Chapter 3

Atomic and Ionic Arrangements

Have You Ever Wondered?

- *What is amorphous silicon and how is it different from the silicon used to make computer chips?*
- *What are liquid crystals?*
- *If you were to pack a cubical box with uniform-sized spheres, what is the maximum packing possible?*
- *How can we calculate the density of different materials?*

Arrangements of atoms and ions play an important role in determining the microstructure and properties of a material. The main objectives of this chapter are to

(a) learn to classify materials based on atomic/ionic arrangements; and
(b) describe the arrangements in crystalline solids according to the concepts of the **lattice, basis**, and **crystal structure**.

For crystalline solids, we will illustrate the concepts of Bravais lattices, unit cells, and crystallographic directions and planes by examining the arrangements of atoms or ions in many technologically important materials. These include metals (e.g., Cu, Al, Fe, W, Mg, etc.), semiconductors (e.g., Si, Ge, GaAs, etc.), advanced ceramics (e.g., ZrO_2, Al_2O_3, $BaTiO_3$, etc.), ceramic superconductors, diamond, and other materials. We will develop the necessary nomenclature used to characterize atomic or ionic arrangements in crystalline materials. We will examine the use of **x-ray diffraction** (XRD), **transmission electron microscopy** (TEM), and **electron diffraction**. These techniques allow us to probe the arrangements of atoms/ions in different materials. We will present an overview of different types of **amorphous materials** such as amorphous silicon, metallic glasses, polymers, and inorganic glasses.

Chapter 2 highlighted how interatomic bonding influences certain properties of materials. This chapter will underscore the influence of atomic and ionic arrangements on the properties of engineered materials. In particular, we will concentrate on "perfect" arrangements of atoms or ions in crystalline solids.

The concepts discussed in this chapter will prepare us for understanding how *deviations* from these perfect arrangements in crystalline materials create what are described as **atomic level defects**. The term **defect** in this context refers to a lack of perfection in atomic or ionic order of crystals and not to any flaw or quality of an engineered material. In Chapter 4, we will describe how these atomic level defects actually enable the development of formable, strong steels used in cars and buildings, aluminum alloys for aircraft, solar cells and photovoltaic modules for satellites, and many other technologies.

3-1 Short-Range Order versus Long-Range Order

In different states of matter, we can find four types of atomic or ionic arrangements (Figure 3-1).

No Order

In monoatomic gases, such as argon (Ar) or plasma created in a fluorescent tubelight, atoms or ions have no orderly arrangement.

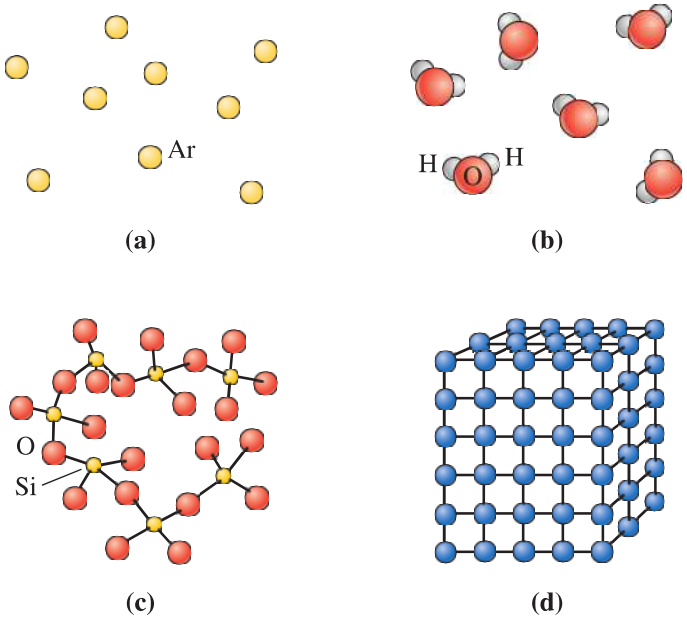


Figure 3-1 Levels of atomic arrangements in materials: (a) Inert monoatomic gases have no regular ordering of atoms. (b,c) Some materials, including water vapor, nitrogen gas, amorphous silicon, and silicate glass, have short-range order. (d) Metals, alloys, many ceramics and some polymers have regular ordering of atoms/ions that extends through the material.

Short-Range Order (SRO)

A material displays **short-range order (SRO)** if the special arrangement of the atoms extends only to the atom's nearest neighbors. Each water molecule in steam has short-range order due to the covalent bonds between the hydrogen and oxygen atoms; that is, each oxygen atom is joined to two hydrogen atoms, forming an angle of 104.5° between the bonds. There is no long-range order, however, because the water molecules in steam have no special arrangement with respect to each other's position.

A similar situation exists in materials known as inorganic glasses. In Chapter 2, we described the **tetrahedral structure** in silica that satisfies the requirement that four oxygen ions be bonded to each silicon ion [Figure 3-2(a)]. As will be discussed later, in a glass, individual tetrahedral units are joined together in a random manner. These tetrahedra may share corners, edges, or faces. Thus, beyond the basic unit of a $(SiO_4)^{4-}$ tetrahedron, there is no periodicity in their arrangement. In contrast, in quartz or other forms of crystalline silica, the $(SiO_4)^{4-}$ tetrahedra are indeed connected in different periodic arrangements.

Many polymers also display short-range atomic arrangements that closely resemble the silicate glass structure. Polyethylene is composed of chains of carbon atoms, with two hydrogen atoms attached to each carbon. Because carbon has a valence of four and the carbon and hydrogen atoms are bonded covalently, a tetrahedral structure is again produced [Figure 3-2(b)]. Tetrahedral units can be joined in a random manner to produce polymer chains.

Long-Range Order (LRO)

Most metals and alloys, semiconductors, ceramics, and some polymers have a crystalline structure in which the atoms or ions display **long-range order (LRO)**; the special atomic arrangement extends over much larger length scales ~ >100 nm. The atoms or ions in these materials form a regular repetitive, grid-like pattern, in three dimensions. We refer to these materials as **crystalline materials**. If a crystalline material consists of only one large crystal, we refer to it as a *single crystal*. Single crystals are useful in many electronic and optical applications. For example, computer chips are made from silicon in the form of large (up to 12 inch diameter) single crystals [Figure 3-3(a)]. Similarly, many useful optoelectronic devices are made from crystals of lithium niobate ($LiNbO_3$). Single crystals can also be made as thin films and used for many electronic and other applications. Certain types of turbine blades may also be made from single crystals of nickel-based superalloys. **A polycrystalline material** is composed of many small crystals with varying orientations in space. These smaller crystals are known as **grains**. The borders between crystals, where the crystals are in misalignment, are known as **grain boundaries**. Figure 3-3(b) shows the microstructure of a polycrystalline stainless steel material.

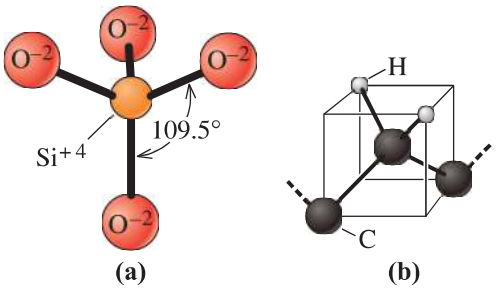
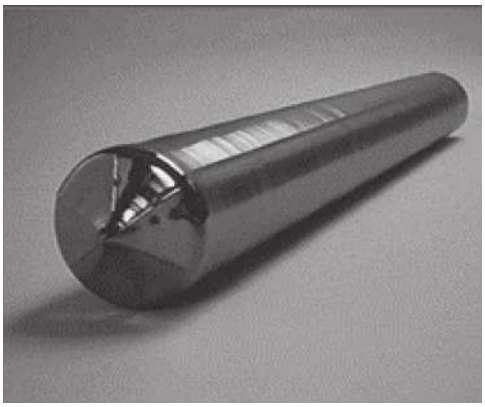
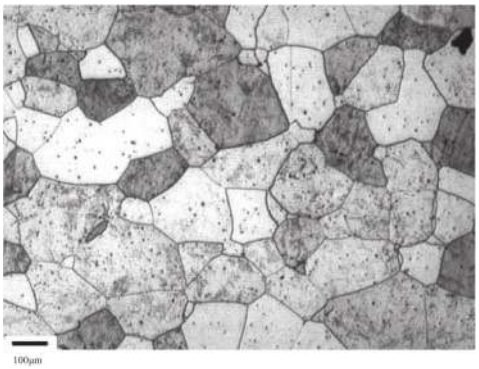


Figure 3-2
(a) Basic Si-O tetrahedron in silicate glass. (b) Tetrahedral arrangement of C-H bonds in polyethylene.



(a)



(b)

Figure 3-3 (a) Photograph of a silicon single crystal. (b) Micrograph of a polycrystalline stainless steel showing grains and grain boundaries (*Courtesy of Dr. A. J. Deardo, Dr. M. Hua and Dr. J. Garcia.*)

Many crystalline materials we deal with in engineering applications are polycrystalline (e.g., steels used in construction, aluminum alloys for aircrafts, etc.). We will learn in later chapters that many properties of polycrystalline materials depend upon the physical and chemical characteristics of both grains and grain boundaries. The properties of single crystal materials depend upon the chemical composition and specific directions within the crystal (known as the crystallographic directions). Long-range order in crystalline materials can be detected and measured using techniques such as **x-ray diffraction** or **electron diffraction** (see Section 3-9).

Liquid crystals (LCs) are polymeric materials that have a special type of order. Liquid crystal polymers behave as amorphous materials (liquid-like) in one state. When an external stimulus (such as an electric field or a temperature change) is provided, some polymer molecules undergo alignment and form small regions that are crystalline, hence the name "liquid crystals." These materials have many commercial applications in liquid crystal display (LCD) technology.

Figure 3-4 shows a summary of classification of materials based on the type of atomic order.

3-2 Amorphous Materials

Any material that exhibits only a short-range order of atoms or ions is an **amorphous material**; that is, a noncrystalline one. In general, most materials want to form periodic arrangements since this configuration maximizes the thermodynamic stability of the material. Amorphous materials tend to form when, for one reason or other, the kinetics of the process by which the material was made did not allow for the formation of periodic arrangements. **Glasses**, which typically form in ceramic and polymer systems, are good examples of amorphous materials. Similarly, certain types of polymeric or colloidal gels, or gel-like materials, are also considered amorphous. Amorphous materials often offer a unique blend of properties since the atoms or ions are not assembled into their "regular" and periodic arrangements. Note that often many engineered

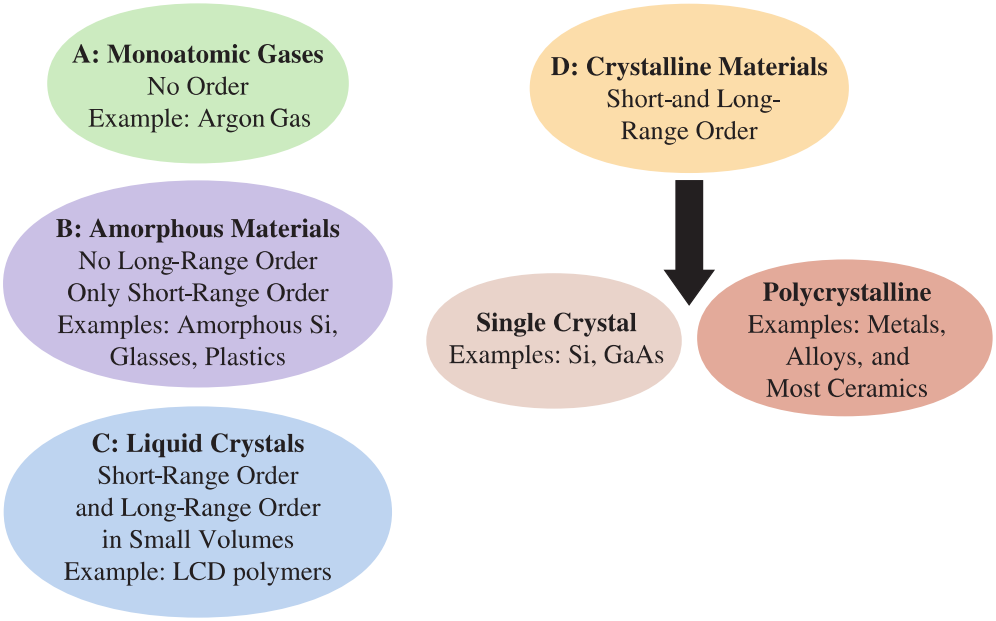


Figure 3-4 Classification of materials based on the type of atomic order.

materials labeled as "amorphous" may contain a fraction that is crystalline. Techniques such as electron diffraction and x-ray diffraction (see Section 3-9) cannot be used to characterize the short-range order in amorphous materials. Scientists use neutron scattering and other methods to investigate the short-range order in amorphous materials.

Crystallization of glasses can be controlled. Materials scientists and engineers, such as Donald Stookey, have developed ways of deliberately nucleating ultrafine crystals in amorphous glasses. The resultant materials, known as **glass-ceramics**, can be made up to ~99.9% crystalline and are quite strong. Some glass-ceramics can be made optically transparent by keeping the size of the crystals extremely small (~ <100 nm). The major advantage of glass-ceramics is that they are shaped using glass-forming techniques, yet they are ultimately transformed into crystalline materials that do not shatter like glass. We will consider this topic in greater detail in Chapter 9.

Similar to inorganic glasses, many plastics are amorphous. They do contain small portions of material that are crystalline. During processing, relatively large chains of polymer molecules get entangled with each other, like spaghetti. Entangled polymer molecules do not organize themselves into crystalline materials. During processing of polymeric beverage bottles, mechanical stress is applied to the preform of the bottle (e.g., the manufacturing of a standard 2-liter soft drink bottle using polyethylene terephthalate (PET plastic)). This process is known as **blow-stretch forming**. The radial (blowing) and longitudinal (stretching) stresses during bottle formation actually untangle some of the polymer chains, causing **stress-induced crystallization**. The formation of crystals adds to the strength of the PET bottles.

Compared to plastics and inorganic glasses, metals and alloys tend to form crystalline materials rather easily. As a result, special efforts must be made to quench the metals and alloys quickly in order to prevent crystallization; for some alloys, a cooling rate of $>10^6$°C/s is required to form **metallic glasses**. This technique of cooling metals and alloys very fast is known as **rapid solidification**. Many metallic glasses have both useful and

unusual properties. The mechanical properties of metallic glasses will be discussed in Chapter 6.

To summarize, amorphous materials can be made by restricting the atoms/ions from assuming their "regular" periodic positions. This means that amorphous materials do not have a long-range order. This allows us to form materials with many different and unusual properties. Many materials labeled as "amorphous" can contain some level of crystallinity. Since atoms are assembled into nonequilibrium positions, the natural tendency of an amorphous material is to crystallize (i.e., since this leads to a thermodynamically more stable material). This can be done by providing a proper thermal (e.g., a silicate glass), thermal and mechanical (e.g., PET polymer), or electrical (e.g., liquid crystal polymer) driving force.

3-3 Lattice, Basis, Unit Cells, and Crystal Structures

A typical solid contains on the order of 10^{23} atoms/cm^3. In order to communicate the spatial arrangements of atoms in a crystal, it is clearly not necessary or practical to specify the position of each atom. We will discuss two complementary methodologies for simply describing the three-dimensional arrangements of atoms in a crystal. We will refer to these as the **lattice and basis concept** and the **unit cell** concept. These concepts rely on the principles of **crystallography**. In Chapter 2, we discussed the structure of the atom. An atom consists of a nucleus of protons and neutrons surrounded by electrons, but for the purpose of describing the arrangements of atoms in a solid, we will envision the atoms as hard spheres, much like ping-pong balls. We will begin with the lattice and basis concept.

A lattice is a collection of points, called **lattice points**, which are arranged in a periodic pattern so that the surroundings of each point in the lattice are identical. A lattice is a purely mathematical construct and is infinite in extent. A lattice may be one-, two-, or three-dimensional. In one dimension, there is only one possible lattice: It is a line of points with the points separated from each other by an equal distance, as shown in Figure 3-5(a). A group of one or more atoms located in a particular way with respect to each other and associated with each lattice point is known as the **basis** or **motif**. The basis must contain at least one atom, but it may contain many atoms of one or more types. A basis of one atom is shown in Figure 3-5(b). We obtain a **crystal structure** by placing the atoms of the basis on every lattice point (i.e., crystal structure = lattice + basis), as shown in Figure 3-5(c). A hypothetical one-dimensional crystal that has a basis of two different atoms is shown in Figure 3-5(d). The larger atom is located on every lattice point with the smaller atom located a fixed distance above each lattice point. Note that it is not necessary that one of the basis atoms be located on each lattice point, as shown in Figure 3-5(e). Figures 3-5(d) and (e) represent the same one-dimensional crystal; the atoms are simply shifted relative to one another. Such a shift does not change the atomic arrangements in the crystal.

There is only one way to arrange points in one dimension such that each point has identical surroundings—an array of points separated by an equal distance as discussed above. There are five distinct ways to arrange points in two dimensions such that each point has identical surroundings; thus, there are five two-dimensional lattices. There are only fourteen unique ways to arrange points in three dimensions. These unique three-dimensional arrangements of lattice points are known as the **Bravais lattices**, named after Auguste Bravais (1811–1863) who was an early French crystallographer.

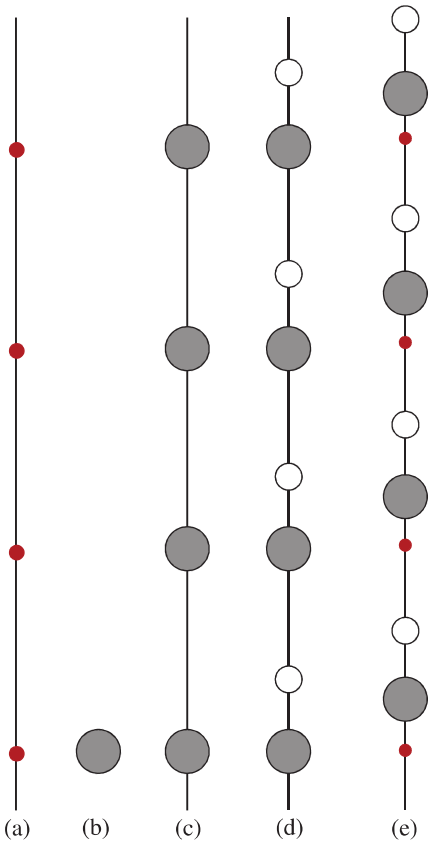


Figure 3-5
Lattice and basis. (a) A one-dimensional lattice. The lattice points are separated by an equal distance. (b) A basis of one atom. (c) A crystal structure formed by placing the basis of (b) on every lattice point in (a). (d) A crystal structure formed by placing a basis of two atoms of different types on the lattice in (a). (e) The same crystal as shown in (d); however, the basis has been shifted relative to each lattice point.

The fourteen Bravais lattices are shown in Figure 3-6. As stated previously, a lattice is infinite in extent, so a single unit cell is shown for each lattice. The unit cell is a subdivision of a lattice that still retains the overall characteristics of the entire lattice. Lattice points are located at the corners of the unit cells and, in some cases, at either the faces or the center of the unit cell.

The fourteen Bravais lattices are grouped into seven **crystal systems**. The seven crystal systems are known as cubic, tetragonal, orthorhombic, rhombohedral (also known as trigonal), hexagonal, monoclinic, and triclinic. Note that for the cubic crystal system, we have simple cubic (SC), face-centered cubic (FCC), and body-centered cubic (BCC) Bravais lattices. These names describe the arrangement of lattice points in the unit cell. Similarly, for the tetragonal crystal system, we have simple tetragonal and body-centered tetragonal lattices. Again remember that the concept of a lattice is mathematical and does not mention atoms, ions, or molecules. It is only when a basis is associated with a lattice that we can describe a crystal structure. For example, if we take the face-centered cubic lattice and position a basis of one atom on every lattice point, then the face-centered cubic crystal structure is reproduced.

Note that although we have only fourteen Bravais lattices, we can have an infinite number of bases. Hundreds of different crystal structures are observed in nature or can be synthesized. Many different materials can have the same crystal structure. For example, copper and nickel have the face-centered cubic crystal structure for which only one atom is associated with each lattice point. In more complicated structures, particularly polymer, ceramic, and biological materials, several atoms may be associated with each lattice point (i.e., the basis is greater than one), forming very complex unit cells.

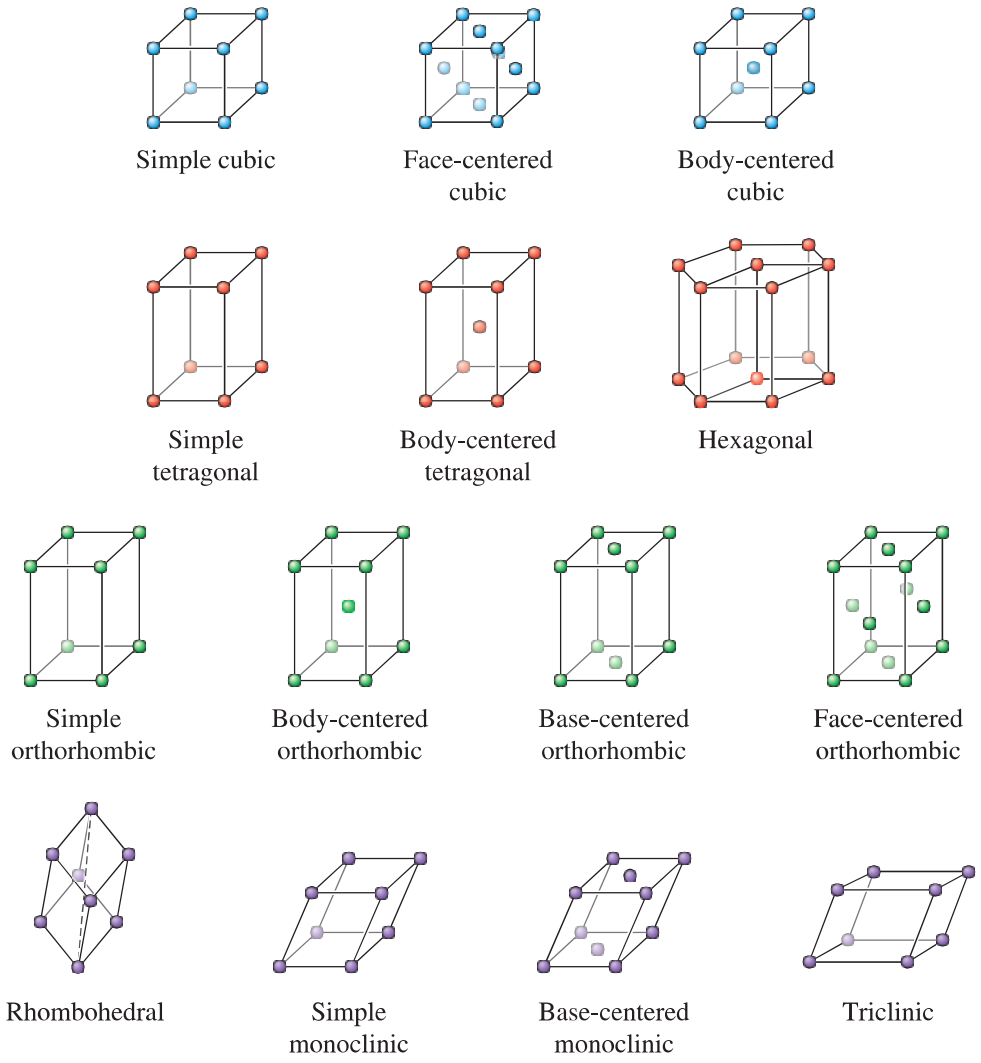


Figure 3-6 The fourteen types of Bravais lattices grouped in seven crystal systems. The actual unit cell for a hexagonal system is shown in Figures 3-8 and 3-13.

Unit Cell

Our goal is to develop a notation to model crystalline solids that simply and completely conveys how the atoms are arranged in space. The unit cell concept complements the lattice and basis model for representing a crystal structure. Although the methodologies of the lattice and basis and unit cell concepts are somewhat different, the end result—a description of a crystal—is the same.

Our goal in choosing a unit cell for a crystal structure is to find the single repeat unit that, when duplicated and translated, reproduces the entire crystal structure. For example, imagine the crystal as a three-dimensional puzzle for which each piece of the puzzle is exactly the same. If we know what one puzzle piece looks like, we know what the entire puzzle looks like, and we don't have to put the entire puzzle together to solve it. We just need one piece! To understand the unit cell concept, we start with the crystal. Figure 3-7(a) depicts a hypothetical two-dimensional crystal that consists of atoms all of the same type.

Next, we add a grid that mimics the symmetry of the arrangements of atoms. There is an infinite number of possibilities for the grid, but by convention, we usually choose the simplest. For the square array of atoms shown in Figure 3-7(a), we choose a

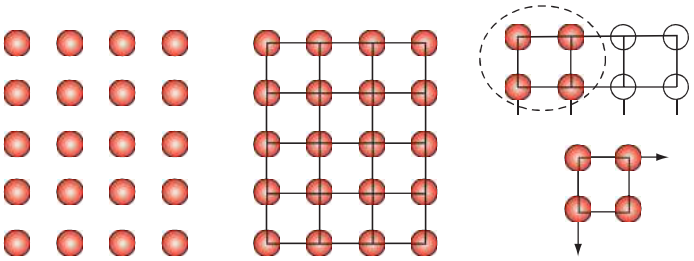


Figure 3-7 The unit cell. (a) A two-dimensional crystal. (b) The crystal with an overlay of a grid that reflects the symmetry of the crystal. (c) The repeat unit of the grid known as the unit cell. Each unit cell has its own origin.

square grid as is shown in Figure 3-7(b). Next, we select the repeat unit of the grid, which is also known as the unit cell. This is the unit that, when duplicated and translated by integer multiples of the axial lengths of the unit cell, recreates the entire crystal. The unit cell is shown in Figure 3-7(c); note that for each unit cell, there is only one quarter of an atom at each corner in two dimensions. We will always draw full circles to represent atoms, but it is understood that only the fraction of the atom that is contained inside the unit cell contributes to the total number of atoms per unit cell. Thus, there is 1/4 atom / corner * 4 corners = 1 atom per unit cell, as shown in Figure 3-7(c). It is also important to note that, if there is an atom at one corner of a unit cell, there must be an atom at every corner of the unit cell in order to maintain the translational symmetry. Each unit cell has its own origin, as shown in Figure 3-7(c).

Lattice Parameters and Interaxial Angles

The **lattice parameters** are the axial lengths or dimensions of the unit cell and are denoted by convention as a, b, and c. The angles between the axial lengths, known as the interaxial angles, are denoted by the Greek letters α, β, and γ. By convention, α is the angle between the lengths b and c, β is the angle between a and c, and γ is the angle between a and b, as shown in Figure 3-8. (Notice that for each combination, there is a letter a, b, and c whether it be written in Greek or Roman letters.)

In a cubic crystal system, only the length of one of the sides of the cube need be specified (it is sometimes designated a_0). The length is often given in nanometers (nm) or angstrom (Å) units, where

$$1 \text{ nanometer (nm)} = 10^{-9} \text{ m} = 10^{-7} \text{ cm} = 10 \text{ Å}$$
$$1 \text{ angstrom (Å)} = 0.1 \text{ nm} = 10^{-10} \text{ m} = 10^{-8} \text{ cm}$$

The lattice parameters and interaxial angles for the unit cells of the seven crystal systems are presented in Table 3-1.

To fully define a unit cell, the lattice parameters or ratios between the axial lengths, interaxial angles, and atomic coordinates must be specified. In specifying atomic coordinates, whole atoms are placed in the unit cell. The coordinates are specified as fractions of the axial lengths. Thus, for the two-dimensional cell represented in Figure 3-7(c), the unit cell is fully specified by the following information:

Axial lengths: $a = b$
Interaxial angle: $\gamma = 90°$
Atomic coordinate: (0, 0)

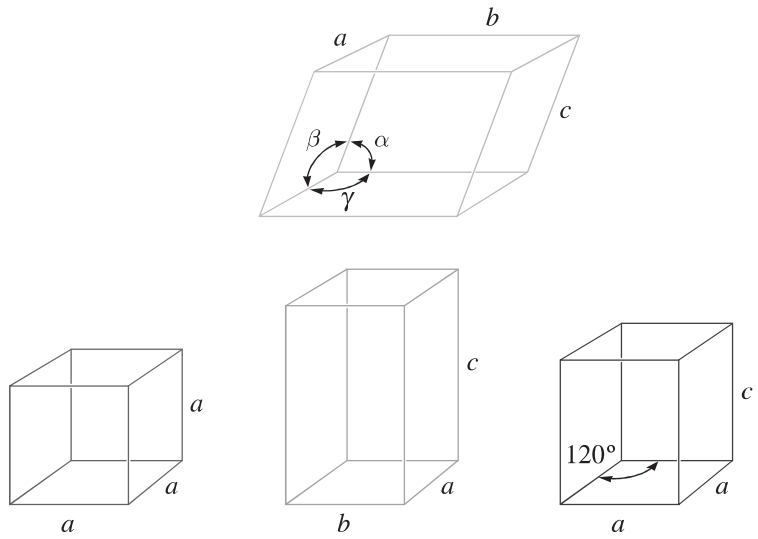


Figure 3-8 Definition of the lattice parameters and their use in cubic, orthorhombic, and hexagonal crystal systems.

Again, only 1/4 of the atom at each origin (0, 0) contributes to the number of atoms per unit cell; however, each corner acts as an origin and contributes 1/4 atom per corner for a total of one atom per unit cell. (Do you see why with an atom at (0, 0) of each unit cell it would be repetitive to also give the coordinates of (1, 0), (0, 1), and (1, 1)?)

Similarly, a cubic unit cell with an atom at each corner is fully specified by the following information:

Axial lengths: $a = b = c$
Interaxial angles: $\alpha = \beta = \gamma = 90°$
Atomic coordinate: (0, 0, 0)

TABLE 3-1 ■ *Characteristics of the seven crystal systems*

Structure	Axes	Angles between Axes	Volume of the Unit Cell
Cubic	$a = b = c$	All angles equal 90°.	a^3
Tetragonal	$a = b \neq c$	All angles equal 90°.	a^2c
Orthorhombic	$a \neq b \neq c$	All angles equal 90°.	abc
Hexagonal	$a = b \neq c$	Two angles equal 90°. The angle between a and b equals 120°.	$0.866a^2c$
Rhombohedral or trigonal	$a = b = c$	All angles are equal and none equals 90°.	$a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}$
Monoclinic	$a \neq b \neq c$	Two angles equal 90°. One angle (β) is not equal to 90°.	$abc \sin\beta$
Triclinic	$a \neq b \neq c$	All angles are different and none equals 90°.	$abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$

Now in three dimensions, each corner contributes 1/8 atom per each of the eight corners for a total of one atom per unit cell. Note that the number of atomic coordinates required is equal to the number of atoms per unit cell. For example, if there are two atoms per unit cell, with one atom at the corners and one atom at the body-centered position, two atomic coordinates are required: (0, 0, 0) and (1/2, 1/2, 1/2).

Number of Atoms per Unit Cell

Each unit cell contains a specific number of lattice points. When counting the number of lattice points belonging to each unit cell, we must recognize that, like atoms, lattice points may be shared by more than one unit cell. A lattice point at a corner of one unit cell is shared by seven adjacent unit cells (thus a total of eight cells); only one-eighth of each corner belongs to one particular cell. Thus, the number of lattice points from all corner positions in one unit cell is

$$\left(\frac{1/8 \text{ lattice point}}{\text{corner}}\right)\left(\frac{8 \text{ corners}}{\text{cell}}\right) = \frac{1 \text{ lattice point}}{\text{unit cell}}$$

Corners contribute 1/8 of a point, faces contribute 1/2, and body-centered positions contribute a whole point [Figure 3-9(a)].

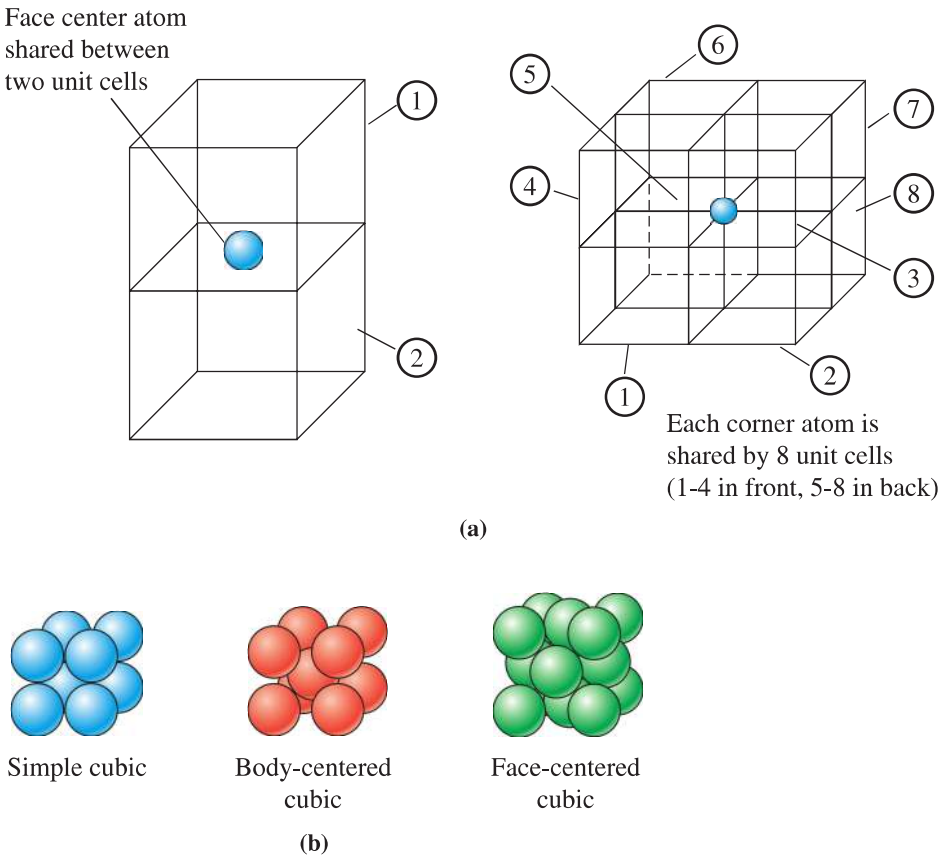


Figure 3-9 (a) Illustration showing sharing of face and corner atoms. (b) The models for simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) unit cells, assuming only one atom per lattice point.

The number of atoms per unit cell is the product of the number of atoms per lattice point and the number of lattice points per unit cell. The structures of simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) unit cells (with one atom located at each lattice point) are shown in Figure 3-9(b). Example 3-1 illustrates how to determine the number of lattice points in cubic crystal systems.

Example 3-1 *Determining the Number of Lattice Points in Cubic Crystal Systems*

Determine the number of lattice points per cell in the cubic crystal systems. If there is only one atom located at each lattice point, calculate the number of atoms per unit cell.

SOLUTION

In the SC unit cell, lattice points are located only at the corners of the cube:

$$\frac{\text{lattice points}}{\text{unit cell}} = (8 \text{ corners})\left(\frac{1}{8}\right) = 1$$

In BCC unit cells, lattice points are located at the corners and the center of the cube:

$$\frac{\text{lattice points}}{\text{unit cell}} = (8 \text{ corners})\left(\frac{1}{8}\right) + (1 \text{ body-center})(1) = 2$$

In FCC unit cells, lattice points are located at the corners and faces of the cube:

$$\frac{\text{lattice points}}{\text{unit cell}} = (8 \text{ corners})\left(\frac{1}{8}\right) + (6 \text{ faces})\left(\frac{1}{2}\right) = 4$$

Since we are assuming there is only one atom located at each lattice point, the number of atoms per unit cell would be 1, 2, and 4, for the simple cubic, body-centered cubic, and face-centered cubic unit cells, respectively.

Example 3-2 *The Cesium Chloride Structure*

Crystal structures usually are assigned names of a representative element or compound that has that structure. Cesium chloride (CsCl) is an ionic, crystalline compound. A unit cell of the CsCl crystal structure is shown in Figure 3-10. Chlorine anions are located at the corners of the unit cell, and a cesium cation is located at the body-centered position of each unit cell. Describe this structure as a lattice and basis and also fully define the unit cell for cesium chloride.

SOLUTION

The unit cell is cubic; therefore, the lattice is either SC, FCC, or BCC. There are no atoms located at the face-centered positions; therefore, the lattice is either SC or BCC. Each Cl anion is surrounded by eight Cs cations at the body-centered positions

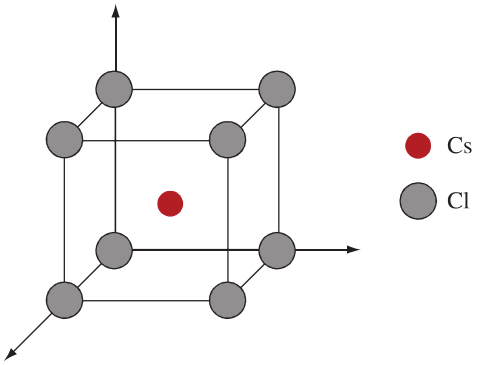


Figure 3-10
The CsCl crystal structure. *Note*: Ion sizes not to scale.

of the adjoining unit cells. Each Cs cation is surrounded by eight Cl anions at the corners of the unit cell. Thus, the corner and body-centered positions do not have identical surroundings; therefore, they both cannot be lattice points. The lattice must be simple cubic.

The simple cubic lattice has lattice points only at the corners of the unit cell. The cesium chloride crystal structure can be described as a simple cubic lattice with a basis of two atoms, Cl (0, 0, 0) and Cs (1/2, 1/2, 1/2). Note that the atomic coordinates are listed as fractions of the axial lengths, which for a cubic crystal structure are equal. The basis atom of Cl (0, 0, 0) placed on every lattice point (i.e., each corner of the unit cell) fully accounts for every Cl atom in the structure. The basis atom of Cs (1/2, 1/2, 1/2), located at the body-centered position with respect to each lattice point, fully accounts for every Cs atom in the structure.

Thus there are two atoms per unit cell in CsCl:

$$\frac{1 \text{ lattice point}}{\text{unit cell}} * \frac{2 \text{ atoms}}{\text{lattice point}} = \frac{2 \text{ atoms}}{\text{unit cell}}$$

To fully define a unit cell, the lattice parameters or ratios between the axial lengths, interaxial angles, and atomic coordinates must be specified. The CsCl unit cell is cubic; therefore,

$$\text{Axial lengths: } a = b = c$$
$$\text{Interaxial angles: } \alpha = \beta = \gamma = 90°$$

The Cl anions are located at the corners of the unit cell, and the Cs cations are located at the body-centered positions. Thus,

$$\text{Atomic coordinates: Cl (0, 0, 0) and Cs (1/2, 1/2, 1/2)}$$

Counting atoms for the unit cell,

$$\frac{8 \text{ corners}}{\text{unit cell}} * \frac{1/8 \text{ Cl atom}}{\text{corner}} + \frac{1 \text{ body-center}}{\text{unit cell}} * \frac{1 \text{ Cs atom}}{\text{body-center}} = \frac{2 \text{ atoms}}{\text{unit cell}}$$

As expected, the number of atoms per unit cell is the same regardless of the method used to count the atoms.

Atomic Radius versus Lattice Parameter

Directions in the unit cell along which atoms are in continuous contact are **close-packed directions**. In simple structures, particularly those with only one atom per lattice point, we use these directions to calculate the relationship between the apparent size of the atom and the size of the unit cell. By geometrically determining the length of the direction relative to the lattice parameters, and then adding the number of **atomic radii** along this direction, we can determine the desired relationship. Example 3-3 illustrates how the relationships between lattice parameters and atomic radius are determined.

Example 3-3 *Determining the Relationship between Atomic Radius and Lattice Parameters*

Determine the relationship between the atomic radius and the lattice parameter in SC, BCC, and FCC structures when one atom is located at each lattice point.

SOLUTION

If we refer to Figure 3-11, we find that atoms touch along the edge of the cube in SC structures. The corner atoms are centered on the corners of the cube, so

$$a_0 = 2r \tag{3-1}$$

In BCC structures, atoms touch along the body diagonal, which is $\sqrt{3}a_0$ in length. There are two atomic radii from the center atom and one atomic radius from each of the corner atoms on the body diagonal, so

$$a_0 = \frac{4r}{\sqrt{3}} \tag{3-2}$$

In FCC structures, atoms touch along the face diagonal of the cube, which is $\sqrt{2}a_0$ in length. There are four atomic radii along this length—two radii from the face-centered atom and one radius from each corner, so

$$a_0 = \frac{4r}{\sqrt{2}} \tag{3-3}$$

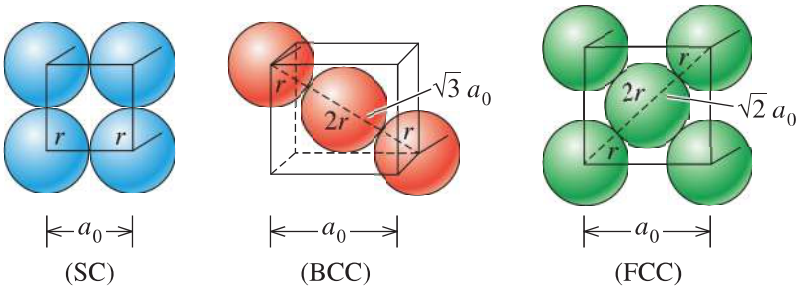


Figure 3-11 The relationships between the atomic radius and the lattice parameter in cubic systems (for Example 3-3).

The Hexagonal Lattice and Unit Cell

The image of the hexagonal lattice in Figure 3-6 reflects the underlying symmetry of the lattice, but unlike the other images in Figure 3-6, it does not represent the unit cell of the lattice. The hexagonal unit cell is shown in Figure 3-8. If you study the image of the hexagonal lattice in Figure 3-6, you can find the hexagonal unit cell. The lattice parameters for the hexagonal unit cell are

$$\text{Axial lengths: } a = b \neq c$$

$$\text{Interaxial angles: } \alpha = \beta = 90°,\ \gamma = 120°$$

When the atoms of the unit cell are located only at the corners, the atomic coordinate is (0, 0, 0).

Coordination Number

The **coordination number** is the number of atoms touching a particular atom, or the number of nearest neighbors for that particular atom. This is one indication of how tightly and efficiently atoms are packed together. For ionic solids, the coordination number of cations is defined as the number of nearest anions. The coordination number of anions is the number of nearest cations. We will discuss the crystal structures of different ionic solids and other materials in Section 3-7.

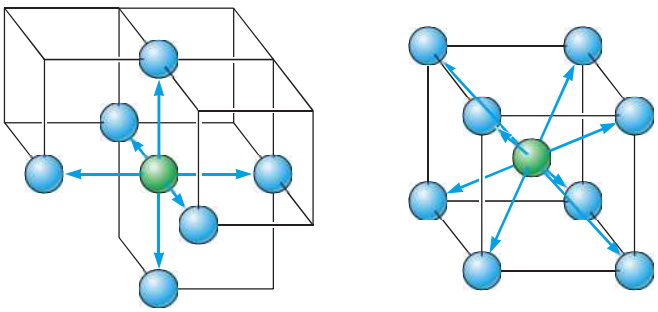
In cubic structures containing only one atom per lattice point, atoms have a coordination number related to the lattice structure. By inspecting the unit cells in Figure 3-12, we see that each atom in the SC structure has a coordination number of six, while each atom in the BCC structure has eight nearest neighbors. In Section 3-5, we will show that each atom in the FCC structure has a coordination number of twelve, which is the maximum.

Packing Factor

The **packing factor** or **atomic packing fraction** is the fraction of space occupied by atoms, assuming that the atoms are hard spheres. The general expression for the packing factor is

$$\text{Packing factor} = \frac{(\text{number of atoms/cell})(\text{volume of each atom})}{\text{volume of unit cell}} \tag{3-4}$$

Example 3-4 illustrates how to calculate the packing factor for the FCC unit cell.



(a) (b)

Figure 3-12 Illustration of the coordination number in (a) SC and (b) BCC unit cells. Six atoms touch each atom in SC, while eight atoms touch each atom in the BCC unit cell.

Example 3-4 *Calculating the Packing Factor*

Calculate the packing factor for the FCC unit cell.

SOLUTION

In the FCC unit cell, there are four lattice points per cell; if there is one atom per lattice point, there are also four atoms per cell. The volume of one atom is $4\pi r^3/3$ and the volume of the unit cell is a_0^3, where r is the radius of the atom and a_0 is the lattice parameter.

$$\text{Packing factor} = \frac{(4 \text{ atoms/cell})\left(\frac{4}{3}\pi r^3\right)}{a_0^3}$$

Since for FCC unit cells, $a_0 = 4r/\sqrt{2}$:

$$\text{Packing factor} = \frac{(4)\left(\frac{4}{3}\pi r^3\right)}{(4r/\sqrt{2})^3} = \frac{\pi}{\sqrt{18}} \cong 0.74$$

The packing factor of $\pi/\sqrt{18} \cong 0.74$ in the FCC unit cell is the most efficient packing possible. BCC cells have a packing factor of 0.68, and SC cells have a packing factor of 0.52. Notice that the packing factor is independent of the radius of atoms, as long as we assume that all atoms have a fixed radius. What this means is that it does not matter whether we are packing atoms in unit cells or packing basketballs or table tennis balls in a cubical box. The maximum achievable packing factor is $\pi/\sqrt{18}$! This discrete geometry concept is known as **Kepler's conjecture**. Johannes Kepler proposed this conjecture in the year 1611, and it remained an unproven conjecture until 1998 when Thomas C. Hales actually proved this to be true.

The FCC arrangement represents a **close-packed structure** (CP) (i.e., the packing fraction is the highest possible with atoms of one size). The SC and BCC structures are relatively open. We will see in the next section that it is possible to have a hexagonal structure that has the same packing efficiency as the FCC structure. This structure is known as the hexagonal close-packed structure (HCP). Metals with only metallic bonding are packed as efficiently as possible. Metals with mixed bonding, such as iron, may have unit cells with less than the maximum packing factor. No commonly encountered engineering metals or alloys have the SC structure, although this structure is found in ceramic materials.

Density

The theoretical **density** of a material can be calculated using the properties of the crystal structure. The general formula is

$$\text{Density } \rho = \frac{(\text{number of atoms/cell})(\text{atomic mass})}{(\text{volume of unit cell})(\text{Avogadro constant})} \tag{3-5}$$

If a material is ionic and consists of different types of atoms or ions, this formula will have to be modified to reflect these differences. Example 3-5 illustrates how to determine the density of BCC iron.

Example 3-5 Determining the Density of BCC Iron

Determine the density of BCC iron, which has a lattice parameter of 0.2866 nm.

SOLUTION

For a BCC cell,

$$\text{Atoms/cell} = 2$$

$$a_0 = 0.2866 \text{ nm} = 2.866 \times 10^{-8} \text{ cm}$$

$$\text{Atomic mass} = 55.847 \text{ g/mol}$$

$$\text{Volume of unit cell} = a_0 = (2.866 \times 10^{-8} \text{ cm})^3 = 23.54 \times 10^{-24} \text{ cm}^3/\text{cell}$$

$$\text{Avogadro constant } N_A = 6.022 \times 10^{23} \text{ atoms/mol}$$

$$\text{Density } \rho = \frac{(\text{number of atoms/cell})(\text{atomic mass of iron})}{(\text{volume of unit cell})(\text{Avogadro constant})}$$

$$\rho = \frac{(2)(55.847)}{(23.54 \times 10^{-24})(6.022 \times 10^{23})} = 7.879 \text{ g/cm}^3$$

The measured density is 7.870 g/cm^3. The slight discrepancy between the theoretical and measured densities is a consequence of defects in the material. As mentioned before, the term "defect" in this context means imperfections with regard to the atomic arrangement.

The Hexagonal Close-Packed Structure

The hexagonal close-packed structure (HCP) is shown in Figure 3-13. The lattice is hexagonal with a basis of two atoms of the same type: one located at (0, 0, 0) and one located at (2/3, 1/3, 1/2). (These coordinates are always fractions of the axial lengths *a, b*, and *c* even if the axial lengths are not equal.) The hexagonal lattice has one lattice point per unit cell located at the corners of the unit cell. In the HCP structure, two atoms are associated with every lattice point; thus, there are two atoms per unit cell.

An equally valid representation of the HCP crystal structure is a hexagonal lattice with a basis of two atoms of the same type: one located at (0, 0, 0) and one located at (1/3, 2/3, 1/2). The (2/3, 1/3, 1/2) and (1/3, 2/3, 1/2) coordinates are equivalent, meaning that they cannot be distinguished from one another.

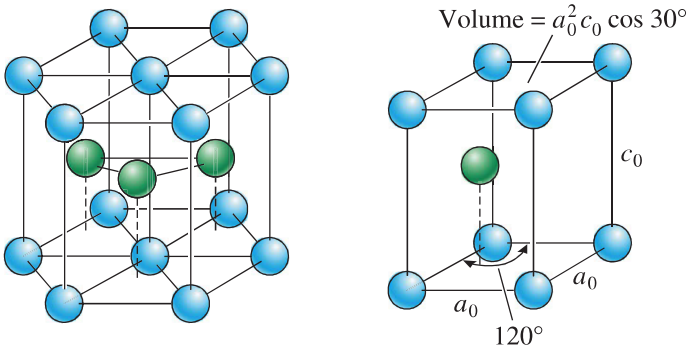


Figure 3-13 The hexagonal close-packed (HCP) structure (left) and its unit cell.

TABLE 3-2 ■ *Crystal structure characteristics of some metals at room temperature*

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α-Mo
Body-centered cubic (BCC)	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, W, Mo, Nb, Ta, K, Na, V, Cr
Face-centered cubic (FCC)	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed (HCP)	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd

In metals with an ideal HCP structure, the a_0 and c_0 axes are related by the ratio $c_0/a_0 = \sqrt{8/3} = 1.633$. Most HCP metals, however, have c_0/a_0 ratios that differ slightly from the ideal value because of mixed bonding. Because the HCP structure, like the FCC structure, has the most efficient packing factor of 0.74 and a coordination number of 12, a number of metals possess this structure. Table 3-2 summarizes the characteristics of crystal structures of some metals.

Structures of ionically bonded materials can be viewed as formed by the packing (cubic or hexagonal) of anions. Cations enter into the interstitial sites or holes that remain after the packing of anions. Section 3-7 discusses this in greater detail.

3-4 Allotropic or Polymorphic Transformations

Materials that can have more than one crystal structure are called allotropic or polymorphic. The term **allotropy** is normally reserved for this behavior in pure elements, while the term **polymorphism** is used for compounds. We discussed the allotropes of carbon in Chapter 2. Some metals, such as iron and titanium, have more than one crystal structure. At room temperature, iron has the BCC structure, but at higher temperatures, iron transforms to an FCC structure. These transformations result in changes in properties of materials and form the basis for the heat treatment of steels and many other alloys.

Many ceramic materials, such as silica (SiO_2) and zirconia (ZrO_2), also are polymorphic. A volume change may accompany the transformation during heating or cooling; if not properly controlled, this volume change causes the brittle ceramic material to crack and fail. For zirconia (ZrO_2), for instance, the stable form at room temperature (~25°C) is monoclinic. As we increase the temperature, more symmetric crystal structures become stable. At 1170°C, the monoclinic zirconia transforms into a tetragonal structure. The tetragonal form is stable up to 2370°C. At that temperature, zirconia transforms into a cubic form. The cubic form remains stable from 2370°C to a melting temperature of 2680°C. Zirconia also can have the orthorhombic form when high pressures are applied.

Ceramics components made from pure zirconia typically will fracture as the temperature is lowered and as zirconia transforms from the tetragonal to monoclinic form because of volume expansion (the cubic to tetragonal phase change does not cause much change in volume). As a result, pure monoclinic or tetragonal polymorphs of zirconia are not used. Instead, materials scientists and engineers have found that adding dopants such as yttria (Y_2O_3) make it possible to stabilize the cubic phase of zirconia, even at room temperature. This yttria stabilized zirconia (YSZ) contains up to 8 mol.% Y_2O_3. Stabilized zirconia formulations are used in many applications, including thermal barrier coatings (TBCs) for turbine blades and electrolytes for oxygen sensors and solid oxide fuel cells. Virtually every car

made today uses an oxygen sensor that is made using stabilized zirconia compositions. Example 3-6 illustrates how to calculate volume changes in polymorphs of zirconia.

Example 3-6 *Calculating Volume Changes in Polymorphs of Zirconia*

Calculate the percent volume change as zirconia transforms from a tetragonal to monoclinic structure [9]. The lattice constants for the monoclinic unit cells are $a = 5.156$, $b = 5.191$, and $c = 5.304$ Å, respectively. The angle β for the monoclinic unit cell is 98.9°. The lattice constants for the tetragonal unit cell are $a = 5.094$ and $c = 5.304$ Å. [10] Does the zirconia expand or contract during this transformation? What is the implication of this transformation on the mechanical properties of zirconia ceramics?

SOLUTION

From Table 3-1, the volume of a tetragonal unit cell is given by

$$V = a^2c = (5.094)^2(5.304) = 137.63 \text{ Å}^3$$

and the volume of a monoclinic unit cell is given by

$$V = abc \sin \beta = (5.156)(5.191)(5.304) \sin(98.9) = 140.25 \text{ Å}^3$$

Thus, there is an expansion of the unit cell as ZrO_2 transforms from a tetragonal to monoclinic form.

$$\text{The percent change in volume} = (\text{final volume} - \text{initial volume})/(\text{initial volume}) * 100 = (140.25 - 137.63 \text{ Å}^3)/137.63 \text{ Å}^3 * 100 = 1.9\%$$

Most ceramics are very brittle and cannot withstand more than a 0.1% change in volume. (We will discuss mechanical behavior of materials in Chapters 6, 7, and 8.) The conclusion here is that ZrO_2 ceramics cannot be used in their monoclinic form since, when zirconia does transform to the tetragonal form, it will most likely fracture. Therefore, ZrO_2 is often stabilized in a cubic form using different additives such as CaO, MgO, and Y_2O_3.

3-5 Points, Directions, and Planes in the Unit Cell

Coordinates of Points

We can locate certain points, such as atom positions, in the lattice or unit cell by constructing the right-handed coordinate system in Figure 3-14. Distance is measured in terms of the number of lattice parameters we must move in each of the x, y, and z coordinates to get from the origin to the point in question. The coordinates are written as the three distances, with commas separating the numbers.

Directions in the Unit Cell

Certain directions in the unit cell are of particular importance. **Miller indices** for directions are the shorthand notation used to describe these directions. The procedure for finding the Miller indices for directions is as follows:

1. Using a right-handed coordinate system, determine the coordinates of two points that lie on the direction.
2. Subtract the coordinates of the "tail" point from the coordinates of the "head" point to obtain the number of lattice parameters traveled in the direction of each axis of the coordinate system.

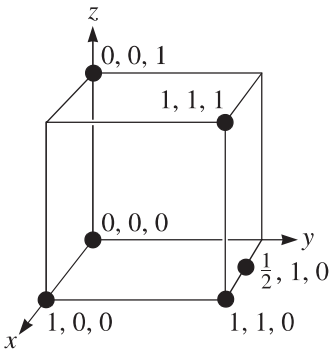


Figure 3-14
Coordinates of selected points in the unit cell. The number refers to the distance from the origin in terms of lattice parameters.

3. Clear fractions and/or reduce the results obtained from the subtraction to lowest integers.
4. Enclose the numbers in square brackets [ ]. If a negative sign is produced, represent the negative sign with a bar over the number.

Example 3-7 illustrates a way of determining the Miller indices of directions.

Example 3-7 *Determining Miller Indices of Directions*

Determine the Miller indices of directions *A*, *B*, and *C* in Figure 3-15.

SOLUTION

Direction *A*

1. Two points are 1, 0, 0, and 0, 0, 0
2. 1, 0, 0 − 0, 0, 0 = 1, 0, 0
3. No fractions to clear or integers to reduce
4. [100]

Direction *B*

1. Two points are 1, 1, 1 and 0, 0, 0
2. 1, 1, 1 − 0, 0, 0 = 1, 1, 1
3. No fractions to clear or integers to reduce
4. [111]

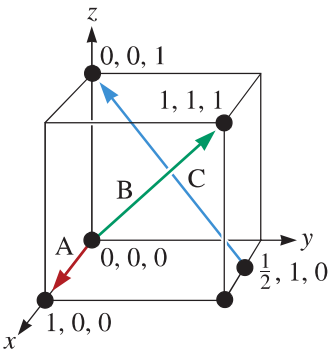


Figure 3-15
Crystallographic directions and coordinates (for Example 3-7).

Direction *C*

1. Two points are 0, 0, 1 and $\frac{1}{2}$, 1, 0
2. 0, 0, 1 $-\frac{1}{2}$, 1, 0 = $-\frac{1}{2}$, −1, 1
3. 2 $(-\frac{1}{2}, -1, 1) = -1, -2, 2$
4. $[\bar{1}\bar{2}2]$

Several points should be noted about the use of Miller indices for directions:

1. Because directions are vectors, a direction and its negative are not identical; [100] is not equal to $[\bar{1}00]$. They represent the same line, but opposite directions.
2. A direction and its multiple are *identical*; [100] is the same direction as [200].
3. Certain groups of directions are *equivalent*; they have their particular indices because of the way we construct the coordinates. For example, in a cubic system, a [100] direction is a [010] direction if we redefine the coordinate system as shown in Figure 3-16. We may refer to groups of equivalent directions as **directions of a form** or **family**. The special brackets ⟨ ⟩ are used to indicate this collection of directions. All of the directions of the form ⟨110⟩ are listed in Table 3-3. We expect a material to have the same properties in each of these twelve directions of the form ⟨110⟩.

Significance of Crystallographic Directions

Crystallographic directions are used to indicate a particular orientation of a single crystal or of an oriented polycrystalline material. Knowing how to describe these can be useful in many applications. Metals deform more easily, for example, in directions along which atoms are in closest contact. Another real-world example is the dependence of the magnetic properties of iron and other magnetic materials on the crystallographic directions. It is much easier to magnetize iron in the [100] direction compared to the [111] or [110] directions. This is why the grains in Fe-Si steels used in magnetic applications (e.g., transformer cores) are oriented in the [100] or equivalent directions.

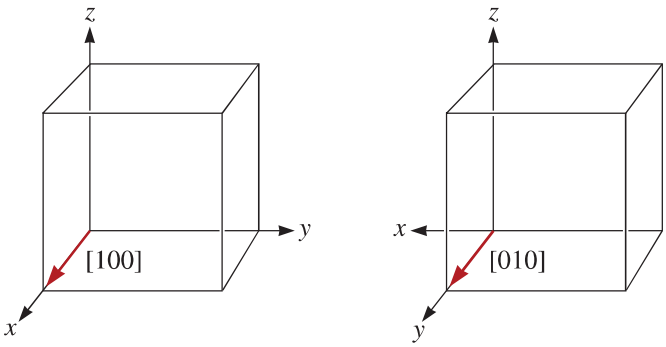


Figure 3-16 Equivalency of crystallographic directions of a form in cubic systems.

TABLE 3-3 ■ *Directions of the form* $\langle 110 \rangle$ *in cubic systems*

$$\langle 110 \rangle = \begin{cases} [110]\,[\bar{1}\,\bar{1}0] \\ [101]\,[\bar{1}0\bar{1}] \\ [011]\,[0\bar{1}\,\bar{1}] \\ [1\,\bar{1}0]\,[\bar{1}\,10] \\ [10\bar{1}]\,[\bar{1}\,01] \\ [01\,\bar{1}]\,[0\bar{1}\,1] \end{cases}$$

Repeat Distance, Linear Density, and Packing Fraction

Another way of characterizing directions is by the **repeat distance** or the distance between lattice points along the direction. For example, we could examine the [110] direction in an FCC unit cell (Figure 3-17); if we start at the 0, 0, 0 location, the next lattice point is at the center of a face, or a 1/2, 1/2, 0 site. The distance between lattice points is therefore one-half of the face diagonal, or $\frac{1}{2}\sqrt{2}a_0$. In copper, which has a lattice parameter of 0.3615 nm, the repeat distance is 0.2556 nm.

The **linear density** is the number of lattice points per unit length along the direction. In copper, there are two repeat distances along the [110] direction in each unit cell; since this distance is $\sqrt{2}a_0 = 0.5112$ nm, then

$$\text{Linear density} = \frac{2 \text{ repeat distances}}{0.5112 \text{ nm}} = 3.91 \text{ lattice points/nm}$$

Note that the linear density is also the reciprocal of the repeat distance.

Finally, we can compute the **packing fraction** of a particular direction, or the fraction actually covered by atoms. For copper, in which one atom is located at each lattice point, this fraction is equal to the product of the linear density and twice the atomic radius. For the [110] direction in FCC copper, the atomic radius $r = \sqrt{2}a_0/4 = 0.1278$ nm. Therefore, the packing fraction is

$$\begin{aligned} \text{Packing fraction} &= (\text{linear density})(2r) \\ &= (3.91)(2)(0.1278) \\ &= (1.0) \end{aligned}$$

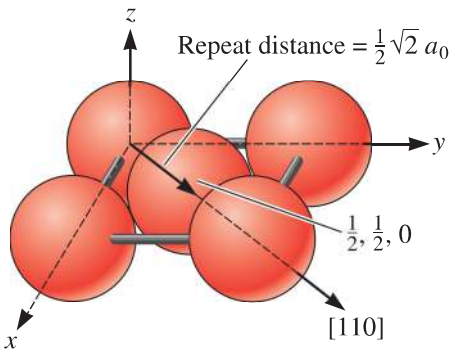


Figure 3-17
Determining the repeat distance, linear density, and packing fraction for a [110] direction in FCC copper.

Atoms touch along the [110] direction, since the [110] direction is close-packed in FCC metals.

Planes in the Unit Cell

Certain planes of atoms in a crystal also carry particular significance. For example, metals deform along planes of atoms that are most tightly packed together. The surface energy of different faces of a crystal depends upon the particular crystallographic planes. This becomes important in crystal growth. In thin film growth of certain electronic materials (e.g., Si or GaAs), we need to be sure the substrate is oriented in such a way that the thin film can grow on a particular crystallographic plane.

Miller indices are used as a shorthand notation to identify these important planes, as described in the following procedure.

1. Identify the points at which the plane intercepts the x, y, and z coordinates in terms of the number of lattice parameters. If the plane passes through the origin, the origin of the coordinate system must be moved to that of an adjacent unit cell.
2. Take reciprocals of these intercepts.
3. Clear fractions but do not reduce to lowest integers.
4. Enclose the resulting numbers in parentheses (). Again, negative numbers should be written with a bar over the number.

The following example shows how Miller indices of planes can be obtained.

Example 3-8 Determining Miller Indices of Planes

Determine the Miller indices of planes A, B, and C in Figure 3-18.

SOLUTION

Plane A

1. $x = 1, y = 1, z = 1$
2. $\frac{1}{x} = 1, \frac{1}{y} = 1, \frac{1}{z} = 1$
3. No fractions to clear
4. (111)

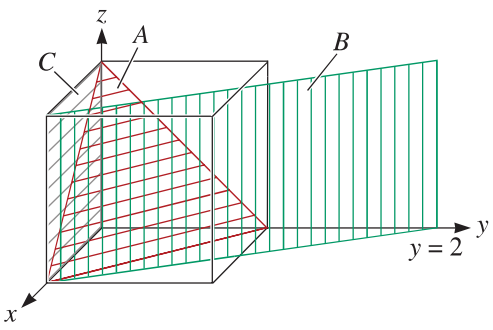


Figure 3-18
Crystallographic planes and intercepts (for Example 3-8).

Plane *B*

1. The plane never intercepts the z axis, so $x = 1$, $y = 2$, and $z = \infty$
2. $\frac{1}{x} = 1, \frac{1}{y} = \frac{1}{2}, \frac{1}{z} = 0$
3. Clear fractions: $\frac{1}{x} = 2, \frac{1}{y} = 1, \frac{1}{z} = 0$
4. (210)

Plane *C*

1. We must move the origin, since the plane passes through 0, 0, 0. Let's move the origin one lattice parameter in the y-direction. Then, $x = \infty$, $y = -1$, and $z = \infty$.
2. $\frac{1}{x} = 0, \frac{1}{y} = -1, \frac{1}{z} = 0$
3. No fractions to clear.
4. $(0\bar{1}0)$

Several important aspects of the Miller indices for planes should be noted:

1. Planes and their negatives are identical (this was not the case for directions) because they are parallel. Therefore, $(020) = (0\bar{2}0)$.
2. Planes and their multiples are not identical (again, this is the opposite of what we found for directions). We can show this by defining planar densities and planar packing fractions. The **planar density** is the number of atoms per unit area with centers that lie on the plane; the packing fraction is the fraction of the area of that plane actually covered by these atoms. Example 3-9 shows how these can be calculated.
3. In each unit cell, **planes of a form** or **family** represent groups of equivalent planes that have their particular indices because of the orientation of the coordinates. We represent these groups of similar planes with the notation {}. The planes of the form {110} in cubic systems are shown in Table 3-4.
4. In cubic systems, a direction that has the same indices as a plane is perpendicular to that plane.

TABLE 3-4 ■ *Planes of the form {110} in cubic systems*

$$\{110\}\begin{cases}(110)\\(101)\\(011)\\(1\bar{1}0)\\(10\bar{1})\\(01\bar{1})\end{cases}$$

Note: The negatives of the planes are not unique planes.

Example 3-9 *Calculating the Planar Density and Packing Fraction*

Calculate the planar density and planar packing fraction for the (010) and (020) planes in simple cubic polonium, which has a lattice parameter of 0.334 nm.

SOLUTION

The two planes are drawn in Figure 3-19. On the (010) plane, the atoms are centered at each corner of the cube face, with 1/4 of each atom actually in the face of the unit cell. Thus, the total atoms on each face is one. The planar density is

$$\text{Planar density (010)} = \frac{\text{atoms per face}}{\text{area of face}} = \frac{1 \text{ atom per face}}{(0.334)^2}$$
$$= 8.96 \text{ atoms/nm}^2 = 8.96 \times 10^{14} \text{ atoms/cm}^2$$

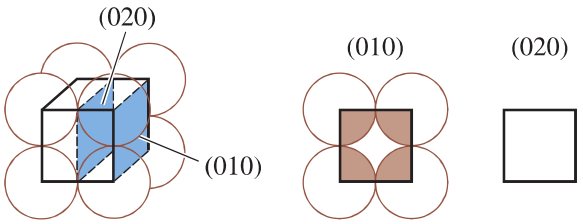


Figure 3-19
The planar densities of the (010) and (020) planes in SC unit cells are not identical (for Example 3-9).

The planar packing fraction is given by

$$\text{Packing fraction (010)} = \frac{\text{area of atoms per face}}{\text{area of face}} = \frac{(1 \text{ atom})(\pi r^2)}{(a_0)^2}$$
$$= \frac{\pi r^2}{(2r)^2} = 0.79$$

No atoms are centered on the (020) planes. Therefore, the planar density and the planar packing fraction are both zero. The (010) and (020) planes are not equivalent!

Construction of Directions and Planes

To construct a direction or plane in the unit cell, we simply work backwards. Example 3-10 shows how we might do this.

Example 3-10 *Drawing a Direction and Plane*

Draw (a) the $[1\bar{2}1]$ direction and (b) the $(\bar{2}10)$ plane in a cubic unit cell.

SOLUTION

a. Because we know that we will need to move in the negative *y*-direction, let's locate the origin at 0, +1, 0. The "tail" of the direction will be located at this new origin. A second point on the direction can be determined by moving +1 in the *x*-direction, −2 in the *y*-direction, and +1 in the *z*-direction [Figure 3-20(a)].

b. To draw in the $(\bar{2}10)$ plane, first take reciprocals of the indices to obtain the intercepts, that is

$$x = \frac{1}{-2} = -\frac{1}{2}; y = \frac{1}{1} = 1; z = \frac{1}{0} = \infty$$

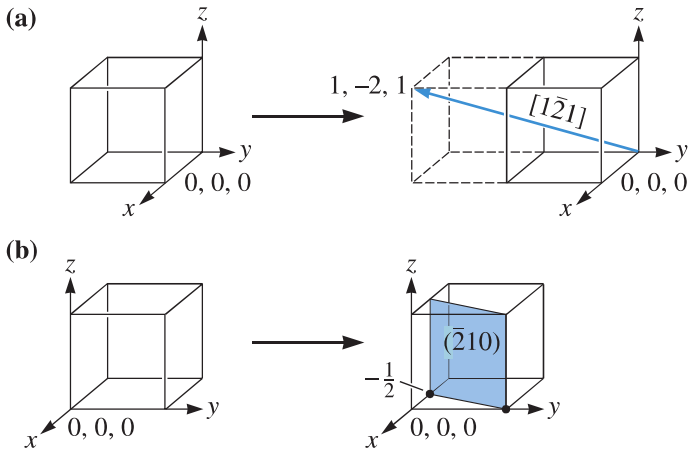


Figure 3-20 Construction of a (a) direction and (b) plane within a unit cell (for Example 3-10).

Since the x-intercept is in a negative direction, and we wish to draw the plane within the unit cell, let's move the origin +1 in the x-direction to 1, 0, 0.

Then we can locate the x-intercept at $-1/2$ and the y-intercept at +1. The plane will be parallel to the z-axis [Figure 3-20(b)].

Miller Indices for Hexagonal Unit Cells

A special set of **Miller-Bravais indices** has been devised for hexagonal unit cells because of the unique symmetry of the system (Figure 3-21). The coordinate system uses four axes instead of three, with the a_3 axis being redundant. The axes a_1, a_2, and a_3 lie in a plane that is perpendicular to the fourth axis. The procedure for finding the indices of planes is exactly the same as before, but four intercepts are required, giving indices of the form $(hkil)$. Because of the redundancy of the a_3 axis and the special geometry of the system, the first three integers in the designation, corresponding to the a_1, a_2, and a_3 intercepts, are related by $h + k = -i$.

Directions in HCP cells are denoted with either the three-axis or four-axis system. With the three-axis system, the procedure is the same as for conventional Miller indices; examples of this procedure are shown in Example 3-11. A more complicated procedure,

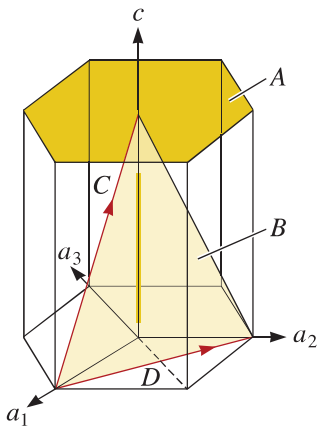


Figure 3-21 Miller-Bravais indices are obtained for crystallographic planes in HCP unit cells by using a four-axis coordinate system. The planes labeled *A* and *B* and the directions labeled *C* and *D* are those discussed in Example 3-11.

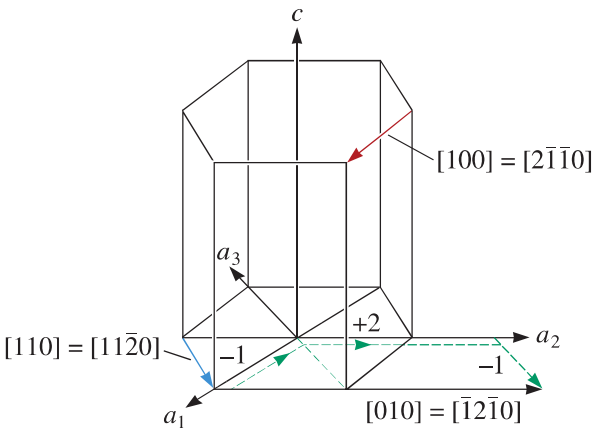


Figure 3-22
Typical directions in the HCP unit cell, using both three- and four-axis systems. The dashed lines show that the [$\bar{1}$2$\bar{1}$0] direction is equivalent to a [010] direction.

by which the direction is broken up into four vectors, is needed for the four-axis system. We determine the number of lattice parameters we must move in each direction to get from the "tail" to the "head" of the direction, while for consistency still making sure that $h + k = -i$. This is illustrated in Figure 3-22, showing that the [010] direction is the same as the [$\bar{1}$2$\bar{1}$0] direction.

We can also convert the three-axis notation to the four-axis notation for directions by the following relationships, where h', k', and l' are the indices in the three-axis system:

$$\left.\begin{aligned} h &= \frac{1}{3}(2h' - k') \\ k &= \frac{1}{3}(2k' - h') \\ i &= -\frac{1}{3}(h' + k') \\ l &= l' \end{aligned}\right\} \tag{3-6}$$

After conversion, the values of h, k, i, and l may require clearing of fractions or reducing to lowest integers.

Example 3-11 *Determining the Miller-Bravais Indices for Planes and Directions*

Determine the Miller-Bravais indices for planes A and B and directions C and D in Figure 3-21.

SOLUTION

Plane *A*

1. $a_1 = a_2 = a_3 = \infty$, $c = 1$
2. $\dfrac{1}{a_1} = \dfrac{1}{a_2} = \dfrac{1}{a_3} = 0, \dfrac{1}{c} = 1$
3. No fractions to clear
4. (0001)

Plane *B*

1. $a_1 = 1, a_2 = 1, a_3 = -\frac{1}{2}, c = 1$
2. $\frac{1}{a_1} = 1, \frac{1}{a_2} = 1, \frac{1}{a_3} = -2, \frac{1}{c} = 1$
3. No fractions to clear.
4. $(11\bar{2}1)$

Direction *C*

1. Two points are 0, 0, 1 and 1, 0, 0.
2. 0, 0, 1 − 1, 0, 0 = −1, 0, 1
3. No fractions to clear or integers to reduce.
4. $[\bar{1}01]$ or $[\bar{2}113]$

Direction *D*

1. Two points are 0, 1, 0 and 1, 0, 0.
2. 0, 1, 0 − 1, 0, 0 = −1, 1, 0
3. No fractions to clear or integers to reduce.
4. $[\bar{1}10]$ or $[\bar{1}100]$

Close-Packed Planes and Directions

In examining the relationship between atomic radius and lattice parameter, we looked for close-packed directions, where atoms are in continuous contact. We can now assign Miller indices to these close-packed directions, as shown in Table 3-5.

We can also examine FCC and HCP unit cells more closely and discover that there is at least one set of close-packed planes in each. Close-packed planes are shown in Figure 3-23. Notice that a hexagonal arrangement of atoms is produced in two dimensions. The close-packed planes are easy to find in the HCP unit cell; they are the (0001) and (0002) planes of the HCP structure and are given the special name **basal planes**. In fact, we can build up an HCP unit cell by stacking together close-packed planes in an . . . *ABABAB* . . . **stacking sequence** (Figure 3-23). Atoms on plane *B*, the (0002) plane, fit into the valleys between atoms on plane *A*, the bottom (0001) plane. If another plane identical in orientation to plane *A* is placed in the valleys of plane *B* directly above plane *A*, the HCP structure is created. Notice that all of the possible close-packed planes are parallel to one another. Only the basal planes—(0001) and (0002)—are close-packed.

TABLE 3-5 ■ *Close-packed planes and directions*

Structure	Directions	Planes
SC	⟨100⟩	None
BCC	⟨111⟩	None
FCC	⟨110⟩	{111}
HCP	⟨100⟩, ⟨110⟩ or $\langle 11\bar{2}0 \rangle$	(0001), (0002)

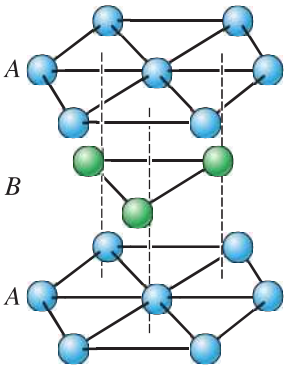


Figure 3-23
The *ABABAB* stacking sequence of close-packed planes produces the HCP structure.

From Figure 3-23, we find the coordination number of the atoms in the HCP structure. The center atom in a basal plane touches six other atoms in the same plane. Three atoms in a lower plane and three atoms in an upper plane also touch the same atom. The coordination number is twelve.

In the FCC structure, close-packed planes are of the form {111} (Figure 3-24). When parallel (111) planes are stacked, atoms in plane *B* fit over valleys in plane *A* and atoms in plane *C* fit over valleys in both planes *A* and *B*. The fourth plane fits directly over atoms in plane *A*. Consequently, a stacking sequence . . . *ABCABCABC* . . . is produced using the (111) plane. Again, we find that each atom has a coordination number of twelve.

Unlike the HCP unit cell, there are four sets of nonparallel close-packed planes—(111), (11$\bar{1}$), (1$\bar{1}$1), and ($\bar{1}$11)—in the FCC cell. This difference between the FCC and HCP unit cells—the presence or absence of intersecting close-packed planes—affects the mechanical behavior of metals with these structures.

Isotropic and Anisotropic Behavior

Because of differences in atomic arrangement in the planes and directions within a crystal, some properties also vary with direction. A material is crystallographically **anisotropic** if its properties depend on the crystallographic direction along which the property is measured. For example, the modulus of elasticity of aluminum is 75.9 GPa (11×10^6 psi) in ⟨111⟩ directions, but only 63.4 GPa (9.2×10^6 psi) in ⟨100⟩ directions. If the properties are

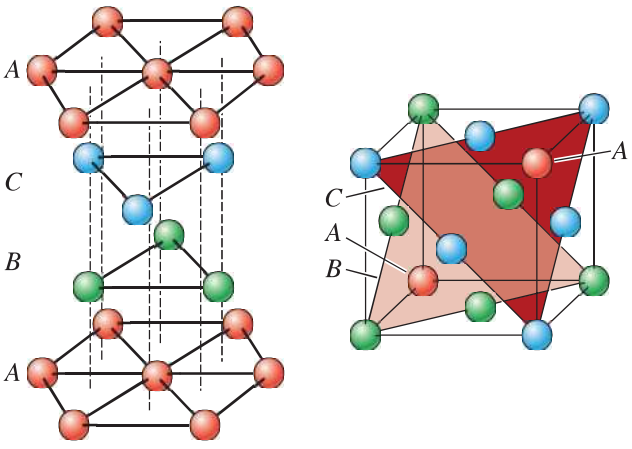


Figure 3-24
The *ABCABCABC* stacking sequence of close-packed planes produces the FCC structure.

identical in all directions, the material is crystallographically **isotropic**. Note that a material such as aluminum, which is crystallographically anisotropic, may behave as an isotropic material if it is in a polycrystalline form. This is because the random orientations of different crystals in a polycrystalline material will mostly cancel out any effect of the anisotropy as a result of crystal structure. In general, most polycrystalline materials will exhibit isotropic properties. Materials that are single crystals or in which many grains are oriented along certain directions (naturally or deliberately obtained by processing) will typically have anisotropic mechanical, optical, magnetic, and dielectric properties.

Interplanar Spacing

The distance between two adjacent parallel planes of atoms with the same Miller indices is called the **interplanar spacing** (d_{hkl}). The interplanar spacing in *cubic* materials is given by the general equation

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}, \tag{3-7}$$

where a_0 is the lattice parameter and h, k, and l represent the Miller indices of the adjacent planes being considered. The interplanar spacings for non-cubic materials are given by more complex expressions.

3-6 Interstitial Sites

In all crystal structures, there are small holes between the usual atoms into which smaller atoms may be placed. These locations are called **interstitial sites**.

An atom, when placed into an interstitial site, touches two or more atoms in the lattice. This interstitial atom has a coordination number equal to the number of atoms it touches. Figure 3-25 shows interstitial locations in the SC, BCC, and FCC structures. The **cubic site**, with a coordination number of eight, occurs in the SC structure at the body-centered position. **Octahedral sites** give a coordination number of six (not eight). They are known as octahedral sites because the atoms contacting the interstitial atom form an octahedron. **Tetrahedral sites** give a coordination number of four. As an example, the octahedral sites in BCC unit cells are located at the faces of the cube; a small atom placed in the octahedral site touches the four atoms at the corners of the face, the atom at the center of the unit cell, plus another atom at the center of the adjacent unit cell, giving a coordination number of six. In FCC unit cells, octahedral sites occur at the center of each edge of the cube, as well as at the body center of the unit cell.

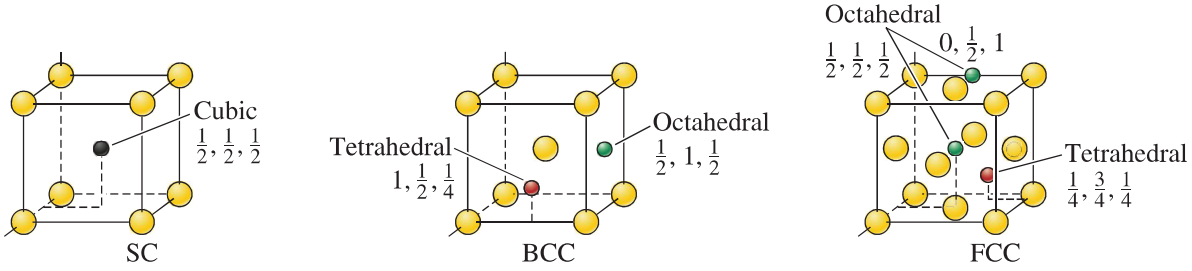


Figure 3-25 The location of the interstitial sites in cubic unit cells. Only representative sites are shown.

Example 3-12 *Calculating Octahedral Sites*

Calculate the number of octahedral sites that *uniquely* belong to one FCC unit cell.

SOLUTION

The octahedral sites include the twelve edges of the unit cell, with the coordinates

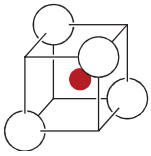
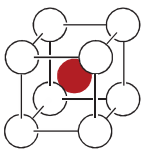
$$\begin{array}{cccc} \frac{1}{2},0,0 & \frac{1}{2},1,0 & \frac{1}{2},0,1 & \frac{1}{2},1,1 \\ 0,\frac{1}{2},0 & 1,\frac{1}{2},0 & 1,\frac{1}{2},1 & 0,\frac{1}{2},1 \\ 0,0,\frac{1}{2} & 1,0,\frac{1}{2} & 1,1,\frac{1}{2} & 0,1,\frac{1}{2} \end{array}$$

plus the center position, 1/2, 1/2, 1/2. Each of the sites on the edge of the unit cell is shared between four unit cells, so only 1/4 of each site belongs uniquely to each unit cell. Therefore, the number of sites belonging uniquely to each cell is

$$\frac{12 \text{ edges}}{\text{cell}} \cdot \frac{\frac{1}{4} \text{ site}}{\text{edge}} + \frac{1 \text{ body-center}}{\text{cell}} \cdot \frac{1 \text{ site}}{\text{body-center}} = 4 \text{ octahedral sites/cell}$$

Interstitial atoms or ions whose radii are slightly larger than the radius of the interstitial site may enter that site, pushing the surrounding atoms slightly apart. Atoms with radii smaller than the radius of the hole are not allowed to fit into the interstitial site because the ion would "rattle" around in the site. If the interstitial atom becomes too large, it prefers to enter a site having a larger coordination number (Table 3-6). Therefore,

TABLE 3-6 *The coordination number and the radius ratio*

Coordination Number	Location of Interstitial	Radius Ratio	Representation
2	Linear	0–0.155	
3	Center of triangle	0.155–0.225	
4	Center of tetrahedron	0.225–0.414	
6	Center of octahedron	0.414–0.732	
8	Center of cube	0.732–1.000	

an atom with a radius ratio between 0.225 and 0.414 enters a tetrahedral site; if its radius is somewhat larger than 0.414, it enters an octahedral site instead.

Many ionic crystals (see Section 3-7) can be viewed as being generated by close packing of larger anions. Cations then can be viewed as smaller ions that fit into the interstitial sites of the close-packed anions. Thus, the radius ratios described in Table 3-6 also apply to the ratios of the radius of the cation to that of the anion. The packing in ionic crystals is not as tight as that in FCC or HCP metals.

3-7 Crystal Structures of Ionic Materials

Ionic materials must have crystal structures that ensure electrical neutrality, yet permit ions of different sizes to be packed efficiently. As mentioned before, ionic crystal structures can be viewed as close-packed structures of anions. Anions form tetrahedra or octahedra, allowing the cations to fit into their appropriate interstitial sites. In some cases, it may be easier to visualize coordination polyhedra of cations with anions going to the interstitial sites. Recall from Chapter 2 that very often in real materials with engineering applications, the bonding is never 100% ionic. We still use this description of the crystal structure, though, to discuss the crystal structure of most ceramic materials. The following factors need to be considered in order to understand crystal structures of ionically bonded solids.

Ionic Radii

The crystal structures of ionically bonded compounds often can be described by placing the anions at the normal lattice points of a unit cell, with the cations then located at one or more of the interstitial sites described in Section 3-6 (or vice versa). The ratio of the sizes of the ionic radii of anions and cations influences both the manner of packing and the coordination number (Table 3-6). Note that the radii of atoms and ions are different. For example, the radius of an oxygen atom is 0.6 Å; however, the radius of an oxygen anion (O^{2-}) is 1.32 Å. This is because an oxygen anion has acquired two additional electrons and has become larger. As a general rule, anions are larger than cations. Cations, having acquired a positive charge by losing electrons, are expected to be smaller. Strictly speaking, the radii of cations and anions also depend upon the coordination number. For example, the radius of an Al^{+3} ion is 0.39 Å when the coordination number is four (tetrahedral coordination); however, the radius of Al^{+3} is 0.53 Å when the coordination number is 6 (octahedral coordination). Also, note that the coordination number for cations is the number of nearest anions and vice versa. The radius of an atom also depends on the coordination number. For example, the radius of an iron atom in the FCC and BCC polymorphs is different! This tells us that atoms and ions are not "hard spheres" with fixed atomic radii. Appendix B in this book contains the atomic and ionic radii for different elements.

Electrical Neutrality

The overall material has to be electrically neutral. If the charges on the anion and the cation are identical and the coordination number for each ion is identical to ensure a proper balance of charge, then the compound will have a formula AX (A: cation, X: anion). As an example, each cation may be surrounded by six anions, while each anion is, in turn, surrounded by six cations. If the valence of the cation is +2 and that of the anion is −1, then twice as many anions must be present, and the formula is AX_2. The structure of the AX_2 compound must ensure that the coordination number of the cation is twice the coordination number of the anion. For example, each cation may have eight anion nearest neighbors, while only four cations touch each anion.

Connection between Anion Polyhedra

As a rule, the coordination polyhedra (formed by the close packing of anions) will share corners, as opposed to faces or edges. This is because in corner sharing polyhedra, electrostatic repulsion between cations is reduced considerably and this leads to the formation of a more stable crystal structure. A number of common structures in ceramic materials are described in the following discussions. Compared to metals, ceramic structures are more complex. The lattice constants of ceramic materials tend to be larger than those for metallic materials because electrostatic repulsion between ions prevents close packing of both anions and cations.

Example 3-13 Radius Ratio for KCl

For potassium chloride (KCl), (a) verify that the compound has the cesium chloride structure and (b) calculate the packing factor for the compound.

SOLUTION

a. From Appendix B, $r_{K^+} = 0.113$ nm and $r_{Cl^-} = 0.181$ nm, so

$$\frac{r_{K^+}}{r_{Cl^-}} = \frac{0.133}{0.181} = 0.735$$

Since $0.732 < 0.735 < 1.000$, the coordination number for each type of ion is eight, and the CsCl structure is likely.

b. The ions touch along the body diagonal of the unit cell, so

$$\sqrt{3}a_0 = 2r_{K^+} + 2r_{Cl^-} = 2(0.133) + 2(0.181) = 0.628 \text{ nm}$$

$$a_0 = 0.363 \text{ nm}$$

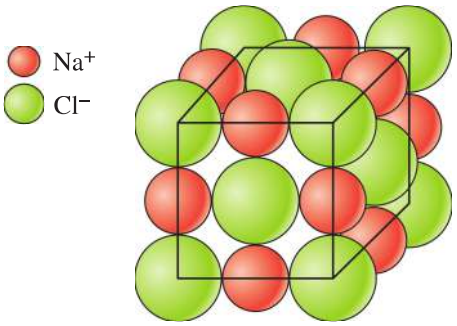
$$\text{Packing factor} = \frac{\frac{4}{3}\pi r_{K^+}^3(1 \text{ K ion}) + \frac{4}{3}\pi r_{Cl^-}^3(1 \text{ Cl ion})}{a_0^3}$$

$$= \frac{\frac{4}{3}\pi(0.133)^3 + \frac{4}{3}\pi(0.181)^3}{(0.363)^3} = 0.73$$

This structure is shown in Figure 3-10.

Sodium Chloride Structure

The radius ratio for sodium and chloride ions is $r_{Na^+}/r_{Cl^-} = 0.097 \text{ nm}/0.181 \text{ nm} = 0.536$; the sodium ion has a charge of +1; the chloride ion has a charge of −1. Therefore, based on the charge balance and radius ratio, each anion and cation must have a coordination number of six. The FCC structure, with Cl^{-1} ions at FCC positions and Na^+ at the four octahedral sites, satisfies these requirements (Figure 3-26). We can also consider this structure to be FCC with two ions—one Na^{+1} and one Cl^{-1}—associated with each lattice point. Many ceramics, including magnesium oxide (MgO), calcium oxide (CaO), and iron oxide (FeO) have this structure.



NaCl

Figure 3-26
The sodium chloride structure, a FCC unit cell with two ions (Na^+ and Cl^-) per lattice point. *Note*: ion sizes not to scale.

Example 3-14 *Illustrating a Crystal Structure and Calculating Density*

Show that MgO has the sodium chloride crystal structure and calculate the density of MgO.

SOLUTION

From Appendix B, $r_{Mg^{+2}} = 0.066$ nm and $r_{O^{-2}} = 0.132$ nm, so

$$\frac{r_{Mg^{+2}}}{r_{O^{-2}}} = \frac{0.066}{0.132} = 0.50$$

Since $0.414 < 0.50 < 0.732$, the coordination number for each ion is six, and the sodium chloride structure is possible.

The atomic masses are 24.312 and 16.00 g/mol for magnesium and oxygen, respectively. The ions touch along the edge of the cube, so

$$a_0 = 2r_{Mg^{+2}} + 2r_{O^{-2}} = 2(0.066) + 2(0.132) = 0.396 \text{ nm} = 3.96 \times 10^{-8} \text{ cm}$$

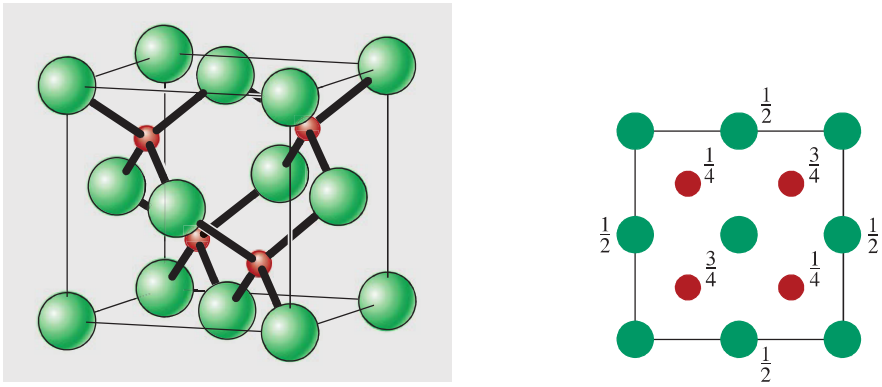
$$\rho = \frac{(4\ Mg^{+2})\,(24.312) + (4\ O^{-2})\,(16.00)}{(3.96 \times 10^{-8}\ cm^3)^3(6.022 \times 10^{23})} = 4.31\ g/cm^3$$

Zinc Blende Structure

Zinc blende is the name of the crystal structure adopted by ZnS. Although the Zn ions have a charge of +2 and S ions have a charge of −2, zinc blende (ZnS) cannot have the sodium chloride structure because

$$\frac{r_{Zn^{+2}}}{r_{S^{-2}}} = 0.074 \text{ nm}/0.184 \text{ nm} = 0.402$$

This radius ratio demands a coordination number of four, which in turn means that the zinc ions enter tetrahedral sites in a unit cell (Figure 3-27). The FCC structure, with S anions at the normal lattice points and Zn cations at half of the tetrahedral sites, can accommodate the restrictions of both charge balance and coordination number. A variety of materials, including the semiconductor GaAs and many other III–V semiconductors (Chapter 2), have this structure.



(a) (b)

Figure 3-27 (a) The zinc blende unit cell, (b) plan view. The fractions indicate the positions of the atoms out of the page relative to the height of one unit cell.

Example 3-15 *Calculating the Theoretical Density of GaAs*

The lattice constant of gallium arsenide (GaAs) is 5.65 Å. Show that the theoretical density of GaAs is 5.33 g/cm^3.

SOLUTION

For the "zinc blende" GaAs unit cell, there are four Ga and four As atoms per unit cell.

From the periodic table (Chapter 2):
Each mole (6.022×10^{23} atoms) of Ga has a mass of 69.72 g. Therefore, the mass of four Ga atoms will be 4×69.72 (6.022×10^{23}) g.
Each mole (6.022×10^{23} atoms) of As has a mass of 74.91 g. Therefore, the mass of four As atoms will be 4×74.91 (6.022×10^{23}) g.
These atoms occupy a volume of $(5.65 \times 10^{-8})^3$ cm^3.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{4(69.72 + 74.91)/(6.022 \times 10^{23})}{(5.65 \times 10^{-8})^3} = 5.33 \text{ g/cm}^3$$

Therefore, the theoretical density of GaAs is 5.33 g/cm^3.

Fluorite Structure The fluorite structure is FCC, with anions located at all eight of the tetrahedral positions (Figure 3-28). Thus, there are four cations and eight anions per cell, and the ceramic compound must have the formula AX_2, as in calcium fluorite, or CaF_2. In the designation AX_2, A is the cation and X is the anion. The coordination number of the calcium ions is eight, but that of the fluoride ions is four, therefore ensuring a balance of charge. One of the polymorphs of ZrO_2 known as cubic zirconia exhibits this crystal structure. Other compounds that exhibit this structure include UO_2, ThO_2, and CeO_2.

Corundum Structure This is one of the crystal structures of alumina known as alpha alumina (α-Al_2O_3). In alumina, the oxygen anions pack in a hexagonal arrangement, and the aluminum cations occupy some of the available octahedral positions (Figure 3-29).

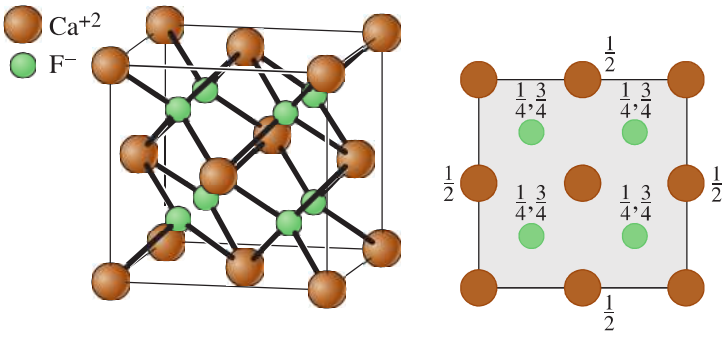


Figure 3-28 (a) Fluorite unit cell, (b) plan view. The fractions indicate the positions of the atoms out of the page relative to the height of the unit cell.

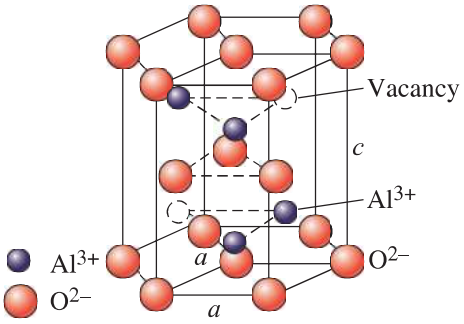


Figure 3-29
Corundum structure of alpha-alumina (α-Al_2O_3).

Alumina is probably the most widely used ceramic material. Applications include, but are not limited to, spark plugs, refractories, electronic packaging substrates, and abrasives.

Example 3-16 *The Perovskite Crystal Structure*

Perovskite is a mineral containing calcium, titanium, and oxygen. The unit cell is cubic and has a calcium atom at each corner, an oxygen atom at each face center, and a titanium atom at the body-centered position. The atoms contribute to the unit cell in the usual way (1/8 atom contribution for each atom at the corners, etc.).

(a) Describe this structure as a lattice and a basis. (b) How many atoms of each type are there per unit cell? (c) An alternate way of drawing the unit cell of perovskite has calcium at the body-centered position of each cubic unit cell. What are the positions of the titanium and oxygen atoms in this representation of the unit cell? (d) By counting the number of atoms of each type per unit cell, show that the formula for perovskite is the same for both unit cell representations.

SOLUTION

(a) The lattice must belong to the cubic crystal system. Since different types of atoms are located at the corner, face-centered, and body-centered positions, the lattice must be simple cubic. The structure can be described as a simple cubic lattice

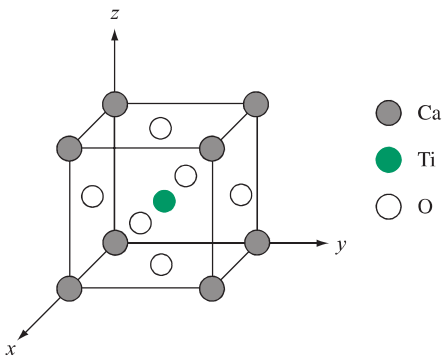


Figure 3-30
The perovskite unit cell.

with a basis of Ca (0, 0, 0), Ti (1/2, 1/2, 1/2), and O (0, 1/2, 1/2), (1/2, 0, 1/2), and (1/2, 1/2, 0). The unit cell is shown in Figure 3-30.

(b) There are two methods for calculating the number of atoms per unit cell. Using the lattice and basis concept,

$$\frac{1 \text{ lattice point}}{\text{unit cell}} * \frac{5 \text{ atoms}}{\text{lattice point}} = \frac{5 \text{ atoms}}{\text{unit cell}}$$

Using the unit cell concept,

$$\frac{8 \text{ corners}}{\text{unit cell}} * \frac{1/8 \text{ Ca atom}}{\text{corner}} + \frac{1 \text{ body-center}}{\text{unit cell}} * \frac{1 \text{ Ti atom}}{\text{body-center}}$$
$$+ \frac{6 \text{ face–centers}}{\text{unit cell}} * \frac{1/2 \text{ O atom}}{\text{face-center}} = \frac{5 \text{ atoms}}{\text{unit cell}}$$

As expected, the number of atoms per unit cell is the same regardless of which method is used. The chemical formula for perovskite is $CaTiO_3$ (calcium titanate). Compounds with the general formula ABO_3 and this structure are said to have the perovskite crystal structure. One of the polymorphs of barium titanate, which is used to make capacitors for electronic applications, and one form of lead zirconate exhibit this structure.

(c) If calcium is located at the body-centered position rather than the corners of the unit cell, then titanium must be located at the corners of the unit cell, and the oxygen atoms must be located at the edge centers of the unit cell, as shown in Figure 3-31. Note that this is equivalent to shifting each atom in the basis given in part (a) by the

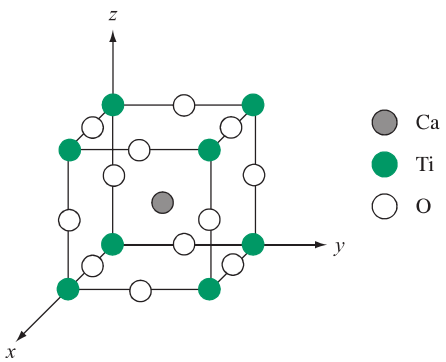


Figure 3-31
An alternate representation of the unit cell of perovskite.

vector [1/2 1/2 1/2]. The Ca atom is shifted from (0, 0, 0) to (1/2, 1/2, 1/2), and the Ti atom is shifted from (1/2, 1/2, 1/2) to (1, 1, 1), which is equivalent to the origin of an adjacent unit cell or (0, 0, 0). Note that the crystal has not been changed; only the coordinates of the atoms in the basis are different. Another lattice and basis description of perovskite is thus a simple cubic lattice with a basis of Ca (1/2, 1/2, 1/2), Ti (0, 0, 0), and O (1/2, 0, 0), (0, 1/2, 0), and (0, 0, 1/2).

Using the lattice and basis concept to count the number of atoms per unit cell,

$$\frac{1 \text{ lattice point}}{\text{unit cell}} * \frac{5 \text{ atoms}}{\text{lattice point}} = \frac{5 \text{ atoms}}{\text{unit cell}}$$

Using the unit cell concept,

$$\frac{1 \text{ body-center}}{\text{unit cell}} * \frac{1 \text{ Ca atom}}{\text{body-center}} + \frac{8 \text{ corners}}{\text{unit cell}} * \frac{1/8 \text{ Ti atom}}{\text{corner}} + \frac{12 \text{ edge centers}}{\text{unit cell}} * \frac{1/4 \text{ O atom}}{\text{edge-center}} = \frac{5 \text{ atoms}}{\text{unit cell}}$$

Again we find that the chemical formula is $CaTiO_3$.

3-8 Covalent Structures

Covalently bonded materials frequently have complex structures in order to satisfy the directional restraints imposed by the bonding.

Diamond Cubic Structure

Elements such as silicon, germanium (Ge), α-Sn, and carbon (in its diamond form) are bonded by four covalent bonds and produce a **tetrahedron** [Figure 3-32(a)]. The coordination number for each silicon atom is only four because of the nature of the covalent bonding.

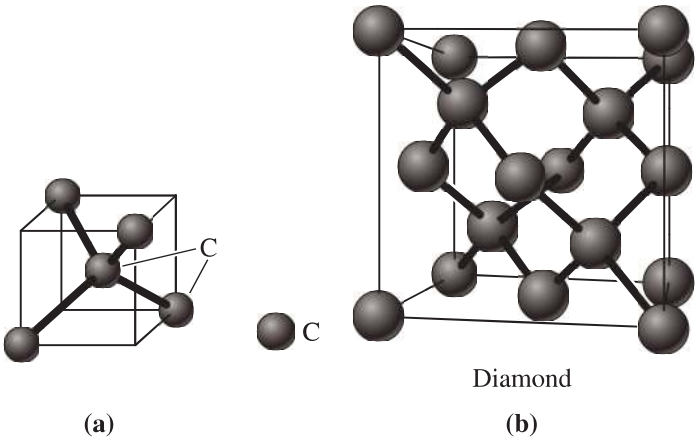


Figure 3-32 (a) Tetrahedron and (b) the diamond cubic (DC) unit cell. This open structure is produced because of the requirements of covalent bonding.

As these tetrahedral groups are combined, a large cube can be constructed [Figure 3-32(b)]. This large cube contains eight smaller cubes that are the size of the tetrahedral cube; however, only four of the cubes contain tetrahedra. The large cube is the **diamond cubic** (DC) unit cell. The atoms at the corners of the tetrahedral cubes provide atoms at the regular FCC lattice points. Four additional atoms are present within the DC unit cell from the atoms at the center of the tetrahedral cubes. We can describe the DC crystal structure as an FCC lattice with two atoms associated with each lattice point (or a basis of 2). Therefore, there are eight atoms per unit cell.

Example 3-17 *Determining the Packing Factor for the Diamond Cubic Structure*

Describe the diamond cubic structure as a lattice and a basis and determine its packing factor.

SOLUTION

The diamond cubic structure is a face-centered cubic lattice with a basis of two atoms of the same type located at (0, 0, 0) and (1/4, 1/4, 1/4). The basis atom located at (0, 0, 0) accounts for the atoms located at the FCC lattice points, which are (0, 0, 0), (0, 1/2, 1/2), (1/2, 0, 1/2), and (1/2, 1/2, 0) in terms of the coordinates of the unit cell. By adding the vector [1/4 1/4 1/4] to each of these points, the four additional atomic coordinates in the interior of the unit cell are determined to be (1/4, 1/4, 1/4), (1/4, 3/4, 3/4), (3/4, 1/4, 3/4), and (3/4, 3/4, 1/4). There are eight atoms per unit cell in the diamond cubic structure:

$$\frac{4 \text{ lattice points}}{\text{unit cell}} * \frac{2 \text{ atoms}}{\text{lattice point}} = \frac{8 \text{ atoms}}{\text{unit cell}}$$

The atoms located at the (1/4, 1/4, 1/4) type positions sit at the centers of tetrahedra formed by atoms located at the FCC lattice points. The atoms at the (1/4, 1/4, 1/4) type positions are in direct contact with the four surrounding atoms. Consider the distance between the center of the atom located at (0, 0, 0) and the center of the atom located at (1/4, 1/4, 1/4). This distance is equal to one-quarter of the body diagonal or two atomic radii, as shown in Figure 3-33. Thus,

$$\frac{a_0\sqrt{3}}{4} = 2r$$

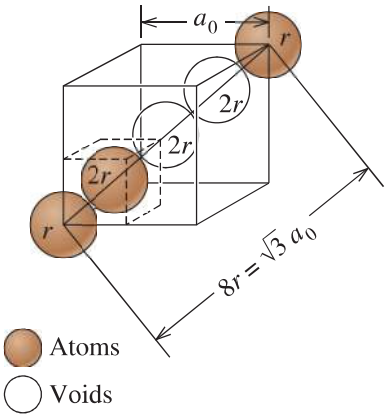


Figure 3-33
Determining the relationship between the lattice parameter and atomic radius in a diamond cubic cell (for Example 3-17).

or

$$a_0 = \frac{8r}{\sqrt{3}}$$

The packing factor is the ratio of the volume of space occupied by the atoms in the unit cell to the volume of the unit cell:

$$\text{Packing factor} = \frac{(8 \text{ atoms/cell})\left(\frac{4}{3}\pi r^3\right)}{a_0^3}$$

$$\text{Packing factor} = \frac{(8 \text{ atoms/cell})\left(\frac{4}{3}\pi r^3\right)}{(8r/\sqrt{3})^3}$$

$$\text{Packing factor} = 0.34$$

This is a relatively open structure compared to close-packed structures. In Chapter 5, we will learn that the openness of a structure is one of the factors that affects the rate at which different atoms can diffuse in a given material.

Example 3-18 *Calculating the Radius, Density, and Atomic Mass of Silicon*

The lattice constant of Si is 5.43 Å. Calculate the radius of a silicon atom and the theoretical density of silicon. The atomic mass of Si is 28.09 g/mol.

SOLUTION

Silicon has the diamond cubic structure. As shown in Example 3-17 for the diamond cubic structure,

$$r = \frac{a_0\sqrt{3}}{8}$$

Therefore, substituting $a_0 = 5.43$ Å, the radius of the silicon atom = 1.176 Å. This is the same radius listed in Appendix B. For the density, we use the same approach as in Example 3-15. Recognizing that there are eight Si atoms per unit cell, then

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{8(28.09)/(6.022 \times 10^{23})}{(5.43 \times 10^{-8} \text{ cm})^3} = 2.33 \text{ g/cm}^3$$

This is the same density value listed in Appendix A.

Crystalline Silica In a number of its forms, silica (or SiO_2) has a crystalline ceramic structure that is partly covalent and partly ionic. Figure 3-34 shows the crystal structure of one of the forms of silica, β-cristobalite, which is a complicated structure with an FCC lattice. The ionic radii of silicon and oxygen are 0.042 nm and 0.132 nm, respectively, so the radius ratio is $r_{Si^{+4}}/r_{O^{-2}} = 0.318$ and the coordination number is four.

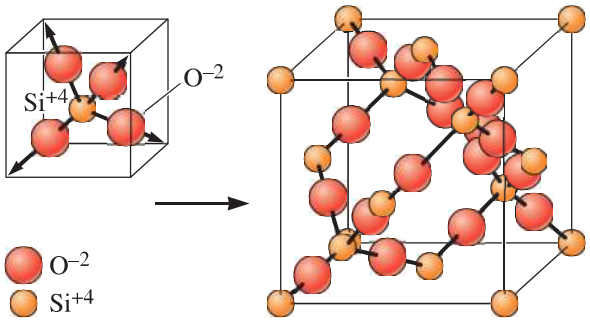


Figure 3-34
The silicon-oxygen tetrahedron and the resultant β-cristobalite form of silica.

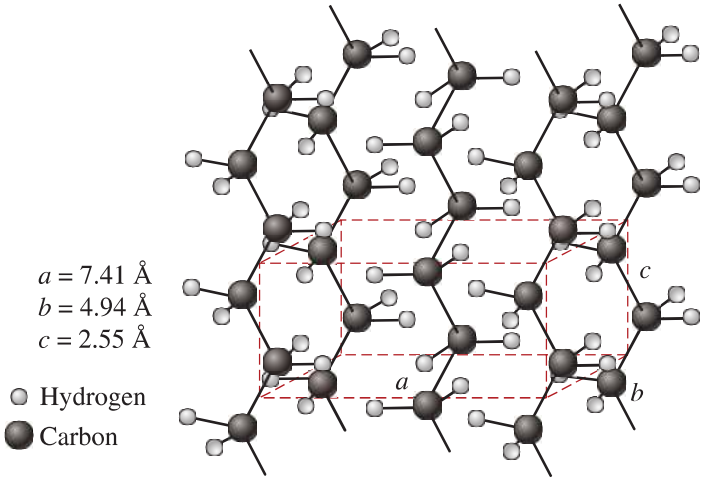


Figure 3-35 The unit cell of crystalline polyethylene (not to scale).

Crystalline Polymers

A number of polymers may form a crystalline structure. The dashed lines in Figure 3-35 outline the unit cell for the lattice of polyethylene. Polyethylene is obtained by joining C_2H_4 molecules to produce long polymer chains that form an orthorhombic unit cell. Some polymers, including nylon, can have several polymorphic forms. Most engineered plastics are partly amorphous and may develop crystallinity during processing. It is also possible to grow single crystals of polymers.

Example 3-19 *Calculating the Number of Carbon and Hydrogen Atoms in Crystalline Polyethylene*

How many carbon and hydrogen atoms are in each unit cell of crystalline polyethylene? There are twice as many hydrogen atoms as carbon atoms in the chain. The density of polyethylene is about 0.9972 g/cm^3.

SOLUTION

If we let x be the number of carbon atoms, then $2x$ is the number of hydrogen atoms. From the lattice parameters shown in Figure 3-35:

$$\rho = \frac{(x)(12 \text{ g/mol}) + (2x)(1 \text{ g/mol})}{(7.41 \times 10^{-8} \text{ cm})(4.94 \times 10^{-8} \text{ cm})(2.55 \times 10^{-8} \text{ cm})(6.022 \times 10^{23})}$$

$$0.9972 = \frac{14x}{56.2}$$

$$x = 4 \text{ carbon atoms per cell}$$

$$2x = 8 \text{ hydrogen atoms per cell}$$

3-9 Diffraction Techniques for Crystal Structure Analysis

A crystal structure of a crystalline material can be analyzed using **x-ray diffraction (XRD)** or electron diffraction. Max von Laue (1879–1960) won the Nobel Prize in 1914 for his discovery related to the diffraction of x-rays by a crystal. William Henry Bragg (1862–1942) and his son William Lawrence Bragg (1890–1971) won the 1915 Nobel Prize for their contributions to XRD.

When a beam of x-rays having a single wavelength on the same order of magnitude as the atomic spacing in the material strikes that material, x-rays are scattered in all directions. Most of the radiation scattered from one atom cancels out radiation scattered from other atoms; however, x-rays that strike certain crystallographic planes at specific angles are reinforced rather than annihilated. This phenomenon is called **diffraction**. The x-rays are diffracted, or the beam is reinforced, when conditions satisfy **Bragg's law**,

$$\sin\theta = \frac{\lambda}{2d_{hkl}} \tag{3-8}$$

where the angle θ is half the angle between the diffracted beam and the original beam direction, λ is the wavelength of the x-rays, and d_{hkl} is the interplanar spacing between the planes that cause constructive reinforcement of the beam (see Figure 3-36).

When the material is prepared in the form of a fine powder, there are always at least some powder particles (crystals or aggregates of crystals) with planes (hkl) oriented at the proper θ angle to satisfy Bragg's law. Therefore, a diffracted beam, making an angle of 2θ with the incident beam, is produced. In a *diffractometer*, a moving x-ray detector records the 2θ angles at which the beam is diffracted, giving a characteristic diffraction pattern (see Figure 3-37 on page 98). If we know the wavelength of the x-rays, we can determine the interplanar spacings and, eventually, the identity of the planes that cause the diffraction. In an XRD instrument, x-rays are produced by bombarding a metal target with a beam of high-energy electrons. Typically, x-rays emitted from copper have a wavelength $\lambda \cong 1.54060$ Å (K-α_1 line) and are used.

In the Laue method, which was the first diffraction method ever used, the specimen is in the form of a single crystal. A beam of "white radiation" consisting of x-rays of different wavelengths is used. Each diffracted beam has a different wavelength. In the transmission Laue method, photographic film is placed behind the crystal. In the