crystals, however, the local atomic bonding units are distorted so that some of the NN atoms are closer than others. Examples of structures with distorted bonding units are given later. The concept of local atomic bonding units will be useful even in amorphous or disordered materials where no lattice or LRO exists. In such materials a type of SRO can still exist if the local atomic bonding units retain their identity (e.g., the same number of NNs as in the crystal, even if the bond lengths and bond angles are distorted from their crystalline values).

Important information for the local atomic bonding units described here is summarized in Table 1.2, specifically the number and identity of the NNs, examples of specific bonding units in real solids, and the *coordination polyhedra* or regular geometrical figures which are often used to represent the bonding units. Note that these coordination polyhedra illustrate the symmetry of the bonding units but are not in general the unit cells for the structures.

These bonding units are each described below and the distinguishing features of each are stressed. In general, the central A atom and the NN A and B atoms are considered to be rigid spheres in contact with each other. Atoms (and ions) are, in fact, somewhat compressible, so that this model of atoms as rigid spheres will need to be modified in order to understand many crystal structures. The types of bonding occurring between the atoms or ions in these units are described in Chapter 2.

**TABLE 1.2 Local Atomic Bonding Units in Solid-State Materials**

Coordination Number n	Bonding Unit	Examples	Coordination Polyhedra
12	$A-A_{12}(cub)$	Al, Ar, C_{60}	Cubo-octahedron
	$A-A_{12}(hex)$	Mg	Twinned cubo-octahedron
	$A-A_{12}(icos)$		Icosahedron
	$A-B_{12}(icos)$	$Sn-Nb_{12}(Nb_3Sn)$	Icosahedron
8	$A-A_8$	Na, Cr, W	Cube
	$A-B_8$	$Cs^+-Cl_8^-$ (CsCl)	Cube
6	$A-A_6$	Po	Octahedron
	$A-B_6$	$Na^+-Cl_6^-$ (NaCl)	Octahedron
	$A-B_6$	$C-Fe_6$ (Fe_3C)	Triangular prism
4	$A-A_4$	C (diamond), Si	Tetrahedron
	$A-B_4$	$Ga-As_4$ (GaAs)	Tetrahedron
		$Si-O_4(SiO_2)$	Tetrahedron
		$Cu-O_4$ (CuO)	Square
3	$A-A_3$	C (graphite)	Triangle or
	$A-B_3$	$B-N_3$ (BN)	pyramid
		$N-Si_3$ (Si_3N_4)	
2	$A-A_2$	S, Se	Link or
		CH_2 (polyethylene)	bridge
	$A-B_2$	$O-Si_2$ (SiO_2)	

$A-A_{12}$(cub), $A-A_{12}$(hex), $A-A_{12}$(icos), and $A-B_{12}$(icos). An atom can be bonded to the 12 identical NN atoms in an $A-A_{12}$ bonding unit in at least three distinct ways, of which the cubic $A-A_{12}$(cub) and hexagonal $A-A_{12}$(hex) cases are referred to as close-packed units. In close-packed units the *packing fraction*, defined as the fraction of space occupied by hard-sphere atoms, has its maximum possible value for identical atoms of 0.74. The structures of these bonding units are shown in Fig. 1.9, with the central A atom in both cases first placed in contact with six other A atoms, all lying in the same plane. Note that pairs of adjacent NN A atoms in the plane are also in contact with each other.

Six additional A atoms then are placed in contact with the central A atom, with three in a plane above and three more in a plane below the original plane. This can be done in two distinct ways, as shown in Fig. 1.9b and c. In Fig. 1.9b the three atoms in the upper plane lie in depressions adjacent to the central A atom and directly above the three A atoms in the lower plane. The structure of the resulting $A-A_{12}$ unit is consistent with a hexagonal lattice so the notation $A-A_{12}$(hex) is used. The coordination polyhedron for the $A-A_{12}$(hex) unit is a twinned *cubo-octahedron* with 14 sides, 8 being equilateral triangles and 6 being squares. In Fig. 1.9c the three atoms in the upper plane are displaced from those in the lower plane by placing them into the remaining three depressions adjacent to the central A atom. The notation $A-A_{12}$(cub) is used for this unit since all the atoms lie on an FCC lattice. In addition, these planes of atoms coincide with (111) planes of the FCC lattice. The cubo-octahedron shown in Fig. 1.10 is the coordination polyhedron for the $A-A_{12}$(cub) unit and corresponds to a cube with the eight corners cut off. The cubic symmetry of this bonding unit is

(a)   (b)   (c)
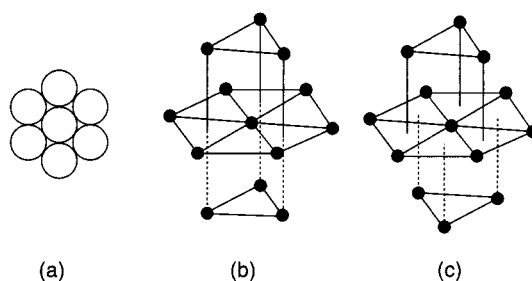
Figure 1.9. Structures of $A-A_{12}$(hex) and $A-A_{12}$(cub) bonding units. (*a*) A central A atom is in contact with six NN A atoms, all in the same plane (viewed from above). (*b*) An $A-A_{12}$(hex) bonding unit is obtained when the three upper A atoms lie directly above the three lower A atoms, as shown. For clarity, the atoms are not shown in contact with each other. (*c*) An $A-A_{12}$(cub) bonding unit obtained when the three upper A atoms are displaced laterally from the three lower A atoms, as shown.
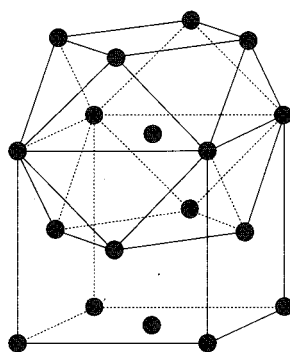
Figure 1.10. The cubo-octahedron shown is the coordination polyhedron for the $A-A_{12}$(cub) bonding unit. The FCC cubic unit cell is also shown. (After W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, copyright 1972 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

evident from this figure, where the atoms are reduced from their normal size and so are not in contact with each other.
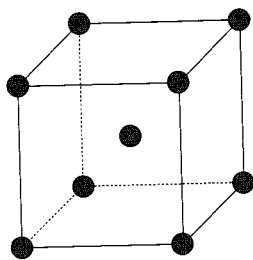
The coordination polyhedron for the $A-A_{12}$(icos) and $A-B_{12}$(icos) icosahedral units is the regular *icosahedron* containing a central A atom (Fig. 1.11). Here A (or B) atoms are located at the 12 vertices of the regular icosahedron, which has 20 triangular faces. An icosahedron therefore consists of 20 tetrahedra sharing a common vertex and has a total of six five-fold symmetry axes. For the $A-A_{12}$(icos) unit shown, the 12 NN A atoms will not be in contact with each other unless there is some compression at their points of contact with the central A atom. Bonding units related to these icosahedral units and which also have coordination polyhedra with triangular faces include those with a central atom surrounded by 14, 15, or 16 NN atoms (i.e., $A-B_{14}$, $A-B_{15}$, and $A-B_{16}$). These are known as CN 14, CN 15, and CN 16 polyhedra, It should be noted that the set of B atoms in these units can also include some A atoms. These units, together with $A-A_{12}$(icos) and $A-B_{12}$(icos), are found in topologically close packed
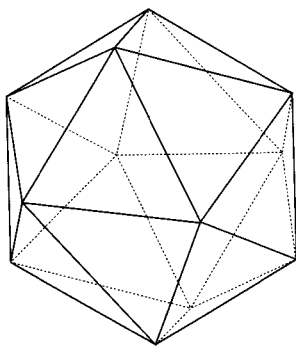
Figure 1.11. The regular icosahedron is the coordination polyhedron for the $A-A_{12}$(icos) and $A-B_{12}$(icos) bonding units. (After W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, copyright 1972 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

phases (e.g., *Frank–Kasper* and *Laves* phases). For a discussion of these phases, see Pearson (1972).

$A-A_8$ and $A-B_8$. An A atom can be bonded to eight other A atoms or to eight B atoms in a symmetric way when the central A atom is placed at the body-centered position of a cube and the eight NN A or B atoms are placed at the corners of the cube (Fig. 1.12). The *cube* is therefore the coordination polyhedron for the $A-A_8$ and $A-B_8$ bonding units. When the B atoms are larger than the A atom, they will come into contact with each other when the radius of a B atom, r_B, is equal to 1.366 times r_A, the radius of an A atom. This establishes the requirement that the *radius ratio* $r_B/r_A \leq$ 1.366 for the central A atom to remain in contact with all eight of its NN B atoms in the $A-B_8$ unit. This requirement can also be expressed as $r_A/r_B \geq 0.732$ ($= \sqrt{3} - 1$). For $r_A/r_B < 0.732$, the $A-B_8$ bonding unit may become unstable, resulting in a possible transformation to an $A-B_6$ unit. The reasons for this instability in ionic crystals are presented in Chapter 2, where ionic bonding is discussed.[†] The radius ratios for several crystal structures are discussed further in Chapter 2.

Figure 1.12. The $A-A_8$ bonding unit is shown with the central A atom at the body-centered position and with the eight NN A atoms at the corners of a cube. The cube is the coordination polyhedron for these bonding units.

[†] See Table 2.3 for a summary of the radius ratios for various bonding units and crystal structures.

(a)   (b)
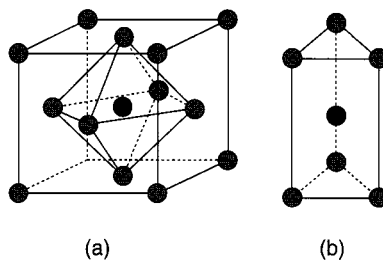
Figure 1.13. $A-A_6$ and $A-B_6$ bonding units. (*a*) The central A atom is at the body-centered position and the six NN A or B atoms are at the face-centered positions of a cube. The regular octahedron shown is the coordination polyhedron for these bonding units. (*b*) An $A-B_6$ unit in the form of a body-centered triangular or trigonal prism is shown. The central A atom is in contact with three B atoms in a lower plane and also with three B atoms in an upper plane.

$A-A_6$ and $A-B_6$. An A atom can be bonded to six other A atoms or to six B atoms in a symmetric way when the central A atom is placed at the body-centered position of a cube and the six NN A or B atoms are placed at the six face-centered positions of the same cube (Fig. 1.13a). When the positions of these six NN atoms are connected as shown, the resulting regular *octahedron* with eight identical triangular faces is seen to be the coordination polyhedron. Using an argument similar to that presented above for the $A-B_8$ unit, it is required that $r_B/r_A \leq 2.414$ (or that $r_A/r_B \geq 0.414 = \sqrt{2} - 1$) for the A atom to remain in contact with all six NN B atoms in the $A-B_6$ unit.

Another example of an $A-B_6$ bonding unit is the body-centered triangular or trigonal *prism* (Fig. 1.13b). This unit consists of a central A atom in contact with three B atoms in a lower plane and three B atoms in an upper plane.

$A-A_4$ and $A-B_4$. The symmetric bonding of an A atom to four other A atoms or to four B atoms can be visualized by placing the central A atom at the body-centered position of a cube and the four NN A or B atoms at four of the eight corners of the cube in such a way that all four NN atoms are separated from each other by the diagonals of the cube faces (Fig. 1.14). The coordination polyhedron formed when the positions of the four NN atoms are connected is the regular *tetrahedron* with vertex angles of $109.47°$. For the central A atom to remain in contact with its four NN B atoms in an $A-B_4$ unit, it is required that $r_B/r_A \leq 4.45$ (or $r_A/r_B \geq 0.225 = \sqrt{3/2} - 1$). This
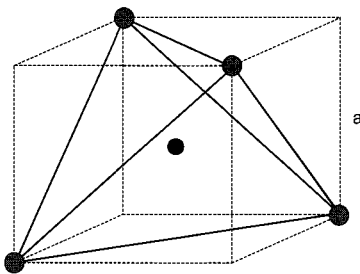
Figure 1.14. The $A-A_4$ and $A-B_4$ bonding units are shown with the central A atom at the body-centered position and with the four NN A or B atoms at four of the eight corners of a cube. The regular tetrahedron shown is the coordination polyhedron for these bonding units.
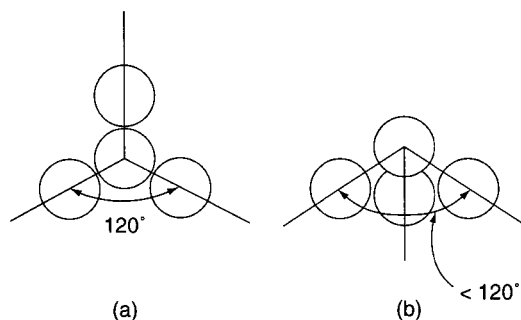
Figure 1.15. Structures of A–A$_3$ and A–B$_3$ bonding units. (*a*) planar triangular structure with central A atom and three NN A or B atoms lying in the same plane; (*b*) pyramidal structure with central A atom lying above the triangular base of three NN A or B atoms.
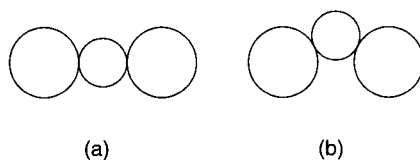
Figure 1.16. Structures of A–A$_2$ and A–B$_2$ bonding units: (*a*) linear structure with central A atom and two NN A or B atoms lying in a straight line; (*b*) nonlinear structure.

stability criterion may have some validity for crystals in which the approximation of spherical atoms or ions is reasonable. It is of less use in covalent crystals with the diamond or zincblende crystal structures, where the bonding tends to be directional and the resulting charge distributions are non spherical. Another type of A–B$_4$ bonding unit has square-planar symmetry, with the A atom surrounded by four NN B atoms at the corners of a square.

A–A$_3$ and A–B$_3$. The A–A$_3$ and A–B$_3$ bonding units can be formed with all the atoms lying in the same plane (Fig. 1.15*a*), or with the central A atom removed from the plane of the other three atoms (Fig. 1.15*b*). In the first case, the central A atom lies at the center of an equilateral triangle, while in the second case it lies above the triangular base at the vertex of a pyramidal bonding unit. The condition $r_B/r_A \leq 6.46$ (or $r_A/r_B \geq 0.155 = \sqrt{4/3} - 1$) can be shown to apply to the first case.

A–A$_2$ and A–B$_2$. A central A atom can be bonded to just two NN A or B atoms in a linear unit (Fig. 1.16*a*), or in a unit with a bond angle of less than 180° (Fig. 1.16*b*). These bonding units are called *linking* or *bridging units* since they can correspond either to a single link in a long chain of similar units or to a bridging unit connecting two larger bonding units.

1.7 Crystal Structures

Important crystal structures based on a single type of bonding unit are described next. Examples of solid-state materials with each crystal structure are also given. The types

of bonding occurring within local atomic bonding units and in crystals are discussed in Chapter 2. Other important crystal structures based on more than one type of bonding unit and some based on the $A-B_{12}$ and $A-A_2$ bonding units are presented in later chapters.

As indicated in Eq. (1.4), crystal structures will be defined by specifying how the local atomic bonding units are placed on a given lattice. The viewpoint taken here is that the lattice of a given crystal structure simply allows the bonding units to fill space efficiently, with low strain.

Crystal Structures Based on $A-A_{12}$(hex). The central A atom and the 12 NN A atoms of the $A-A_{12}$(hex) bonding unit all lie on adjacent points of an hexagonal Bravais lattice, with the planes of atoms parallel to the (0001) lattice planes (see Fig. 1.6). The resulting crystal structure (Fig. 1.17a) is known as *hexagonal close-packed* (HCP). In the HCP crystal structure it can be seen that every atom is at the center of an $A-A_{12}$(hex) bonding unit. The hexagonal primitive unit cell for HCP (Fig. 1.17b) contains a basis of two identical A atoms at the positions (0,0,0) and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. The coordinates refer to the primitive translation vectors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$.

The close-packed planes of atoms in the HCP crystal structure are the (0002) planes of the lattice and are stacked along the c direction in the sequence **ABABAB**. . . . This stacking sequence is consistent with the structure of the $A-A_{12}$(hex) unit, where the central A atom and six of its NN atoms lie in an **A** plane. The three A atoms above the **A** plane and the remaining three A atoms below the **A** plane lie in **B** planes.

The ratio c/a of the lattice constants for the hexagonal unit cell has the value $\sqrt{\frac{8}{3}} = 1.633$ for the ideal HCP crystal structure when the atoms are taken to be hard spheres in contact with each other. The actual c/a ratio for crystals with HCP crystal structures can deviate from this ideal value when the atoms are not perfectly spherical, as when

(a)   (b)
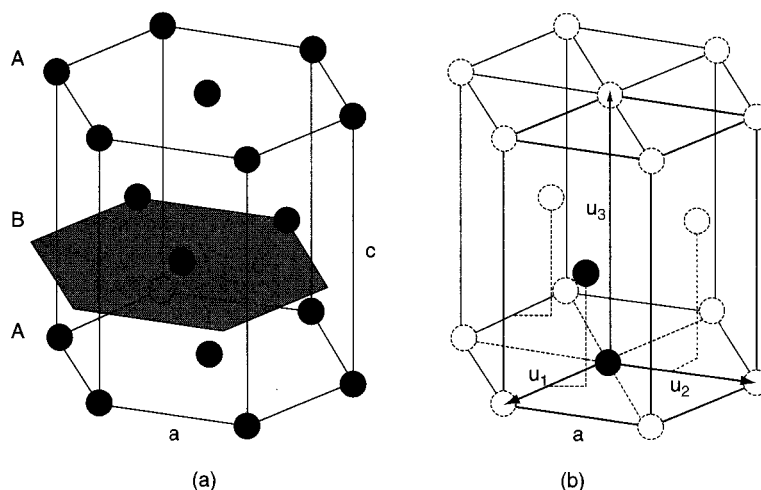
Figure 1.17. (a) Hexagonal close-packed (HCP) crystal structure based on the $A-A_{12}$(hex) bonding unit; (b) primitive unit cell for HCP with a basis of two A atoms at the positions (0,0,0) and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$, where the coordinates refer to the u_1, u_2, and u_3 axes, as shown. (After C. Kittel, *Introduction to Solid State Physics*, 7th ed., copyright 1995 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

TABLE 1.3 Elemental Crystals with the HCP Crystal Structure

Element	a (nm)[a]	c/a	Element	a (nm)[a]	c/a
Be	0.229	1.568	Mg	0.321	1.624
Ti	0.295	1.587	Co	0.251	1.623
Zn	0.267	1.856	Zr	0.323	1.593
Tl	0.346	1.598	Gd	0.363	1.591
Ho	0.358	1.570			

[a]Lattice constants are values at room temperature.

bonding between atoms in the solid state involves nonspherical electron orbitals. Some examples of elemental crystals with the HCP crystal structure are given in Table 1.3, along with the lattice constants a and c/a ratios observed at room temperature (as is the case for all the lattice constants given in tables in this chapter). Information on the structures and lattice constants of crystals of the elements is given in Table 1.4. Metallic bonding tends to dominate in elemental crystals that have the HCP crystal structure, with the result that the A atoms are actually positively charged ions (cations). An exception is the inert-gas solid He, where van der Waals bonding occurs between neutral He atoms.

As mentioned earlier, the packing fraction for the $A-A_{12}$(hex) bonding unit and therefore for the ideal HCP crystal structure has the value 0.74. An introduction to the calculation of packing fractions for important crystal structures is presented later.

Several metallic rare earth elements (e.g., La, Pr, Nd, Pm, and Am) can have crystal structures in which the stacking of the close-packed planes of atoms along the c axis is **ABACABAC....** These crystal structures are known as *double HCP* (DHCP). In DHCP half the planes of atoms have the cubic stacking sequence (**ABCABC...**) while the other half have hexagonal stacking (**ABAB...**). Thus elements with the DHCP crystal structure contain both the $A-A_{12}$(cub) and $A-A_{12}$(hex) local bonding units. The DHCP crystal structure is analogous to the hexagonal 4H–SiC crystal structure in which the stacking of planes of atoms along the c axis is also **ABACABAC...**, where, in this case, $A = A(Si)A(C)$, and so on. The local bonding units in 4H–SiC, however, are tetrahedral $Si-C_4$ and $C-Si_4$ units.

Crystal Structures Based on $A-A_{12}$(cub). The crystal structure based on the $A-A_{12}$(cub) bonding unit is the close-packed *FCC structure*, also known as *cubic close-packed* (ccp). In this crystal structure the central A atom and its 12 NN A atoms all lie on adjacent points of an FCC lattice. In the FCC crystal structure every atom is the center of an $A-A_{12}$(cub) unit. The planes of atoms in the bonding unit are parallel to the (111) planes of the lattice (Fig. 1.18). Choosing an FCC lattice for this crystal structure corresponds to a basis of a single A atom at (0,0,0), while choosing a SC lattice corresponds to a basis of four identical A atoms at (0,0,0), $(0\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2},0)$. The latter choice confirms that there are four A atoms per conventional cubic unit cell.

The stacking of the (111) planes of atoms in the FCC crystal structure is **ABCABC...** since the atoms in the upper and lower planes within the $A-A_{12}$(cub) bonding unit are displaced from each other. Deviations from this ideal stacking sequence can occur and are known as *stacking faults* (see Chapter 4).

TABLE 1.4 Crystal Structures and Lattice Constants (nm) of the Elemental Solids[a]

1	2	3–12	13	14	15	16	17	18
1 14K H₂ HCP 0.378 0.616								2 4K He HCP 0.356 0.580
3 Li BCC 0.351	4 Be HCP 0.229 0.358		5 B trig. 1.017 65.1°	6 C graphite 0.246 0.671	7 36K N₂ cubic 0.566	8 55K O₂ cubic 0.683	9 54K F₂ cubic 0.667	10 30K Ne FCC 0.446
11 Na BCC 0.429	12 Mg HCP 0.321 0.521		13 Al FCC 0.405	14 Si diamond 0.543	15 P ortho. 0.331 1.048 0.438	16 S ortho. 1.046 1.287 2.449	17 113K Cl₂ ortho. 0.624 0.448 0.826	18 34K Ar FCC 0.532

(dashed box, separately listed) 6 C diamond 0.357

19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
19 K BCC 0.532	20 Ca FCC 0.559	21 Sc HCP 0.331 0.527	22 Ti HCP 0.295 0.468	23 V BCC 0.302	24 Cr BCC 0.288	25 Mn cubic 0.891	26 Fe BCC 0.287	27 Co HCP 0.251 0.407	28 Ni FCC 0.352	29 Cu FCC 0.361	30 Zn HCP 0.267 0.495	31 Ga ortho. 0.452 0.766 0.453	32 Ge diamond 0.566	33 As trig. 0.413 54.1°	34 Se hex. 0.437 0.495	35 Br₂ ortho. 0.668 0.449 0.874	36 116K Kr FCC 0.581
37 Rb BCC 0.571	38 Sr FCC 0.608	39 Y HCP 0.365 0.573	40 Zr HCP 0.323 0.515	41 Nb BCC 0.330	42 Mo BCC 0.315	43 Tc HCP 0.274 0.439	44 Ru HCP 0.271 0.428	45 Rh FCC 0.380	46 Pd FCC 0.389	47 Ag FCC 0.409	48 Cd HCP 0.298 0.562	49 In tetr. 0.325 0.595	50 Sn tetr. 0.583 0.318	51 Sb trig. 0.451 57.1°	52 Te hex. 0.446 0.593	53 I₂ ortho. 0.727 0.479 0.979	54 162K Xe FCC 0.635
55 Cs BCC 0.614	56 Ba BCC 0.502	57 La DHCP 0.377 1.217	72 Hf HCP 0.319 0.505	73 Ta BCC 0.330	74 W BCC 0.317	75 Re HCP 0.276 0.446	76 Os HCP 0.273 0.439	77 Ir FCC 0.384	78 Pt FCC 0.392	79 Au FCC 0.408	80 227K Hg trig. 0.301 70.5°	81 Tl HCP 0.346 0.552	82 Pb FCC 0.495	83 Bi trig. 0.475 57.2°	84 Po SC 0.337	85 At —	86 Rn —
87 Fr —	88 Ra BCC 0.571	89 Ac FCC 0.531															

Lanthanides

58	59	60	61	62	63	64	65	66	67	68	69	70	71
58 Ce DHCP 0.368 1.186	59 Pr DHCP 0.367 1.183	60 Nd DHCP 0.366 1.180	61 Pm DHCP 0.365 1.165	62 Sm trig. 0.900 23.2°	63 Eu BCC 0.458	64 Gd HCP 0.363 0.578	65 Tb HCP 0.361 0.570	66 Dy HCP 0.359 0.565	67 Ho HCP 0.358 0.562	68 Er HCP 0.356 0.559	69 Tm HCP 0.354 0.555	70 Yb FCC 0.548	71 Lu HCP 0.351 0.555

Actinides

90	91	92	93	94	95	96	97	98	99	100	101	102	103
90 Th FCC 0.508	91 Pa tetr. 0.392 0.324	92 U ortho. 0.285 0.587 0.495	93 Np ortho. 0.666 0.472 0.487	94 Pu mono. 0.618 0.482 1.096	95 Am DHCP 0.347 1.124	96 Cm DHCP 0.350 1.133	97 Bk DHCP 0.342 1.107	98 Cf DHCP 0.339 1.102	99 Es DHCP ?	100 Fm —	101 Md —	102 No —	103 Lr —

Source: Data from D. R. Lide, ed.-in-chief, *CRC Handbook of Chemistry and Physics*, 79th ed. (CRCnetBASE 1999), CRC Press, Boca Raton, Fla., 1999, pp. 12–19 to 12–21; W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley-Interscience, New York, 1972; and R. W. G. Wyckoff, *Crystal Structures*, Vol. II, 2nd ed., Interscience, New York, 1963.

[a]Values correspond to room temperature, unless stated otherwise.
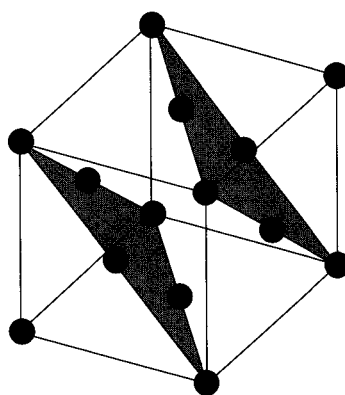
Figure 1.18. Cubic unit cell of the face-centered cubic (FCC) crystal structure based on the $A-A_{12}(cub)$ bonding unit. The planes of atoms in the bonding unit are the (111) planes of the FCC structure.

TABLE 1.5 Elemental Crystals with the FCC Crystal Structure

| Element	a (nm)^a	Element	a (nm)^a
Al	0.405	Ca	0.559
Ni	0.352	Cu	0.361
Pd	0.389	Ag	0.409
Ir	0.384	Au	0.408
Pb	0.495	Yb	0.548

^{a}Lattice constants are values at room temperature.

Some elemental crystals with the FCC crystal structure are listed in Table 1.5. Metallic bonding dominates in these crystals and the A atoms are positively charged ions.

An important property of both hexagonal and cubic close-packed arrays of atoms is the presence of unoccupied *interstitial sites* in the HCP and FCC crystal structures. Even though close-packed arrays of atoms have the maximum possible packing fraction of 0.74 for spheres of a given radius, the fact remains that 26% of the volume of the crystal is in principle still available to be filled, for example, by smaller atoms. Examples of this filling of interstitial sites are given later. These interstitial sites are of two types, tetrahedral and octahedral, according to the symmetry of the NN close-packed atoms surrounding the site.

The tetrahedral and octahedral interstitial sites can easily be identified within the cubic unit cell of the FCC crystal structure (Fig. 1.19). Here the tetrahedron and octahedron of close-packed atoms surrounding the corresponding interstitial sites are shown. A tetrahedral interstitial site is located at the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ position within the unit cell. Eight tetrahedral interstitial sites surround each atom in the FCC crystal structure, with the sites oriented along the set of eight $\langle 111 \rangle$ directions.

As shown in Fig. 1.19, an octahedral interstitial site is located at the body-centered position of the unit cell. Identical interstitial sites are also located at the centers of

(a)   (b)
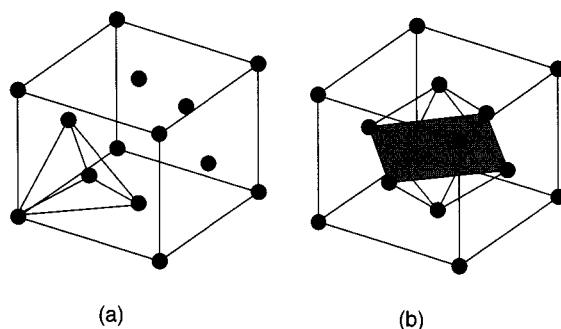
Figure 1.19. Unoccupied interstitial sites in the FCC crystal structure: (*a*) example of an interstitial site with tetrahedral symmetry located at the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ position within the cubic unit cell; (*b*) interstitial site with octahedral symmetry located at the body-centered position of the cubic unit cell. Identical interstitial sites are also located at the centers of the cube edges.

the cube edges. Each atom in the FCC crystal structure is surrounded by six of these octahedral interstitial sites, which are oriented along the six ⟨100⟩ directions. As a result, there are two tetrahedral and one octahedral interstitial site per FCC atom. The same is true for the HCP crystal structure, although the interstitial sites are arranged differently around each atom. The occupation of these interstitial sites by cations occurs in minerals where the close-packed array consists of O^{2-} anions. Crystal structures based on $A-A_{12}$(icos) and $A-B_{12}$(icos) bonding units are described in Chapter W1, at our Web site.

Crystal Structures Based on A–A₈. The crystal structure based on the $A-A_8$ bonding unit is obtained by placing atoms on every point of the BCC lattice (Fig. 1.20). This results in a BCC crystal structure in which every atom is at the center of an $A-A_8$ bonding unit. When a BCC lattice is chosen for this structure, the basis is simply an A atom at (0,0,0). There are, however, two atoms per conventional cubic unit cell
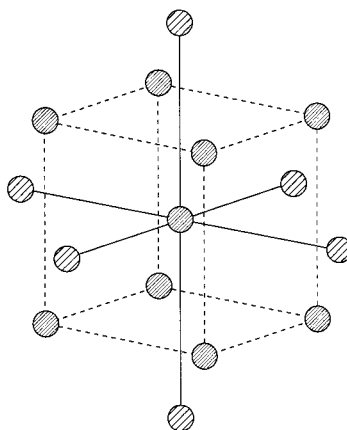
Figure 1.20. Body-centered cubic (BCC) crystal structure based on the $A-A_8$ bonding unit. The eight NN A atoms and the six second-NN A atoms to the central A atom are shown.

**TABLE 1.6   Elemental Crystals with the BCC Crystal Structure**

Element	a (nm)^a	Element	a (nm)^a
Li	0.351	Na	0.429
K	0.532	V	0.302
Cr	0.288	Fe	0.287
Rb	0.571	Nb	0.330
Mo	0.315	Cs	0.614
Ba	0.502	Ta	0.330
W	0.317	Eu	0.458

^{a}Lattice constants are values at room temperature.

of this structure, located at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The packing fraction for the BCC crystal structure is 0.68, only about 10% less than the value of 0.74 for HCP and FCC. As shown in Fig. 1.20, there are six second-NN A atoms arranged octahedrally with respect to the central A atom.

Some elemental crystals with the BCC crystal structure are listed in Table 1.6. Metallic bonding dominates in these crystals and the A atoms are positively charged ions.

Vacant interstitial sites are also present in BCC crystals (Fig. 1.21). There are six distorted octahedral interstitial sites per cubic unit cell, in the middle of each of the six faces (shared by two cells) and also at the midpoint of each of the 12 edges (shared by four cells). In addition, there are six distorted tetrahedral interstitial sites per cubic unit cell, two in each of the six faces. These octahedral and tetrahedral interstitial sites are distorted because the distances from the site to the surrounding atoms are not all the same. The maximum radii of hard-sphere atoms that can occupy the interstitial sites in BCC crystal structures are smaller than the corresponding radii in FCC crystal

(a)   (b)
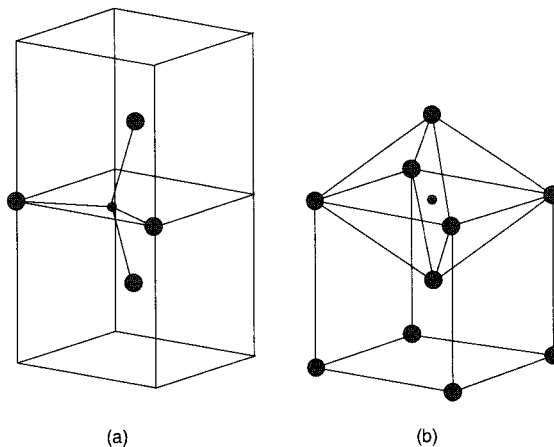
Figure 1.21. Unoccupied interstitial sites in the BCC crystal structure: (a) interstitial site with distorted tetrahedral symmetry; (b) interstitial site with distorted octahedral symmetry located at the face-centered position of the cubic unit cell. Other distorted interstitial sites are located at the centers of the cube edges.
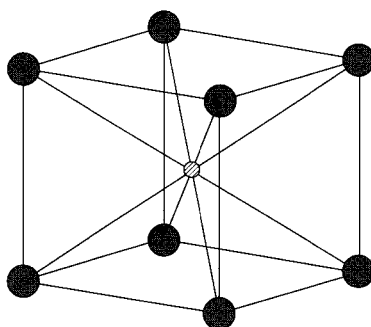
Figure 1.22. Cesium chloride (CsCl) crystal structure based on the $A–B_8$ bonding unit.

structures despite the fact that FCC has a higher packing fraction than BCC. Interstitial carbon atoms in BCC (and FCC) Fe play a crucial role in the properties of cast iron and steels (see Chapter 12).

Crystal Structures Based on $A–B_8$. Crystals that are based on the $A–B_8$ bonding unit are typically binary compounds with a SC lattice and a basis of two atoms in the cubic unit cell: an A atom at $(0,0,0)$ and a B atom at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, or vice versa; (Fig. 1.22). This *cesium chloride* (CsCl) crystal structure can be viewed as two interpenetrating SC lattices, with A atoms on one SC lattice and B atoms on the other lattice, displaced from the first by one-half of a body diagonal. As a result, each B atom is at the center of a $B–A_8$ bonding unit that has the same symmetry as that of the $A–B_8$ unit.

The bonding in crystals with the CsCl crystal structure has a strong ionic component. It is therefore important to recognize that, for example, if the A atom is a positively charged ion (cation) such as Cs^+, the B atom will be a negatively charged ion (anion) such as Cl^-. Examples of crystals based on the $A–B_8$ bonding unit and having the CsCl crystal structure are listed in Table 1.7.

Crystal Structures Based on $A–A_6$. When the central A atom of an $A–A_6$ unit is placed at a lattice point, the six NN A atoms will lie on points of a SC lattice. The resulting crystal structure is SC, with every A atom at the center of an $A–A_6$ unit. The SC crystal structure has a packing fraction of only 0.52 and is therefore a rather open structure with a vacant interstitial site with cubic symmetry located at the body-centered position. Since this site could be occupied by other A atoms, as in BCC crystals, or by B atoms, as in crystals with the CsCl structure, it is not surprising that at most one element, polonium (Po), has the SC crystal structure.

TABLE 1.7   Crystals with the CsCl Crystal Structure

Compound	a (nm)[a]	Compound	a (nm)[a]
CsCl	0.411	NH_4Cl	0.387
CuZn (β-brass)	0.294	AlNi	0.288
TlBr	0.397	BeCu	0.270

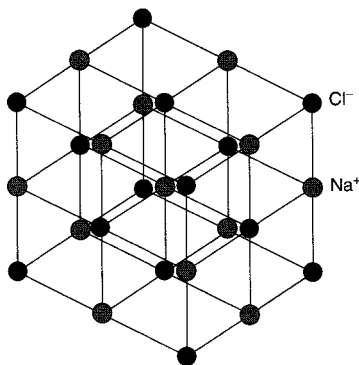[a]Lattice constants are values at room temperature.

Figure 1.23. Sodium chloride (NaCl) crystal structure based on the $A-B_6$ bonding unit.

Crystal Structures Based on A–B₆. When the central A atoms of $A-B_6$ bonding units are placed on the lattice points of an FCC lattice, with the six NN B atoms oriented along the six $\langle 100 \rangle$ directions, the resulting crystal structure (Fig. 1.23) is *NaCl*, or *rocksalt*. This crystal structure, in fact, consists of two interpenetrating FCC lattices with A atoms on one lattice and the B atoms on the other lattice. The A and B lattices are displaced from each other by, for example, one half of the lattice constant a along the [100] direction or by one half of the body diagonal in the [111] direction. The basis for this structure consists of an A atom at (0,0,0) and a B atom at either $(\frac{1}{2},0,0)$ or $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. As a result, B atoms are also at the centers of $B-A_6$ units having the same symmetry as the $A-B_6$ units.

Another useful way to view the NaCl crystal structure is to recognize that the larger Cl^- anions lie on a close-packed FCC lattice containing two tetrahedral and one octahedral interstitial site per Cl^- ion, as described earlier for the FCC crystal structure. When the smaller Na^+ cations are placed in all the octahedral interstitial sites, the resulting crystal structure is electrically neutral (as required), contains both $Na^+-Cl_6^-$ and $Cl^--Na_6^+$ bonding units, and is in fact the NaCl crystal structure. It is apparent that this arrangement of two oppositely charged ions in the NaCl crystal structure makes use of the efficient close-packing solution to filling space.

Table 1.8 presents examples of important crystals with the NaCl crystal structure. Since ionic bonding dominates in these crystals, the A atoms may be considered to be the cations and the B atoms, the anions.

Crystal Structures Based on A–A₄. $A-A_4$ bonding units can be placed at the lattice points of an FCC lattice so that every A atom is at the center of a tetrahedral

TABLE 1.8 Crystals with the NaCl Crystal Structure

Compound	a (nm)^a	Compound	a (nm)^a
NaCl	0.563	LiH	0.408
AgBr	0.577	MgO	0.420
PbS	0.592	MnO	0.443
KCl	0.629	KBr	0.659

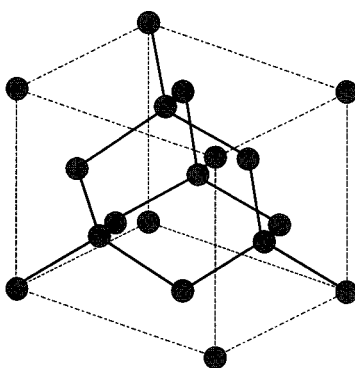^{a}Lattice constants are values at room temperature.

Figure 1.24. Diamond crystal structure based on the A–A$_4$ bonding unit.

A–A$_4$ unit. The resulting crystal structure (Fig. 1.24), known as the *diamond crystal structure*, consists of two interpenetrating FCC lattices of A atoms separated from each other by one-fourth of a body diagonal (i.e., along the [111] direction). With the choice of an FCC lattice the basis consists of two A atoms at (0,0,0) and $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ within the cubic unit cell. There are eight A atoms per conventional cubic unit cell and the structure is quite open, with a packing fraction of only 0.34. There are a total of eight interstitial sites with tetrahedral symmetry in the cubic unit cell, four on the body diagonal [e.g., at $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$], three on the cube edges, and one in the body-centered position. The stacking of the (111) planes of A atoms in the diamond crystal structure is **AABBCCAABBCC**... , which is a doubling of the FCC sequence of **ABCABC**.... Another view of the diamond crystal structure corresponds to an FCC lattice of A atoms with additional A atoms placed at four of the eight otherwise vacant tetrahedral interstitial sites.

The four elements having the diamond crystal structure are listed in Table 1.9. The bonding in these crystals is covalent. It should be noted that the stable form of Sn at room temperature is white Sn (β-Sn), which has a tetragonal structure and is metallic. Gray Sn (α-Sn) is semimetallic.

A hexagonal crystal structure based on the A–A$_4$ unit which differs from the cubic diamond crystal structure in the distribution of second-NN atoms is also possible, and for the case of carbon is known as *lonsdaleite*. In this "hexagonal diamond" the stacking sequence of planes of atoms is **AABBAABB**... , which is a doubling of the **ABAB**... sequence for the HCP crystal structure.

Crystal Structures Based on A–B$_4$. A–B$_4$ bonding units can be placed at the lattice points of an FCC lattice in the same way as was done for the A–A$_4$ units

TABLE 1.9 Elemental Crystals with the Diamond Crystal Structure

Element	a (nm)^a	Element	a (nm)^a
C	0.3567	Si	0.543
Ge	0.5657	Sn (gray)	0.649

^{a}Lattice constants are values at room temperature.
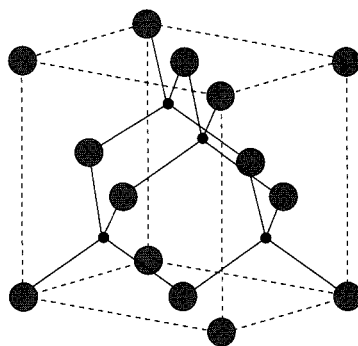
Figure 1.25. Zincblende (sphalerite or cubic ZnS) crystal structure based on the $A-B_4$ bonding unit.

of the diamond crystal structure. The resulting crystal structure, known as *zincblende* (*sphalerite*) or cubic ZnS, consists of a FCC lattice of A atoms and a second FCC lattice of B atoms displaced from each other by one-fourth of a body diagonal, along the [111] direction (Fig. 1.25). This crystal structure pos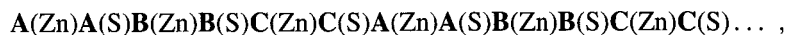sesses both $A-B_4$ and $B-A_4$ tetrahedral units. With the choice of the FCC lattice the basis consists of an A atom at $(0,0,0)$ and a B atom at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, with four A and four B atoms per conventional cubic unit cell. The stacking sequence for the (111) planes of the cubic ZnS structure is

$$A(Zn)A(S)B(Zn)B(S)C(Zn)C(S)A(Zn)A(S)B(Zn)B(S)C(Zn)C(S)\ldots,$$

where alternating (111) planes consist of either Zn or S atoms. Cubic ZnS can also be thought of as consisting of an FCC lattice of the larger S "anions" with four of the eight otherwise vacant tetrahedral interstitial sites occupied by the smaller Zn "cations".

Important examples of compounds that have the zincblende or cubic ZnS crystal structure are presented in Table 1.10. Both semiconductors and insulators are represented here, with bonding that has both ionic and covalent components. Additional examples are given in Table 11.9.

A hexagonal crystal structure based on the $A-B_4$ bonding unit also exists and is analogous to the hexagonal crystal structure discussed earlier for the $A-A_4$ unit. This structure, known as *wurtzite* or hexagonal ZnS (Fig. 1.26), can be seen also to consist of tetrahedral $A-B_4$ and $B-A_4$ bonding units. In the wurtzite structure the S "anions" lie on an HCP lattice in which the Zn "cations" occupy four of the eight otherwise vacant

TABLE 1.10 Crystals with the Zincblende (Cubic ZnS) Crystal Structure

Compound	a (nm)^a	Compound	a (nm)^a
ZnS	0.541	ZnSe	0.567
β-SiC	0.435	GaAs	0.565
CdS	0.583	AlAs	0.566
InSb	0.648	AlP	0.545
BN	0.362	GaP	0.545
BP	0.454		

^{a}Lattice constants are values at room temperature.
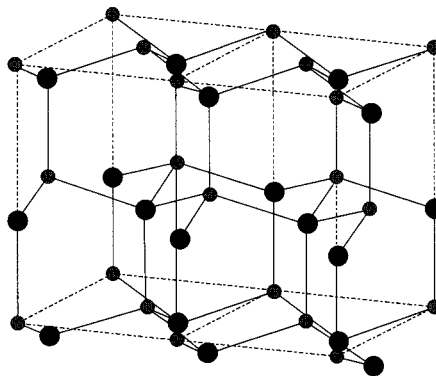
Figure 1.26. Wurtzite (hexagonal ZnS) crystal structure based on the $A-B_4$ bonding unit. (After R. J. Borg and G. J. Dienes, *The Physical Chemistry of Solids*, copyright 1992. Reprinted by permission of Academic Press, Inc.)

tetrahedral interstitial sites. With a hexagonal lattice, the basis of atoms for wurtzite within the hexagonal unit cell (see Fig. 1.17) can be chosen to be A atoms at $(0,0,0)$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$, as for the HCP structure, but also with B atoms at $(0,0,u)$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{2} + u)$ where $u = \frac{3}{8}$ when $c/a = \sqrt{\frac{8}{3}}$. The stacking of planes of atoms perpendicular to the c axis for hexagonal ZnS occurs in the sequence

$$A(Zn)A(S)B(Zn)B(S)A(Zn)A(S)B(Zn)B(S)\ldots .$$

Examples of binary compounds with the wurtzite crystal structure are also presented in Table 11.9.

Crystal Structures Based on A–A₃. When the central A atom of a planar $A-A_3$ unit is placed at every point of a HCP lattice, the *graphite* crystal structure results (Fig. 1.27). In this crystal structure every A atom is at the center of a planar $A-A_3$
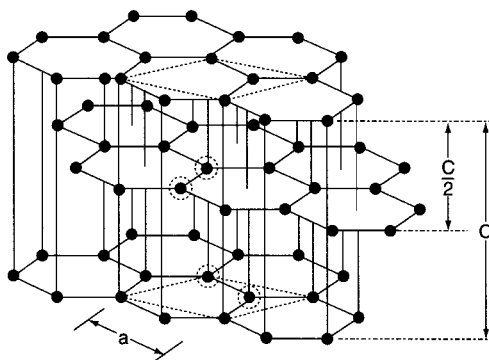
Figure 1.27. Graphite crystal structure based on the $A-A_3$ bonding unit. The hexagonal unit cell containing four identical atoms at $(0,0,0)$, $(\frac{1}{3},\frac{2}{3},0)$, $(0,0,\frac{1}{2})$, and $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$ is indicated. (After R. J. Borg and G. J. Dienes, *The Physical Chemistry of Solids*, copyright 1992. Reprinted by permission of Academic Press, Inc.)
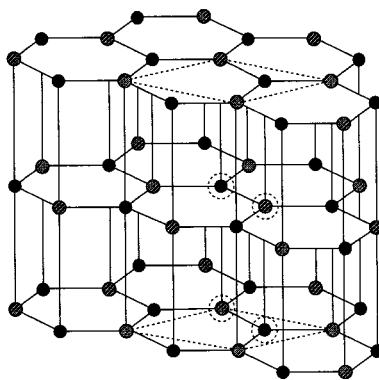
Figure 1.28. Crystal structure of hexagonal BN based on the A–B$_3$ bonding unit. The hexagonal unit cell containing two identical A atoms at $(0,0,0)$ and $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$ and two identical B atoms at $(\frac{1}{3},\frac{2}{3},0)$ and $(0,0,\frac{1}{2})$ is indicated.

unit and the stacking sequence of planes of atoms along the c axis is **ABABAB**. . . . The lattice constants for graphite are $a = 0.246$ nm and $c = 0.671$ nm. The resulting c/a ratio of 2.73 is quite high and results from the positioning of one-half of the atoms in a given layer directly above and below atoms in the adjacent layers. Choosing a hexagonal lattice and unit cell, the basis of atoms for this structure consists of four A atoms at $(0,0,0)$, $(\frac{1}{3},\frac{2}{3},0)$, $(0,0,\frac{1}{2})$, and $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$. No other element has the graphite crystal structure.

Crystal Structures Based on A–B$_3$. A crystal structure similar to graphite can be formed with every A atom at the center of an planar A–B$_3$ unit and every B atom at the center of a planar B–A$_3$ unit (Fig. 1.28). The stacking sequence of planes of atoms along the c axis is again **ABABAB**. . . . The basis of atoms corresponding to a hexagonal lattice and unit cell consists of A atoms at $(0,0,0)$ and $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$, as for HCP, and B atoms at $(0,0,\frac{1}{2})$ and $(\frac{1}{3},\frac{2}{3},0)$. The stoichiometry of crystals with this structure is therefore AB. Note that unlike atoms lie above and below each other in this structure. A crystal with this structure is hexagonal boron nitride (α-BN), which is isoelectronic with graphite. With lattice constants $a = 0.2504$ nm and $c = 0.6661$ nm, the c/a ratio for hexagonal BN is 2.66, quite close to that of graphite. Although the crystal structure is similar in appearance to that of graphite, the relative arrangement of atoms in adjacent planes is very different.

It is found that solids typically take on crystal structures that have the highest packing fraction and therefore the highest density consistent with the bonding present in the crystal. These two properties of crystals are defined and illustrated next.

1.8   Packing Fractions and Densities

Packing Fractions. The *packing fraction* of a crystal structure corresponds to the fraction of space filled by its atoms. The assumptions typically made are that the atoms

TABLE 1.11 Densities (10^3 kg/m^3) and Atomic Concentrations (10^{28} atoms/m^3) of the Elemental Solids[a]

Z	Symbol	Density	Concentration
1 (14K)	H	0.088	5.26
2 (4K)	He	0.209	3.15
3	Li	0.533	4.63
4	Be	1.84	12.33
5	B	2.28	12.70
6	C (graphite)	2.27	11.37
6	C (diamond)	3.52	17.63
7 (30K)	N	1.03	4.41
8 (55K)	O	1.33	5.02
9 (54K)	F	1.70	5.39
10 (30K)	Ne	1.51	4.50
11	Na	0.967	2.53
12	Mg	1.74	4.30
13	Al	2.70	6.02
14	Si	2.33	5.00
15	P	2.71	5.27
16	S	2.07	3.88
17 (113K)	Cl	2.04	3.64
18 (34K)	Ar	1.77	2.66
19	K	0.862	1.33
20	Ca	1.53	2.29
21	Sc	2.99	4.00
22	Ti	4.51	5.66
23	V	6.12	7.23
24	Cr	7.19	8.33
25	Mn	7.47	8.19
26	Fe	7.87	8.49
27	Co	8.84	9.03
28	Ni	8.91	9.14
29	Cu	8.94	8.47
30	Zn	7.14	6.57
31	Ga	5.91	5.11
32	Ge	5.33	4.42
33	As	5.78	4.65
34	Se	4.81	3.67
35 (123K)	Br	4.05	3.05
36 (116K)	Kr	2.84	2.04
37	Rb	1.53	1.08
38	Sr	2.58	1.78
39	Y	4.47	3.03
40	Zr	6.51	4.30
41	Nb	8.58	5.56
42	Mo	10.22	6.42
43	Tc	11.4	7.01
44	Ru	12.36	7.37
45	Rh	12.43	7.27
46	Pd	12.00	6.79
47	Ag	10.51	5.86
48	Cd	8.64	4.63
49	In	7.28	3.82
50	Sn	7.29	3.70
51	Sb	6.69	3.31
52	Te	6.24	2.94
53	I	4.94	2.35
54 (162K)	Xe	3.41	1.56
55	Cs	1.91	0.864
56	Ba	3.60	1.58
57	La	6.15	2.66
72	Hf	13.28	4.48
73	Ta	16.68	5.55
74	W	19.25	6.31
75	Re	21.01	6.80
76	Os	22.22	7.03
77	Ir	22.56	7.07
78	Pt	21.45	6.62
79	Au	19.29	5.90
80	Hg	14.26	4.28
81	Tl	11.87	3.50
82	Pb	11.35	3.30
83	Bi	9.81	2.83
84	Po	9.10	2.62
85	At	—	
86	Rd	—	
87	Fr	—	
88	Ra	5.50	1.47
89	Ac	10.07	2.67
58	Ce	6.69	2.87
59	Pr	6.77	2.89
60	Nd	7.01	2.93
61	Pm	7.17	2.98
62	Sm	7.54	3.02
63	Eu	5.24	2.08
64	Gd	7.90	3.03
65	Tb	8.23	3.12
66	Dy	8.55	3.17
67	Ho	8.80	3.21
68	Er	9.05	3.26
69	Tm	9.32	3.32
70	Yb	6.97	2.42
71	Lu	9.84	3.39
90	Th	11.73	3.04
91	Pa	15.43	4.02
92	U	19.05	4.82
93	Np	20.48	5.20
94	Pu	20.3	5.00
95	Am	13.8	3.42
96	Cm	13.7	3.35
97	Bk	14.7	3.58
98	Cf	15.2	3.65
99	Es	—	
100	Fm	—	
101	Md	—	
102	No	—	
103	Lr	—	

[a]Values correspond to room temperature, unless stated otherwise, and have been calculated using the structural data presented in Table 1.4.

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can be represented by hard spheres that are in contact with each other. The definition used here is

$$\text{packing fraction (PF)} = \frac{(\text{no. atoms per unit cell})(\text{volume per atom})}{\text{unit cell volume}}$$

$$= \frac{N(\text{atom})V(\text{atom}).}{V(\text{unit cell})} \tag{1.5}$$

This equation can easily be generalized for crystal structures containing more than one type of atom, as can be seen in Chapter W1. The volume $V(\text{atom}) = 4\pi r^3/3$ for spherical atoms of radius r.

As an example of the calculation of packing fractions, consider the simple cubic (SC) crystal structure. With one atom per cubic unit cell, it follows that $N(\text{atom}) = 1$ and $V(\text{unit cell}) = a^3$. To find the relationship between the atom radius r and the lattice constant a, note that two atoms are in contact along the edge of the cube in the [001] direction, as shown in Fig. W1.2a at our Web site. It follows that $a = 2r$, so that $V(\text{atom}) = \pi a^3/6$. Therefore,

$$\text{PF(SC)} = \frac{(1)(\pi a^3/6)}{a^3} = \frac{\pi}{6} = 0.52. \tag{1.6}$$

This relatively low PF for the SC crystal structure is due primarily to the presence of a vacant cubic interstitial site at the body-centered position.

Densities. For a crystal with a single type of atom, the number density or concentration of atoms $n(\text{atom})$ and the mass density ρ are defined as

$$n(\text{atom}) = \frac{N(\text{atom})}{V(\text{unit cell})}, \tag{1.7}$$

$$\rho(\text{kg/m}^3) = \frac{N(\text{atom})m(\text{atom})}{V(\text{unit cell})} = n(\text{atom})m(\text{atom}). \tag{1.8}$$

The generalizations to crystals with more than one type of atom is obvious.

The mass densities and atomic concentrations of crystals of the elements are given in Table 1.11. The crystalline element with the highest concentration of atoms is C in the form of diamond with $n = 1.76 \times 10^{29}$ atoms/m^3, a somewhat surprising result given the low packing fraction of 0.34 for this crystal structure. Crystals of Cs have the lowest atom concentrations, less than 1×10^{28} atoms/m^3, due to the large size of the atoms. Mass densities are found to be highest for crystals of the close-packed 5d transition metals Os and Ir, where ρ is over 22,000 kg/m^3. The elemental crystal with the lowest mass density is Li, with $\rho = 533$ kg/m^3.

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PROBLEMS

1.1 Using the primitive translation vectors given in Figs. 1.4 and 1.5, calculate the volumes of the BCC and FCC primitive unit cells.

1.2 Show that the face-centered tetragonal lattice is equivalent to the body-centered tetragonal lattice.

1.3 Show that the spacing $d(hkl)$ between adjacent lattice planes with Miller indices (hkl) is equal to $a/\sqrt{h^2 + k^2 + l^2}$ for cubic Bravais lattices and to $1/\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}$ for orthorhombic Bravais lattices.

1.4 Calculate the densities of lattice points in the (100), (110), (111), and (hkl) lattice planes of a simple cubic lattice.

1.5 Write a computer program that will determine the distance $d(n)$ from a given atom to the nth nearest neighbor (NN) in a Bravais lattice. Also compute $N(n)$, the number of nth NNs. Carry out the calculation for the SC, BCC, and FCC lattices.

1.6 Calculate the packing fractions for the following crystal structures: FCC, HCP, and diamond.

1.7 Show that the B atoms in an A–B_8 bonding unit come into contact with each other when $r_B = 1.366 r_A$ [i.e., when $r_A = (\sqrt{3} - 1)r_B$]. Here r_A and r_B are the radii of the hard-sphere A and B atoms, respectively. Find the analogous conditions on the radii for the A–B_6 and A–B_4 bonding units.

1.8 Prove for hard-sphere atoms in the HCP crystal structure that $c/a = \sqrt{8/3} = 1.633$.

1.9 Assuming that the atoms in the FCC crystal structure are hard spheres of radius R in contact with each other, calculate the maximum radii r of the smaller hard-sphere atoms that could occupy the octahedral and tetrahedral interstitial sites in the FCC crystal structure.

Note: An additional problem is given in Chapter W1.