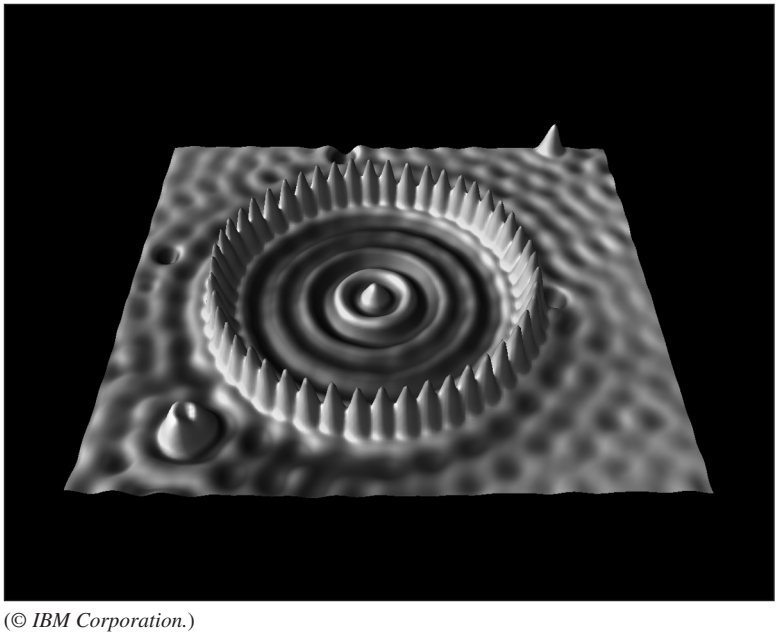
CHAPTER 3

Crystal Structures and Crystal Geometry

It is possible to map the surfaces of conducting solids at the atomic level using an instrument called the scanning tunneling microscope (STM). The STM allows the observation and manipulation of adsorbate molecules and chemical reactions on the atomic scale. This is accomplished by manipulating and monitoring a small amount of current passing through the extremely small STM tip (single-atom tungsten nanotip). The current is amplified and used to measure the size of the gap



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between the nanotip and the atoms on the surface. The chapter-opening image is an example of the resolution achieved using the STM technology.

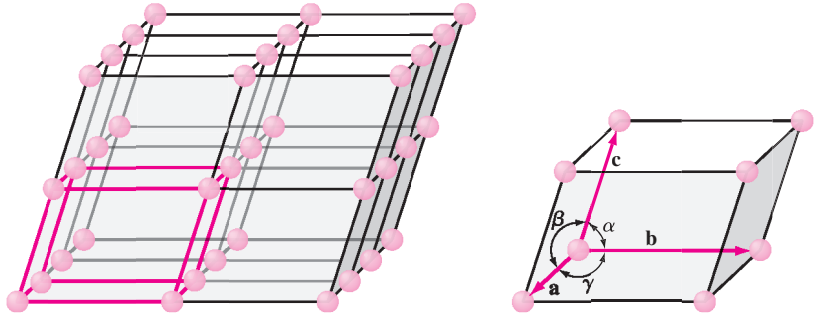
Scientists discovered a new method for confining electrons to artificial structures at the nanometer lengthscale. Surface state electrons on Cu(111) were confined to closed structures (corrals) defined by barriers built from Fe adatoms. The barriers were assembled by individually positioning Fe adatoms using the tip of a low temperature scanning tunneling microscope (STM). A circular corral of radius 71.3 Angstrom was constructed in this way out of 48 Fe adatoms.[1] ■

3.1 THE SPACE LATTICE AND UNIT CELLS

The physical structure of solid materials of engineering importance depends mainly on the arrangements of the atoms, ions, or molecules that make up the solid and the bonding forces between them. If the atoms or ions of a solid are arranged in a pattern that repeats itself in three dimensions, they form a solid that is said to have a *crystal structure* and is referred to as a *crystalline solid* or *crystalline material*. Examples of crystalline materials are metals, alloys, and some ceramic materials.

Atomic arrangements in crystalline solids can be described by referring the atoms to the points of intersection of a network of lines in three dimensions. Such a network is called a *space lattice* (Fig. 3.1*a*), and it can be described as an infinite three-dimensional array of points. Each point in the space lattice has identical surroundings. In an ideal crystal the grouping of lattice points about any given point are identical with the grouping about any other lattice point in the crystal lattice. Each space lattice can thus be described by specifying the atom positions in a repeating *unit cell,* such as the one heavily outlined in Fig. 3.1*a*. The size and shape of the unit cell can be described by three lattice vectors **a**, **b**,

[1] www.sljus.lu.se/stm/NonTech.html



(*a*) (*b*)

Figure 3.1
(*a*) Space lattice of ideal crystalline solid. (*b*) Unit cell showing lattice constants.

and **c**, originating from one corner of the unit cell (Fig. 3.1*b*). The axial lengths a, b, and c and the interaxial angles α, β, and γ are the *lattice constants* of the unit cell.

3.2 CRYSTAL SYSTEMS AND BRAVAIS LATTICES

By assigning specific values for axial lengths and interaxial angles, unit cells of different types can be constructed. Crystallographers have shown that only seven different types of unit cells are necessary to create all point lattices. These crystal systems are listed in Table 3.1.

Many of the seven crystal systems have variations of the basic unit cell. A. J. Bravais[2] showed that 14 standard unit cells could describe all possible lattice networks. These Bravais lattices are illustrated in Fig. 3.2. There are four basic types of unit cells: (1) simple, (2) body-centered, (3) face-centered, and (4) base-centered.

In the cubic system there are three types of unit cells: simple cubic, body-centered cubic, and face-centered cubic. In the orthorhombic system all four

[2]August Bravais (1811–1863). French crystallographer who derived the 14 possible arrangements of points in space.

Table 3.1 Classification of Space Lattices by Crystal System

Crystal system	Axial lengths and interaxial angles	Space lattice
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90^\circ$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple tetragonal Body-centered tetragonal
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	Simple rhombohedral
Hexagonal	Two equal axes at 120°, third axis at right angles $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Simple hexagonal
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$	Simple monoclinic Base-centered monoclinic
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple triclinic

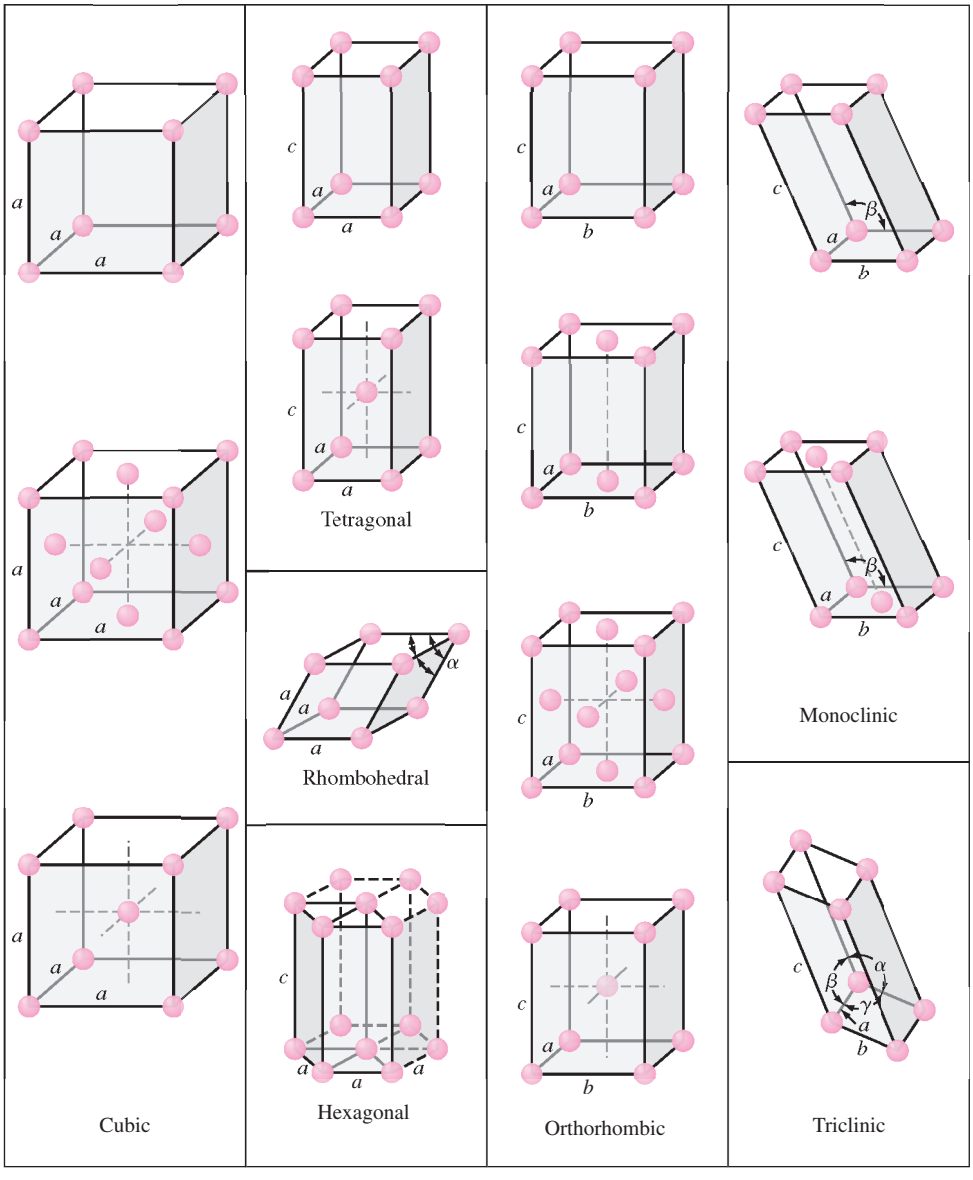


Figure 3.2
The 14 Bravais conventional unit cells grouped according to crystal system. The dots indicate lattice points that, when located on faces or at corners, are shared by other identical lattice unit cells.
(*After W. G. Moffatt, G. W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p. 47.*)

types are represented. In the tetragonal system there are only two: simple and body-centered. The face-centered tetragonal unit cell appears to be missing but can be constructed from four body-centered tetragonal unit cells. The monoclinic system has simple and base-centered unit cells, and the rhombohedral, hexagonal, and triclinic systems have only one simple type of unit cell.

3.3 PRINCIPAL METALLIC CRYSTAL STRUCTURES

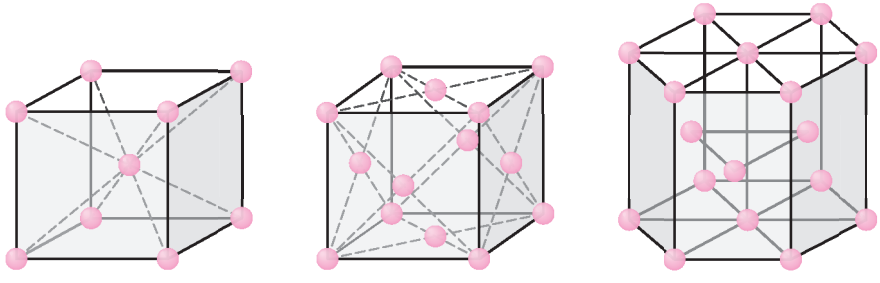
In this chapter the principal crystal structures of elemental metals will be discussed in detail. In Chap. 10 the principal ionic and covalent crystal structures that occur in ceramic materials will be treated.

Most elemental metals (about 90 percent) crystallize upon solidification into three densely packed crystal structures: *body-centered cubic (BCC)* (Fig. 3.3*a*), *face-centered cubic (FCC)* (Fig. 3.3*b*) and *hexagonal close-packed (HCP)* (Fig. 3.3*c*). The HCP structure is a denser modification of the simple hexagonal crystal structure shown in Fig. 3.2. Most metals crystallize in these dense-packed structures because energy is released as the atoms come closer together and bond more tightly with each other. Thus, the densely packed structures are in lower and more stable energy arrangements.

The extremely small size of the unit cells of crystalline metals that are shown in Fig. 3.3 should be emphasized. The cube side of the unit cell of body-centered cubic iron, for example, at room temperature is equal to 0.287×10^{-9} m, or 0.287 nanometer (nm).[3] Therefore, if unit cells of pure iron are lined up side by side, in 1 mm there will be

$$1 \text{ mm} \times \frac{1 \text{ unit cell}}{0.287 \text{ nm} \times 10^{-6} \text{ mm/nm}} = 3.48 \times 10^{6} \text{ unit cells!}$$

[3] 1 nanometer $= 10^{-9}$ meter.



(*a*) (*b*) (*c*)

Figure 3.3
Principal metal crystal structure unit cells: (*a*) body-centered cubic, (*b*) face-centered cubic, (*c*) hexagonal close-packed.

Let us now examine in detail the arrangement of the atoms in the three principal crystal structure unit cells. Although an approximation, we shall consider atoms in these crystal structures to be hard spheres. The distance between the atoms (interatomic distance) in crystal structures can be determined experimentally by x-ray diffraction analysis.[4] For example, the interatomic distance between two aluminum atoms in a piece of pure aluminum at 20°C is 0.2862 nm. The radius of the aluminum atom in the aluminum metal is assumed to be half the interatomic distance, or 0.143 nm. The atomic radii of selected metals are listed in Tables 3.2 to 3.4.

3.3.1 Body-Centered Cubic (BCC) Crystal Structure

First, consider the atomic-site unit cell for the BCC crystal structure shown in Fig. 3.4*a*. In this unit cell the solid spheres represent the centers where atoms are located and clearly indicate their relative positions. If we represent the atoms in this cell as hard spheres, then the unit cell appears as shown in Fig. 3.4*b*. In this

[4]Some of the principles of x-ray diffraction analysis will be studied in Sec. 3.11.

Table 3.2 Selected Metals That Have the BCC Crystal Structure at Room Temperature (20°C) and Their Lattice Constants and Atomic Radii

Metal	Lattice constant a (nm)	Atomic radius R^* (nm)
Chromium	0.289	0.125
Iron	0.287	0.124
Molybdenum	0.315	0.136
Potassium	0.533	0.231
Sodium	0.429	0.186
Tantalum	0.330	0.143
Tungsten	0.316	0.137
Vanadium	0.304	0.132

*Calculated from lattice constants by using Eq. (3.1), $R = \sqrt{3}a/4$.

Table 3.3 Selected Metals That Have the FCC Crystal Structure at Room Temperature (20°C) and Their Lattice Constants and Atomic Radii

Metal	Lattice constant a (nm)	Atomic radius R^* (nm)
Aluminum	0.405	0.143
Copper	0.3615	0.128
Gold	0.408	0.144
Lead	0.495	0.175
Nickel	0.352	0.125
Platinum	0.393	0.139
Silver	0.409	0.144

*Calculated from lattice constants by using Eq. (3.3), $R = \sqrt{2}a/4$.

Table 3.4 Selected Metals That Have the HCP Crystal Structure at Room Temperature (20°C) and Their Lattice Constants, Atomic Radii, and *c*/*a* Ratios

Metal	Lattice constants (nm)		Atomic radius *R* (nm)	*c*/*a* ratio	% deviation from ideality
	a	*c*			
Cadmium	0.2973	0.5618	0.149	1.890	+15.7
Zinc	0.2665	0.4947	0.133	1.856	+13.6
Ideal HCP				1.633	0
Magnesium	0.3209	0.5209	0.160	1.623	−0.66
Cobalt	0.2507	0.4069	0.125	1.623	−0.66
Zirconium	0.3231	0.5148	0.160	1.593	−2.45
Titanium	0.2950	0.4683	0.147	1.587	−2.81
Beryllium	0.2286	0.3584	0.113	1.568	−3.98

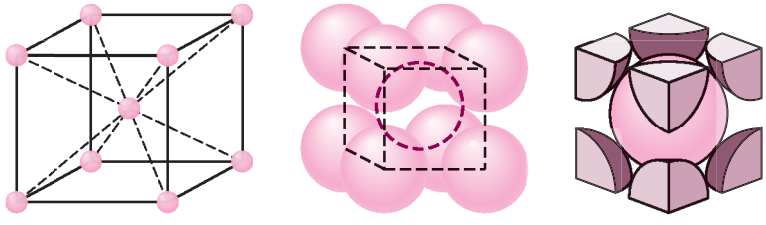


Figure 3.4
BCC unit cells: (*a*) atomic-site unit cell, (*b*) hard-sphere unit cell, and (*c*) isolated unit cell.

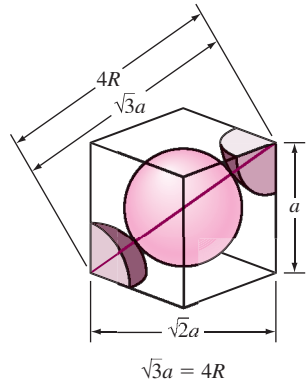


Figure 3.5
BCC unit cell showing relationship between the lattice constant *a* and the atomic radius *R*.

unit cell we see that the central atom is surrounded by eight nearest neighbors and is said to have a coordination number of 8.

If we isolate a single hard-sphere unit cell, we obtain the model shown in Fig. 3.4*c*. Each of these cells has the equivalent of two atoms per unit cell. One complete atom is located at the center of the unit cell, and an eighth of a sphere is located at each corner of the cell, making the equivalent of another atom. Thus there is a total of 1 (at the center) + 8 × $\frac{1}{8}$ (at the corners) = 2 atoms per unit cell. The atoms in the BCC unit cell contact each other across the cube diagonal, as indicated in Fig. 3.5, so that the relationship between the length of the cube side *a* and the atomic radius *R* is

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

EXAMPLE PROBLEM 3.1

Iron at 20°C is BCC with atoms of atomic radius 0.124 nm. Calculate the lattice constant a for the cube edge of the iron unit cell.

■ **Solution**

From Fig. 3.5 it is seen that the atoms in the BCC unit cell touch across the cube diagonals. Thus, if a is the length of the cube edge, then

$$\sqrt{3}a = 4R \tag{3.1}$$

where R is the radius of the iron atom. Therefore

$$a = \frac{4R}{\sqrt{3}} = \frac{4(0.124\text{ nm})}{\sqrt{3}} = 0.2864\text{ nm} \blacktriangleleft$$

If the atoms in the BCC unit cell are considered to be spherical, an atomic packing factor (APF) can be calculated by using the equation

$$\text{Atomic packing factor (APF)} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}} \tag{3.2}$$

Using this equation, the APF for the BCC unit cell (Fig. 3.3*a*) is calculated to be 68 percent (see Example Problem 3.2). That is, 68 percent of the volume of the BCC unit cell is occupied by atoms and the remaining 32 percent is empty space. The BCC crystal structure is *not* a close-packed structure since the atoms could be packed closer together. Many metals such as iron, chromium, tungsten, molybdenum, and vanadium have the BCC crystal structure at room temperature. Table 3.2 lists the lattice constants and atomic radii of selected BCC metals.

EXAMPLE PROBLEM 3.2

Calculate the atomic packing factor (APF) for the BCC unit cell, assuming the atoms to be hard spheres.

■ **Solution**

$$\text{APF} = \frac{\text{volume of atoms in BCC unit cell}}{\text{volume of BCC unit cell}} \tag{3.2}$$

Since there are two atoms per BCC unit cell, the volume of atoms in the unit cell of radius R is

$$V_{\text{atoms}} = (2)\left(\tfrac{4}{3}\pi R^3\right) = 8.373\,R^3$$

The volume of the BCC unit cell is

$$V_{\text{unit cell}} = a^3$$

where a is the lattice constant. The relationship between a and R is obtained from Fig. 3.5, which shows that the atoms in the BCC unit cell touch each other across the cubic diagonal. Thus

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

Thus

$$V_{\text{unit cell}} = a^3 = 12.32R^3$$

The atomic packing factor for the BCC unit cell is, therefore,

$$\text{APF} = \frac{V_{\text{atoms}}/\text{unit cell}}{V_{\text{unit cell}}} = \frac{8.373R^3}{12.32R^3} = 0.68 \blacktriangleleft$$

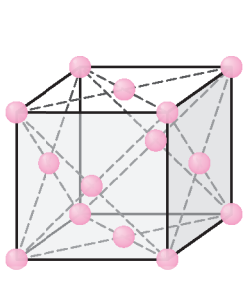
3.3.2 Face-Centered Cubic (FCC) Crystal Structure

Consider next the FCC lattice-point unit cell of Fig. 3.6*a*. In this unit cell there is one lattice point at each corner of the cube and one at the center of each cube face. The hard-sphere model of Fig. 3.6*b* indicates that the atoms in the FCC crystal structure are packed as close together as possible. The APF for this close-packed structure is 0.74 as compared to 0.68 for the BCC structure, which is not close-packed.

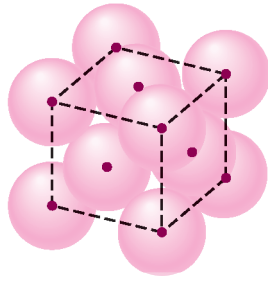
The FCC unit cell as shown in Fig. 3.6*c* has the equivalent of four atoms per unit cell. The eight corner octants account for one atom ($8 \times \frac{1}{8} = 1$), and the six half-atoms on the cube faces contribute another three atoms, making a total of four atoms per unit cell. The atoms in the FCC unit cell contact each other across the cubic face diagonal, as indicated in Fig. 3.7, so that the relationship between the length of the cube side a and the atomic radius R is

$$\sqrt{2}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{2}} \tag{3.3}$$

The APF for the FCC crystal structure is 0.74, which is greater than the 0.68 factor for the BCC structure. The APF of 0.74 is for the closest packing possible of "spherical atoms." Many metals such as aluminum, copper, lead,



(*a*)



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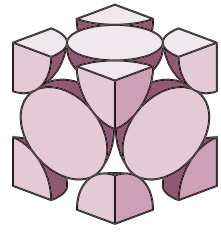

(*c*)

Figure 3.6
FCC unit cells: (*a*) atomic-site unit cell, (*b*) hard-sphere unit cell, and (*c*) isolated unit cell.

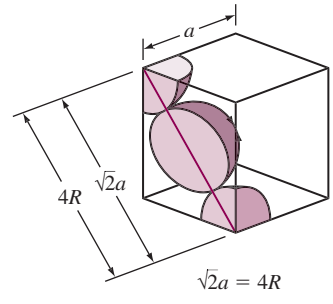

Figure 3.7
FCC unit cell showing relationship between the lattice constant a and atomic radius R. Since the atoms touch across the face diagonals, $\sqrt{2}a = 4R$.

nickel, and iron at elevated temperatures (912 to 1394°C) crystallize with the FCC crystal structure. Table 3.3 lists the lattice constants and atomic radii for some selected FCC metals.

3.3.3 Hexagonal Close-Packed (HCP) Crystal Structure

The third common metallic crystal structure is the HCP structure shown in Fig. 3.8. Metals do not crystallize into the simple hexagonal crystal structure shown in Fig. 3.2 because the APF is too low. The atoms can attain a lower energy and a more stable condition by forming the HCP structure of Fig. 3.8. The APF of the HCP crystal structure is 0.74, the same as that for the FCC crystal structure since in both structures the atoms are packed as tightly as possible. In both the HCP and FCC crystal structures each atom is surrounded by 12 other atoms, and thus both structures have a coordination number of 12. The differences in the atomic packing in FCC and HCP crystal structures will be discussed in Sec. 3.8.

The isolated HCP unit cell is shown in Fig. 3.8*c* and has the equivalent of six atoms per unit cell. Three atoms form a triangle in the middle layer, as indicated by the atomic sites in Fig. 3.8*a*. There are six $\frac{1}{6}$-atom sections on both the top and bottom layers, making an equivalent of two more atoms ($2 \times 6 \times \frac{1}{6} = 2$). Finally, there is one-half of an atom in the center of both the top and bottom layers, making the equivalent of one more atom. The total number of atoms in the HCP crystal structure unit cell is thus $3 + 2 + 1 = 6$.

The ratio of the height c of the hexagonal prism of the HCP crystal structure to its basal side a is called the c/a *ratio* (Fig. 3.8*a*). The c/a *ratio* for an ideal HCP crystal structure consisting of uniform spheres packed as tightly together as possible is 1.633. Table 3.4 lists some important HCP metals and their c/a ratios. Of the metals listed, cadmium and zinc have c/a ratios higher than ideality, which

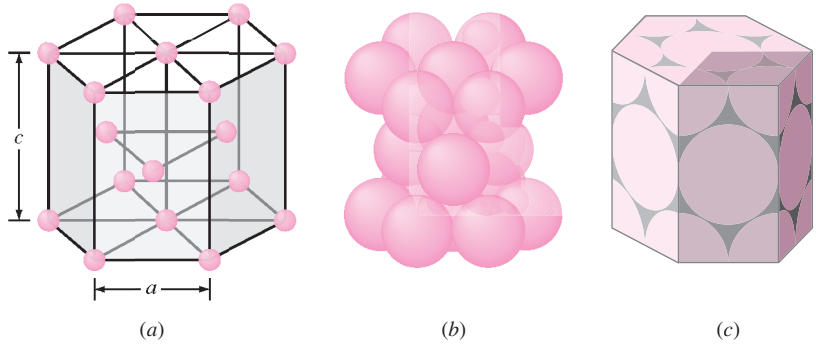

Figure 3.8
HCP unit cells: (*a*) atomic-site unit cell, (*b*) hard-sphere unit cell, and (*c*) isolated unit cell.
[*(b) and (c) After F. M. Miller, "Chemistry: Structure and Dynamics," McGraw-Hill, 1984, p. 296.*]

indicates that the atoms in these structures are slightly elongated along the c axis of the HCP unit cell. The metals magnesium, cobalt, zirconium, titanium, and beryllium have c/a ratios less than the ideal ratio. Therefore, in these metals the atoms are slightly compressed in the direction along the c axis. Thus, for the HCP metals listed in Table 3.4 there is a certain amount of deviation from the ideal hard-sphere model.

EXAMPLE PROBLEM 3.3

Calculate the volume of the zinc crystal structure unit cell by using the following data: pure zinc has the HCP crystal structure with lattice constants $a = 0.2665$ nm and $c = 0.4947$ nm.

■ Solution

The volume of the zinc HCP unit cell can be obtained by determining the area of the base of the unit cell and then multiplying this by its height (Fig. 3.9).

The area of the base of the unit cell is area $ABDEFG$ of Fig. 3.9a and b. This total area consists of the areas of six equilateral triangles of area ABC of Fig. 3.9b. From Fig. 3.9c,

$$\text{Area of triangle } ABC = \tfrac{1}{2}(\text{base})(\text{height}) = \tfrac{1}{2}(a)(a \sin 60^\circ) = \tfrac{1}{2}a^2 \sin 60^\circ$$

From Fig. 3.9b,

$$\text{Total area of HCP base} = (6)\left(\tfrac{1}{2}a^2 \sin 60^\circ\right) = 3a^2 \sin 60^\circ$$

From Fig. 3.9a,

$$\begin{aligned}\text{Volume of zinc HCP unit cell} &= (3a^2 \sin 60^\circ)(c)\\ &= (3)(0.2665 \text{ nm})^2(0.8660)(0.4947 \text{ nm})\\ &= 0.0913 \text{ nm}^3 \blacktriangleleft\end{aligned}$$

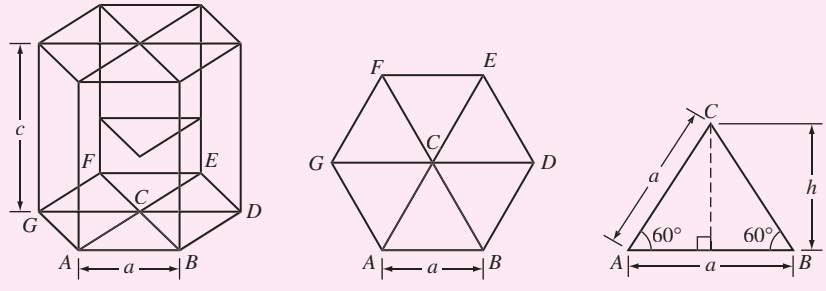

Figure 3.9
Diagrams for calculating the volume of an HCP unit cell. (*a*) HCP unit cell. (*b*) Base of HCP unit cell. (*c*) Triangle *ABC* removed from base of unit cell.

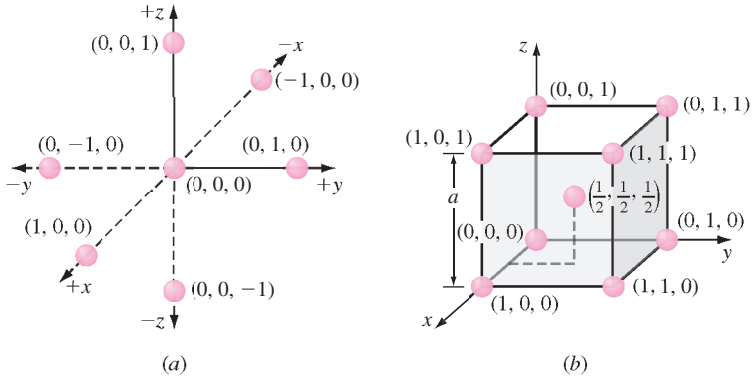

Figure 3.10
(*a*) Rectangular *x*, *y*, and *z* axes for locating atom positions in cubic unit cells. (*b*) Atom positions in a BCC unit cell.

3.4 ATOM POSITIONS IN CUBIC UNIT CELLS

To locate atom positions in cubic unit cells, we use rectangular *x*, *y*, and *z* axes. In crystallography the positive *x* axis is usually the direction coming out of the paper, the positive *y* axis is the direction to the right of the paper, and the positive *z* axis is the direction to the top (Fig. 3.10). Negative directions are opposite to those just described.

Atom positions in unit cells are located by using unit distances along the *x*, *y*, and *z* axes, as indicated in Fig. 3.10*a*. For example, the position coordinates for the atoms in the BCC unit cell are shown in Fig. 3.10*b*. The atom positions for the eight corner atoms of the BCC unit cell are

(0, 0, 0) (1, 0, 0) (0, 1, 0) (0, 0, 1)
(1, 1, 1) (1, 1, 0) (1, 0, 1) (0, 1, 1)

The center atom in the BCC unit cell has the position coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For simplicity sometimes only two atom positions in the BCC unit cell are specified which are (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The remaining atom positions of the BCC unit cell are assumed to be understood. In the same way the atom positions in the FCC unit cell can be located.

3.5 DIRECTIONS IN CUBIC UNIT CELLS

Often it is necessary to refer to specific directions in crystal lattices. This is especially important for metals and alloys with properties that vary with crystallographic orientation. *For cubic crystals the crystallographic direction indices are the vector components of the direction resolved along each of the coordinate axes and reduced to the smallest integers.*

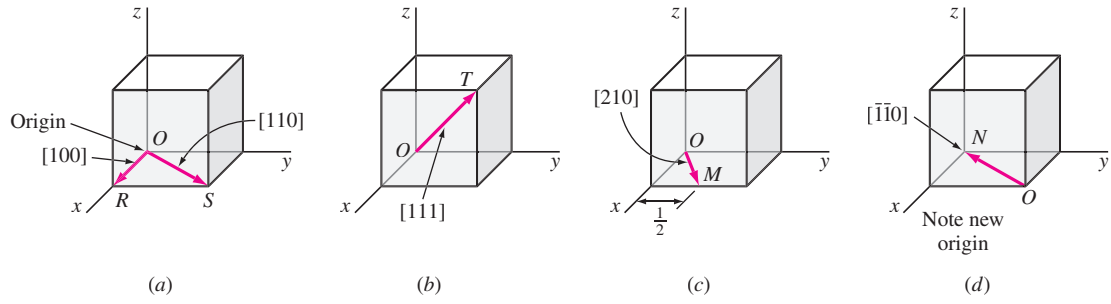

Figure 3.11
Some directions in cubic unit cells.

To diagrammatically indicate a direction in a cubic unit cell, we draw a direction vector from an origin, which is usually a corner of the cubic cell, until it emerges from the cube surface (Fig. 3.11). The position coordinates of the unit cell where the direction vector emerges from the cube surface after being converted to integers are the direction indices. The direction indices are enclosed by square brackets with no separating commas.

For example, the position coordinates of the direction vector *OR* in Fig. 3.11*a* where it emerges from the cube surface are (1, 0, 0), and so the direction indices for the direction vector *OR* are [100]. The position coordinates of the direction vector *OS* (Fig. 3.11*a*) are (1, 1, 0), and so the direction indices for *OS* are [110]. The position coordinates for the direction vector *OT* (Fig. 3.11*b*) are (1, 1, 1), and so the direction indices of *OT* are [111].

The position coordinates of the direction vector *OM* (Fig. 3.11*c*) are $(1, \frac{1}{2}, 0)$, and since the direction vectors must be integers, these position coordinates must be multiplied by 2 to obtain integers. Thus, the direction indices of *OM* become $2(1, \frac{1}{2}, 0) = [210]$. The position coordinates of the vector *ON* (Fig. 3.11*d*) are $(-1, -1, 0)$. A negative direction index is written with a bar over the index. Thus, the direction indices for the vector *ON* are $[\bar{1}\bar{1}0]$. Note that to draw the direction *ON* inside the cube the origin of the direction vector had to be moved to the front lower-right corner of the unit cube (Fig. 3.11*d*). Further examples of cubic direction vectors are given in Example Problem 3.4.

The letters *u*, *v*, *w* are used in a general sense for the direction indices in the *x*, *y*, and *z* directions, respectively, and are written as [*uvw*]. It is also important to note that *all parallel direction vectors have the same direction indices*.

Directions are said to be *crystallographically equivalent* if the atom spacing along each direction is the same. For example, the following cubic edge directions are crystallographic equivalent directions:

$$[100],\ [010],\ [001],\ [0\bar{1}0],\ [00\bar{1}],\ [\bar{1}00] \equiv \langle 100 \rangle$$

Equivalent directions are called *indices of a family or form*. The notation $\langle 100 \rangle$ is used to indicate cubic edge directions collectively. Other directions of a form are the cubic body diagonals $\langle 111 \rangle$ and the cubic face diagonals $\langle 110 \rangle$.

EXAMPLE PROBLEM 3.4

Draw the following direction vectors in cubic unit cells:

(*a*) [100] and [110]
(*b*) [112]
(*c*) $[\bar{1}10]$
(*d*) $[\bar{3}2\bar{1}]$

■ Solution

(*a*) The position coordinates for the [100] direction are (1, 0, 0) (Fig. 3.12*a*). The position coordinates for the [110] direction are (1, 1, 0) (Fig. 3.12*a*).

(*b*) The position coordinates for the [112] direction are obtained by dividing the direction indices by 2 so that they will lie within the unit cube. Thus they are $(\frac{1}{2}, \frac{1}{2}, 1)$ (Fig. 3.12*b*).

(*c*) The position coordinates for the $[\bar{1}10]$ direction are $(-1, 1, 0)$ (Fig. 3.12*c*). Note that the origin for the direction vector must be moved to the lower-left front corner of the cube.

(*d*) The position coordinates for the $[\bar{3}2\bar{1}]$ direction are obtained by first dividing all the indices by 3, the largest index. This gives $-1, \frac{2}{3}, -\frac{1}{3}$ for the position coordinates of the exit point of the direction $[\bar{3}2\bar{1}]$, which are shown in Fig. 3.12*d*.

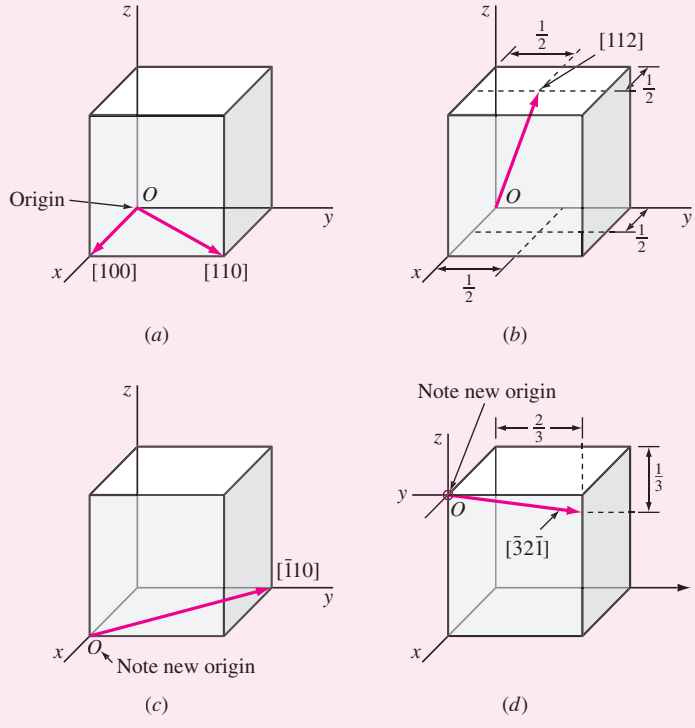

Figure 3.12
Direction vectors in cubic unit cells.

EXAMPLE PROBLEM 3.5

Determine the direction indices of the cubic direction shown in Fig. EP3.5*a*.

■ Solution

Parallel directions have the same direction indices, and so we move the direction vector in a parallel manner until its tail reaches the nearest corner of the cube, still keeping the vector within the cube. Thus, in this case, the upper-left front corner becomes the new origin for the direction vector (Fig. EP3.5*b*). We can now determine the position coordinates where the direction vector leaves the unit cube. These are $x = -1$, $y = +1$, and $z = -\frac{1}{6}$. The position coordinates of the direction where it leaves the unit cube are thus $(-1, +1, -\frac{1}{6})$. The direction indices for this direction are, after clearing the fraction $6x$, $(-1, +1, -\frac{1}{6})$, or $[\bar{6}6\bar{1}]$.

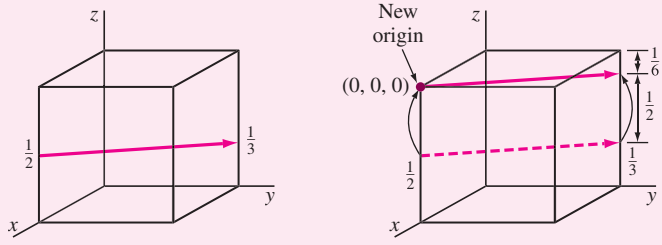

Figure EP3.5

EXAMPLE PROBLEM 3.6

Determine the direction indices of the cubic direction between the position coordinates $(\frac{3}{4}, 0, \frac{1}{4})$ and $(\frac{1}{4}, \frac{1}{2}, \frac{1}{2})$.

■ Solution

First we locate the origin and termination points of the direction vector in a unit cube, as shown in Fig. EP3.6. The fraction vector components for this direction are

$$x = -\left(\tfrac{3}{4} - \tfrac{1}{4}\right) = -\tfrac{1}{2}$$
$$y = \left(\tfrac{1}{2} - 0\right) = \tfrac{1}{2}$$
$$z = \left(\tfrac{1}{2} - \tfrac{1}{4}\right) = \tfrac{1}{4}$$

Thus, the vector direction has fractional vector components of $-\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$. The direction indices will be in the same ratio as their fractional components. By multiplying the fraction vector components by 4, we obtain $[\bar{2}21]$ for the direction indices of this vector direction.

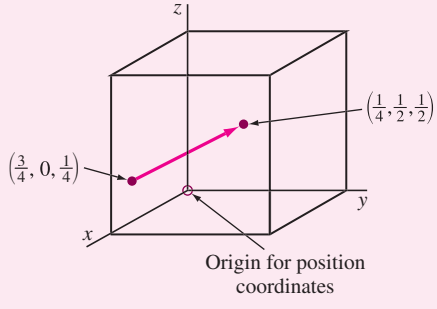

Figure EP3.6

3.6 MILLER INDICES FOR CRYSTALLOGRAPHIC PLANES IN CUBIC UNIT CELLS

Sometimes it is necessary to refer to specific lattice planes of atoms within a crystal structure, or it may be of interest to know the crystallographic orientation of a plane or group of planes in a crystal lattice. To identify crystal planes in cubic crystal structures, the *Miller notation system*[5] is used. The *Miller indices of a crystal plane* are defined as the *reciprocals of the fractional intercepts (with fractions cleared) that the plane makes with the crystallographic x, y, and z axes of the three nonparallel edges of the cubic unit cell.* The cube edges of the unit cell represent unit lengths, and the intercepts of the lattice planes are measured in terms of these unit lengths.

The procedure for determining the Miller indices for a cubic crystal plane is as follows:

1. Choose a plane that does *not* pass through the origin at (0, 0, 0).
2. Determine the intercepts of the plane in terms of the crystallographic x, y, and z axes for a unit cube. These intercepts may be fractions.
3. Form the reciprocals of these intercepts.
4. Clear fractions and determine the *smallest* set of whole numbers that are in the same ratio as the intercepts. These whole numbers are the Miller indices of the crystallographic plane and are enclosed in parentheses without the use of commas. The notation (*hkl*) is used to indicate Miller indices in a general sense, where h, k, and l are the Miller indices of a cubic crystal plane for the x, y, and z axes, respectively.

Figure 3.13 shows three of the most important crystallographic planes of cubic crystal structures. Let us first consider the shaded crystal plane in Fig. 3.13*a*, which has the intercepts 1, ∞, ∞ for the x, y, and z axes, respectively. We take the reciprocals of these intercepts to obtain the Miller indices, which are therefore 1, 0, 0. Since these numbers do not involve fractions, the Miller indices for this plane are (100), which is read as the one-zero-zero plane. Next let us consider the second plane shown in Fig. 3.13*b*. The intercepts of this plane are 1, 1, ∞. Since the reciprocals of these numbers are 1, 1, 0, which do not involve fractions, the Miller indices of this plane are (110). Finally, the third plane (Fig. 3.13*c*) has the intercepts 1, 1, 1, which give the Miller indices (111) for this plane.

Consider now the cubic crystal plane shown in Fig. 3.14 which has the intercepts $\frac{1}{3}$, $\frac{2}{3}$, 1. The reciprocals of these intercepts are 3, $\frac{3}{2}$, 1. Since fractional intercepts are not allowed, these fractional intercepts must be multiplied by 2 to clear the $\frac{3}{2}$ fraction. Thus, the reciprocal intercepts become 6, 3, 2 and the Miller

[5]William Hallowes Miller (1801–1880). English crystallographer who published a "Treatise on Crystallography" in 1839, using crystallographic reference axes that were parallel to the crystal edges and using reciprocal indices.

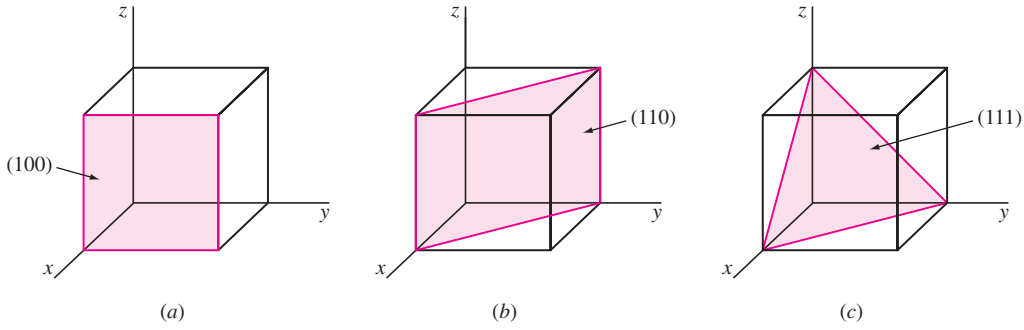

Figure 3.13
Miller indices of some important cubic crystal planes: (*a*) (100), (*b*) (110), and (*c*) (111).

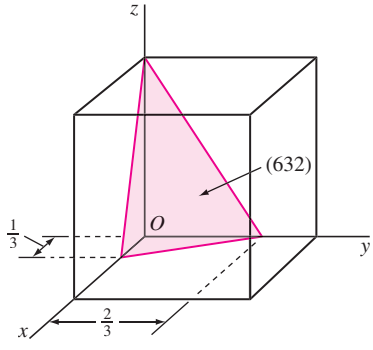

Figure 3.14
Cubic crystal plane (632), which has fractional intercepts.

indices are (632). Further examples of cubic crystal planes are shown in Example Problem 3.7.

If the crystal plane being considered passes through the origin so that one or more intercepts are zero, the plane must be moved to an equivalent position in the same unit cell and the plane must remain parallel to the original plane. This is possible because all equispaced parallel planes are indicated by the same Miller indices.

If sets of equivalent lattice planes are related by the symmetry of the crystal system, they are called *planes of a family or form,* and the indices of one plane of the family are enclosed in braces as $\{hkl\}$ to represent the indices of a family of symmetrical planes. For example, the Miller indices of the cubic surface planes (100), (010), and (001) are designated collectively as a family or form by the notation {100}.

EXAMPLE PROBLEM 3.7

Draw the following crystallographic planes in cubic unit cells:

(*a*) (101) (*b*) $(1\bar{1}0)$ (*c*) (221)

(*d*) Draw a (110) plane in a BCC atomic-site unit cell, and list the position coordinates of the atoms whose centers are intersected by this plane.

■ Solutions

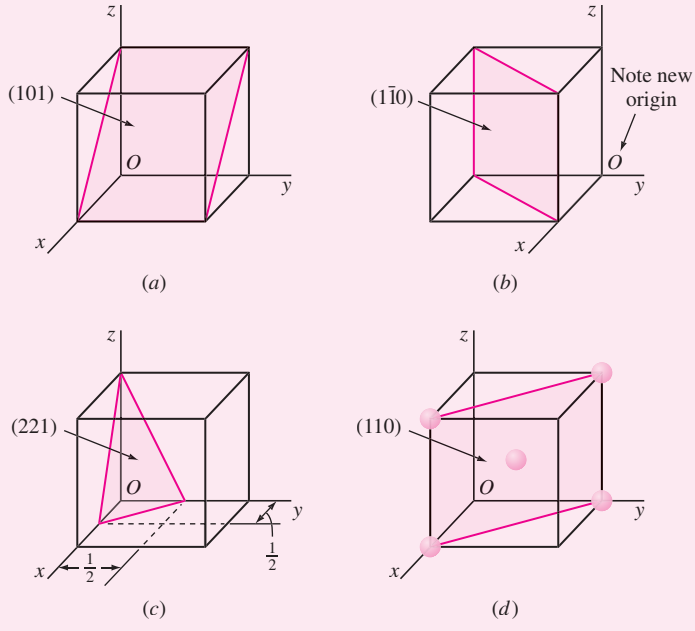

Figure EP3.7
Various important cubic crystal planes.

(*a*) First determine the reciprocals of the Miller indices of the (101) plane. These are 1, ∞, 1. The (101) plane must pass through a unit cube at intercepts $x = 1$ and $z = 1$ and be parallel to the y axis.

(*b*) First determine the reciprocals of the Miller indices of the $(1\bar{1}0)$ plane. These are 1, -1, ∞. The $(1\bar{1}0)$ plane must pass through a unit cube at intercepts $x = 1$ and $y = -1$ and be parallel to the z axis. Note that the origin of axes must be moved to the lower-right back side of the cube.

(*c*) First determine the reciprocals of the Miller indices of the (221) plane. These are $\frac{1}{2}$, $\frac{1}{2}$, 1. The (221) plane must pass through a unit cube at intercepts $x = \frac{1}{2}$, $y = \frac{1}{2}$, and $z = 1$.

(*d*) Atom positions whose centers are intersected by the (110) plane are (1, 0, 0), (0, 1, 0), (1, 0, 1), (0, 1, 1), and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. These positions are indicated by the solid circles.

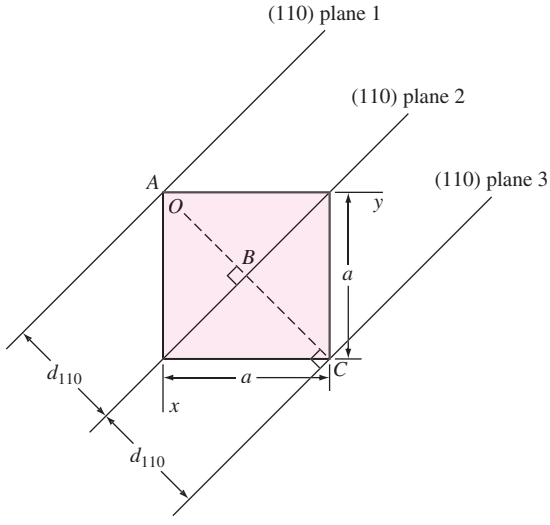

Figure 3.15
Top view of cubic unit cell showing the distance between (110) crystal planes, d_{110}.

An important relationship for the cubic system, and *only the cubic system,* is that the direction indices of a direction *perpendicular* to a crystal plane are the same as the Miller indices of that plane. For example, the [100] direction is perpendicular to the (100) crystal plane.

In cubic crystal structures the *interplanar spacing* between two closest parallel planes with the same Miller indices is designated d_{hkl}, where h, k, and l are the Miller indices of the planes. This spacing represents the distance from a selected origin containing one plane and another parallel plane with the same indices that is closest to it. For example, the distance between (110) planes 1 and 2, d_{110}, in Fig. 3.15 is AB. Also, the distance between (110) planes 2 and 3 is d_{110} and is length BC in Fig. 3.15. From simple geometry, it can be shown that for cubic crystal structures

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{3.4}$$

where d_{hkl} = interplanar spacing between parallel closest planes with Miller indices h, k, and l
a = lattice constant (edge of unit cube)
h, k, l = Miller indices of cubic planes being considered

EXAMPLE PROBLEM 3.8

Determine the Miller indices of the cubic crystallographic plane shown in Fig. EP3.8*a*.

■ **Solution**

First, transpose the plane parallel to the z axis $\frac{1}{4}$ unit to the right along the y axis as shown in Fig. EP3.8*b* so that the plane intersects the x axis at a unit distance from the

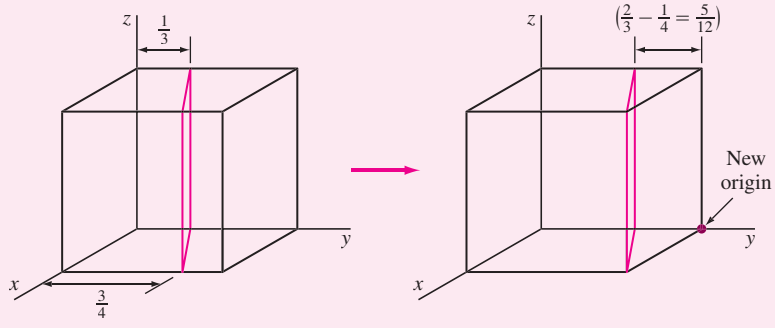

Figure EP3.8

new origin located at the lower-right back corner of the cube. The new intercepts of the transposed plane with the coordinate axes are now $(+1, -\frac{5}{12}, \infty)$. Next, we take the reciprocals of these intercepts to give $(1, -\frac{12}{5}, 0)$. Finally, we clear the $\frac{12}{5}$ fraction to obtain $(5\bar{1}20)$ for the Miller indices of this plane.

EXAMPLE PROBLEM 3.9

Determine the Miller indices of the cubic crystal plane that intersects the position coordinates $(1, \frac{1}{4}, 0)$, $(1, 1, \frac{1}{2})$, $(\frac{3}{4}, 1, \frac{1}{4})$, and all coordinate axes.

■ Solution

First, we locate the three position coordinates as indicated in Fig. EP3.9 at A, B, and C. Next, we join A and B and extend AB to D and then join A and C. Finally, we join A to C to complete plane ACD. The origin for this plane in the cube can be chosen at E, which gives axial intercepts for plane ACD at $x = -\frac{1}{2}$, $y = -\frac{3}{4}$, and $z = \frac{1}{2}$. The reciprocals of these axial intercepts are -2, $-\frac{4}{3}$, and 2. Multiplying these intercepts by 3 clears the fraction, giving Miller indices for the plane of $(\bar{6}\bar{4}6)$.

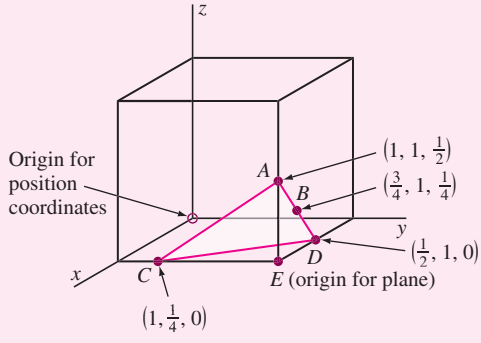

Figure EP3.9

EXAMPLE PROBLEM 3.10

Copper has an FCC crystal structure and a unit cell with a lattice constant of 0.361 nm. What is its interplanar spacing d_{220}?

■ **Solution**

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.361 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.128 \text{ nm} \blacktriangleleft$$

3.7 CRYSTALLOGRAPHIC PLANES AND DIRECTIONS IN HEXAGONAL UNIT CELLS

3.7.1 Indices for Crystal Planes in HCP Unit Cells

Crystal planes in HCP unit cells are commonly identified by using four indices instead of three. The HCP crystal plane indices, called *Miller-Bravais indices,* are denoted by the letters h, k, i, and l and are enclosed in parentheses as ($hkil$). These four-digit hexagonal indices are based on a coordinate system with four axes, as shown in Fig. 3.16 in an HCP unit cell. There are three basal axes, a_1, a_2, and a_3, which make 120° with each other. The fourth axis or c axis is the vertical axis located at the center of the unit cell. The a unit of measurement along the a_1, a_2, and a_3 axes is the distance between the atoms along these axes and is indicated in Fig. 3.16. The unit of measurement along the c axis is the height of the unit cell. The reciprocals of the intercepts that a crystal plane makes with the a_1, a_2, and a_3 axes give the h, k, and i indices, while the reciprocal of the intercept with the c axis gives the l index.

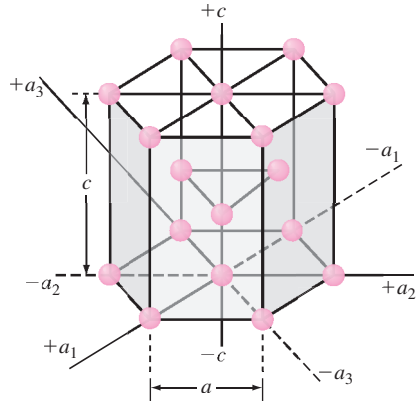

Figure 3.16
The four coordinate axes (a_1, a_2, a_3, and c) of the HCP crystal structure unit cell.

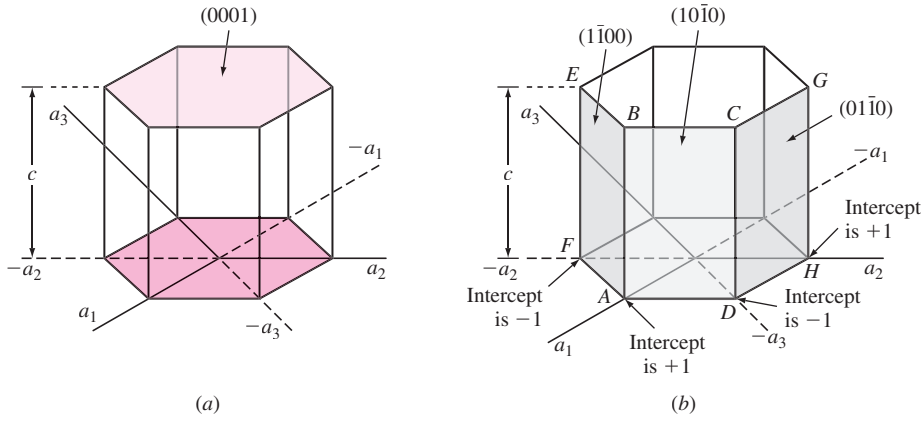

Figure 3.17
Miller-Bravais indices of hexagonal crystal planes: (*a*) basal planes, and (*b*) prism planes.

Basal Planes The basal planes of the HCP unit cell are very important planes for this unit cell and are indicated in Fig. 3.17*a*. Since the basal plane on the top of the HCP unit cell in Fig. 3.17*a* is parallel to the a_1, a_2, and a_3 axes, the intercepts of this plane with these axes will all be infinite. Thus, $a_1 = \infty$, $a_2 = \infty$, and $a_3 = \infty$. The c axis, however, is unity since the top basal plane intersects the c axis at unit distance. Taking the reciprocals of these intercepts gives the Miller-Bravais indices for the HCP basal plane. Thus $h = 0$, $k = 0$, $i = 0$, and $l = 1$. The HCP basal plane is, therefore, a zero-zero-zero-one or (0001) plane.

Prism Planes Using the same method, the intercepts of the front prism plane (*ABCD*) of Fig. 3.17*b* are $a_1 = +1$, $a_2 = \infty$, $a_3 = -1$, and $c = \infty$. Taking the reciprocals of these intercepts gives $h = 1$, $k = 0$, $i = -1$, and $l = 0$, or the $(10\bar{1}0)$ plane. Similarly, the *ABEF* prism plane of Fig. 3.17*b* has the indices $(1\bar{1}00)$ and the *DCGH* plane the indices $(01\bar{1}0)$. All HCP prism planes can be identified collectively as the $\{10\bar{1}0\}$ family of planes.

Sometimes HCP planes are identified only by three indices (*hkl*) since $h + k = -i$. However, the (*hkil*) indices are used more commonly because they reveal the hexagonal symmetry of the HCP unit cell.

3.7.2 Direction Indices in HCP Unit Cells[6]

Directions in HCP unit cells are also usually indicated by four indices u, v, t, and w enclosed by square brackets as [*uvtw*]. The u, v, and t indices are lattice

[6]The topic of direction indices for hexagonal unit cells is not normally presented in an introductory course in materials but is included here for advanced students.

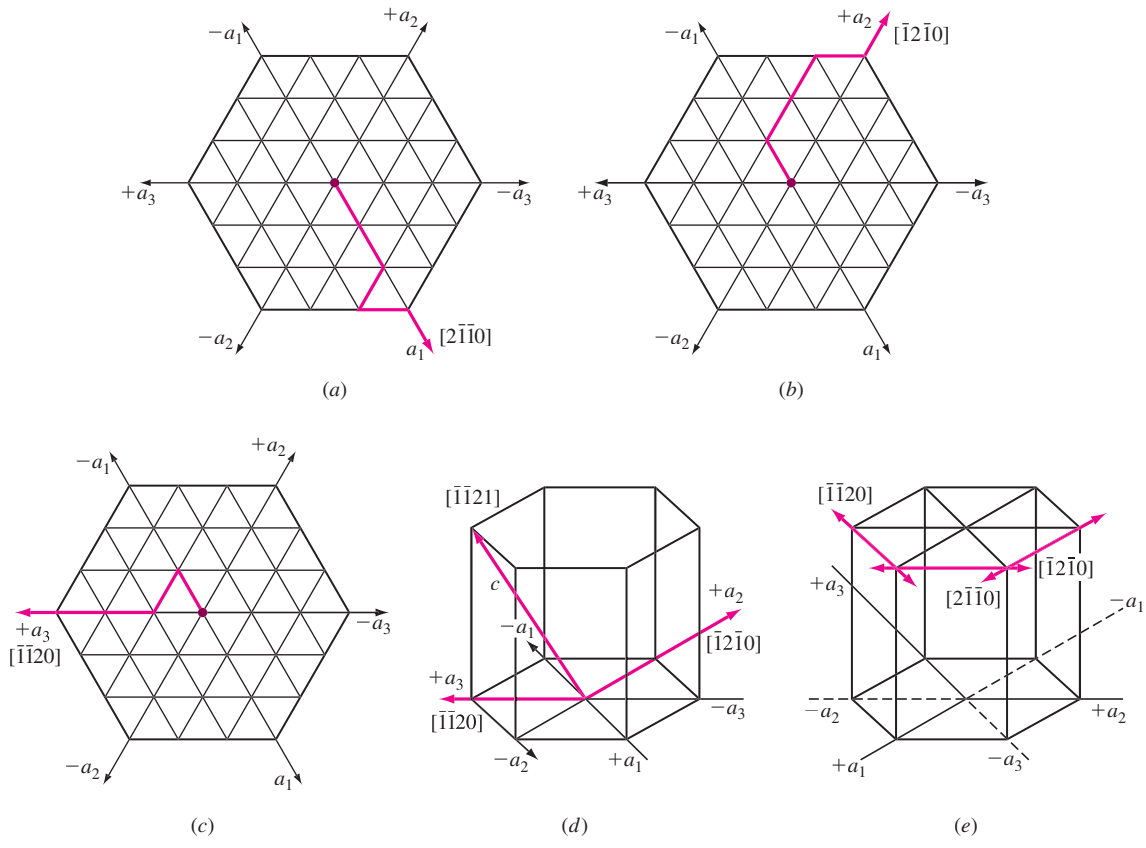

Figure 3.18
Miller-Bravais hexagonal crystal structure direction indices for principal directions: (*a*) $+a_1$ axis direction on basal plane, (*b*) $+a_2$ axis direction on basal plane, (*c*) $+a_3$ direction axis on basal plane, and (*d*) $+a_3$ direction axis incorporating *c* axis. (*e*) Positive and negative Miller-Bravais directions are indicated in simple hexagonal crystal structure on upper basal plane.

vectors in the a_1, a_2, and a_3 directions, respectively (Fig. 3.16), and the w index is a lattice vector in the c direction. To maintain uniformity for both HCP indices for planes and directions, it has been agreed that $u + v = -t$ for directions.

Let us now determine the Miller-Bravais hexagonal indices for the directions a_1, a_2, and a_3, which are the positive basal axes of the hexagonal unit cell. The a_1 direction indices are given in Fig. 3.18*a*, the a_2 direction indices in Fig. 3.18*b* and the a_3 direction indices in Fig. 3.18*c*. If we need to indicate a c direction also for the a_3 direction, this is shown in Fig. 3.18*d*. Fig. 3.18*e* summarizes the positive and negative directions on the upper basal plane of the simple hexagonal crystal structure.

3.8 COMPARISON OF FCC, HCP, AND BCC CRYSTAL STRUCTURES

3.8.1 Face-Centered Cubic and Hexagonal Close-Packed Crystal Structures

As previously pointed out, both the HCP and FCC crystal structures are close-packed structures. That is, their atoms, which are considered approximate "spheres," are packed together as closely as possible so that an atomic packing factor of 0.74 is attained.[7] The (111) planes of the FCC crystal structure shown in Fig. 3.19*a* have the identical packing arrangement as the (0001) planes of the HCP crystal structure shown in Fig. 3.19*b*. However, the three-dimensional FCC and HCP crystal structures are not identical because there is a difference in the stacking arrangement of their atomic planes, which can best be described by considering the stacking of hard spheres representing atoms. As a useful analogy, one can imagine the stacking of planes of equal-sized marbles on top of each other, minimizing the space between the marbles.

Consider first a plane of close-packed atoms designated the *A* plane, as shown in Fig. 3.20*a*. Note that there are two different types of empty spaces or

[7]As pointed out in Sec. 3.3, the atoms in the HCP structure deviate to varying degrees from ideality. In some HCP metals the atoms are elongated along the *c* axis, and in other cases they are compressed along the *c* axis (see Table 3.4).

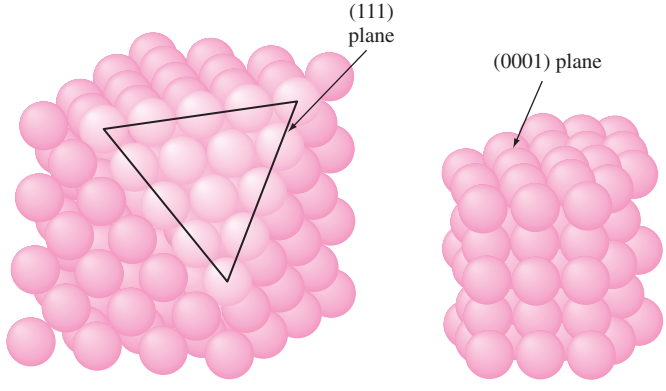

Figure 3.19
Comparison of the (a) FCC crystal structure showing the close-packed (111) planes, and (b) the HCP crystal structure showing the close-packed (0001) planes.
(*After W. G. Moffatt, G. W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p. 51.*)

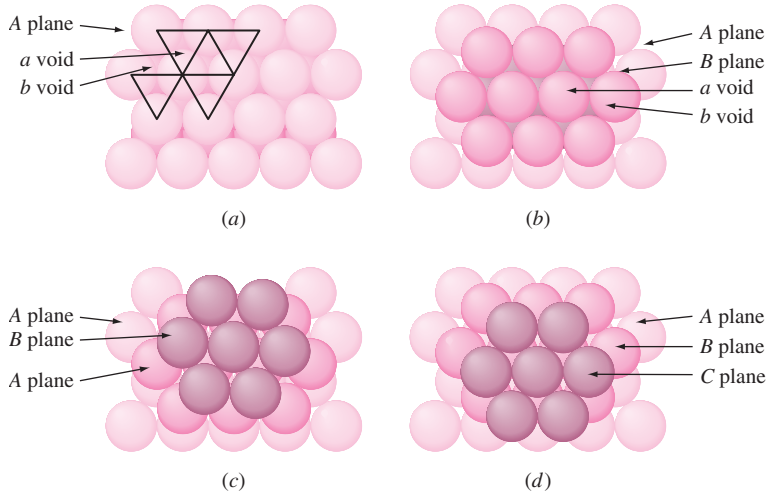

Figure 3.20
Formation of the HCP and FCC crystal structures by the stacking of atomic planes. (*a*) *A* plane showing the *a* and *b* voids. (*b*) *B* plane placed in *a* voids of plane *A*. (*c*) Third plane placed in *b* voids of *B* plane, making another *A* plane and forming the HCP crystal structure. (*d*) Third plane placed in the *a* voids of *B* plane, making a new *C* plane and forming the FCC crystal structure.
(*Adapted from P. Ander and A. J. Sonnessa, "Principles of Chemistry," Macmillan, 1965, p. 661.*)

voids between the atoms. The voids pointing to the top of the page are designated *a* voids and those pointing to the bottom of the page, *b* voids. A second plane of atoms can be placed over the *a* or *b* voids and the same three-dimensional structure will be produced. Let us place plane *B* over the *a* voids, as shown in Fig. 3.20*b*. Now if a third plane of atoms is placed over plane *B* to form a closest-packed structure, it is possible to form two different close-packed structures. One possibility is to place the atoms of the third plane in the *b* voids of the *B* plane. Then the atoms of this third plane will lie directly over those of the *A* plane and thus can be designated another *A* plane (Fig. 3.20*c*). If subsequent planes of atoms are placed in this same alternating stacking arrangement, then the stacking sequence of the three-dimensional structure produced can be denoted by *ABABAB*. . . . Such a stacking sequence leads to the HCP crystal structure (Fig. 3.19*b*).

The second possibility for forming a simple close-packed structure is to place the third plane in the *a* voids of plane *B* (Fig. 3.20*d*). This third plane is designated the *C* plane since its atoms do not lie directly above those of the *B* plane or the *A* plane. The stacking sequence in this close-packed structure is thus designated *ABCABCABC* . . . and leads to the FCC structure shown in Fig. 3.19*a*.

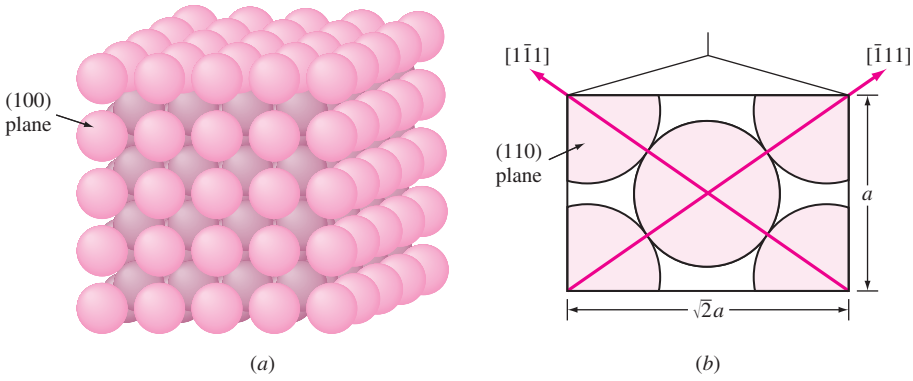

Figure 3.21
BCC crystal structure showing (*a*) the (100) plane and (*b*) a section of the (110) plane. Note that this is not a close-packed structure but that diagonals are close-packed directions.
[*(a) After W. G. Moffatt, G. W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p. 51.*]

3.8.2 Body-Centered Cubic Crystal Structure

The BCC structure is not a close-packed structure and hence does not have close-packed planes like the {111} planes in the FCC structure and the {0001} planes in the HCP structure. The most densely packed planes in the BCC structure are the {110} family of planes of which the (110) plane is shown in Fig. 3.21*b*. However, the atoms in the BCC structure do have close-packed directions along the cube diagonals, which are the ⟨111⟩ directions.

3.9 VOLUME, PLANAR, AND LINEAR DENSITY UNIT-CELL CALCULATIONS

3.9.1 Volume Density

Using the hard-sphere atomic model for the crystal structure unit cell of a metal and a value for the atomic radius of the metal obtained from x-ray diffraction analysis, a value for the volume density of a metal can be obtained by using the equation

$$\text{Volume density of metal} = \rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} \qquad \textbf{(3.5)}$$

In Example Problem 3.11 a value of 8.98 Mg/m^3 (8.98 g/cm^3) is obtained for the density of copper. The handbook experimental value for the density of copper is 8.96 Mg/m^3 (8.96 g/cm^3). The slightly lower density of the experimental value could be attributed to the absence of atoms at some atomic sites (vacancies),

line defects, and mismatch where grains meet (grain boundaries). These crystalline defects are discussed in Chap. 4. Another cause of the discrepancy could also be due to the atoms not being perfect spheres.

EXAMPLE PROBLEM 3.11

Copper has an FCC crystal structure and an atomic radius of 0.1278 nm. Assuming the atoms to be hard spheres that touch each other along the face diagonals of the FCC unit cell as shown in Fig. 3.7, calculate a theoretical value for the density of copper in megagrams per cubic meter. The atomic mass of copper is 63.54 g/mol.

■ **Solution**

For the FCC unit cell, $\sqrt{2}a = 4R$, where a is the lattice constant of the unit cell and R is the atomic radius of the copper atom. Thus

$$a = \frac{4R}{\sqrt{2}} = \frac{(4)(0.1278\ \text{nm})}{\sqrt{2}} = 0.361\ \text{nm}$$

$$\text{Volume density of copper} = \rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} \qquad \textbf{(3.5)}$$

In the FCC unit cell there are four atoms/unit cell. Each copper atom has a mass of (63.54 g/mol)/(6.02×10^{23} atoms/mol). Thus the mass m of Cu atoms in the FCC unit cell is

$$m = \frac{(4\ \text{atoms})(63.54\ \text{g/mol})}{6.02 \times 10^{23}\ \text{atoms/mol}} \left(\frac{10^{-6}\ \text{Mg}}{\text{g}}\right) = 4.22 \times 10^{-28}\ \text{Mg}$$

The volume V of the Cu unit cell is

$$V = a^3 = \left(0.361\ \text{nm} \times \frac{10^{-9}\ \text{m}}{\text{nm}}\right)^3 = 4.70 \times 10^{-29}\ \text{m}^3$$

Thus the density of copper is

$$\rho_v = \frac{m}{V} = \frac{4.22 \times 10^{-28}\ \text{Mg}}{4.70 \times 10^{-29}\ \text{m}^3} = 8.98\ \text{Mg/m}^3 \quad (8.98\ \text{g/cm}^3) \blacktriangleleft$$

3.9.2 Planar Atomic Density

Sometimes it is important to determine the atomic densities on various crystal planes. To do this a quantity called the *planar atomic density* is calculated by using the relationship

$$\text{Planar atomic density} = \rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}} \qquad \textbf{(3.6)}$$

For convenience the area of a plane that intersects a unit cell is usually used in these calculations, as shown, for example, in Fig. 3.22 for the (110) plane in a BCC unit cell. In order for an atom area to be counted in this calculation, the plane of interest must intersect the center of an atom. In Example Problem 3.12

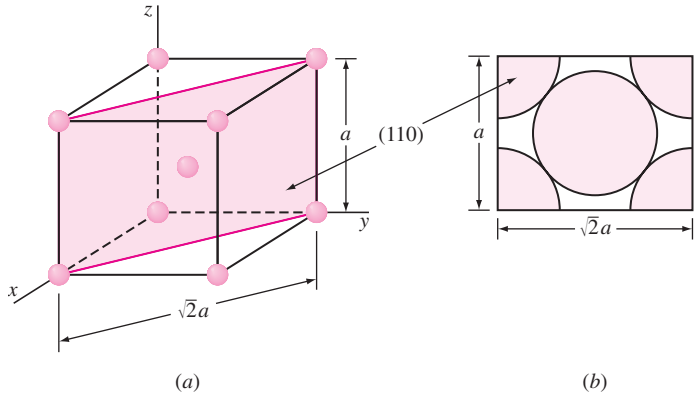

Figure 3.22
(*a*) A BCC atomic-site unit cell showing a shaded (110) plane.
(*b*) Areas of atoms in BCC unit cell cut by the (110) plane.

the (110) plane intersects the centers of five atoms, but the equivalent of only two atoms is counted since only one-quarter of each of the four corner atoms is included in the area inside the unit cell.

EXAMPLE PROBLEM 3.12

Calculate the planar atomic density ρ_p on the (110) plane of the α iron BCC lattice in atoms per square millimeter. The lattice constant of α iron is 0.287 nm.

■ **Solution**

$$\rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}} \tag{3.6}$$

The equivalent number of atoms intersected by the (110) plane in terms of the surface area inside the BCC unit cell is shown in Fig. 3.22 and is

$$1 \text{ atom at center} + 4 \times \tfrac{1}{4} \text{ atoms at four corners of plane} = 2 \text{ atoms}$$

The area intersected by the (110) plane inside the unit cell (selected area) is

$$(\sqrt{2}a)(a) = \sqrt{2}a^2$$

Thus the planar atomic density is

$$\rho_p = \frac{2 \text{ atoms}}{\sqrt{2}(0.287 \text{ nm})^2} = \frac{17.2 \text{ atoms}}{\text{nm}^2}$$

$$= \frac{17.2 \text{ atoms}}{\text{nm}^2} \times \frac{10^{12} \text{ nm}^2}{\text{mm}^2}$$

$$= 1.72 \times 10^{13} \text{ atoms/mm}^2 \blacktriangleleft$$

3.9.3 Linear Atomic Density

Sometimes it is important to determine the atomic densities in various directions in crystal structures. To do this a quantity called the *linear atomic density* is calculated by using the relationship

$$\text{Linear atomic density} = \rho_l = \frac{\text{no. of atomic diam. intersected by selected length of line in direction of interest}}{\text{selected length of line}} \tag{3.7}$$

Example Problem 3.13 shows how the linear atomic density can be calculated in the [110] direction in a pure copper crystal lattice.

EXAMPLE PROBLEM 3.13

Calculate the linear atomic density ρ_l in the [110] direction in the copper crystal lattice in atoms per millimeter. Copper is FCC and has a lattice constant of 0.361 nm.

■ **Solution**

The atoms whose centers the [110] direction intersects are shown in Fig. 3.23. We shall select the length of the line to be the length of the face diagonal of the FCC unit cell, which is $\sqrt{2}a$. The number of atomic diameters intersected by this length of line are $\frac{1}{2} + 1 + \frac{1}{2} = 2$ atoms. Thus using Eq. 3.7, the linear atomic density is

$$\rho_l = \frac{2 \text{ atoms}}{\sqrt{2}a} = \frac{2 \text{ atoms}}{\sqrt{2}(0.361 \text{ nm})} = \frac{3.92 \text{ atoms}}{\text{nm}}$$

$$= \frac{3.92 \text{ atoms}}{\text{nm}} \times \frac{10^6 \text{ nm}}{\text{mm}}$$

$$= 3.92 \times 10^6 \text{ atoms/mm} \blacktriangleleft$$

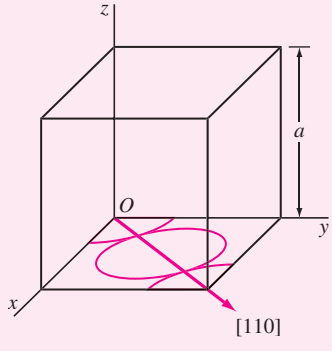

Figure 3.23
Diagram for calculating the atomic linear density in the [110] direction in an FCC unit cell.

3.10 POLYMORPHISM OR ALLOTROPY

Many elements and compounds exist in more than one crystalline form under different conditions of temperature and pressure. This phenomenon is termed *polymorphism,* or *allotropy*. Many industrially important metals such as iron, titanium, and cobalt undergo allotropic transformations at elevated temperatures at atmospheric pressure. Table 3.5 lists some selected metals that show allotropic transformations and the structure changes that occur.

Iron exists in both BCC and FCC crystal structures over the temperature range from room temperature to its melting point at 1539°C, as shown in Fig. 3.24. Alpha (α) iron exists from −273 to 912°C and has the BCC crystal structure. Gamma (γ) iron exists from 912 to 1394°C and has the FCC crystal

Table 3.5 Allotropic Crystalline Forms of Some Metals

Metal	Crystal structure at room temperature	At other temperatures
Ca	FCC	BCC (> 447°C)
Co	HCP	FCC (> 427°C)
Hf	HCP	BCC (> 1742°C)
Fe	BCC	FCC (912–1394°C)
		BCC (> 1394°C)
Li	BCC	HCP (< −193°C)
Na	BCC	HCP (< −233°C)
Tl	HCP	BCC (> 234°C)
Ti	HCP	BCC (> 883°C)
Y	HCP	BCC (> 1481°C)
Zr	HCP	BCC (> 872°C)

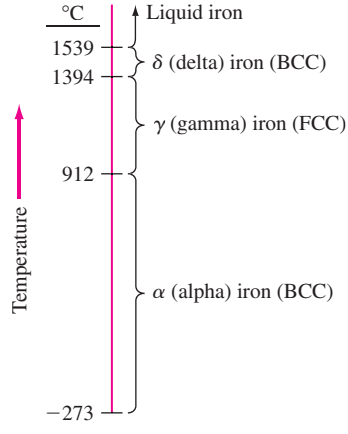

Figure 3.24
Allotropic crystalline forms of iron over temperature ranges at atmospheric pressure

structure. Delta (δ) iron exists from 1394 to 1539°C, which is the melting point of iron. The crystal structure of δ iron is also BCC but with a larger lattice constant than α iron.

EXAMPLE PROBLEM 3.14

Calculate the theoretical volume change accompanying a polymorphic transformation in a pure metal from the FCC to BCC crystal structure. Assume the hard-sphere atomic model and that there is no change in atomic volume before and after the transformation.

■ **Solution**

In the FCC crystal structure unit cell, the atoms are in contact along the face diagonal of the unit cell, as shown in Fig. 3.7. Hence

$$\sqrt{2}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{2}} \tag{3.3}$$

In the BCC crystal structure unit cell, the atoms are in contact along the body diagonal of the unit cell as shown in Fig. 3.5. Hence

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

The volume per atom for the FCC crystal lattice, since it has four atoms per unit cell, is

$$V_{FCC} = \frac{a^3}{4} = \left(\frac{4R}{\sqrt{2}}\right)^3 \left(\frac{1}{4}\right) = 5.66R^3$$

The volume per atom for the BCC crystal lattice, since it has two atoms per unit cell, is

$$V_{BCC} = \frac{a^3}{2} = \left(\frac{4R}{\sqrt{3}}\right)^3 \left(\frac{1}{2}\right) = 6.16R^3$$

The change in volume associated with the transformation from the FCC to BCC crystal structure, assuming no change in atomic radius, is

$$\frac{\Delta V}{V_{FCC}} = \frac{V_{BCC} - V_{FCC}}{V_{FCC}}$$

$$= \left(\frac{6.16R^3 - 5.66R^3}{5.66R^3}\right) 100\% = +8.8\% \blacktriangleleft$$

3.11 CRYSTAL STRUCTURE ANALYSIS

Our present knowledge of crystal structures has been obtained mainly by x-ray diffraction techniques that use x-rays about the same wavelength as the distance between crystal lattice planes. However, before discussing the manner in which

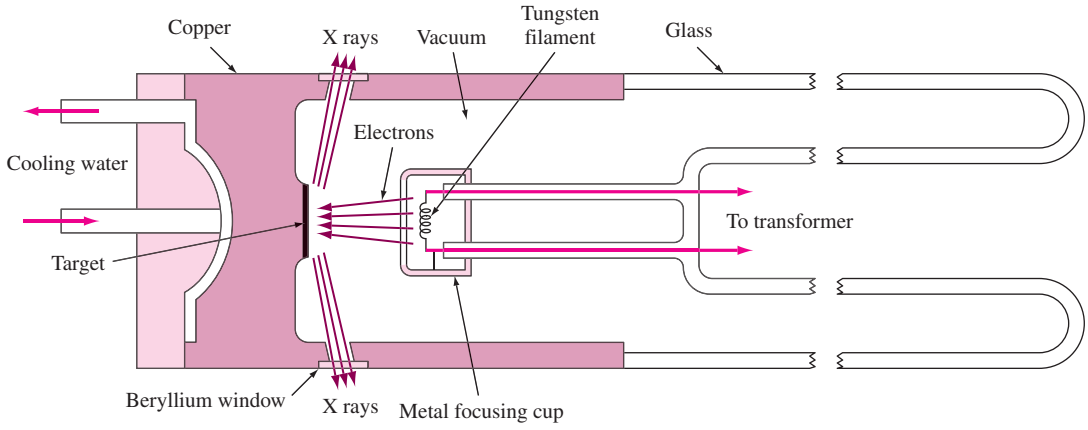

Figure 3.25
Schematic diagram of the cross section of a sealed-off filament x-ray tube.
(*After B. D. Cullity, "Elements of X-Ray Diffraction," 2d ed., Addison-Wesley, 1978, p. 23.*)

x-rays are diffracted in crystals, let us consider how x-rays are produced for experimental purposes.

3.11.1 X-Ray Sources

X-rays used for diffraction are electromagnetic waves with wavelengths in the range 0.05 to 0.25 nm (0.5 to 2.5 Å). By comparison, the wavelength of visible light is of the order of 600 nm (6000 Å). In order to produce x-rays for diffraction purposes, a voltage of about 35 kV is necessary and is applied between a cathode and an anode target metal, both of which are contained in a vacuum, as shown in Fig. 3.25. When the tungsten filament of the cathode is heated, electrons are released by thermionic emission and accelerated through the vacuum by the large voltage difference between the cathode and anode, thereby gaining kinetic energy. When the electrons strike the target metal (e.g., molybdenum), x-rays are given off. However, most of the kinetic energy (about 98 percent) is converted into heat, so the target metal must be cooled externally.

The x-ray spectrum emitted at 35 kV using a molybdenum target is shown in Fig. 3.26. The spectrum shows continuous x-ray radiation in the wavelength range from about 0.2 to 1.4 Å (0.02 to 0.14 nm) and two spikes of characteristic radiation that are designated the K_α and K_β lines. The wavelengths of the K_α and K_β lines are characteristic for an element. For molybdenum, the K_α line occurs at a wavelength of about 0.7 Å (0.07 nm). The origin of the characteristic radiation is explained as follows. First, K electrons (electrons in the $n = 1$ shell) are knocked out of the atom by highly energetic electrons bombarding the target, leaving excited atoms. Next, some electrons in higher shells (that is, $n = 2$ or 3) drop down to lower energy levels to replace the lost K electrons, emitting energy

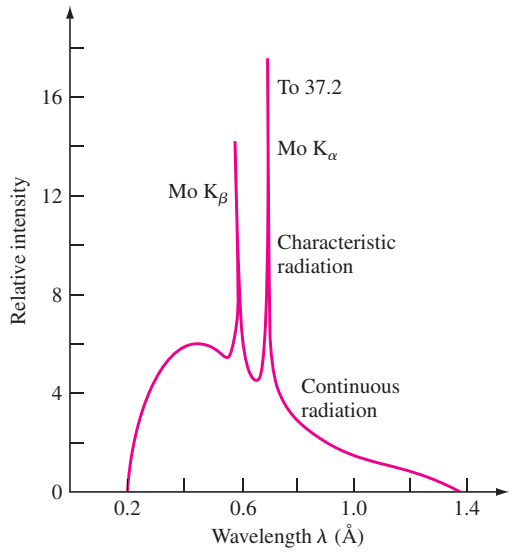

Figure 3.26
X-ray emission spectrum produced when molybdenum metal is used as the target metal in an x-ray tube operating at 35 kV.

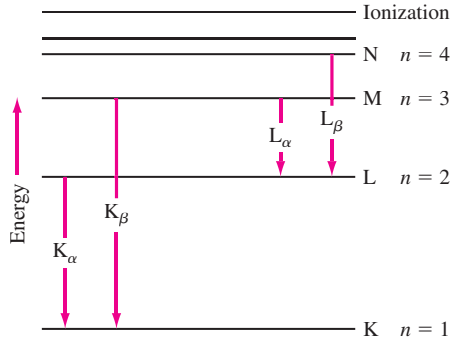

Figure 3.27
Energy levels of electrons in molybdenum showing the origin of K_α and K_β radiation.

of a characteristic wavelength. The transition of electrons from the L ($n = 2$) shell to the K ($n = 1$) shell creates energy of the wavelength of the K_α line, as indicated in Fig. 3.27.

3.11.2 X-Ray Diffraction

Since the wavelengths of some x-rays are about equal to the distance between planes of atoms in crystalline solids, reinforced diffraction peaks of radiation of varying intensities can be produced when a beam of x-rays strikes a crystalline solid. However, before considering the application of x-ray diffraction techniques to crystal structure analysis, let us examine the geometric conditions necessary to produce diffracted or reinforced beams of reflected x-rays.

Consider a monochromatic (single-wavelength) beam of x-rays to be incident on a crystal, as shown in Fig. 3.28. For simplification let us allow the crystal planes of atomic scattering centers to be replaced by crystal planes that act as mirrors in reflecting the incident x-ray beam. In Fig. 3.28 the horizontal lines represent a set of parallel crystal planes with Miller indices (*hkl*). When an incident beam of monochromatic x-rays of wavelength λ strikes this set of planes at an angle such that the wave patterns of the beam leaving the various planes are *not in phase, no reinforced beam will be produced* (Fig. 3.28*a*). Thus destructive interference occurs. If the reflected wave patterns of the beam leaving the various

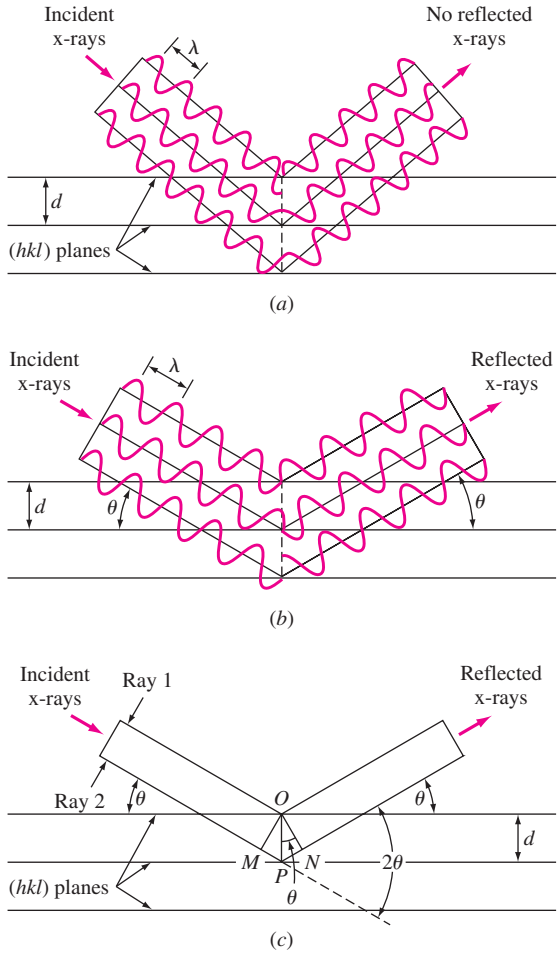

Figure 3.28
The reflection of an x-ray beam by the (*hkl*) planes of a crystal. (*a*) No reflected beam is produced at an arbitrary angle of incidence. (*b*) At the Bragg angle θ, the reflected rays are in phase and reinforce one another. (*c*) Similar to (*b*) except that the wave representation has been omitted.
(*After A. G. Guy and J. J. Hren, "Elements of Physical Metallurgy," 3d ed., Addison-Wesley, 1974, p. 201.*)

planes are in phase, then reinforcement of the beam or constructive interference occurs (Fig. 3.28*b*).

Let us now consider incident x-rays 1 and 2 as indicated in Fig. 3.28*c*. For these rays to be in phase, the extra distance of travel of ray 2 is equal to $MP + PN$, which must be an integral number of wavelengths λ. Thus

$$n\lambda = MP + PN \tag{3.8}$$

where $n = 1, 2, 3, \ldots$ and is called the *order of the diffraction*. Since both *MP* and *PN* equal $d_{hkl} \sin\theta$, where d_{hkl} is the interplanar spacing of the crystal planes of indices (*hkl*), the condition for constructive interference (i.e., the production of a diffraction peak of intense radiation) must be

$$n\lambda = 2d_{hkl} \sin\theta \tag{3.9}$$

This equation, known as *Bragg's law*,[8] gives the relationship among the angular positions of the reinforced diffracted beams in terms of the wavelength λ of the incoming x-ray radiation and of the interplanar spacings d_{hkl} of the crystal planes. In most cases, the first order of diffraction where $n = 1$ is used, and so for this case Bragg's law takes the form

$$\lambda = 2d_{hkl} \sin\theta \tag{3.10}$$

EXAMPLE PROBLEM 3.15

A sample of BCC iron was placed in an x-ray diffractometer using incoming x-rays with a wavelength $\lambda = 0.1541$ nm. Diffraction from the {110} planes was obtained at $2\theta = 44.704°$. Calculate a value for the lattice constant a of BCC iron. (Assume first-order diffraction with $n = 1$.)

■ **Solution**

$$2\theta = 44.704° \qquad \theta = 22.35°$$

$$\lambda = 2d_{hkl} \sin\theta$$

$$d_{110} = \frac{\lambda}{2\sin\theta} = \frac{0.1541 \text{ nm}}{2(\sin 22.35°)} \tag{3.10}$$

$$= \frac{0.1541 \text{ nm}}{2(0.3803)} = 0.2026 \text{ nm}$$

Rearranging Eq. 3.4 gives

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$$

Thus

$$a(\text{Fe}) = d_{110}\sqrt{1^2 + 1^2 + 0^2}$$

$$= (0.2026 \text{ nm})(1.414) = 0.287 \text{ nm} \blacktriangleleft$$

3.11.3 X-Ray Diffraction Analysis of Crystal Structures

The Powder Method of X-Ray Diffraction Analysis The most commonly used x-ray diffraction technique is the *powder method*. In this technique a powdered specimen is utilized so that there will be a random orientation of many crystals to ensure that some of the particles will be oriented in the x-ray beam to

[8]William Henry Bragg (1862–1942). English physicist who worked in x-ray crystallography.

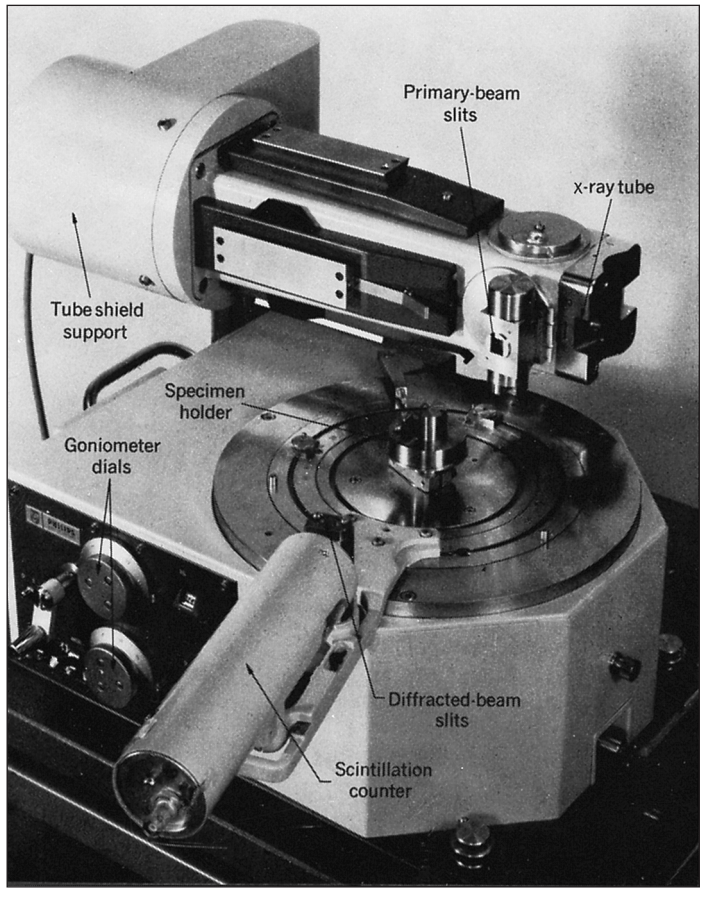

Figure 3.29
An x-ray diffractometer (with x-radiation shields removed). (*Philips Electronic Instruments, Inc.*)

satisfy the diffraction conditions of Bragg's law. Modern x-ray crystal analysis uses an x-ray diffractometer that has a radiation counter to detect the angle and intensity of the diffracted beam (Fig. 3.29). A recorder automatically plots the intensity of the diffracted beam as the counter moves on a goniometer[9] circle (Fig. 3.30) that is in synchronization with the specimen over a range of 2θ values. Figure 3.31 shows an x-ray diffraction recorder chart for the intensity of the diffracted beam versus the diffraction angles 2θ for a powdered pure-metal specimen. In this way both the angles of the diffracted beams and their intensities can be recorded at one time. Sometimes a powder camera with an enclosed

[9]A goniometer is an instrument for measuring angles.

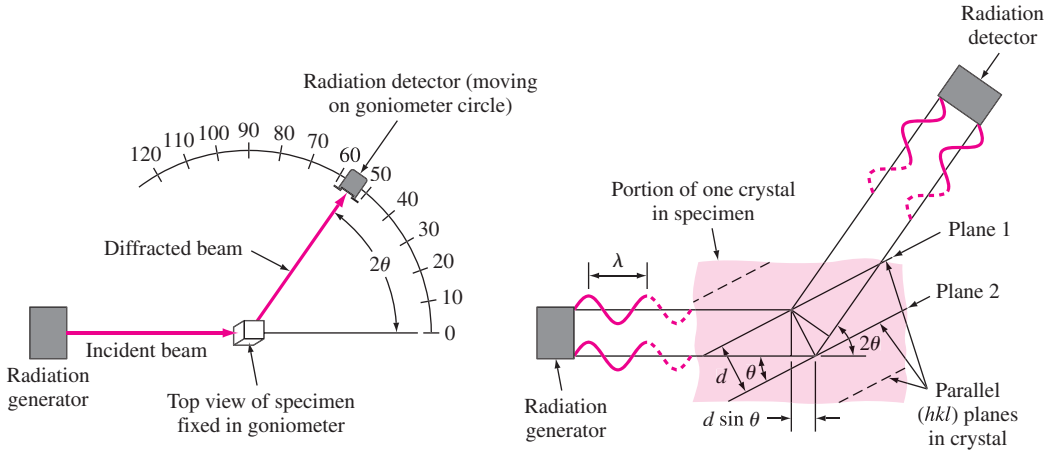

Figure 3.30
Schematic illustration of the diffractometer method of crystal analysis and of the conditions necessary for diffraction.
(*After A. G. Guy, "Essentials of Materials Science," McGraw-Hill, 1976.*)

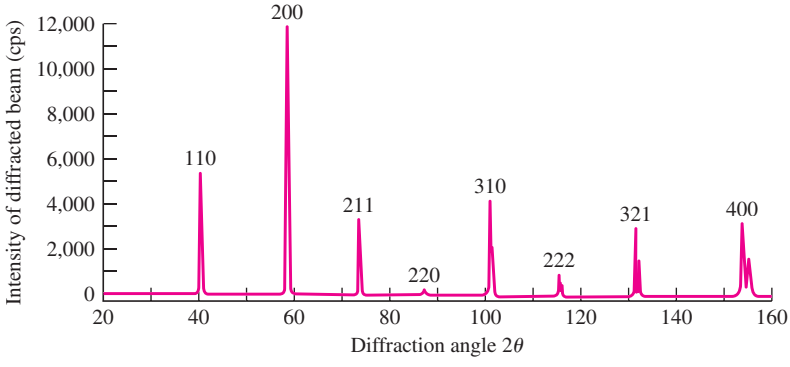

Figure 3.31
Record of the diffraction angles for a tungsten sample obtained by the use of a diffractometer with copper radiation.
(*After A. G. Guy and J. J. Hren, "Elements of Physical Metallurgy," 3d ed., Addison-Wesley, 1974, p. 208.*)

filmstrip is used instead of the diffractometer, but this method is much slower and in most cases less convenient.

Diffraction Conditions for Cubic Unit Cells X-ray diffraction techniques enable the structures of crystalline solids to be determined. The interpretation of x-ray diffraction data for most crystalline substances is complex and beyond the scope of this book, and so only the simple case of diffraction in pure cubic metals

will be considered. The analysis of x-ray diffraction data for cubic unit cells can be simplified by combining Eq. 3.4,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

with the Bragg equation $\lambda = 2d \sin\theta$, giving

$$\lambda = \frac{2a \sin\theta}{\sqrt{h^2 + k^2 + l^2}} \tag{3.11}$$

This equation can be used along with x-ray diffraction data to determine if a cubic crystal structure is body-centered or face-centered cubic. The rest of this subsection will describe how this is done.

To use Eq. 3.11 for diffraction analysis, we must know which crystal planes are the diffracting planes for each type of crystal structure. For the simple cubic lattice, reflections from all (*hkl*) planes are possible. However, for the BCC structure diffraction occurs only on planes whose Miller indices when added together $(h + k + l)$ total to an even number (Table 3.6). Thus, for the BCC crystal structure the principal diffracting planes are {110}, {200}, {211}, etc., which are listed in Table 3.7. In the case of the FCC crystal structure, the principal diffracting planes are those whose Miller indices are either all even or all odd (zero is con-

Table 3.6 Rules for Determining the Diffracting {*hkl*} Planes in Cubic Crystals

Bravais lattice	Reflections present	Reflections absent
BCC	$(h + k + l) =$ even	$(h + k + l) =$ odd
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

Table 3.7 Miller Indices of the Diffracting Planes for BCC and FCC Lattices

Cubic planes {*hkl*}	$h^2 + k^2 + l^2$	Sum $\Sigma[h^2 + k^2 + l^2]$	Cubic diffracting planes {*hkl*}	
			FCC	BCC
{100}	$1^2 + 0^2 + 0^2$	1		
{110}	$1^2 + 1^2 + 0^2$	2	···	110
{111}	$1^2 + 1^2 + 1^2$	3	111	
{200}	$2^2 + 0^2 + 0^2$	4	200	200
{210}	$2^2 + 1^2 + 0^2$	5		
{211}	$2^2 + 1^2 + 1^2$	6	···	211
···		7		
{220}	$2^2 + 2^2 + 0^2$	8	220	220
{221}	$2^2 + 2^2 + 1^2$	9		
{310}	$3^2 + 1^2 + 0^2$	10	···	310

sidered even). Thus, for the FCC crystal structure the diffracting planes are {111}, {200}, {220}, etc., which are listed in Table 3.7.

Interpreting Experimental X-Ray Diffraction Data for Metals with Cubic Crystal Structures We can use x-ray diffractometer data to determine crystal structures. A simple case to illustrate how this analysis can be used is to distinguish between the BCC and FCC crystal structures of a cubic metal. Let us assume that we have a metal with either a BCC or an FCC crystal structure and that we can identify the principal diffracting planes and their corresponding 2θ values, as indicated for the metal tungsten in Fig. 3.3.

By squaring both sides of Eq. 3.11 and solving for $\sin^2\theta$, we obtain

$$\sin^2\theta = \frac{\lambda^2(h^2 + k^2 + l^2)}{4a^2} \tag{3.12}$$

From x-ray diffraction data we can obtain experimental values of 2θ for a series of principal diffracting $\{hkl\}$ planes. Since the wavelength of the incoming radiation and the lattice constant a are both constants, we can eliminate these quantities by forming the ratio of two $\sin^2\theta$ values as

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{h_A^2 + k_A^2 + l_A^2}{h_B^2 + k_B^2 + l_B^2} \tag{3.13}$$

where θ_A and θ_B are two diffracting angles associated with the principal diffracting planes $\{h_Ak_Al_A\}$ and $\{h_Bk_Bl_B\}$, respectively.

Using Eq. 3.13 and the Miller indices of the first two sets of principal diffracting planes listed in Table 3.7 for BCC and FCC crystal structures, we can determine values for the $\sin^2\theta$ ratios for both BCC and FCC structures.

For the BCC crystal structure the first two sets of principal diffracting planes are the {110} and {200} planes (Table 3.7). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. 3.13 gives

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{1^2 + 1^2 + 0^2}{2^2 + 0^2 + 0^2} = 0.5 \tag{3.14}$$

Thus, if the crystal structure of the unknown cubic metal is BCC, the ratio of the $\sin^2\theta$ values that correspond to the first two principal diffracting planes will be 0.5.

For the FCC crystal structure the first two sets of principal diffracting planes are the {111} and {200} planes (Table 3.7). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. 3.13 gives

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{1^2 + 1^2 + 1^2}{2^2 + 0^2 + 0^2} = 0.75 \tag{3.15}$$

Thus, if the crystal structure of the unknown cubic metal is FCC, the ratio of the $\sin^2\theta$ values that correspond to the first two principal diffracting planes will be 0.75.

Example Problem 3.16 uses Eq. 3.13 and experimental x-ray diffraction data for the 2θ values for the principal diffracting planes to determine whether an unknown cubic metal is BCC or FCC. X-ray diffraction analysis is usually much more complicated than Example Problem 3.16, but the principles used are the same. Both experimental and theoretical x-ray diffraction analysis has been and continues to be used for the determination of the crystal structure of materials.

EXAMPLE PROBLEM 3.16

An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure shows diffraction peaks at the following 2θ angles: 40, 58, 73, 86.8, 100.4, and 114.7. The wavelength of the incoming x-ray used was 0.154 nm.

(*a*) Determine the cubic structure of the element.
(*b*) Determine the lattice constant of the element.
(*c*) Identify the element.

■ **Solution**

(*a*) *Determination of the crystal structure of the element*. First, the $\sin^2\theta$ values are calculated from the 2θ diffraction angles.

2θ(deg)	θ(deg)	$\sin\theta$	$\sin^2\theta$
40	20	0.3420	0.1170
58	29	0.4848	0.2350
73	36.5	0.5948	0.3538
86.8	43.4	0.6871	0.4721
100.4	50.2	0.7683	0.5903
114.7	57.35	0.8420	0.7090

Next the ratio of the $\sin^2\theta$ values of the first and second angles is calculated:

$$\frac{\sin^2\theta}{\sin^2\theta} = \frac{0.117}{0.235} = 0.498 \approx 0.5$$

The crystal structure is BCC since this ratio is ≈ 0.5. If the ratio had been ≈ 0.75, the structure would have been FCC.

(*b*) *Determination of the lattice constant*. Rearranging Eq. 3.12 and solving for a^2gives

$$a^2 = \frac{\lambda^2}{4}\frac{h^2+k^2+l^2}{\sin^2\theta} \tag{3.16}$$

or

$$a = \frac{\lambda}{2}\sqrt{\frac{h^2+k^2+l^2}{\sin^2\theta}} \tag{3.17}$$

Substituting into Eq. 3.17 $h = 1$, $k = 1$, and $l = 0$ for the h, k, l Miller indices of the first set of principal diffracting planes for the BCC crystal structure, which are the {110} planes, the corresponding value for $\sin^2\theta$, which is 0.117, and 0.154 nm for λ, the incoming radiation, gives

$$a = \frac{0.154 \text{ nm}}{2}\sqrt{\frac{1^2 + 1^2 + 0^2}{0.117}} = 0.318 \text{ nm} \blacktriangleleft$$

(*c*) *Identification of the element.* The element is tungsten since this element has a lattice constant of 0.316 nm and is BCC.

3.12 SUMMARY

Atomic arrangements in crystalline solids can be described by a network of lines called a *space lattice.* Each space lattice can be described by specifying the atom positions in a repeating *unit cell.* There are seven crystal systems based on the geometry of the axial lengths and interaxial angles of the unit cells. These seven systems have a total of 14 sublattices (unit cells) based on the internal arrangements of atomic sites within the unit cells.

In metals the most common crystal structure unit cells are: *body-centered cubic* (BCC), *face-centered cubic* (FCC), and *hexagonal close-packed* (HCP) (which is a dense variation of the simple hexagonal structure).

Crystal directions in cubic crystals are the vector components of the directions resolved along each of the component axes and reduced to smallest integers. They are indicated as [*uvw*]. Families of directions are indexed by the direction indices enclosed by pointed brackets as $\langle uvw \rangle$. *Crystal planes* in cubic crystals are indexed by the reciprocals of the axial intercepts of the plane (followed by the elimination of fractions) as (*hkl*). Cubic crystal planes of a form (family) are indexed with braces as {*hkl*}. Crystal planes in hexagonal crystals are commonly indexed by four indices *h*, *k*, *i*, and *l* enclosed in parentheses as (*hkil*). These indices are the reciprocals of the intercepts of the plane on the a_1, a_2, a_3, and c axes of the hexagonal crystal structure unit cell. Crystal directions in hexagonal crystals are the vector components of the direction resolved along each of the four coordinate axes and reduced to smallest integers as [*uvtw*].

Using the hard-sphere model for atoms, calculations can be made for the volume, planar, and linear density of atoms in unit cells. Planes in which atoms are packed as tightly as possible are called *close-packed planes,* and directions in which atoms are in closest contact are called *close-packed directions*. Atomic packing factors for different crystal structures can also be determined by assuming the hard-sphere atomic model. Some metals have different crystal structures at different ranges of temperature and pressure, a phenomenon called *polymorphism*.

Crystal structures of crystalline solids can be determined by using x-ray diffraction analysis techniques. X-rays are diffracted in crystals when the *Bragg's law* ($n\lambda = 2d \sin\theta$) conditions are satisfied. By using the x-ray diffractometer and the *powder method,* the crystal structure of many crystalline solids can be determined.

3.13 DEFINITIONS

Sec. 3.1

Crystal: a solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions.

Crystal structure: a regular three-dimensional pattern of atoms or ions in space.

Space lattice: a three-dimensional array of points each of which has identical surroundings.

Lattice point: one point in an array in which all the points have identical surroundings.

Unit cell: a convenient repeating unit of a space lattice. The axial lengths and axial angles are the lattice constants of the unit cell.

Sec. 3.3

Body-centered cubic (BCC) unit cell: a unit cell with an atomic packing arrangement in which one atom is in contact with eight identical atoms located at the corners of an imaginary cube.

Face-centered cubic (FCC) unit cell: a unit cell with an atomic packing arrangement in which 12 atoms surround a central atom. The stacking sequence of layers of close-packed planes in the FCC crystal structure is *ABCABC*. . . .

Hexagonal close-packed (HCP) unit cell: a unit cell with an atomic packing arrangement in which 12 atoms surround a central identical atom. The stacking sequence of layers of close-packed planes in the HCP crystal structure is *ABABAB*. . . .

Atomic packing factor (APF): the volume of atoms in a selected unit cell divided by the volume of the unit cell.

Sec. 3.5

Indices of direction in a cubic crystal: a direction in a cubic unit cell is indicated by a vector drawn from the origin at one point in a unit cell through the surface of the unit cell; the position coordinates (x, y, and z) of the vector where it leaves the surface of the unit cell (with fractions cleared) are the indices of direction. These indices, designated u, v, and w are enclosed in brackets as $[uvw]$. Negative indices are indicated by a bar over the index.

Sec. 3.6

Indices for cubic crystal planes (Miller indices): the reciprocals of the intercepts (with fractions cleared) of a crystal plane with the x, y, and z axes of a unit cube are called the Miller indices of that plane. They are designated h, k, and l for the x, y, and z axes, respectively, and are enclosed in parentheses as (hkl). Note that the selected crystal plane must *not* pass through the origin of the x, y, and z axes.

Sec. 3.9

Volume density ρ_v: mass per unit volume; this quantity is usually expressed in Mg/m^3 or g/cm^3.

Planar density ρ_p: the equivalent number of atoms whose centers are intersected by a selected area divided by the selected area.

Linear density ρ_l: the number of atoms whose centers lie on a specific direction on a specific length of line in a unit cube.

Sec. 3.10

Polymorphism (as pertains to metals): the ability of a metal to exist in two or more crystal structures. For example, iron can have a BCC or an FCC crystal structure, depending on the temperature.

3.14 PROBLEMS

3.1 Define a crystalline solid.

3.2 Define a crystal structure. Give examples of materials that have crystal structures.

3.3 Define a space lattice.

3.4 Define a unit cell of a space lattice. What lattice constants define a unit cell?

3.5 What are the 14 Bravais unit cells?

3.6 What are the three most common metal crystal structures? List five metals that have each of these crystal structures.

3.7 How many atoms per unit cell are there in the BCC crystal structure?

3.8 What is the coordination number for the atoms in the BCC crystal structure?

3.9 What is the relationship between the length of the side a of the BCC unit cell and the radius of its atoms?

3.10 Molybdenum at 20°C is BCC and has an atomic radius of 0.140 nm. Calculate a value for its lattice constant a in nanometers.

3.11 Niobium at 20°C is BCC and has an atomic radius of 0.143 nm. Calculate a value for its lattice constant a in nanometers.

3.12 Lithium at 20°C is BCC and has a lattice constant of 0.35092 nm. Calculate a value for the atomic radius of a lithium atom in nanometers.

3.13 Sodium at 20°C is BCC and has a lattice constant of 0.42906 nm. Calculate a value for the atomic radius of a sodium atom in nanometers.

3.14 How many atoms per unit cell are there in the FCC crystal structure?

3.15 What is the coordination number for the atoms in the FCC crystal structure?

3.16 Gold is FCC and has a lattice constant of 0.40788 nm. Calculate a value for the atomic radius of a gold atom in nanometers.

3.17 Platinum is FCC and has a lattice constant of 0.39239 nm. Calculate a value for the atomic radius of a platinum atom in nanometers.

3.18 Palladium is FCC and has an atomic radius of 0.137 nm. Calculate a value for its lattice constant a in nanometers.

3.19 Strontium is FCC and has an atomic radius of 0.215 nm. Calculate a value for its lattice constant a in nanometers.

3.20 Calculate the atomic packing factor for the FCC structure.

3.21 How many atoms per unit cell are there in the HCP crystal structure?

3.22 What is the coordination number for the atoms in the HCP crystal structure?

3.23 What is the ideal c/a ratio for HCP metals?

3.24 Of the following HCP metals, which have higher or lower c/a ratios than the ideal ratio: Zr, Ti, Zn, Mg, Co, Cd, and Be?

3.25 Calculate the volume in cubic nanometers of the titanium crystal structure unit cell. Titanium is HCP at 20°C with $a = 0.29504$ nm and $c = 0.46833$ nm.

3.26 Rhenium at 20°C is HCP. The height c of its unit cell is 0.44583 nm and its c/a ratio is 1.633. Calculate a value for its lattice constant a in nanometers.

3.27 Osmium at 20°C is HCP. Using a value of 0.135 nm for the atomic radius of osmium atoms, calculate a value for its unit-cell volume. Assume a packing factor of 0.74.

3.28 How are atomic positions located in cubic unit cells?

3.29 List the atom positions for the eight corner and six face-centered atoms of the FCC unit cell.

3.30 How are the indices for a crystallographic direction in a cubic unit cell determined?

3.31 Draw the following directions in a BCC unit cell and list the position coordinates of the atoms whose centers are intersected by the direction vector:
(*a*) [100] (*b*) [110] (*c*) [111]

3.32 Draw direction vectors in unit cubes for the following cubic directions:
(*a*) $[1\bar{1}\bar{1}]$ (*b*) $[1\bar{1}0]$ (*c*) $[\bar{1}2\bar{1}]$ (*d*) $[\bar{1}\bar{1}3]$

3.33 Draw direction vectors in unit cubes for the following cubic directions:
(*a*) $[1\bar{1}\bar{2}]$ (*c*) $[\bar{3}31]$ (*e*) $[2\bar{1}2]$ (*g*) $[\bar{1}01]$ (*i*) [321] (*k*) $[1\bar{2}\bar{2}]$
(*b*) $[1\bar{2}3]$ (*d*) $[0\bar{2}1]$ (*f*) $[2\bar{3}3]$ (*h*) $[12\bar{1}]$ (*j*) $[10\bar{3}]$ (*l*) $[\bar{2}\bar{2}3]$

3.34 What are the indices of the directions shown in the unit cubes of Fig. P3.34?

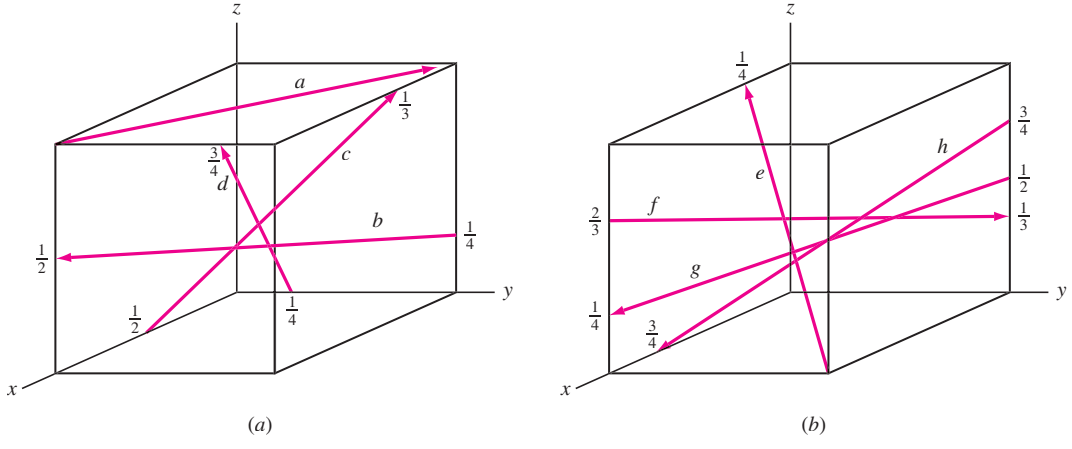

Figure P3.34

3.35 A direction vector passes through a unit cube from the $(\frac{3}{4}, 0, \frac{1}{4})$ to the $(\frac{1}{2}, 1, 0)$ positions. What are its direction indices?

3.36 A direction vector passes through a unit cube from the $(1, 0, \frac{3}{4})$ to the $(\frac{1}{4}, 1, \frac{1}{4})$ positions. What are its direction indices?

3.37 What are the crystallographic directions of a family or form? What generalized notation is used to indicate them?

3.38 What are the directions of the ⟨100⟩ family or form for a unit cube?

3.39 What are the directions of the ⟨111⟩ family or form for a unit cube?

3.40 What ⟨110⟩-type directions lie on the (111) plane of a cubic unit cell?

3.41 What ⟨111⟩-type directions lie on the (110) plane of a cubic unit cell?

3.42 How are the Miller indices for a crystallographic plane in a cubic unit cell determined? What generalized notation is used to indicate them?

3.43 Draw in unit cubes the crystal planes that have the following Miller indices:

(*a*) $(1\bar{1}\bar{1})$ (*c*) $(1\bar{2}\bar{1})$ (*e*) $(3\bar{2}1)$ (*g*) $(20\bar{1})$ (*i*) $(\bar{2}32)$ (*k*) $(3\bar{1}2)$

(*b*) $(10\bar{2})$ (*d*) $(21\bar{3})$ (*f*) $(30\bar{2})$ (*h*) $(\bar{2}1\bar{2})$ (*j*) $(13\bar{3})$ (*l*) $(\bar{3}3\bar{1})$

3.44 What are the Miller indices of the cubic crystallographic planes shown in Fig. P3.44?

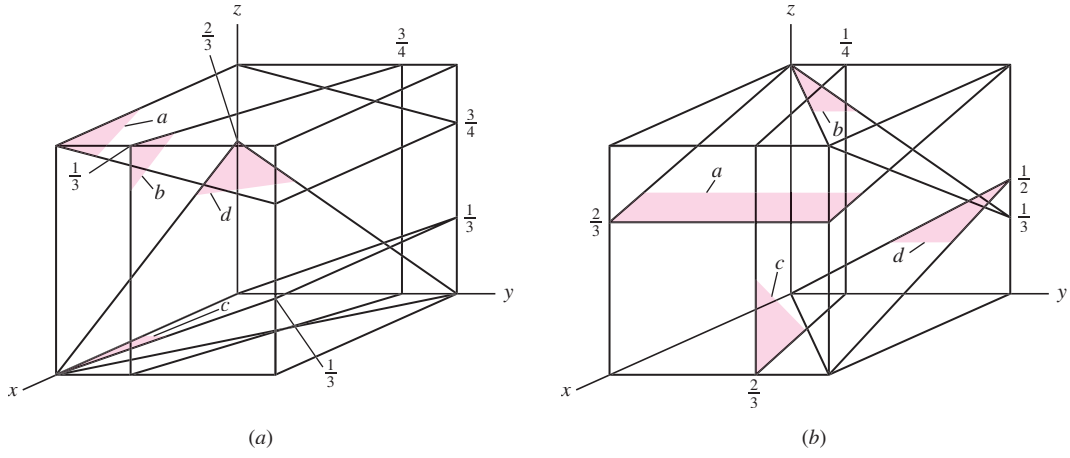

Figure P3.44

3.45 What is the notation used to indicate a family or form of cubic crystallographic planes?

3.46 What are the {100} family of planes of the cubic system?

3.47 Draw the following crystallographic planes in a BCC unit cell and list the position of the atoms whose centers are intersected by each of the planes:

(*a*) (100) (*b*) (110) (*c*) (111)

3.48 Draw the following crystallographic planes in an FCC unit cell and list the position coordinates of the atoms whose centers are intersected by each of the planes:

(*a*) (100) (*b*) (110) (*c*) (111)

3.49 A cubic plane has the following axial intercepts: $a = \frac{1}{3}, b = -\frac{2}{3}, c = \frac{1}{2}$. What are the Miller indices of this plane?

3.50 A cubic plane has the following axial intercepts: $a = -\frac{1}{2}, b = -\frac{1}{2}, c = \frac{2}{3}$. What are the Miller indices of this plane?

3.51 A cubic plane has the following axial intercepts: $a = 1, b = \frac{2}{3}, c = -\frac{1}{2}$. What are the Miller indices of this plane?

3.52 Determine the Miller indices of the cubic crystal plane that intersects the following position coordinates: (1, 0, 0); (1, $\frac{1}{2}$, $\frac{1}{4}$); ($\frac{1}{2}$, $\frac{1}{2}$, 0).

3.53 Determine the Miller indices of the cubic crystal plane that intersects the following position coordinates: ($\frac{1}{2}$, 0, $\frac{1}{2}$); (0, 0, 1); (1, 1, 1).

3.54 Determine the Miller indices of the cubic crystal plane that intersects the following position coordinates: (1, $\frac{1}{2}$, 1); ($\frac{1}{2}$, 0, $\frac{3}{4}$); (1, 0, $\frac{1}{2}$).

3.55 Determine the Miller indices of the cubic crystal plane that intersects the following position coordinates: (0, 0, $\frac{1}{2}$); (1, 0, 0); ($\frac{1}{2}$, $\frac{1}{4}$, 0).

3.56 Rodium is FCC and has a lattice constant a of 0.38044 nm. Calculate the following interplanar spacings:

(a) d_{111} (b) d_{200} (c) d_{220}

3.57 Tungsten is BCC and has a lattice constant a of 0.31648 nm. Calculate the following interplanar spacings:

(a) d_{110} (b) d_{220} (c) d_{310}

3.58 The d_{310} interplanar spacing in a BCC element is 0.1587 nm. (a) What is its lattice constant a? (b) What is the atomic radius of the element? (c) What could this element be?

3.59 The d_{422} interplanar spacing in an FCC metal is 0.083397 nm. (a) What is its lattice constant a? (b) What is the atomic radius of the metal? (c) What could this metal be?

3.60 How are crystallographic planes determined in HCP unit cells?

3.61 What notation is used to describe HCP crystal planes?

3.62 Draw the hexagonal crystal planes whose Miller-Bravais indices are:

(a) $(10\bar{1}1)$ (d) $(1\bar{2}12)$ (g) $(\bar{1}2\bar{1}2)$ (j) $(\bar{1}100)$

(b) $(01\bar{1}1)$ (e) $(2\bar{1}\bar{1}1)$ (h) $(2\bar{2}00)$ (k) $(\bar{2}111)$

(c) $(\bar{1}2\bar{1}0)$ (f) $(1\bar{1}01)$ (i) $(10\bar{1}2)$ (l) $(\bar{1}012)$

3.63 Determine the Miller-Bravais indices of the hexagonal crystal planes in Fig. P3.63.

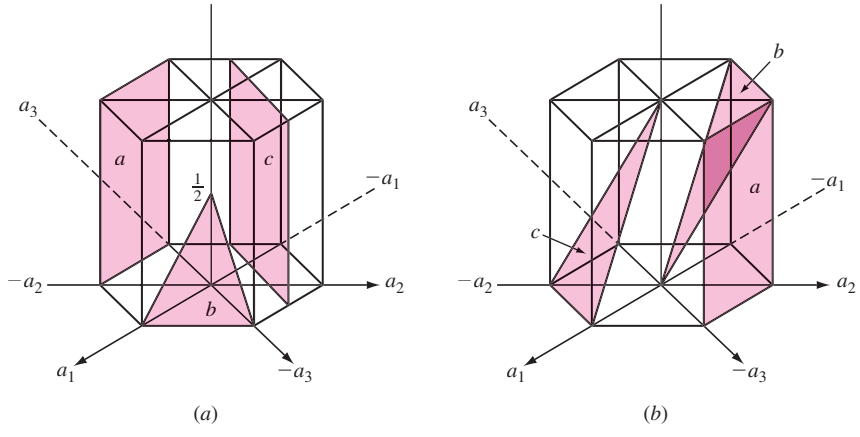

Figure P3.63

3.64 Determine the Miller-Bravais direction indices of the $-a_1$, $-a_2$, and $-a_3$ directions.

3.65 Determine the Miller-Bravais direction indices of the vectors originating at the center of the lower basal plane and ending at the endpoints of the upper basal plane as indicated in Fig. 3.18*d*.

3.66 Determine the Miller-Bravais direction indices of the basal plane of the vectors originating at the center of the lower basal plane and exiting at the midpoints between the principal planar axes.

3.67 Determine the Miller-Bravais direction indices of the directions indicated in Fig. P3.67.

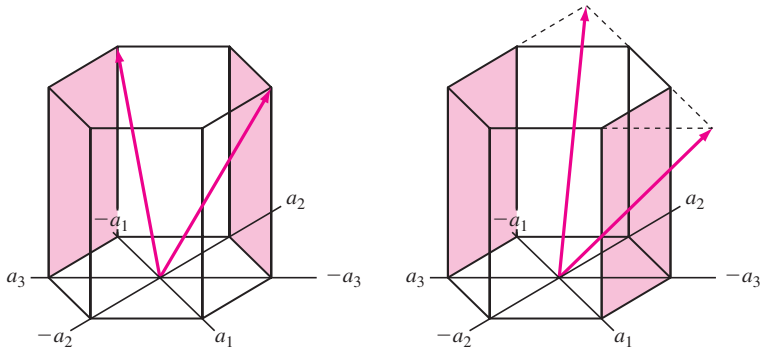

Figure P3.67

3.68 What is the difference in the stacking arrangement of close-packed planes in (*a*) the HCP crystal structure and (*b*) the FCC crystal structure?

3.69 What are the most densely packed planes in (*a*) the FCC structure and (*b*) the HCP structure?

3.70 What are the closest-packed directions in (*a*) the FCC structure and (*b*) the HCP structure?

3.71 The lattice constant for BCC tantalum at 20°C is 0.33026 nm and its density is 16.6 g/cm^3. Calculate a value for its atomic mass.

3.72 Calculate a value for the density of FCC platinum in grams per cubic centimeter from its lattice constant a of 0.39239 nm and its atomic mass of 195.09 g/mol.

3.73 Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in BCC chromium, which has a lattice constant of 0.28846 nm: (*a*) (100), (*b*) (110), (*c*) (111).

3.74 Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in FCC gold, which has a lattice constant of 0.40788 nm: (*a*) (100), (*b*) (110), (*c*) (111).

3.75 Calculate the planar atomic density in atoms per square millimeter for the (0001) plane in HCP beryllium, which has a constant $a = 0.22856$ nm and a c constant of 0.35832 nm.

3.76 Calculate the linear atomic density in atoms per millimeter for the following directions in BCC vanadium, which has a lattice constant of 0.3039 nm:
(*a*) [100], (*b*) [110], (*c*) [111].

3.77 Calculate the linear atomic density in atoms per millimeter for the following directions in FCC iridium, which has a lattice constant of 0.38389 nm:
(*a*) [100], (*b*) [110], (*c*) [111].

3.78 What is polymorphism with respect to metals?

3.79 Titanium goes through a polymorphic change from BCC to HCP crystal structure upon cooling through 882°C. Calculate the percentage change in volume when the crystal structure changes from BCC to HCP. The lattice constant a of the BCC unit cell at 882°C is 0.332 nm, and the HCP unit cell has $a = 0.2950$ nm and $c = 0.4683$ nm.

3.80 Pure iron goes through a polymorphic change from BCC to FCC upon heating through 912°C. Calculate the volume change associated with the change in crystal structure from BCC to FCC if at 912°C the BCC unit cell has a lattice constant $a = 0.293$ nm and the FCC unit cell $a = 0.363$ nm.

3.81 What are x-rays, and how are they produced?

3.82 Draw a schematic diagram of an x-ray tube used for x-ray diffraction, and indicate on it the path of the electrons and x-rays.

3.83 What is the characteristic x-ray radiation? What is its origin?

3.84 Distinguish between destructive interference and constructive interference of reflected x-ray beams through crystals.

3.85 Derive Bragg's law by using the simple case of incident x-ray beams being diffracted by parallel planes in a crystal.

3.86 A sample of BCC metal was placed in an x-ray diffractometer using x-rays with a wavelength of $\lambda = 0.1541$ nm. Diffraction from the {221} planes was obtained at $2\theta = 88.838°$. Calculate a value for the lattice constant a for this BCC elemental metal. (Assume first-order diffraction, $n = 1$.)

3.87 X-rays of an unknown wavelength are diffracted by a gold sample. The 2θ angle was 64.582° for the {220} planes. What is the wavelength of the x-rays used? (The lattice constant of gold = 0.40788 nm; assume first-order diffraction, $n = 1$.)

3.88 An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 41.069°, 47.782°, 69.879°, and 84.396°. (The wavelength of the incoming radiation was 0.15405 nm.)[10]
(*a*) Determine the crystal structure of the element.
(*b*) Determine the lattice constant of the element.
(*c*) Identify the element.

3.89 An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 38.60°, 55.71°, 69.70°, 82.55°, 95.00°, and 107.67°. (Wavelength λ of the incoming radiation was 0.15405 nm.)

[10]X-ray diffraction data courtesy of the International Centre for Diffraction Data.

(*a*) Determine the crystal structure of the element.

(*b*) Determine the lattice constant of the element.

(*c*) Identify the element.

3.90 An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 36.191°, 51.974°, 64.982°, and 76.663°. (The wavelength of the incoming radiation was 0.15405 nm.)

(*a*) Determine the crystal structure of the element.

(*b*) Determine the lattice constant of the element.

(*c*) Identify the element.

3.91 An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 40.663°, 47.314°, 69.144°, and 83.448°. (The wavelength λ of the incoming radiation was 0.15405 nm.)

(*a*) Determine the crystal structure of the element.

(*b*) Determine the lattice constant of the element.

(*c*) Identify the element.

3.15 MATERIALS SELECTION AND DESIGN PROBLEMS

1. In the design of computer chips and microelectronic devices, single crystal silicon wafers are used as the building blocks of the system. (*a*) To which class of materials does silicon belong? (*b*) Discuss the bonding and crystal structure of the silicon crystal. (*c*) Propose a process by which single silicon crystals can be manufactured.

2. Steel is manufactured by adding smaller carbon atoms to the crystal structure of iron. It is possible to add more carbon to the structure when the structure of iron is FCC. However, the normal room-temperature structure of iron is BCC. Design a process that allows the introduction of more carbon to the structure of iron in a solid state.

3. You are given an unknown material and are asked to identify it to the best of your ability. What are some of the tests that you can perform to help identify the material?

4. Often, turbine blades operating at high temperature and high stress levels are manufactured in the form of a large single crystal. (*a*) Speculate on the advantages of a single-crystal turbine blade. (*b*) What properties should the selected material have? (*c*) What specific material would you select to make the single-crystal turbine blade?

5. Name as many carbon allotropes as you can and discuss their crystal structure.

6. Silicon wafers are sometimes coated with a thin layer of aluminum nitride at high temperatures (1000°C). The coefficient of thermal expansion of the silicon crystal is significantly different than that of aluminum nitride. Will this cause a problem? Explain.