Basic Properties of Crystals

CHAPTER OUTLINE

1.1 CRYSTAL LATTICES

A crystal lattice (Bravais lattice) is defined as an infinite array of discrete points that appear exactly the same from whichever of the points the array is viewed. If one starts from some point, all other points can be reached from it by the basic translations known as the lattice sites. For a three-dimensional lattice, these are defined by the set

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

where $\mathbf{R}$ is the lattice translation vector and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are three fundamental translation vectors that are not in the same plane. They are also known as primitive vectors that generate the lattice. Here, n_1, n_2, and n_3 are integers that can be zero, positive, or negative. In fact, a lattice is a mathematical concept used to identify crystal structures. Theoretically, a lattice spans the entire space.

It may be noted from Figure 1.1 that there is an infinite number of nonequivalent choices of primitive vectors and consequently primitive cells for any Bravais lattice (in two dimensions).
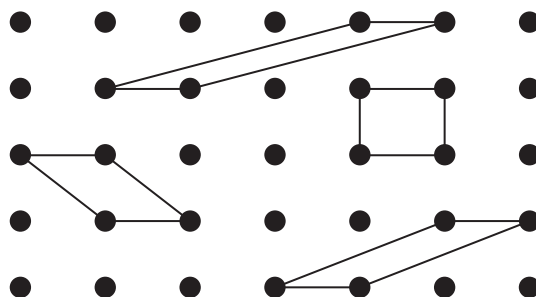

FIGURE 1.1

Possible choices of primitive cells for a two-dimensional square Bravais lattice.

1.1.1 Primitive Cell

The parallelepiped defined by the primitive axes $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ is called a primitive lattice cell. The volume of a primitive cell is $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$, and it has a density of one lattice point per unit cell. There are a variety of ways in which a primitive cell with the symmetry of the Bravais lattice can be chosen.

1.1.2 Unit Cell

A unit cell is defined as a cell that would define all space under the action of suitable crystal translation operators. Thus, a primitive cell is a minimum-volume unit cell. The difference between a primitive cell and a unit cell is shown in Figure 1.2. As we will see later, it is sometimes more convenient (especially in the case of cubic lattices) to define three-dimensional lattices in terms of unit cells rather than primitive cells.

1.1.3 Wigner–Seitz Cell

The Wigner–Seitz cell is obtained by drawing lines to connect a lattice point to all the neighboring lattice points and then by drawing new lines or planes at the midpoint and normal to these lines. The Wigner–Seitz cell is the smallest volume enclosed in this way. Figure 1.3 illustrates a Wigner–Seitz cell for a two-dimensional Bravais lattice. The Wigner–Seitz cell about a lattice point is the region of space that is closer to that point than to any other lattice point (except for points on the common surface of two or more Wigner–Seitz cells).

1.1.4 Lattice Point Group

A lattice point group is defined as the collection of the symmetry operations that leave the lattice invariant when applied about a lattice point. They include one-, two-, three-, four-, and six-fold rotations that correspond to rotations by 2π, π, $2\pi/3$, $\pi/2$, and $\pi/3$ radians as well as integral multiples of these rotations. These rotation axes are denoted as symbols 1, 2, 3, 4, and 6. A lattice point group also includes mirror reflections $\mathbf{m}$ about a lattice point. The inversion operation consists of a rotation of π and a reflection in a plane normal to the rotation axis such that $\mathbf{r}$ is replaced by $-\mathbf{r}$.
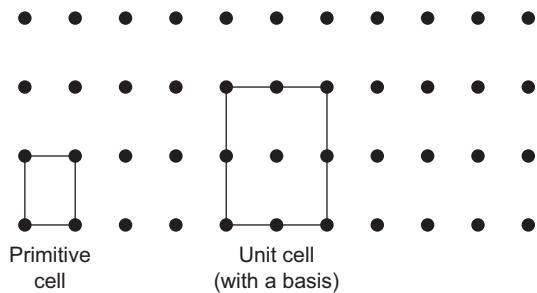

FIGURE 1.2

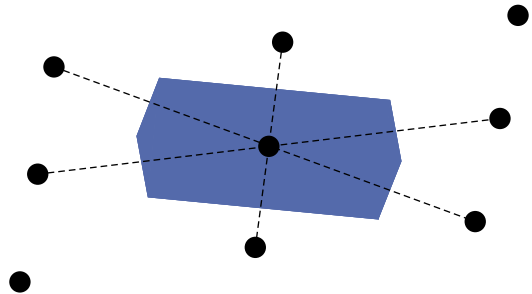Difference between a primitive cell and a unit cell for a rectangular lattice.

FIGURE 1.3

Wigner–Seitz primitive cell for a two-dimensional lattice.

1.2 BRAVAIS LATTICES IN TWO AND THREE DIMENSIONS

It can be shown that there are 5 distinct Bravais lattice types in two dimensions and 14 distinct Bravais lattices in three dimensions. These 14 Bravais lattices in three dimensions can be grouped into seven types of conventional unit cells. They are known as cubic (3), tetragonal (2), orthorhombic (4), monoclinic (2), triclinic (1), trigonal (1), and hexagonal (1). Later, we will discuss some of these Bravais lattices, an understanding of which is necessary in the study of commonly used solids. The three cubic Bravais lattices are simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) cells. These are shown in Figure 1.4. They all have cubic point groups, but their space groups are not equivalent.

1.2.1 Simple Cubic (sc) Lattice

The simple cubic lattice (Figure 1.4a) is generated by the primitive lattice vectors $a\hat{\mathbf{x}}$, $a\hat{\mathbf{y}}$, and $a\hat{\mathbf{z}}$, where a is a side of the cube (known as the lattice constant) and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are the three orthonormal vectors. It may be easily seen that the entire cubic lattice can be obtained by using the lattice translation vectors $\mathbf{R}$, as defined in Eq. (1.1), to connect any lattice point to another lattice point. In fact, the simple cubic (sc) lattice is the simplest three-dimensional Bravais lattice.

It may be noted that although there are eight lattice points at the corners of each cubic primitive cell, each lattice point is shared by eight such primitive cells. Considering that eight lattice points are shared by eight primitive cells, on the average, each primitive cell has one lattice point. However, not one of the lattice points belongs uniquely to any simple cubic primitive cell.

The Wigner–Seitz cell of a simple cubic Bravais lattice is also a simple cubic cell. However, the primitive cell is closer to its own lattice point except for points on the nearest-neighbor surface of two or more Wigner–Seitz cells. Therefore, each lattice point has its own Wigner–Seitz cell. When a Wigner–Seitz cell is translated by all the lattice vectors, it will fill the lattice without overlapping. In that sense, the Wigner–Seitz cell is extremely convenient to describe a primitive cell around each lattice point.

Only one known element, the alpha phase of polonium, crystallizes in the simple cubic form.

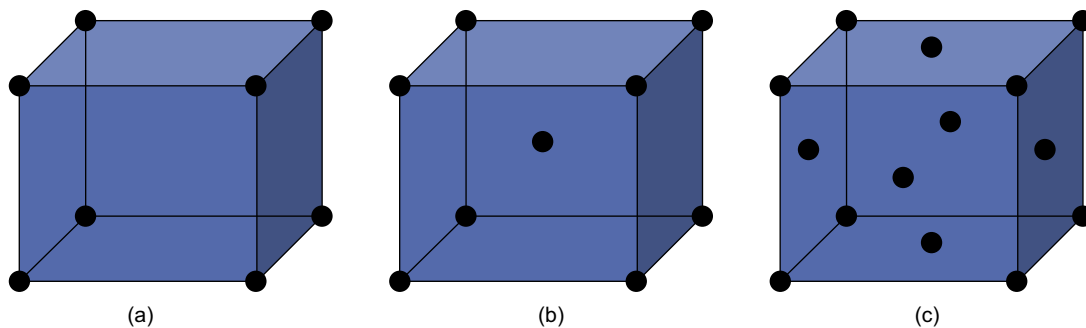(a)   (b)   (c)

FIGURE 1.4

Unit cells of the three cubic lattices: (a) simple cubic lattice (sc), (b) body-centered cubic lattice (bcc), and (c) face-centered cubic lattice (fcc).

1.2.2 **Lattice Constants**

The lattice constants are the numbers that specify the size of a unit cell. For example, the lattice constant for cubic crystals is a, the side of the cube. The maximum number of lattice constants for a unit cell can be three. These are, in general, on the order of a few angstroms and are experimentally determined by crystallographers using X-rays. There are a variety of reference texts in which the lattice constants of different crystal structures have been noted.

1.2.3 **Coordination Numbers**

The number of nearest neighbors of each lattice point in a Bravais lattice is the same because of its periodic nature and is known as the coordination number. The coordination number is a property of the lattice. For example, the coordination number of a square or rectangular lattice (in two dimensions) is 4, whereas the coordination number of a simple cubic lattice is 6.

1.2.4 **Body-Centered Cubic (bcc) Lattice**

The body-centered cubic (bcc) lattice (Figure 1.4b) can be obtained by adding a second lattice point at the center of each cubic cell of a simple cubic lattice. Thus, the unit cell of each bcc lattice can be considered as two interpenetrating simple cubic primitive lattices. In fact, there are two alternate ways of considering a bcc lattice, either with a simple cubic lattice formed from the corner points with a lattice point at the cube center, or with the simple cubic lattice formed from the lattice points at the center and the corner points located at the center of the new cubic lattice. In either case, each one of the eight lattice points at the corner of a cubic cell is shared by eight adjacent cubic cells, while the lattice point at the center of the cubic cell exclusively belongs to that cell. Therefore, the bcc lattice can be considered as a unit cubic cell with two lattice points per cell. The number of nearest neighbors of each lattice point is 8. Alternately, one can state that the coordination number is 8.

However, the primitive cell of a bcc lattice can also be easily obtained. In fact, there are a variety of ways in which the primitive vectors of the bcc lattice can be described. The most symmetric set of primitive vectors is given as follows:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \ \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \ \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \mathbf{y} - \hat{\mathbf{z}}), \tag{1.2}$$

where a is the lattice constant (the side of the unit cubic cell), and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are orthonormal vectors. It is important to note that $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are not orthogonal vectors. The parallelepiped drawn with these three vectors (shown in Figure 1.5) is the primitive cell of the bcc lattice. The eight corners of this primitive cell have eight lattice points, each shared by eight primitive cells.

It can be shown that the volume of the primitive Bravais cell is (Problem 1.1)

$$V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{a^3}{2}. \tag{1.3}$$

Because the volume of the unit cubic cell is a^3, and each unit cell has two lattice points, the primitive cell of the bcc lattice is half of the volume of the unit cell. However, not one of the lattice points uniquely belongs to any primitive cell shown in Figure 1.5. The lattice constants of bcc lattices at low temperatures are shown in Table 1.1. To be able to specify the primitive cell around each lattice point, one has to draw the Wigner–Seitz cell of the bcc lattice.

It can be easily shown that the Wigner–Seitz cell of a body-centered cubic Bravais lattice is a truncated octahedron (see Figure 1.6). The octahedron has four square faces and four hexagonal faces. The square faces bisect the lines joining the central point of a cubic cell to the central points of the six neighboring cubic cells. The hexagonal faces bisect the lines joining the central point of a

FIGURE 1.5

Symmetric set of primitive vectors for the bcc Bravais lattice.
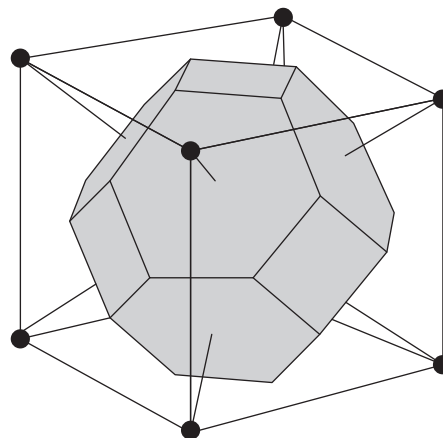
FIGURE 1.6

Wigner–Seitz cell of a bcc Bravais lattice.

Table 1.1 Lattice Constants of bcc Lattices at Low Temperatures	
Element	**Lattice Constant ($A°$)**
Barium	5.02
Chromium	2.88 (Cr also has fcc and hcp phases)
Cesium	6.05
Europium	4.61
Iron	2.87 (Fe also has fcc phase)
Potassium	5.23
Lithium	3.50
Molybdenum	3.15 (Mo also has fcc phase)
Sodium	4.29
Niobidium	3.30
Rubidium	5.59
Tantalum	3.31
Thallium	3.88 (T1 also has fcc and hcp phases)
Uranium	3.47
Vanadium	3.02
Tungsten	3.16
Source: R. W. G. Wyckoff, *Crystal Structures*, vol. 1 (J. Wiley, 1963).	

cubic cell to the eight corner points of the same cubic cell. The lattice point at the center of the bcc lattice is also at the center of this octahedron. Any point in the space within the octahedron (except for points on the common surface at two or more Wigner–Seitz cells) is closer to this central lattice point than any other central lattice point.

1.2.5 Face-Centered Cubic (fcc) Lattice

The face-centered cubic (fcc) Bravais lattice (Figure 1.4c) can be constructed from a simple cubic lattice (Figure 1.4a) by adding a lattice point in the center of each square face. Thus, there are eight lattice points, one each at the corner of the cubic unit cell, and six more lattice points, one each at the center of each square face. Each lattice point at the corner is shared by eight cubic cells, and each lattice point at the square face is shared by two cubic cells. Thus, the fcc lattice can be considered as a unit cubic cell with four lattice points per unit cubic cell. However, not one of the lattice points exclusively belongs to any unit cell. Each lattice point has 12 nearest neighbors. Therefore, the coordination number of a fcc lattice is 12.

Alternately, one can obtain the primitive Bravais cell for the fcc lattice. There are a variety of ways in which these primitive vectors can be obtained. The most symmetric set of primitive lattice vectors of a fcc lattice is

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \ \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \ \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}).$$
(1.4)

Here, a is the side of the cubic unit cell (the lattice constant), $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are orthonormal vectors, but $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are not orthogonal vectors. These vectors have been drawn in Figure 1.7. The lattice constants of fcc lattices at low temperatures are shown in Table 1.2.

The volume of the primitive Bravais cell is given by (Problem 1.2)

$$V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{a^3}{4}.$$
(1.5)

Because the volume of the unit cubic cell is a^3, and each unit cell has four lattice points, it is appropriate that the volume of the primitive cell of a fcc lattice is $a^3/4$. However, not one of the lattice points of the fcc Bravais lattice uniquely belongs to a primitive cell. The Wigner–Seitz cell for a fcc Bravais lattice is shown in Figure 1.8.
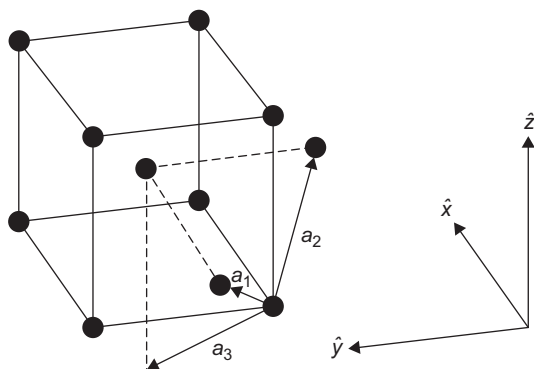

FIGURE 1.7

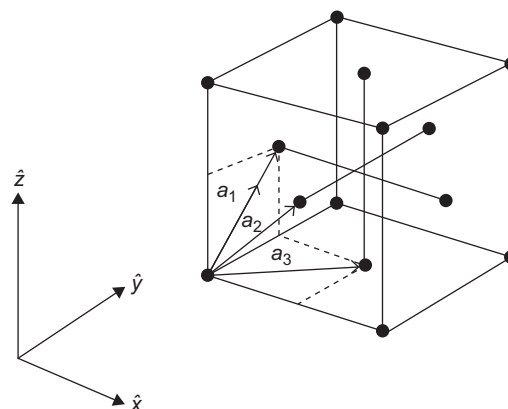Symmetric set of primitive vectors for the fcc Bravais lattice.
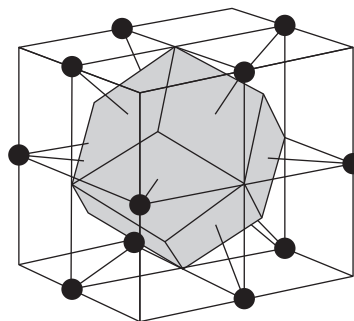

FIGURE 1.8

Wigner–Seitz cell for the fcc Bravais lattice.

As shown in Figure 1.8, the Wigner–Seitz cell of a fcc Bravais lattice is a "rhombic dodecahedron." The lattice points are at the center of the cube as well as at the center of the 12 edges. The Wigner–Seitz cell has 12 congruent faces, each of which is perpendicular to the line joining the center of an edge to the central point. Any point in the "rhombic dodecahedron" (except at the common surface of two or more Wigner–Seitz cells) is closer to this central point than any other central point of an adjacent Wigner–Seitz cell.

Table 1.2 Lattice Constants of fcc Lattices at Low Temperatures	
Element	**Lattice Constant ($A°$)**
Actinium	5.31
Silver	4.09
Aluminum	4.05
Americium	4.89
Argon	5.26
Gold	4.08
Calcium	5.58
Cerium	5.16 (Ce also has two hcp structures)
Cobalt	3.55 (Co also has two hcp structures)
Chromium	3.68 (Cr also has a bcc and an hcp structure)
Copper	3.61
Iron	3.59 (Fe also has a bcc structure)
Iridium	3.84
Krypton	5.72
Lanthanum	5.30 (La also has two hcp structures)
Molybdenum	4.16 (Mo also has a bcc structure)
Neon	4.43
Nickel	3.52 (Ni also has two hcp structures)
Lead	4.95
Palladium	3.89
Praseodymium	5.16 (Pr also has two hcp structures)
Platinum	3.92
Rhodium	3.80
Scandium	4.54 (Sc also has two hcp structures)
Strontium	6.08
Thorium	5.08
Thallium	4.84 (Th also has two hcp structures and a bcc structure)
Xenon	6.20
Ytterbium	5.49
Source: R. W. G. Wyckoff, *Crystal Structures,* vol. 1 (J. Wiley, 1963).	

1.2.6 Other Bravais Lattices

There are 7 crystal systems and 14 Bravais lattices in three dimensions. We have already discussed the 3 cubic Bravais lattices. We will discuss the primitive cells of the other 11 Bravais lattices. We note that sometimes it is more convenient as well as conventional to use a larger unit cell that involves atoms in the end, fcc, or bcc positions. In such cases, the advantage is that one can use orthogonal axes.

(a) Tetragonal Systems

There are two tetragonal systems. If a cube is stretched to make four of the sides into rectangles, an object with the symmetry of the tetragonal group is obtained. The solid is symmetric under reflections about planes that bisect it although the three-fold symmetry and the 90° rotation symmetry about two of the axes are lost. If a simple cubic lattice is stretched, a simple tetragonal lattice, shown in Figure 1.9a, is obtained. It has the sides $a = b \neq c$ and the angles $\alpha = \beta = \gamma$. If either a fcc lattice or a bcc lattice is stretched, a centered tetragonal lattice shown in Figure 1.9b is obtained. It also has the sides $a = b \neq c$ and the angles $\alpha = \beta = \gamma$ and, in addition to the above, a body-centered lattice point.

(b) Orthorhombic Systems

If the top and bottom squares of the tetragonal solid are deformed into rectangles, the 90° rotational symmetry is eliminated. One obtains a solid with orthorhombic symmetry. There are four orthorhombic systems. When a simple tetragonal lattice (Figure 1.9a) is deformed along one of its axes, a simple orthorhombic lattice, as shown in Figure 1.10a, is obtained. When one stretches a simple tetragonal lattice along face diagonals, the base-centered orthorhombic lattice shown in Figure 10b is obtained. When a centered tetragonal lattice (Figure 1.9b) is deformed, a body-centered orthogonal lattice (Figure 1.10c) is obtained. When one stretches the centered tetragonal lattice along the face diagonals, the face-centered orthorhombic lattice (Figure 1.10d) is obtained. All these Bravais lattices shown in Figure 1.10 have lattice constants $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$.
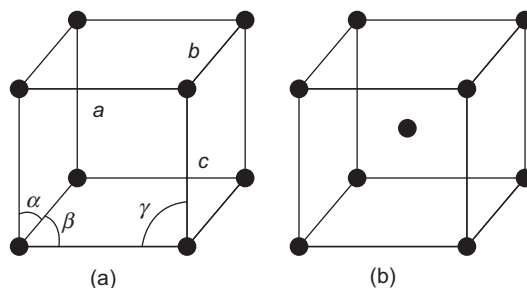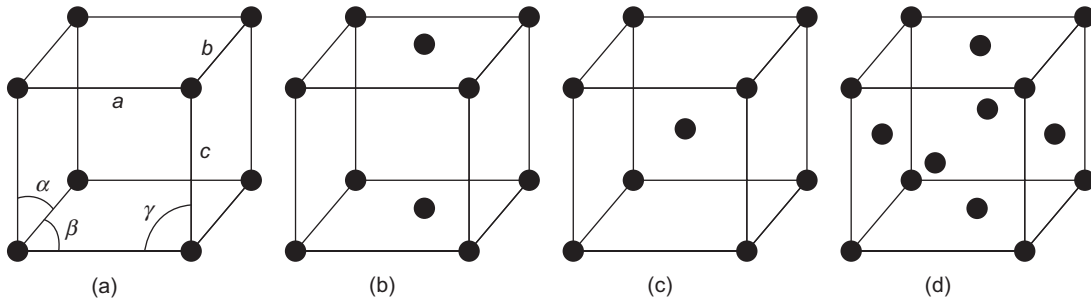

FIGURE 1.9

The two tetragonal Bravais lattices: (a) simple and (b) centered.

FIGURE 1.10

The Bravais lattices for the four orthorhombic systems.
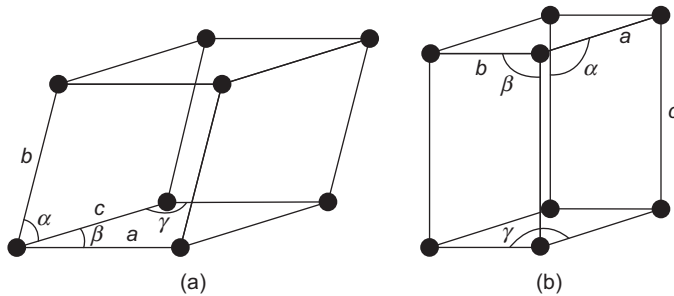
FIGURE 1.11

The Bravais lattices for the rhombohedral or trigonal systems and the hexagonal systems.

(c) Rhombohedral or Trigonal Systems

If a cube is stretched across a body diagonal, one obtains a solid with rhombohedral or trigonal symmetry. Stretching any of the three cubic Bravais lattices produces the same Bravais lattice known as the rhombohedral lattice or the trigonal lattice. The rhombohedral system is shown in Figure 1.11a. In the rhombohedral system, the lattice constants are $a = b = c$ and the angles are $\alpha = \beta = \gamma \neq 90°$.

(d) Hexagonal Systems

A solid can be formed with a hexagon at the base and perpendicular walls such that it has hexagonal symmetry. This Bravais lattice is called the hexagonal lattice. In the hexagonal system, shown in Figure 1.11b, the lattice constants are $a = b \neq c$ and the angles are $\alpha = \beta = 90°$, $\gamma = 120°$.

(e) Monoclinic and Triclinic Systems

A solid with monoclinic symmetry can be generated by squeezing a tetragonal solid across a diagonal in a manner such that the 90° angles on the top and bottom faces are eliminated. However,
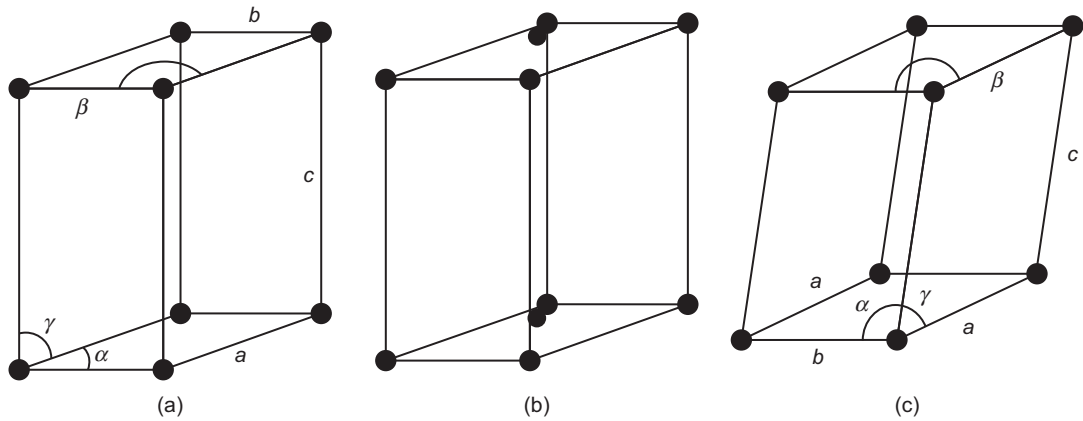
FIGURE 1.12

The Bravais lattices for the monoclinic and triclinic systems.

the sides are built out of rectangles. The simple monoclinic lattice shown in Figure 1.12a is obtained by distorting either the simple orthorhombic lattice or the base-centered orthorhombic lattice. The centered monoclinic lattice shown in Figure 1.12b is obtained from the distortion of either the face-centered orthorhombic lattice or the body-centered orthorhombic lattice. For the two monoclinic systems, the lattice constants are $a \neq b \neq c$ and the angles are $\alpha = \gamma = 90°$, $\beta \neq 90°$. The triclinic system, shown in Figure 1.12c, is obtained by pulling the top of a monoclinic solid sideways relative to the bottom. Thus, all the faces become diamonds, and the only remaining symmetry is inversion symmetry. For the triclinic system, the lattice constants are $a \neq b \neq c$ and the angles are $\alpha, \beta, \gamma \neq 90°$.

1.3 LATTICE PLANES AND MILLER INDICES

A lattice plane is defined to be a plane that has at least three noncollinear Bravais lattice points. In fact, such a plane would contain an infinite number of two-dimensional Bravais lattice points. A three-dimensional Bravais lattice is represented as a family of parallel equally spaced lattice planes. Such lattice planes can be constructed in a lattice in a variety of ways. Figures 1.13a and b represent two ways of representing the same simple cubic Bravais lattice as a family of lattice planes.

The Miller indices are used to label a crystal plane. They are obtained by using the following procedure. All the Bravais lattice points lie on a chosen assembly of equally spaced parallel lattice planes (whether cubic or otherwise). Certain planes of the assembly (sometimes all of them) will always intersect the coordinate axes at the lattice points. Therefore, every plane in this chosen set of parallel planes would intercept the coordinate axes that bear a definite rational ratio to one another. To define the Miller indices, one adopts the following procedure. One

(a)   (b)
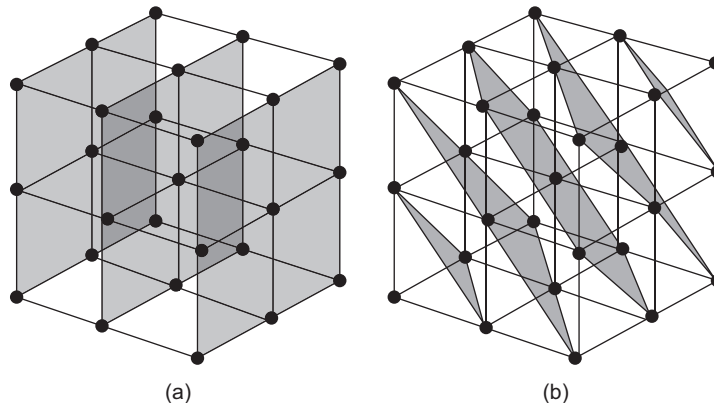
FIGURE 1.13

Lattice planes in a simple cubic lattice. The shaded regions in (a) and (b) are two of the infinite ways in which a family of lattice planes can be represented in the same cubic lattice.

of the lattice points is chosen as the origin, and the coordinate axes are chosen such that they are not coplanar. In some cases, such as the cubic lattices, the coordinate axes are chosen as orthogonal and parallel to the sides of the cubic unit cell. This property of the Bravais lattice was used to define the Miller indices by crystallographers and was later used for the proper definition of reciprocal lattice vectors. The Miller indices are obtained by using the following prescription:

1. Determine the intercepts on the axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ in the units of lattice constants. Here, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ need not be primitive vectors. For example, determine $\frac{a_1}{a}, \frac{a_2}{b}, \frac{a_3}{c}$, where a, b, c are the lattice constants of the three-dimensional lattice (note that $a = b = c$ for a cubic lattice). These intercepts have rational ratios although they are not, in general, integers.
2. Take the reciprocal of each number, i.e., $\frac{a}{a_1}, \frac{b}{a_2}, \frac{c}{a_3}$.
3. Then reduce these numbers to the three smallest integers h, k, l that have the same ratio. The integers h, k, l are called the Miller indices.
4. The parentheses (hkl) denote a single crystal plane or a set of parallel planes.
5. If a plane cuts an axis on the negative side of the origin, the negative index is indicated by placing a minus sign above the index $(h\bar{k}l)$. If a plane is parallel to a particular axis, because the intercept with the axis occurs at infinity, the corresponding Miller index is zero (reciprocal of infinity). Thus, the cube faces of a cubic crystal are (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$.
6. Planes equivalent by symmetry are denoted by curly brackets $\{hkl\}$. Thus, the set of cube faces of a cubic crystal described previously can also be described as $\{100\}$.
7. A direction in a lattice is denoted by square brackets $[hkl]$. In cubic crystals, the direction $[hkl]$ is always perpendicular to a plane (hkl) having the same directions. However, this is not true for other crystals. Figure 1.14 shows the lattice planes and their Miller indices in a simple cubic lattice.
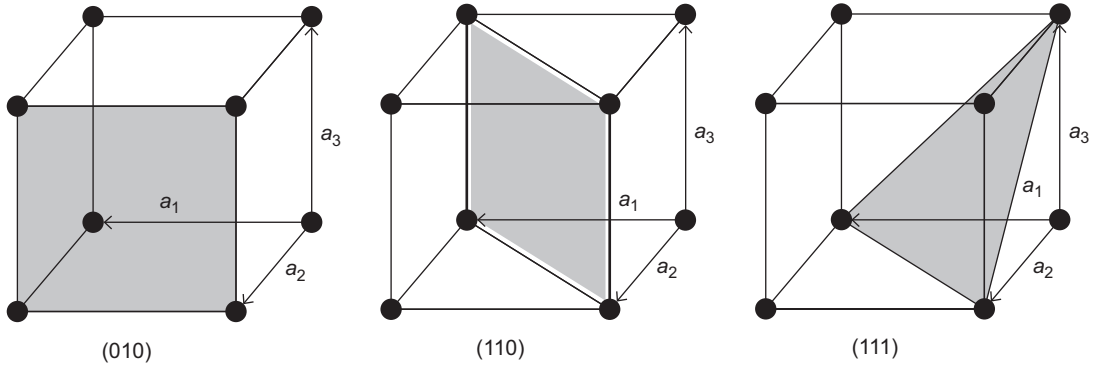
(010) (110) (111)

FIGURE 1.14

Lattice planes and their Miller indices in a simple cubic lattice.

1.4 BRAVAIS LATTICES AND CRYSTAL STRUCTURES

1.4.1 Crystal Structure

A crystal structure is obtained when an identical basis of atoms is attached to each lattice point. We will give a simple example of two atoms A and B (of different types) to illustrate a crystal structure.

Figure 1.15 shows an example of a two-dimensional crystal structure with two types of atoms A and B. Figure 1.15a shows a two-dimensional rectangular lattice. Figure 1.15b shows a basis of two different types of atoms, A and B. It has to be emphasized that the basis is the definition of the same physical unit of atoms or ions (ranging from 1 for some elements to nearly 100 for some complex proteins) that is located symmetrically at each point of the Bravais lattice. Thus, a basis can be translated through all the vectors of a Bravais lattice, and another identical basis with the same location around another lattice point would be reached. The crystal structure is defined (Figure 1.15c) as a lattice with a basis. In fact, this symmetry of the crystals makes it possible to study their physical properties. We note that the lattice points in the rectangular lattice can be symmetrically shifted in the crystal structure as long as the basis of atoms is grouped symmetrically around each lattice point.

1.4.2 Lattice with a Basis

We also note that there is a dichotomy in the usage of the words "lattice with a basis." In addition to describing a crystal structure, in which case the basis is the description of identical atoms or ions based symmetrically around each lattice point, this expression is also used to describe a Bravais lattice as a lattice with a basis. As examples of the most commonly used lattices, the bcc Bravais lattice can be described as a simple cubic lattice (the unit cell) with a two-point basis

$$\mathbf{0}, \ \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}), \tag{1.6}$$

and the fcc lattice can be described as a four-point basis

$$\mathbf{0}, \ \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}), \ \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \ \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}). \tag{1.7}$$
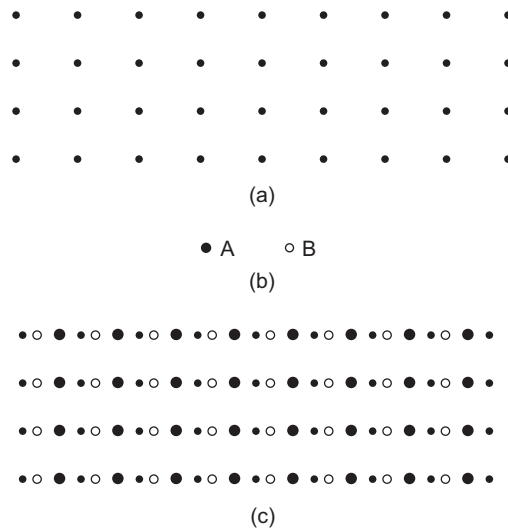
FIGURE 1.15

(a) A two-dimensional rectangular lattice; (b) basis of two atoms, A and B; (c) Crystal structure
(two dimensions): lattice + basis.

1.4.3 Packing Fraction

The packing fraction of a crystal structure is defined as the fraction of space occupied by the atoms
or ions considered as contacting hard spheres. For example, a bcc crystal has a packing fraction of
0.68, and a fcc crystal has a packing fraction of 0.74.

1.5 CRYSTAL DEFECTS AND SURFACE EFFECTS

1.5.1 Crystal Defects

It has to be noted at this point that no crystal, either grown naturally or in the laboratory, is perfect.
There are a certain number of impurities, varying in range depending on the laboratory conditions dur-
ing crystal growth, that are invariably present. The average number of impurities in reasonably pure
crystal is 1 in 10,000. There are also lattice defects in the crystal in the sense that an atom is found not
at the designated lattice point, but either it is missing or found at an interstitial. This is called a lattice
defect, and such defects are also in the range of 1 in 10,000. The crystal impurities and lattice defects,
together known as crystal defects, do play a significant role in certain physical properties of the crystal.

1.5.2 Surface Effects

There is another significant difference between a lattice and a crystal structure even if there are only
single atoms or ions (called monatomic lattice) at each lattice point in the crystal structure. As defined
earlier, a lattice is a mathematical concept that extends to infinity in all dimensions, whereas every

crystal has finite dimensions. In general, a crystal has a huge number of atoms (around 10^{23}). This difference between the infinite lattice and the finite lattice structure is not significant inside the crystal, and as we will discuss later, one gets around the finite size of the crystal by using periodic boundary conditions. Therefore, the concept of a Bravais lattice can be extended to a crystal. However, this concept breaks down when one approaches the surface of the crystal because the periodicity of the lattice, which is the cornerstone of most of the basic theoretical concepts of solid state physics, is no more valid. Therefore, the physical properties at or near the surface of a crystal are very different. The study of these surface properties, constrained by the nonperiodicity in a third dimension perpendicular to the surface, requires application of different techniques and is by itself a vast and fascinating field.

1.6 SOME SIMPLE CRYSTAL STRUCTURES

1.6.1 Sodium Chloride Structure

The sodium chloride structure is shown in Figure 1.16. There are equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice. Each ion has six of the other kind of ions as its nearest neighbor. Thus, the coordination number is 6. The crystal structure can be described as a Bravais fcc lattice with a basis. The basis consists of one sodium ion at **0** and one chlorine ion at the center of the cubic unit cell; i.e., at $(a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$.

The compounds that have the sodium chloride structure include AgBr, AgCl, AgF, BaO, BaS, BaSe, BaTe, CaO, CaS, CaSe, CaTe, CsF, KBr, KCl, KF, KI, LiBr, LiCl, LiF, LiH, LiI, MgO, MgS, MgSe, MnO, NaBr, NaCl, NaF, NaI, RbBr, PbS, RbCl, RbF, RbI, SrO, SrS, SrSe, SrTe, and UO.

1.6.2 Cesium Chloride Structure

The cesium chloride structure is shown in Figure 1.17. There is one molecule per unit cubic cell with the ions in the body-centered positions; i.e., Cs^+: 000 and Cl^-: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Thus, the cesium chloride
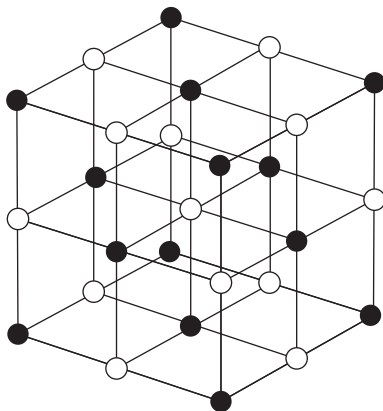

FIGURE 1.16
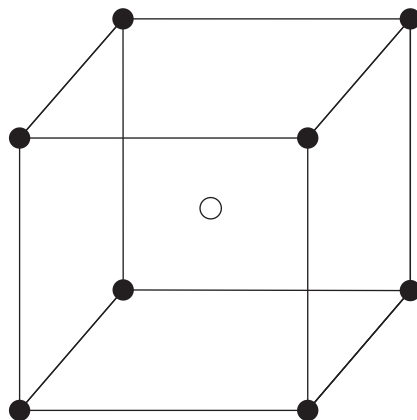
The sodium chloride structure.

FIGURE 1.17

CsCl structure.

structure can be described as a simple cubic lattice with a basis. The cesium ion is at the origin $\mathbf{0}$, and the chlorine ion is at $(a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. Because each ion is at the center of a cube of ions of the other type of ions, the coordination number is 8.

The compounds that have the cesium chloride structure include AlNi, BeCu, CsBr, CsCl, CsI, LiHg, NH_4Cl, RbCl, TlBr, TlCl, and TlI.

1.6.3 Diamond Structure

The diamond structure is shown in Figure 1.18. The diamond cubic structure (Ref. 2a) consists of two interpenetrating fcc Bravais lattices displaced from each other by one-quarter of a body diagonal. Alternately, it can be considered as a fcc lattice with basis at $\mathbf{0}$ and at $(a/4)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. The diamond structure is a result of covalent bonding. The covalent bond between two atoms is a very strong bond between two electrons, one from each atom, with directional properties. The spins of the two electrons are antiparallel, and the electrons forming the bond tend to be localized in the region between the two atoms. Because the C, Ge, and Si atoms each lack four electrons to form filled shells, these elements can have attractive interaction due to charge overlap, a type of interaction not found between atoms with filled shells because of the Pauli exclusion principle and the consequent repulsive interaction. There are eight atoms in a unit cube, and each atom has 4 nearest neighbors and 12 next nearest neighbors in the diamond lattice. Hence, the diamond lattice, which is not a Bravais lattice, is relatively empty. The 4 nearest neighbors of each atom form the vertices of a regular tetrahedron, and the covalent bonding between the neighboring atoms in the diamond structure is also known as tetrahedral bonding. The maximum proportion of the volume that is available to be filled by hard spheres is 0.34. The elements that crystallize in the diamond structure are C (diamond), Si, Ge, and α-Sn (grey). The coordination number of the diamond lattice is 4, and the packing fraction is 0.34.
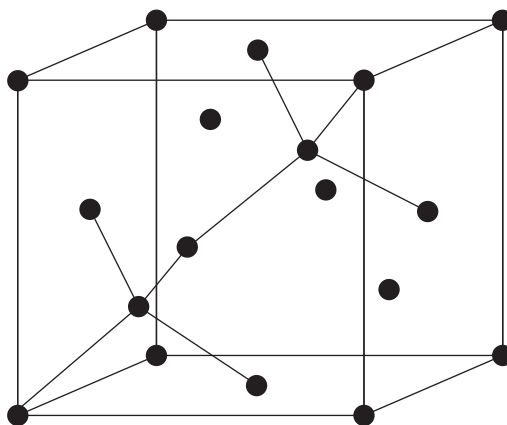

FIGURE 1.18

The diamond cubic structure.

1.6.4 **Zincblende Structure**

The zincblende (or cubic zinc sulfide) structure, shown in Figure 1.19, is obtained from the diamond structure (Figure 1.18) when Zn ions are placed on one fcc lattice and S ions are placed on the other fcc lattice. Thus, each ion has four of the opposite type as nearest neighbors.

Some crystals with zincblende structure are AgI, AlAs, AlP, AlSb, BeS, BeSe, BeTe, CdS, CdTe, CuBr, CuCl, CuF, CuI, GaAs, GaP, GaSb, HgS, HgSe, HgTe, InAs, InP, InSb, MnS(red), MnSe, SiC, ZnS, ZnSe, and ZnTe.

1.6.5 **Hexagonal Close-Packed (hcp) Structure**

The hexagonal close-packed (hcp) structure is not a Bravais lattice, but a large number of elements crystallize in this form. If we assume atoms to be hard spheres, close-packed planes with hexagonal symmetry (see Figure 1.20) can be formed.

If one starts with the atom in position A, there are two other kinds of spaces between the atoms, B or C. If the second plane is placed on the B positions, a third nesting layer can be placed either over site A or site C. The stacking ABABAB… yields the hcp structure while the stacking ABCABC… gives the fcc structure (see Problems 1.8 and 1.11). Both types of stacking have the same density of packing, and the packing fraction is 0.74.

The unit cell of the hcp structure is the hexagonal primitive cell, and the basis contains two elements of the same type. The ideal c/a ratio for hcp structures is $\sqrt{\frac{8}{3}} = 1.633$. Figures 1.21 and 1.22 represent two alternate ways of representing the hcp structure.

In Figure 1.21, the unit cell of the hcp structure is shown. The unit cell of the hcp structure is the hexagonal primitive cell, and the basis contains two atoms. One atom of the basis is at the origin (000), and the other atom is at $\left(\frac{2}{3}\frac{1}{3}\frac{1}{2}\right)$, which means at $\mathbf{r} = 2/3\mathbf{a} + 1/3\mathbf{b} + 1/2\mathbf{c}$. The c/a ratio of hexagonal
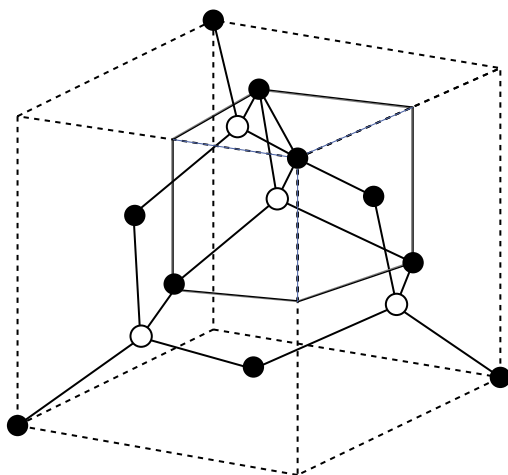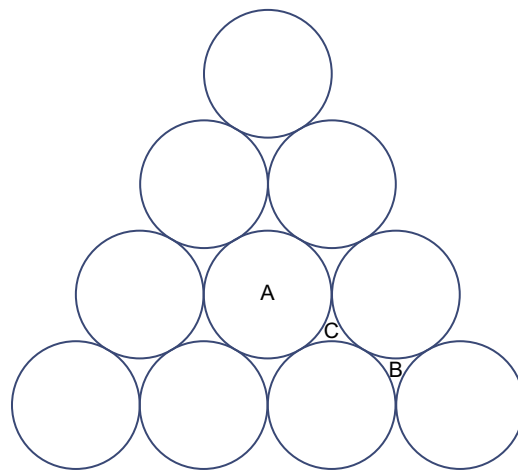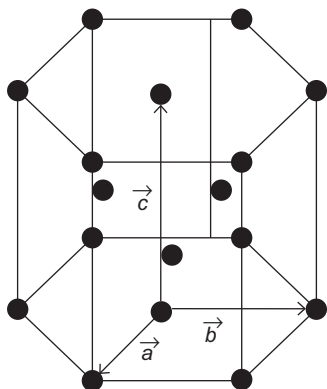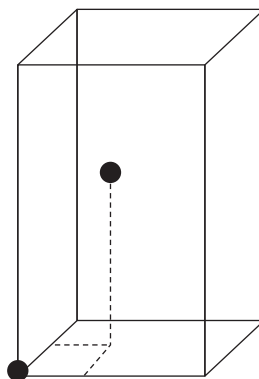

FIGURE 1.19

Zincblende structure.

FIGURE 1.20

The three sites A, B, and C in a close-packed plane of atomic spheres (the [111] plane of a fcc structure or the basal plane of a hcp structure).

FIGURE 1.21

The hexagonal close-packed (hcp) structure.

FIGURE 1.22

The basic unit of hcp structure as a trigonal cell with two identical atoms as the basis at (000) and $(\frac{1}{3}\frac{1}{3}\frac{1}{2})$. (Note the differences in origin between Figures 1.21 and 1.22.)

close-packing of spheres is 1.633. However, several crystals, of which the c/a ratio is quite different, such as zinc with a c/a ratio of 1.85, are also called hcp structures. The lattice constants of elements with hcp structure are shown in Table 1.3.

The coordination number is the same for both fcc and hcp structures. Therefore, at appropriate temperatures, many metals transform easily between fcc and hcp structures. This is called martinestic transformation. However, the alternate way to describe the basic unit of hcp structure is a trigonal cell containing two atoms, which is shown in Figure 1.22.

The basic unit of the unit cell of the hcp structure described in Figure 1.22 is the trigonal cell containing two identical atoms at (000) and $(\frac{1}{3}\frac{1}{3}\frac{1}{2})$. We note that the origins and the lattice vectors are chosen differently in Figures 1.21 and 1.22. The choice of any one of the two alternate methods of representing the same hcp crystal structure depends on convenience.

Table 1.3 Lattice Constants of Elements with hcp Structure		
Element	**a($A°$)**	**c($A°$)**
Beryllium	2.29	3.58
Cadmium	2.98	5.62
Cerium	3.65	5.96
Chromium	2.72	4.43
Cobalt	2.51	4.07
Dysprosium	3.59	5.65
Erbium	3.55	5.59
Gadolinium	3.56	5.80
Hafnium	3.20	5.06
Helium (2 K and 26 atm)	3.57	5.83

(*Continued*)

Table 1.3 Lattice Constants of Elements with hcp Structure—cont'd		
Element	**a($A°$)**	**c($A°$)**
Holmium	3.58	5.62
Hydrogen (molecule)	3.75	6.49
Lanthanum	3.75	6.07
Lutetium	3.50	5.55
Magnesium	3.21	5.21
Neodymium	3.66	5.90
Nickel	2.65	4.33
Osmium	2.74	4.32
Praseodymium	3.67	5.92
Rhenium	2.76	4.46
Ruthenium	2.70	4.28
Scandium	3.31	5.27
Terbium	3.60	5.69
Titanium	2.95	4.69
Thallium	3.46	5.53
Thulium	3.54	5.55
Yttrium	3.65	5.73
Zinc	2.66	4.95
Zirconium	3.23	5.15
Source: R. W. G. Wyckoff, *Crystal Structures,* vol. 1 (J. Wiley, 1963).		

1.7 BRAGG DIFFRACTION

W. L. Bragg considered a crystal as made up of a set of parallel lattice planes of ions spaced equal distances d apart, as shown in Figure 1.23.

If the incident waves are reflected specularly, the reflected rays (also known as diffracted rays) would interfere constructively if the path difference is

$$2d \sin \theta = n\lambda, \tag{1.8}$$

where θ is the angle of incidence and n is an integer, also known as the order of the corresponding reflection. This is the famous Bragg law of X-ray diffraction, (Ref. 2a) although the same law is valid for other types of waves (such as electron waves) as long as there is specular reflection from the ions in the crystal lattice. The Bragg law considers the periodicity of the lattice but does not include the basis of ions or atoms at each lattice point. In fact, it is the composition of the basis that determines the intensity of diffraction for various orders of n. In addition, it is pertinent to note that the crystal planes can be arranged in an infinite number of ways. Even for the same incident ray, both the direction and intensity of the reflected (note that we are using *diffraction* and *reflection* interchangeably) rays would depend on the orientation of the crystal planes.

One immediate consequence of the Bragg law (Eq. 1.8) is that Bragg reflection can occur only for wavelengths $\lambda \leq 2d$. Originally, Bragg diffraction was used by crystallographers to study the
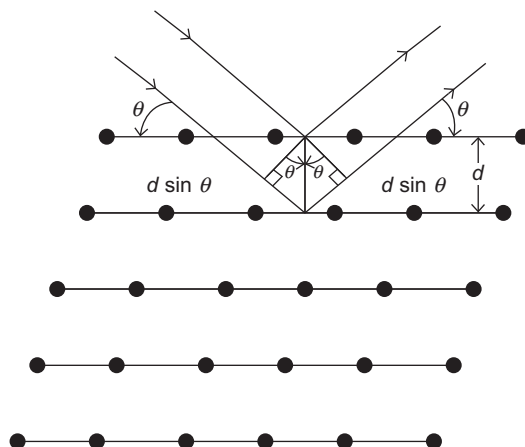
FIGURE 1.23

Bragg reflection from a family of lattice planes.

crystal structure of solids. Later, after the discovery of diffraction of electrons from a periodic crystal by Davisson and Germer, Bragg diffraction became important in understanding the theory of crystalline solids.

1.8 LAUE METHOD

Von Laue considered the X-ray diffraction from a crystal by considering it as composed of identical atoms or ions (basis) placed at the lattice sites **R** of a Bravais lattice. Each ion or atom at these sites would reradiate the incident radiation in all directions (Laue did not make any assumptions about specular reflections). However, sharp peaks would be observed only at appropriate wavelengths and directions when the scattered radiations from the ions or atoms (basis) placed at sites **R** would interfere constructively.

We consider two ions, separated by the vector **d** (see Figure 1.24).

If $\hat{\mathbf{n}}$ is the direction of the incident radiation of wavelength λ, the incident wave vector $\mathbf{k} = 2\pi\,\hat{\mathbf{n}}/\lambda$. If the path difference between the radiation scattered by each of the two ions is $m\lambda$, where m is an integer, the scattered radiation (assuming elastic scattering) would be observed in the direction $\hat{\mathbf{n}}'$ with the same wavelength λ and wave vector $\mathbf{k}' = 2\pi\hat{\mathbf{n}}'/\lambda$. This leads to constructive interference, the condition for which is (Figure 1.24)

$$\mathbf{d} \cdot (\hat{\mathbf{n}} - \hat{\mathbf{n}}') = m\lambda. \tag{1.9}$$
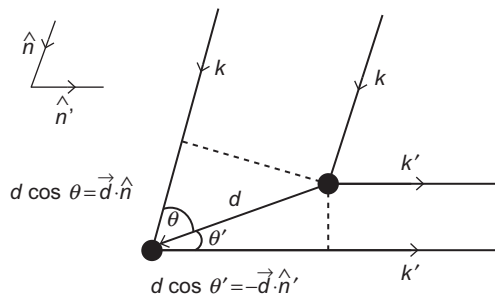
FIGURE 1.24

Path difference of X-rays scattered by two points separated by **d**.

Multiplying Eq. (1.9) by $2\pi/\lambda$ and using the definitions of $\mathbf{k}$ and $\mathbf{k}'$, we can write Eq. (1.9) in the alternate form

$$\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m. \tag{1.10}$$

If we consider all the ions at each site of the Bravais lattice, the condition of constructive interference of all the scattered radiations is obtained from a generalization of Eq. (1.10), which can be written in the form

$$\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m, \tag{1.11}$$

where $\mathbf{R}$ is a direct lattice vector of the Bravais lattice. If we write

$$\mathbf{K} = \mathbf{k} - \mathbf{k}' = \mathbf{k}' - \mathbf{k}, \tag{1.12}$$

where $\mathbf{K}$ is the set of wave vectors that satisfy the condition of constructive interference of all the scattered radiations (Eq. 1.11), i.e.,

$$\mathbf{K} \cdot \mathbf{R} = 2\pi m. \tag{1.13}$$

In Section 1.9, we will study the properties of the reciprocal lattice constructed from the set of wave vectors $\mathbf{K}$ by first constructing them using the basic properties of the direct lattice vectors $\mathbf{R}$.

1.9 **RECIPROCAL LATTICE**
1.9.1 **Definition**

If $\mathbf{R}$ is a set of points that constitute a Bravais lattice as defined in Eq. (1.1),

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

there would exist a particular set of wave vectors $\mathbf{K}$ that would yield plane waves with the periodicity of the lattice. The analytic definition of the set of vectors $\mathbf{K}$ would be

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{1.14}$$

for any vector $\mathbf{r}$ and all direct lattice vectors $\mathbf{R}$ in the Bravais lattice. Eq. (1.14) can be written in the alternate form

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1. \tag{1.15}$$

The set of wave vectors $\mathbf{K}$ that satisfy Eq. (1.14) for any direct lattice vector $\mathbf{R}$ that generates a Bravais lattice is defined as the reciprocal lattice of that Bravais lattice. It is obvious that each Bravais lattice has its own reciprocal lattice.

It can be shown that the reciprocal lattice can be generated from the three primitive vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, where $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are defined by

$$
\begin{aligned}
\mathbf{b}_1 &= 2\pi\,\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\
\mathbf{b}_2 &= 2\pi\,\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\
\mathbf{b}_3 &= 2\pi\,\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.
\end{aligned}
\tag{1.16}
$$

It is easy to show from Eq. (1.16) that (Problem 1.13)

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}, \tag{1.17}$$

where δ_{ij} is the Kronecker delta function, defined by $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i = j$.

We also note from Eqs. (1.16) and (1.17) that the vectors $\mathbf{b}_1, \mathbf{b}_2$, and $\mathbf{b}_3$, are in the reciprocal space and are not in the same plane because the primitive lattice vectors $\mathbf{a}_1, \mathbf{a}_2$, and $\mathbf{a}_3$ are not coplanar. Therefore, any vector $\mathbf{k}$ in the reciprocal space can be written as

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3. \tag{1.18}$$

From Eqs. (1.1), (1.16), and (1.18), we obtain

$$\mathbf{k} \cdot \mathbf{R} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3). \tag{1.19}$$

For Eq. (1.15) to hold true for any $\mathbf{K}$,

$$\mathbf{K} \cdot \mathbf{R} = 2\pi m, \tag{1.20}$$

where m is an integer. Because n_1, n_2, and n_3 are integers, and we obtain from Eqs. (1.19) and (1.20) that

$$m = k_1n_1 + k_2n_2 + k_3n_3, \tag{1.21}$$

whenever $\mathbf{k} = \mathbf{K}$. Eq. (1.21) must hold good for any choice of the integers n_i. It follows that k_1, k_2, and k_3 are also integers whenever $\mathbf{k} = \mathbf{K}$. Thus, we can write m in the alternate form

$$m = m_1 + m_2 + m_3, \tag{1.22}$$

where each m_i is an integer. If we write $m_1 = hn_1, m_2 = kn_2$, and $m_3 = \ln_3$, where h, k, l are integers, the reciprocal lattice vectors can be expressed as

$$\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3, \tag{1.23}$$

Later, we will identify h, k, l as the Miller indices introduced earlier. As mentioned earlier, any Bravais lattice has its own reciprocal lattice. It has sometimes been compared to each person having his or her own shadow.

1.9.2 Properties of the Reciprocal Lattice

We can enumerate some of the properties of the reciprocal lattice from the previous definitions.

a. Each vector of the reciprocal lattice is normal to a set of lattice planes of the direct lattice.
Proof:
We have obtained from Eq. (1.20), $\mathbf{K} \cdot \mathbf{R} = 2\pi m$, where m is an integer. Therefore, the projection of vector $\mathbf{R}$ on the direction of $\mathbf{K}$ has the length d,

$$d = \frac{2\pi m}{|\mathbf{K}|}. \tag{1.24}$$

However, there is an infinite number of points in the direct lattice with the same property. To show this, let us consider a lattice point $\mathbf{R}'$ represented by the integers

$$n_1' = n_1 - pl; \ n_2' = n_2 - pl; \ n_3' = n_1 + p(h+k), \tag{1.25}$$

where p is an arbitrary integer; n_1, n_2, and n_3 are the set of integers that represent a lattice point **R**, and h, k, and l are the integers that define a reciprocal lattice vector. It can be easily shown that

$$\mathbf{K} \cdot \mathbf{R}' = \mathbf{K} \cdot \mathbf{R} = 2\pi m. \tag{1.26}$$

Therefore, $\mathbf{R}'$ has the same projection on $\mathbf{K}$ as $\mathbf{R}$ and is on the plane normal to $\mathbf{K}$, at a distance d from the origin. Thus, there is an infinite number of lattice points on this plane if it has at least one lattice point.

b. $|\mathbf{K}|$ is inversely proportional to the spacing of the lattice planes normal to $\mathbf{K}$, if the components of $\mathbf{K}$ have no common factor.

Proof:

We have shown in Eq. (1.24) that $d = \frac{2\pi m}{|\mathbf{K}|}$. If (h, k, l), the components of $\mathbf{K}$ have no common factor, then a lattice vector $\mathbf{R}''$ with components (n_1'', n_2'', n_3'') can always be found such that

$$\mathbf{K} \cdot \mathbf{R}'' = 2\pi(m + 1). \tag{1.27}$$

Here,

$$m + 1 = hn_1'' + kn_2'' + ln_3''. \tag{1.28}$$

Thus, the lattice plane containing $\mathbf{R}''$ is at a distance

$$d'' = \frac{2\pi(m + 1)}{|\mathbf{K}|} \tag{1.29}$$

from the origin. Comparing Eqs. (1.24) and (1.29), we note that the lattice plane containing $\mathbf{R}''$ is spaced $2\pi / |\mathbf{K}|$ from the lattice plane containing $\mathbf{R}$. The simplest way of identifying the planes of a direct lattice is by their normals, which are the vectors of the reciprocal lattice. The planes that are most densely populated with lattice sites are usually the most prominent planes in a direct lattice. These are also the most widely separated because the density of direct lattice sites is constant. Therefore, the most prominent planes are those with the smallest reciprocal lattice vectors.

c. The Miller indices h, k, l, which identify the direct lattice planes, are also the integers that identify the reciprocal lattice vectors normal to those planes.

Proof:

Consider a lattice plane with normal $\mathbf{K}$ such that $\mathbf{K} \cdot \mathbf{R} = 2\pi m$ (Eq. 1.20) is satisfied by all lattice points identified by $\mathbf{R}$ in that plane. If a lattice point has $n_2 = n_3 = 0$, from Eq. (1.21), we obtain

$$n_1 = m/h. \tag{1.30}$$

The intercept of this plane along the $\mathbf{a}_1$ axis has the length

$$d_1 = n_1 a_1 = \left(\frac{m}{h}\right) a_1. \tag{1.31}$$

One can similarly obtain

$$d_2 = n_2 a_2 = \left(\frac{m}{k}\right) a_2, \tag{1.32}$$

and

$$d_3 = n_3 a_3 = \left(\frac{m}{l}\right) a_3. \tag{1.33}$$

Thus, the intercepts of this plane among the axes, measured in the units of the corresponding basis vectors, are inversely proportional to h, k, l. These integers are precisely the definition of the Miller indices (after removal of common factors) of the plane.

d. The volume of a unit cell of the reciprocal lattice is inversely proportional to the volume of the unit cell of a direct lattice.

Proof:

The primitive vectors of the reciprocal lattice are $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$. The volume of a unit cell of the reciprocal lattice is

$$\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{2\pi(\mathbf{a}_2 \times \mathbf{a}_3) \cdot (\mathbf{b}_2 \times \mathbf{b}_3)}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \tag{1.34}$$

which can be simplified as

$$\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{-2\pi\mathbf{b}_2 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \times \mathbf{b}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \tag{1.35}$$

By using the vector identity $(\mathbf{B} \times \mathbf{C}) \times \mathbf{A} = -\mathbf{B}(\mathbf{A} \cdot \mathbf{C}) + \mathbf{C}(\mathbf{A} \cdot \mathbf{B})$, we obtain

$$(\mathbf{a}_2 \times \mathbf{a}_3) \times \mathbf{b}_3 = -\mathbf{a}_2(\mathbf{b}_3 \cdot \mathbf{a}_3) + \mathbf{a}_3(\mathbf{b}_3 \cdot \mathbf{a}_2). \tag{1.36}$$

From Eqs. (1.17) and (1.36), we obtain

$$(\mathbf{a}_2 \times \mathbf{a}_3) \times \mathbf{b}_3 = -2\pi\mathbf{a}_2. \tag{1.37}$$

From Eqs. (1.17), (1.35), and (1.37), we obtain

$$\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \tag{1.38}$$

Because the volume of the primitive cell in the direct lattice is

$$v = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3), \tag{1.39}$$

we obtain from Eqs. (1.32) and (1.33),

$$\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{v}. \tag{1.40}$$

e. The reciprocal lattice of a simple cubic Bravais lattice with side a is a simple cubic lattice with cubic primitive cell of side $2\pi/a$.
Proof:
For a simple cubic (sc) lattice, the primitive lattice vectors are

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}}. \tag{1.41}$$

From Eqs. (1.11) and (1.35), we obtain the reciprocal lattice vectors of the sc lattice,

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}. \tag{1.42}$$

f. The direct lattice is the reciprocal of its own reciprocal lattice.
Proof:
This can be easily shown by inspection of Eq. (1.40) or (1.42).
g. The reciprocal lattice of a bcc Bravais lattice with conventional unit cell of side a is a fcc lattice with conventional unit cell of side $4\pi/a$.
Proof:
We have seen in Eq. (1.2) that for a bcc lattice, the symmetric set of primitive vectors is

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}); \ \ \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}); \ \ \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}).$$

From Eqs. (1.11), the reciprocal lattice vectors are

$$\mathbf{b}_1 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}); \ \ \mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}); \ \ \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}). \tag{1.43}$$

This has the form of the fcc primitive vectors (Eq. 1.3), provided the side of the cubic cell is taken to be $4\pi/a$.
h. One can similarly show (Problem 1.14) that the reciprocal lattice of the fcc Bravais lattice with conventional unit cell of side a is a bcc lattice with conventional unit cell of side $4\pi/a$.
i. The unit cell of the reciprocal lattice need not be a parallelepiped.

1.9.3 Alternative Formulation of the Laue Condition

We have derived the Laue condition (Eq. 1.12) for constructive interference of the incident radiation reradiated by the ions or atoms in all directions as $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, where $\mathbf{K}$ is a reciprocal lattice vector. Because the incident and scattered radiations have the same wavelengths $\lambda = \lambda'$ for elastic scattering, it follows that

$$|\mathbf{k}| = |\mathbf{k}'| = k. \tag{1.44}$$

From Eqs. (1.12) and (1.44), we obtain

$$k' = |\mathbf{k} - \mathbf{K}| = k. \tag{1.45}$$

By squaring Eq. (1.45), we obtain

$$k^2 = k^2 + K^2 - 2\mathbf{k} \cdot \mathbf{K}, \tag{1.46}$$

which can be written in the alternate form

$$\mathbf{k} \cdot \hat{\mathbf{K}} = 1/2K. \tag{1.47}$$

Eq. (1.47) implies that the incident wave vector $\mathbf{k}$ would satisfy the Laue condition only if the tip of $\mathbf{k}$ is on a plane that is a perpendicular bisector of the line joining the origin to $\mathbf{K}$. This is shown in Figure 1.25, and such planes in k space are known as Bragg planes.

In Figure 1.26, the Laue condition is shown in an alternate way such that its equivalence to Bragg refection can be demonstrated.

In fact, it can be easily shown that the Bragg and Laue formulations of X-ray diffraction from a crystal are equivalent. We write $\mathbf{K} = n\mathbf{K_0}$, where n is an integer and $\mathbf{K}_0$ is the shortest reciprocal lattice vector parallel to $\mathbf{K}$. Further, Eq. (1.24) can be written in the alternate form

$$K = \frac{2\pi n}{d}. \tag{1.48}$$

We can easily show from Figure 1.26,

$$K = 2k \sin\theta. \tag{1.49}$$

From Eqs. (1.48) and (1.49), we obtain

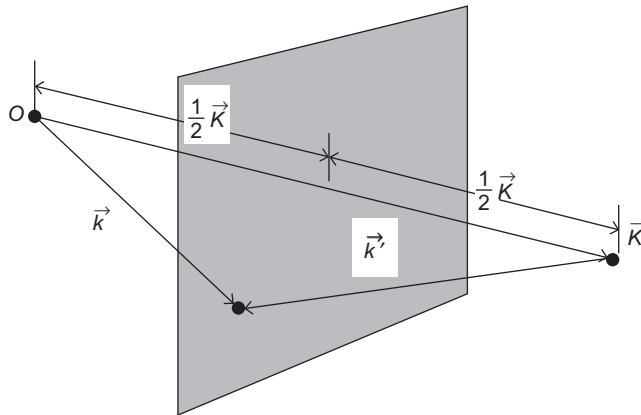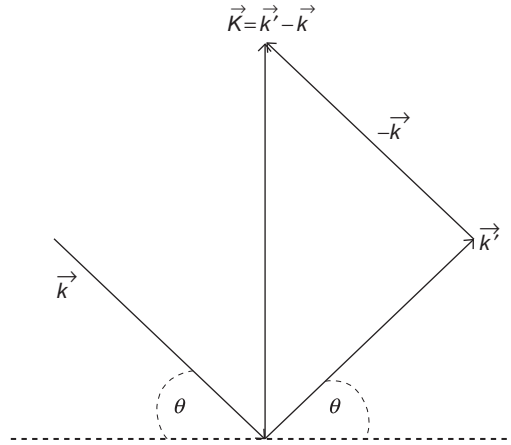$$k \sin\theta = \frac{n\pi}{d}. \tag{1.50}$$

FIGURE 1.25

The Laue condition. A typical Bragg plane is shown in the diagram.

FIGURE 1.26

Because $\mathbf{K} = \mathbf{k}' - \mathbf{k}$ and $|\mathbf{k}| = |\mathbf{k}'|$, $\mathbf{k}$ and $\mathbf{k}'$ have the same angle θ with the plane perpendicular to $\mathbf{K}$.

Using the expression $k = 2\pi/\lambda$, we can write Eq. (1.50) as

$$2d \sin \theta = n\lambda, \tag{1.51}$$

which is precisely Eq. (1.8), the Bragg condition. We have also shown that the order n of the Bragg reflection is $n = |\mathbf{K}|/|\mathbf{K}_0|$.

1.10 BRILLOUIN ZONES
1.10.1 Definition

The Brillouin zone is a very important concept in solid state physics; it plays a major role in the theoretical understanding of the elementary ideas of electronic energy bands. The first Brillouin zone is defined as the Wigner–Seitz primitive cell of the reciprocal lattice. Thus, it is the set of points in the reciprocal space that is closer to $K = 0$ than to any other reciprocal lattice point. We have shown in Figure 1.21 that the Bragg planes bisect the lines joining 0 (the origin) to the reciprocal lattice points. Thus, we can also define the first Brillouin zone as the set of points that can be reached from 0 without crossing any Bragg planes. Here, the points common to the surface of two or more zones have not been considered.

The second Brillouin zone is the set of points that can be reached from the first Brillouin zone by crossing only one plane. Similarly, the nth Brillouin zone can be defined as the set of points that can be reached by crossing $n - 1$ Bragg planes. We will first describe Brillouin zones of one- and two-dimensional (square) lattices to explain the fundamental methods of obtaining the Brillouin zones before describing the Brillouin zones of some important lattices.

1.10.2 One-Dimensional Lattice

Consider a one-dimensional (linear) lattice of lattice constant a, which is taken in the $\hat{\mathbf{x}}$ direction. By definition, the direct lattice vector is $\mathbf{R} = n_1 a \hat{\mathbf{x}}$, where n_1 is an integer. The reciprocal lattice vectors for this linear lattice are

$$\mathbf{K} = (2\pi/a)h\hat{\mathbf{x}}, \tag{1.52}$$

where h is an integer. Thus, the reciprocal lattice is also a linear lattice of side $b = 2\pi/a$. As described earlier, the Bragg planes (points in one dimension also known as zone boundaries) bisect the lines joining a reciprocal lattice point with its neighbors. The first three Brillouin zones of the linear lattice are shown in Figure 1.27.

As we can see from Eq. (1.52), the shortest reciprocal lattice vector $|\mathbf{K}_0| = 2\pi/a$. If the origin $\mathbf{0}$ is chosen at the center, the first Bragg plane (zone boundary) is at $-\pi/a$ and π/a. Similarly, the second Bragg plane is at $-2\pi/a$ and $2\pi/a$, and the third Bragg plane is at $-3\pi/a$ and $3\pi/a$. Thus, the first Brilloun zone (shown by horizontal lines) extends from $-\pi/a$ to π/a, the second Brillouin zone (shown by lines \\\\\\\\\\) is between $-2\pi/a$ and $-\pi/a$ as well as between π/a and $2\pi/a$. Similarly, the third Brillouin zone (shown by lines ////////) is between $-3\pi/a$ and $-2\pi/a$ as well as between $2\pi/a$ and $3\pi/a$. These are consistent with the definition of the Brillouin zones; i.e., a point in the first zone does not cross any Bragg plane (point in one dimension), a point in the second zone crosses only one Bragg plane (zone boundary), and a point in the third Brillouin zone crosses two Bragg planes (zone boundaries).

1.10.3 Two-Dimensional Square Lattice

The direct lattice vectors of a two-dimensional square Bravais lattice are

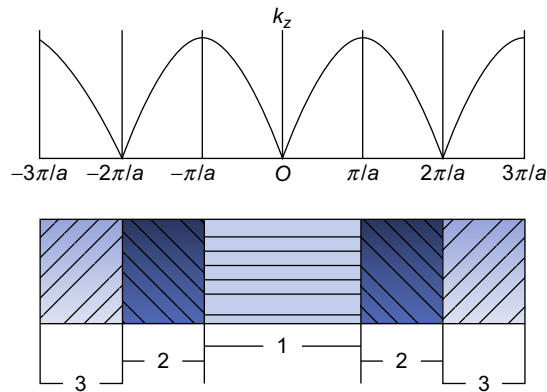$$\mathbf{R} = n_1 a\hat{\mathbf{x}} + n_2 a\hat{\mathbf{y}}, \tag{1.53}$$

FIGURE 1.27

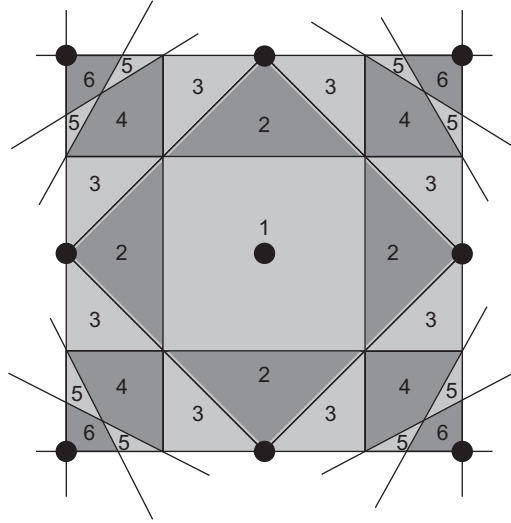The Brillouin zones of the linear lattice.

FIGURE 1.28

The Brillouin zones for a two-dimensional square lattice of side $4\pi/a$ [[$4\pi/\alpha$]].

where n_1 and n_2 are integers and a is the lattice constant. The reciprocal lattice vectors are

$$\mathbf{K} = \frac{2\pi}{a}(h\hat{\mathbf{x}} + k\hat{\mathbf{y}}), \tag{1.54}$$

where h and k are integers. Thus, the reciprocal lattice is also a square lattice of side $b = 2\pi/a$. The Brillouin zones are constructed according to the method outlined earlier. In Figure 1.28, all the Bragg lines (in two dimensions) that are in a square of side $4\pi/a$ centered on the origin are shown. The Bragg lines divide the square into regions belonging to different zones.

1.10.4 bcc Lattice

We have shown in Eq. (1.43) that the primitive translational vectors of the reciprocal lattice of a bcc lattice are given by

$$\mathbf{b}_1 = (2\pi/a)(\hat{\mathbf{y}} + \hat{\mathbf{z}}); \ \ \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{z}} + \hat{\mathbf{x}}); \ \ \mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}}).$$

The reciprocal lattice vectors are

$$\begin{aligned} \mathbf{K} &= h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \\ &= (2\pi/a)[(k+l)\hat{\mathbf{x}} + (h+l)\hat{\mathbf{y}} + (h+k)\hat{\mathbf{z}}] \cdot \end{aligned} \tag{1.55}$$
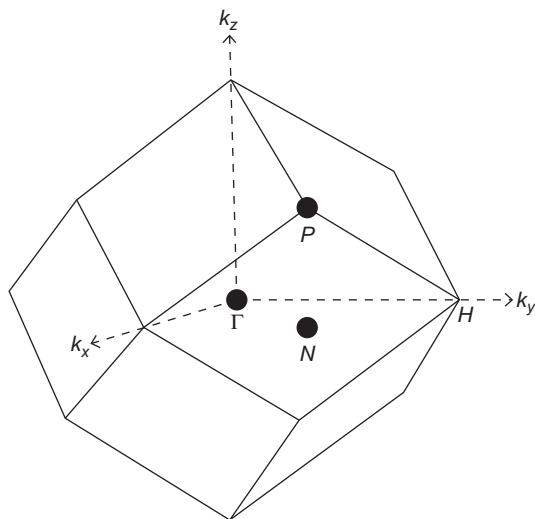
FIGURE 1.29

The first Brillouin zone for the bcc lattice.

From Eq. (1.55), we note that the shortest nonzero $\mathbf{K}'$s are the 12 vectors

$$(2\pi/a)(\pm\hat{\mathbf{x}}\pm\hat{\mathbf{y}}); \quad (2\pi/a)(\pm\hat{\mathbf{y}}\pm\hat{\mathbf{z}}); \quad (2\pi/a)(\pm\hat{\mathbf{z}}\pm\hat{\mathbf{x}}). \tag{1.56}$$

The first Brillouin zone is the primitive cell formed from the planes normal to the 12 vectors (the Bragg planes) of Eq. (1.56). Thus, the 12 vectors from the origin to the center of each face of the first Brillouin zone are

$$(\pi/a)(\pm\hat{\mathbf{x}}\pm\hat{\mathbf{y}}); \quad (\pi/a)(\pm\hat{\mathbf{y}}\pm\hat{\mathbf{z}}); \quad (\pi/a)(\pm\hat{\mathbf{z}}\pm\hat{\mathbf{x}}). \tag{1.57}$$

The first Brillouin zone for the bcc lattice is shown in Figure 1.29. This regular 12-faced solid is a rhombic dodecahedron. The important symmetry points are marked by conventional symbols. By convention, Γ is denoted as the center of a zone.

1.10.5 fcc Lattice

The primitive translation vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ of the reciprocal lattice of the fcc lattice are (Problem 1.14)

$$\begin{aligned}
\mathbf{b}_1 &= (2\pi/a)(\hat{\mathbf{y}}+\hat{\mathbf{z}}-\hat{\mathbf{x}}), \\
\mathbf{b}_2 &= (2\pi/a)(\hat{\mathbf{z}}+\hat{\mathbf{x}}-\hat{\mathbf{y}}), \\
\mathbf{b}_3 &= (2\pi/a)(\hat{\mathbf{x}}+\hat{\mathbf{y}}-\hat{\mathbf{z}}) \cdot
\end{aligned} \tag{1.58}$$

Thus, the reciprocal lattice vectors of the fcc lattice are

$$\begin{aligned}
\mathbf{K} &= h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \\
&= (2\pi/a)[(-h+k+l)\hat{\mathbf{x}} + (h-k+l)\hat{\mathbf{y}} + (h+k-l)\hat{\mathbf{z}}] \cdot
\end{aligned} \tag{1.59}$$
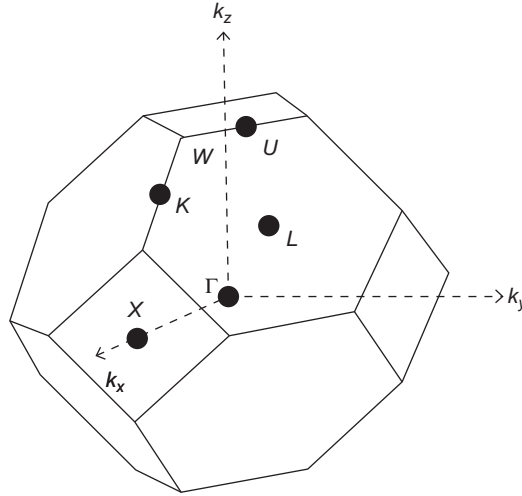
FIGURE 1.30

The first Brillouin zone for the fcc lattice.

While the shortest nonzero $\mathbf{K}'$s are the eight vectors

$$(2\pi/a)(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{y}} \pm \hat{\mathbf{z}}), \tag{1.60}$$

the corners of the octahedron formed by the eight planes normal to these vectors at their midpoints are truncated by the planes that are the perpendicular bisectors of the six reciprocal lattice vectors

$$\pm(4\pi/a)\hat{\mathbf{x}}; \quad \pm(4\pi/a)\hat{\mathbf{y}}; \quad \pm(4\pi/a)\hat{\mathbf{z}}. \tag{1.61}$$

The first Brillouin zone of the fcc lattice is the truncated octahedron shown in Figure 1.30. The conventional symbols of the important symmetry points are also shown in the figure.

1.11 DIFFRACTION BY A CRYSTAL LATTICE WITH A BASIS

The analysis of diffraction of the incident radiation by a crystal lattice with a basis and, consequently, the intensity of radiation in a given Bragg peak is more complicated than a monoatomic crystal because we have to consider the scattering of the radiation from each ion or atom of the basis at each lattice point. A crystal lattice with a basis can have two or more ions or atoms, either of the same type or of different types. In general, each lattice point in a primitive cell would have a basis of atoms or ions associated with it, and the crystal structure consists of a repetitive unit of this basis.

1.11.1 Theory

We consider n scatterers at positions $\mathbf{r}_1$, $\mathbf{r}_2$, ..., $\mathbf{r}_n$, in each primitive cell with the lattice point considered as the origin of $\mathbf{r}_j$. It is important to note that in an ideal crystal, each lattice point has an identical basis

around it so that the scatterers are located at the same relative position in each cell. We have already noted that a Bragg peak is associated with a change in the wave vector $\mathbf{K} = \mathbf{k}' - \mathbf{k}$ and the phase difference between two rays scattered from $\mathbf{r}_i$ and $\mathbf{r}_j$ would be $\mathbf{K} \cdot (\mathbf{r}_i - \mathbf{r}_j)$. The amplitudes of the rays scattered at $\mathbf{r}_1, ..., \mathbf{r}_n$ would be in the ratios $e^{i\mathbf{K}\cdot\mathbf{r}_1}, ..., e^{i\mathbf{K}\cdot\mathbf{r}_n}$. Thus, the amplitude of the scattered ray from the primitive cell, which is the sum of the scattered rays from the n identical scatterers of the primitive cell, will be equal to

$$S = \sum_{\mathbf{R}} \sum_{j} f_j e^{-i(\mathbf{R}+\mathbf{r}_j)\cdot\Delta\mathbf{k}}. \tag{1.62}$$

The amplitude of the scattered rays (Eq. 1.62) can be expressed as

$$S = \sum_{\mathbf{R}} e^{-i\mathbf{R}\cdot\Delta\mathbf{k}} S_K, \tag{1.63}$$

where S_K is the structure factor obtained by the Bragg condition $\Delta\mathbf{k} = \mathbf{K}$,

$$S_{\mathbf{K}} = \sum_{j=1}^{n} f_j \, e^{i\mathbf{K}\cdot\mathbf{r}_j}. \tag{1.64}$$

Here, f_j is the atomic scattering factor or form factor that is a measure of the scattering power of the jth atom or ion in the basis.

1.11.2 Geometrical Structure Factor

We will first consider the basis as consisting of n identical atoms or ions around each lattice point. This is equivalent to stating that each atomic form factor f_j has the same value $f_j \equiv f$. Then we can write Eq. (1.64) in the form

$$S_{\mathbf{K}} = f \sum_{j=1}^{n} e^{i\mathbf{K}\cdot\mathbf{r}_j} \equiv f \mathbb{S}_{\mathbf{K}}. \tag{1.65}$$

$S_{\mathbf{K}}$ is known as the geometrical structure factor. Because $S_{\mathbf{K}}$ is proportional to the amplitude, $|S_{\mathbf{K}}|^2$ is proportional to the intensity of the Bragg peak and indicates the extent to which the waves scattered from the ions or atoms in the basis within the primitive cell interfere to reduce it.

Next, we will discuss the structure factor of a few important lattices.

1.11.3 Application to bcc Lattice

If we consider the bcc lattice as a simple cubic lattice of side a with identical atoms or ions at $\mathbf{r}_1 = \mathbf{0}$ and at $\mathbf{r}_2 = (a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, the structure factor (Eq. 1.65) can be expressed as

$$\mathbb{S}_{\mathbf{K}} = (1 + e^{i\mathbf{K}\cdot[1/2a(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})]}). \tag{1.66}$$

Further, for a simple cubic lattice,

$$\mathbf{K} = \frac{2\pi}{a}(h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}}). \tag{1.67}$$

From Eqs. (1.66) and (1.67), we obtain

$$
\begin{aligned}
\mathbb{S}_{\mathbf{K}} &= (1 + e^{i\pi(h+k+l)}) \\
&= 1 + (-1)^{h+k+l}
\end{aligned}
\tag{1.68}
$$

$$
= \left\{
\begin{array}{ll}
0, & h+k+l \quad \text{odd} \\
2, & h+k+l \quad \text{even}
\end{array}
\right\}.
\tag{1.69}
$$

From Eq. (1.69), we note that whenever $h+k+l$ is odd, there is no Bragg diffraction (reflection). Because in this derivation, the bcc lattice has been considered as a simple cubic lattice with a basis, this implies that the odd reciprocal lattice vectors $h+k+l$ of the reciprocal simple cubic lattice do not exist. Therefore, the actual reciprocal lattice is a fcc lattice, which could have been obtained directly if we had considered the bcc lattice as the primitive lattice.

1.11.4 Application to fcc Lattice

If we consider a fcc lattice as a simple cubic lattice of side a and basis at

$$
\mathbf{r}_1 = \mathbf{0},\ \mathbf{r}_2 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}),\ \mathbf{r}_3 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}),\ \mathbf{r}_4 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}),
$$

the structure factor (Eq. 1.65) can be expressed as

$$
\mathbb{S}_{\mathbf{K}} = 1 + e^{i\mathbf{K}\cdot a/2(\hat{\mathbf{y}}+\hat{\mathbf{z}})} + e^{i\mathbf{K}\cdot a/2(\hat{\mathbf{z}}+\hat{\mathbf{x}})} + e^{i\mathbf{K}\cdot a/2(\hat{\mathbf{x}}+\hat{\mathbf{y}})}.
\tag{1.70}
$$

From Eqs. (1.67) and (1.70), we obtain

$$
\mathbb{S}_{\mathbf{K}} = 1 + e^{i\pi(k+l)} + e^{i\pi(h+l)} + e^{i\pi(h+k)}.
\tag{1.71}
$$

Eq. (1.71) can be written in the alternate form

$$
\mathbb{S}_{\mathbf{K}} = 1 + (-1)^{k+l} + (-1)^{h+l} + (-1)^{h+k}.
\tag{1.72}
$$

From Eq. (1.72), we note that $\mathbb{S}_{\mathbf{K}} = 4$, if each value of the integers $h,\ k,\ l$ is either even or odd. However, $\mathbb{S}_{\mathbf{K}} = 0$, if either only one of the three integers $h,\ k,\ l$ is even and the other two are odd, or one of the three integers is odd and the other two are even. Thus, there can be no Bragg reflection if the indices h, k, l are partly odd and partly even. In contrast, there is Bragg reflection if each of the indices h, k, l is either even or odd. This is true for a reciprocal bcc lattice. Hence, the reciprocal lattice of a fcc lattice is a bcc lattice, which we stated earlier, and has been assigned as a problem.

1.11.5 The Atomic Scattering Factor or Form Factor

In Eq. (1.64), we defined f_j as the atomic scattering factor or form factor, which was a component of the geometrical structure factor. However, in subsequent discussions, we considered that all the atoms or ions in a basis are identical.

Thus, each $f_j = f$ and f are factored out of the summation. We wrote the geometrical structure factor as $S_{\mathbf{K}} = f\,\mathbb{S}_{\mathbf{K}}$, where $\mathbb{S}_{\mathbf{K}}$ is the structure factor.

However, if the atoms or the ions in a basis are not identical, the atomic form factor f_j at the site $\mathbf{d}_j$ in the basis is

$$f_j(\mathbf{K}) = -\frac{1}{e} \int d\mathbf{r} \, e^{i\mathbf{K} \cdot \mathbf{r}} \rho_j(\mathbf{r}). \tag{1.73}$$

Here, $\rho_j(\mathbf{r})$ is the electronic charge density of the ion of type j placed at $\mathbf{r} = \mathbf{0}$. It is evident from Eqs. (1.64) and (1.73) that the geometrical structure factor would no longer vanish.

PROBLEMS

1.1. Show that the volume of the primitive Bravais cell of a bcc lattice is $a^3/2$, where a is the side of the unit cube.

1.2. Show that the volume of the primitive Bravais cell of a fcc lattice is $a^3/4$, where a is the side of the unit cube.

1.3. A plane in a lattice with primitive vectors $\mathbf{a}_1, \mathbf{a}_2$, and $\mathbf{a}_3$ has intercepts at $3\mathbf{a}_1$, $2\mathbf{a}_2$, and $-2\mathbf{a}_3$. Calculate the Miller indices of the plane. Label the direction perpendicular to this plane.

1.4. Draw a sketch of the $(10\bar{2})$ plane in a simple cubic lattice.

1.5. Prove that in a cubic crystal, a direction [hkl] is perpendicular to the plane (hkl) having the same indices.

1.6. Show that the actual volume occupied by the spheres in the simple cubic structure (assuming that they are contacting hard spheres) is 52.4% of the total volume.

1.7. Show that the actual volume occupied by the spheres in the bcc structure (packing fraction: assuming that they are contacting hard spheres) is 0.68.

1.8. Show that the actual volume occupied by the spheres in the fcc structure (packing fraction: assuming that they are contacting hard spheres) is 0.74.

1.9. Show that the angle between any two of the lines (bonds) joining a site of the diamond lattice to its four nearest neighbors is $\cos^{-1}(-1/3)$.

1.10. Show that the ideal c/a ratio of the hexagonal close-packed structure is $\sqrt{8/3}$.

1.11. Show that the packing fraction of the hexagonal close-packed structure is 0.74.

1.12. Sodium transforms from bcc to hcp at about 23 K, which is also known as the "martenistic" transformation. The lattice constant in the cubic phase is $a = 4.23 \, A°$. Determine the lattice constant a of the hexagonal phase. Assume that the c/a ratio in the hexagonal phase is indistinguishable.

1.13. Show that if $\mathbf{a}_i$ are the three direct lattice primitive vectors and $\mathbf{b}_j$ are the three primitive vectors of the reciprocal lattice (as defined in Eq. 1.16), then

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

where δ_{ij} is the Kronecker delta function.

1.14. Show that the primitive translation vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ of the reciprocal lattice of the fcc lattice are $\mathbf{b}_1 = (2\pi/a)(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$, and prove that the reciprocal lattice of a fcc lattice of side a is a bcc lattice of side $4\pi/a$.

1.15. Show that for a monatomic diamond lattice, the structure factor is

$$\mathbb{S}_\mathbf{K} = 1 + e^{i[2\pi(h+k+l)]}$$

$$= \begin{cases} 2, & h+k+l \quad \text{is twice an even number,} \\ 1\pm i, & h+k+l \quad \text{is odd,} \\ 0, & h+k+l \quad \text{is twice an odd number.} \end{cases}$$

Interpret these conditions geometrically.

1.16. a. Show that the reciprocal lattice of the sodium chloride structure is bcc and a reciprocal lattice vector can be written as

$$\mathbf{K} = \frac{4\pi}{a}(n_1\hat{\mathbf{x}} + n_2\hat{\mathbf{y}} + n_3\hat{\mathbf{z}}),$$

where a is the side of the cube and all the coefficients n_i of a of a reciprocal lattice vector are integers or integer+1/2.

b. If the atomic form factors of the two types of ions are f_1 and f_2, show that the geometrical structure factor $S_\mathbf{K} = f_1 + f_2$ if each n_i in a set is an integer and $S_\mathbf{K} = f_1 - f_2$ if each n_i in a set is an integer+1/2.

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