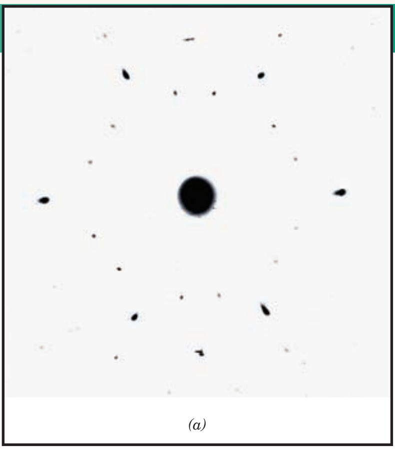
Chapter 3 The Structure of Crystalline Solids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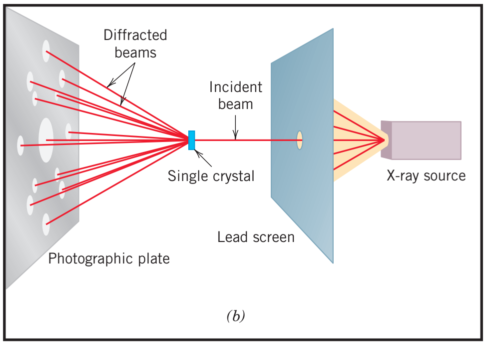

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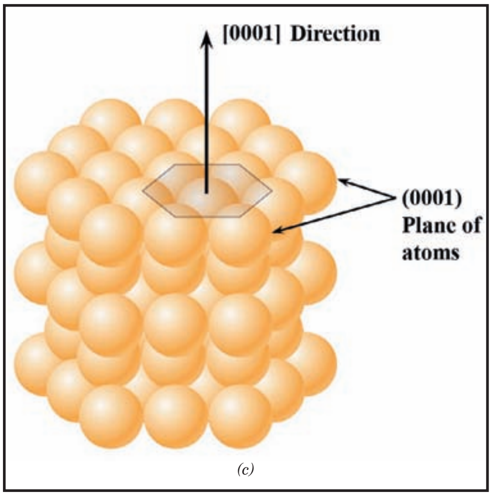

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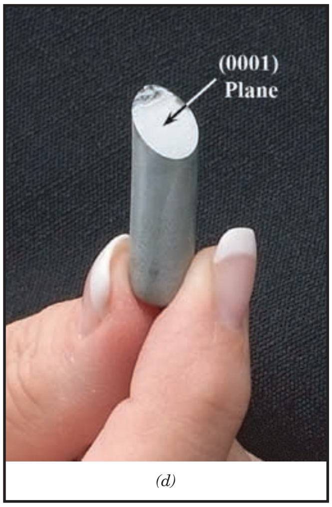


(d)


(e)

(*a*) X-ray diffraction photograph [or Laue photograph (Section 3.16)] for a single crystal of magnesium. (*b*) Schematic diagram illustrating how the spots (i.e., the diffraction pattern) in (*a*) are produced. The lead screen blocks out all beams generated from the x-ray source, except for a narrow beam traveling in a single direction. This incident beam is diffracted by individual crystallographic planes in the single crystal (having different orientations), which gives rise to the various diffracted beams that impinge on the photographic plate. Intersections of these beams with the plate appear as spots when the film is developed. The large spot in the center of (*a*) is from the incident beam, which is parallel to a [0001] crystallographic direction. It should be noted that the hexagonal symmetry of magnesium's hexagonal close-packed crystal structure [shown in (*c*)] is indicated by the diffraction spot pattern that was generated.

(*d*) Photograph of a single crystal of magnesium that was cleaved (or split) along a (0001) plane—the flat surface is a (0001) plane. Also, the direction perpendicular to this plane is a [0001] direction.

(*e*) Photograph of a "mag wheel"—a light-weight automobile wheel that is made of magnesium.

[Figure (*a*) courtesy of J. G. Byrne, Department of Metallurgical Engineering, University of Utah. Figure (*b*) from J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes,* 4th edition. Copyright © 2004 by John Wiley & Sons, Hoboken, NJ. Reprinted by permission of John Wiley & Sons, Inc. Figure(*e*) iStockphoto.]

WHY STUDY The *Structure of Crystalline Solids?*

The properties of some materials are directly related to their crystal structures. For example, pure and undeformed magnesium and beryllium, having one crystal structure, are much more brittle (i.e., fracture at lower degrees of deformation) than are pure and undeformed metals such as gold and silver that have yet another crystal structure (see Section 7.4).

Furthermore, significant property differences exist between crystalline and noncrystalline materials having the same composition. For example, noncrystalline ceramics and polymers normally are optically transparent; the same materials in crystalline (or semicrystalline) form tend to be opaque or, at best, translucent.

In the processing/structure/properties/performance scheme, reasons for studying the structure of crystalline solids are as follows:

- A knowledge of the crystal structure for iron helps us understand transformations that occur when steels are heat treated to improve their mechanical properties (Chapter 10). (Iron is the major constituent of steels.)
- The production of a glass-ceramic (Chapters 12 and 13) involves the formation of a glass that is subsequently transformed into a crystalline solid. This chapter also discusses briefly the structure (on an atomic level) of materials that are noncrystalline (i.e., that form glasses).

Learning Objectives

After studying this chapter you should be able to do the following:

1. **Describe the difference in atomic/molecular structure between crystalline and noncrystalline materials.**
2. **Draw unit cells for face-centered cubic, body-centered cubic, and hexagonal close-packed crystal structures.**
3. **Derive the relationships between unit cell edge length and atomic radius for face-centered cubic and body-centered cubic crystal structures.**
4. **Compute the densities for metals having face-centered cubic and body-centered cubic crystal structures given their unit cell dimensions.**
5. **Given three direction index integers, sketch the direction corresponding to these indices within a unit cell.**
6. **Specify the Miller indices for a plane that has been drawn within a unit cell.**
7. **Describe how face-centered cubic and hexagonal close-packed crystal structures may be generated by the stacking of close-packed planes of atoms.**
8. **Distinguish between single crystals and polycrystalline materials.**
9. **Define *isotropy* and *anisotropy* with respect to material properties.**

3.1 INTRODUCTION

Chapter 2 was concerned primarily with the various types of atomic bonding, which are determined by the electron structures of the individual atoms. The present discussion is devoted to the next level of the structure of materials, specifically, to some of the arrangements that may be assumed by atoms in the solid state. Within this framework, concepts of crystallinity and noncrystallinity are introduced. For crystalline solids the notion of crystal structure is presented, specified in terms of a unit cell. The three common crystal structures found in metals are then detailed, along with the scheme by which crystallographic points, directions, and planes are expressed. Single crystals, polycrystalline materials, and noncrystalline materials are considered. Another section of this chapter briefly describes how crystal structures are determined experimentally using x-ray diffraction techniques.

Crystal Structures

3.2 FUNDAMENTAL CONCEPTS

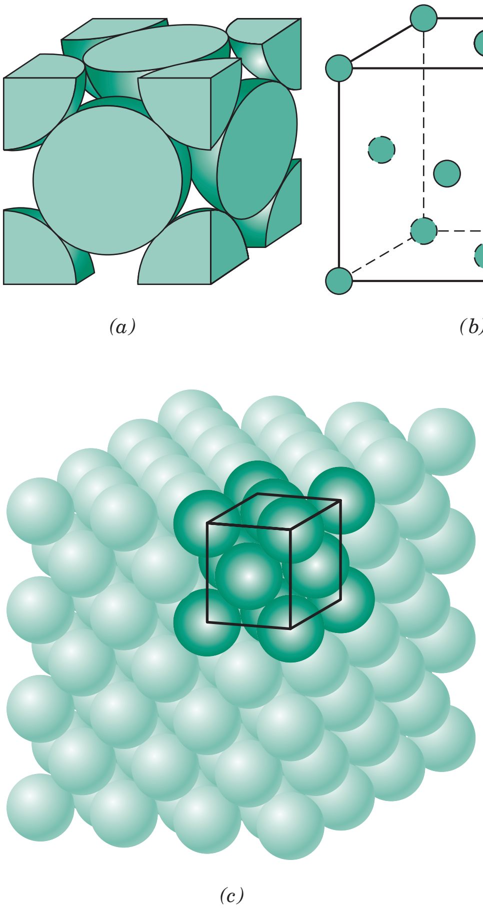
crystalline

Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another. A **crystalline** material is one in which the atoms are situated in a repeating or periodic array over large atomic distances; that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbor atoms. All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; these *noncrystalline* or *amorphous* materials are discussed briefly at the end of this chapter.

crystal structure

Some of the properties of crystalline solids depend on the **crystal structure** of the material, the manner in which atoms, ions, or molecules are spatially arranged. There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials. The present discussion deals with several common metallic crystal structures. Chapters 12 and 14 are devoted to crystal structures for ceramics and polymers, respectively.

When describing crystalline structures, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the *atomic hard-sphere*



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

Figure 3.1 For the face-centered cubic crystal structure, (*a*) a hard-sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms. [Figure (*c*) adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

model in which spheres representing nearest-neighbor atoms touch one another. An example of the hard-sphere model for the atomic arrangement found in some of the common elemental metals is displayed in Figure 3.1*c*. In this particular case all the atoms are identical. Sometimes the term **lattice** is used in the context of crystal structures; in this sense *lattice* means a three-dimensional array of points coinciding with atom positions (or sphere centers).

lattice

3.3 UNIT CELLS

unit cell

The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells.** Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces; one is drawn within the aggregate of spheres (Figure 3.1*c*), which in this case happens to be a cube. A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges. Thus, the unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within. Convenience usually dictates that parallelepiped corners coincide with centers of the hard-sphere atoms. Furthermore, more than a single unit cell may be chosen for a particular crystal structure; however, we generally use the unit cell having the highest level of geometrical symmetry.

3.4 METALLIC CRYSTAL STRUCTURES

The atomic bonding in this group of materials is metallic and thus nondirectional in nature. Consequently, there are minimal restrictions as to the number and position of nearest-neighbor atoms; this leads to relatively large numbers of nearest neighbors and dense atomic packings for most metallic crystal structures. Also, for metals, using the hard-sphere model for the crystal structure, each sphere represents an ion core. Table 3.1 presents the atomic radii for a number of metals. Three relatively simple crystal structures are found for most of the common metals: face-centered cubic, body-centered cubic, and hexagonal close-packed.

The Face-Centered Cubic Crystal Structure

The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces. It is aptly

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

face-centered cubic (FCC)

called the **face-centered cubic (FCC)** crystal structure. Some of the familiar metals having this crystal structure are copper, aluminum, silver, and gold (see also Table 3.1). Figure 3.1*a* shows a hard-sphere model for the FCC unit cell, whereas in Figure 3.1*b* the atom centers are represented by small circles to provide a better perspective of atom positions. The aggregate of atoms in Figure 3.1*c* represents a section of crystal consisting of many FCC unit cells. These spheres or ion cores touch one another across a face diagonal; the cube edge length *a* and the atomic radius *R* are related through

Unit cell edge length for face-centered cubic

$$a = 2R\sqrt{2} \tag{3.1}$$

This result is obtained in Example Problem 3.1.

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Crystal Systems and Unit Cells for Metals

For the FCC crystal structure, each corner atom is shared among eight unit cells, whereas a face-centered atom belongs to only two. Therefore, one-eighth of each of the eight corner atoms and one-half of each of the six face atoms, or a total of four whole atoms, may be assigned to a given unit cell. This is depicted in Figure 3.1*a*, where only sphere portions are represented within the confines of the cube. The cell comprises the volume of the cube, which is generated from the centers of the corner atoms as shown in the figure.

Corner and face positions are really equivalent; that is, translation of the cube corner from an original corner atom to the center of a face atom will not alter the cell structure.

coordination number

atomic packing factor (APF)

Two other important characteristics of a crystal structure are the **coordination number** and the **atomic packing factor (APF).** For metals, each atom has the same number of nearest-neighbor or touching atoms, which is the coordination number. For face-centered cubics, the coordination number is 12. This may be confirmed by examination of Figure 3.1*a*; the front face atom has four corner nearest-neighbor atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front, which is not shown.

The APF is the sum of the sphere volumes of all atoms within a unit cell (assuming the atomic hard-sphere model) divided by the unit cell volume—that is,

Definition of atomic packing factor

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

For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter. Computation of this APF is also included as an example problem. Metals typically have relatively large atomic packing factors to maximize the shielding provided by the free electron cloud.

The Body-Centered Cubic Crystal Structure

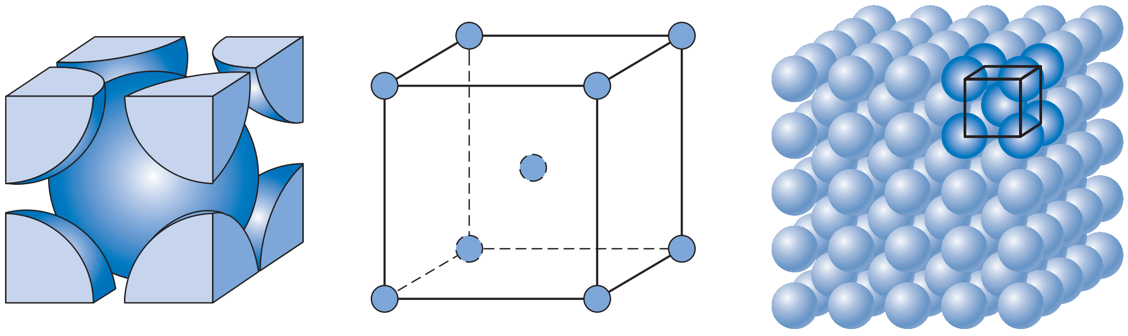
body-centered cubic (BCC)

Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. This is called a **body-centered cubic (BCC)** crystal structure. A collection of spheres depicting this crystal structure is shown in Figure 3.2*c*, whereas Figures 3.2*a* and 3.2*b* are diagrams of BCC unit cells with the atoms represented by hard-sphere and reduced-sphere models, respectively. Center and corner atoms touch one another along cube diagonals, and unit cell length *a* and atomic radius *R* are related through

Unit cell edge length for body-centered cubic

$$a = \frac{4R}{\sqrt{3}} \tag{3.3}$$

Chromium, iron, tungsten, as well as several other metals listed in Table 3.1 exhibit a BCC structure.



(a) (b) (c)

Figure 3.2 For the body-centered cubic crystal structure, (*a*) a hard-sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms. [Figure (*c*) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

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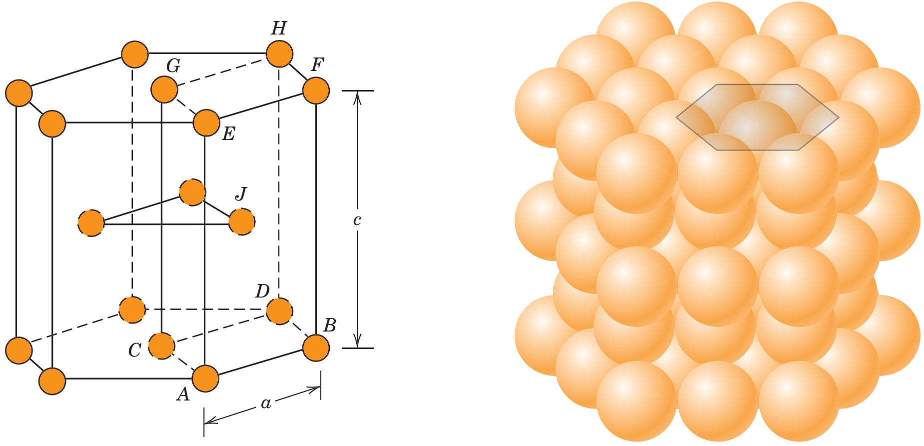
Crystal Systems and Unit Cells for Metals

Two atoms are associated with each BCC unit cell: the equivalent of one atom from the eight corners, each of which is shared among eight unit cells, and the single center atom, which is wholly contained within its cell. In addition, corner and center atom positions are equivalent. The coordination number for the BCC crystal structure is 8; each center atom has as nearest neighbors its eight corner atoms. Because the coordination number is less for BCC than FCC, so also is the atomic packing factor for BCC lower—0.68 versus 0.74.

The Hexagonal Close-Packed Crystal Structure

hexagonal close-packed (HCP)

Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a unit cell that is hexagonal. Figure 3.3*a* shows a reduced-sphere unit cell for this structure, which is termed **hexagonal close-packed (HCP);** an



(a) (b)

Figure 3.3 For the hexagonal close-packed crystal structure, (*a*) a reduced-sphere unit cell (*a* and *c* represent the short and long edge lengths, respectively), and (*b*) an aggregate of many atoms. [Figure (*b*) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

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Crystal Systems and Unit Cells for Metals

assemblage of several HCP unit cells is presented in Figure 3.3*b*.[1] The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes. The equivalent of six atoms is contained in each unit cell; one-sixth of each of the 12 top and bottom face corner atoms, one-half of each of the 2 center face atoms, and all 3 midplane interior atoms. If a and c represent, respectively, the short and long unit cell dimensions of Figure 3.3*a*, the c/a ratio should be 1.633; however, for some HCP metals this ratio deviates from the ideal value.

The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively. The HCP metals include cadmium, magnesium, titanium, and zinc; some of these are listed in Table 3.1.

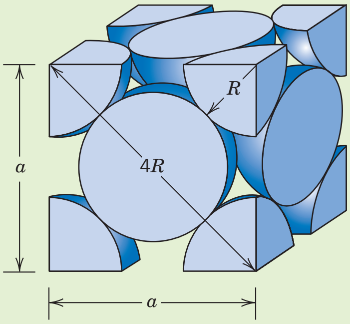
EXAMPLE PROBLEM 3.1

Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R.

Solution

In the FCC unit cell illustrated,



the atoms touch one another across a face-diagonal the length of which is $4R$. Because the unit cell is a cube, its volume is a^3, where a is the cell edge length. From the right triangle on the face,

$$a^2 + a^2 = (4R)^2$$

or, solving for a,

$$a = 2R\sqrt{2} \tag{3.1}$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \tag{3.4}$$

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[1] Alternatively, the unit cell for HCP may be specified in terms of the parallelepiped defined by the atoms labeled A through H in Figure 3.3*a*. Thus, the atom denoted J lies within the unit cell interior.

EXAMPLE PROBLEM 3.2

Computation of the Atomic Packing Factor for FCC

Show that the atomic packing factor for the FCC crystal structure is 0.74.

Solution

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R. The volume for a sphere is $\frac{4}{3}\pi R^3$, and because there are four atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = (4)\tfrac{4}{3}\pi R^3 = \tfrac{16}{3}\pi R^3$$

From Example Problem 3.1, the total unit cell volume is

$$V_C = 16R^3\sqrt{2}$$

Therefore, the atomic packing factor is

$$\text{APF} = \frac{V_S}{V_C} = \frac{\left(\frac{16}{3}\right)\pi R^3}{16R^3\sqrt{2}} = 0.74$$

3.5 DENSITY COMPUTATIONS

A knowledge of the crystal structure of a metallic solid permits computation of its theoretical density ρ through the relationship

Theoretical density for metals

$$\rho = \frac{nA}{V_C N_A} \tag{3.5}$$

where

n = number of atoms associated with each unit cell
A = atomic weight
V_C = volume of the unit cell
N_A = Avogadro's number (6.022×10^{23} atoms/mol)

EXAMPLE PROBLEM 3.3

Theoretical Density Computation for Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density and compare the answer with its measured density.

Solution

Equation 3.5 is employed in the solution of this problem. Because the crystal structure is FCC, n, the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_C for FCC was determined in Example Problem 3.1 as $16R^3\sqrt{2}$, where R, the atomic radius, is 0.128 nm.

Substitution for the various parameters into Equation 3.5 yields

$$\rho = \frac{nA_{\mathrm{Cu}}}{V_C N_{\mathrm{A}}} = \frac{nA_{\mathrm{Cu}}}{(16R^3\sqrt{2})N_{\mathrm{A}}}$$

$$= \frac{(4\ \text{atoms/unit cell})(63.5\ \text{g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8}\ \text{cm})^3/\text{unit cell}](6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 8.89\ \text{g/cm}^3$$

The literature value for the density of copper is 8.94 g/cm^3, which is in very close agreement with the foregoing result.

3.6 POLYMORPHISM AND ALLOTROPY

polymorphism

allotropy

Some metals, as well as nonmetals, may have more than one crystal structure, a phenomenon known as **polymorphism.** When found in elemental solids, the condition is often termed **allotropy.** The prevailing crystal structure depends on both the temperature and the external pressure. One familiar example is found in carbon: graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures. Also, pure iron has a BCC crystal structure at room temperature, which changes to FCC iron at 912°C (1674°F). Most often a modification of the density and other physical properties accompanies a polymorphic transformation.

3.7 CRYSTAL SYSTEMS

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Crystal Systems and Unit Cells for Metals

lattice parameters

Because there are many different possible crystal structures, it is sometimes convenient to divide them into groups according to unit cell configurations and/or atomic arrangements. One such scheme is based on the unit cell geometry, that is, the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell. Within this framework, an xyz coordinate system is established with its origin at one of the unit cell corners; each of the x, y, and z axes coincides with one of the three parallelepiped edges that extend from this corner, as illustrated in Figure 3.4. The unit cell geometry is completely defined in terms of six parameters: the three edge lengths a, b, and c, and the three interaxial angles α, β, and γ. These are indicated in Figure 3.4, and are sometimes termed the **lattice parameters** of a crystal structure.

crystal system

On this basis there are seven different possible combinations of a, b, and c, and α, β, and γ, each of which represents a distinct **crystal system.** These seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral,[2] monoclinic, and triclinic. The lattice parameter relationships and unit cell sketches for each are

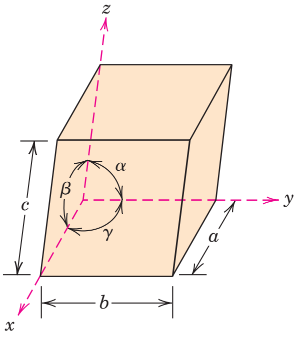

Figure 3.4 A unit cell with x, y, and z coordinate axes, showing axial lengths (a, b, and c) and interaxial angles (α, β, and γ).

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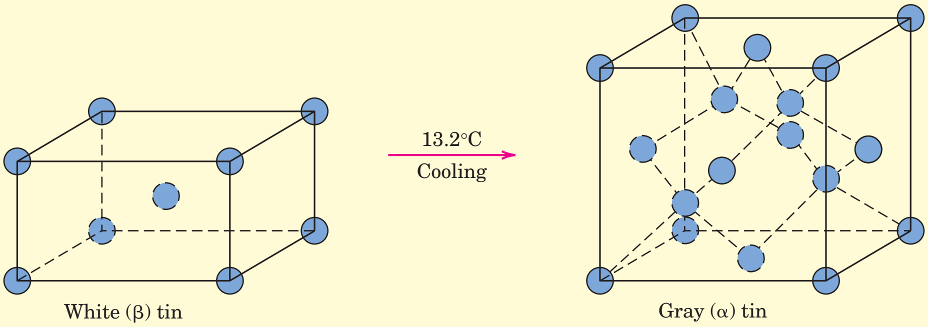
[2] Also called *trigonal*.

MATERIAL OF IMPORTANCE

Tin (Its Allotropic Transformation)

Another common metal that experiences an allotropic change is tin. White (or β) tin, having a body-centered tetragonal crystal structure at room temperature, transforms, at 13.2°C (55.8°F), to gray (or α) tin, which has a crystal structure similar to diamond (i.e., the diamond cubic crystal structure); this transformation is represented schematically as follows:



The rate at which this change takes place is extremely slow; however, the lower the temperature (below 13.2°C) the faster the rate. Accompanying this white-to-gray-tin transformation is an increase in volume (27%), and, accordingly, a decrease in density (from 7.30 g/cm^3 to 5.77 g/cm^3). Consequently, this volume expansion results in the disintegration of the white tin metal into a coarse powder of the gray allotrope. For normal subambient temperatures, there is no need to worry about this disintegration process for tin products, because of the very slow rate at which the transformation occurs.

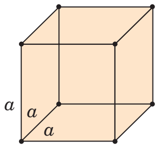
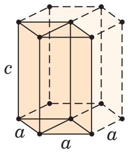
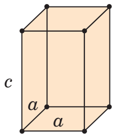
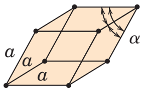
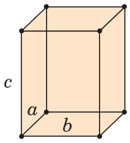
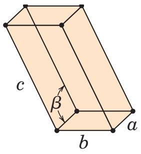
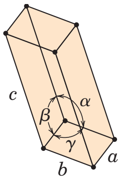
This white-to-gray-tin transition produced some rather dramatic results in 1850 in Russia. The winter that year was particularly cold, and record low temperatures persisted for extended periods of time. The uniforms of some Russian soldiers had tin buttons, many of which crumbled because of these extreme cold conditions, as did also many of the tin church organ pipes. This problem came to be known as the “tin disease.”

Specimen of white tin (left). Another specimen disintegrated upon transforming to gray tin (right) after it was cooled to and held at a temperature below 13.2°C for an extended period of time. (Photograph courtesy of Professor Bill Plumbridge, Department of Materials Engineering, The Open University, Milton Keynes, England.)

represented in Table 3.2. The cubic system, for which $a = b = c$ and $\alpha = \beta = \gamma = 90°$, has the greatest degree of symmetry. The least symmetry is displayed by the triclinic system, because $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$.

From the discussion of metallic crystal structures, it should be apparent that both FCC and BCC structures belong to the cubic crystal system, whereas HCP falls within hexagonal. The conventional hexagonal unit cell really consists of three parallelepipeds situated as shown in Table 3.2.

Table 3.2 **Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems**

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Concept Check 3.1

What is the difference between crystal structure and crystal system?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

It is important to note that many of the principles and concepts addressed in previous discussions in this chapter also apply to crystalline ceramic and polymeric systems (Chapters 12 and 14). For example, crystal structures are most often described in terms of unit cells, which are normally more complex than those for FCC, BCC, and HCP. In addition, for these other systems, we are often interested in determining atomic packing factors and densities, using modified forms of Equations 3.2 and 3.5. Furthermore, according to unit cell geometry, crystal structures of these other material types are grouped within the seven crystal systems.

Crystallographic Points, Directions, and Planes

When dealing with crystalline materials, it often becomes necessary to specify a particular point within a unit cell, a crystallographic direction, or some crystallographic plane of atoms. Labeling conventions have been established in which three numbers or indices are used to designate point locations, directions, and planes. The basis for determining index values is the unit cell, with a right-handed coordinate system consisting of three (x, y, and z) axes situated at one of the corners and coinciding with the unit cell edges, as shown in Figure 3.4. For some crystal systems—namely, hexagonal, rhombohedral, monoclinic, and triclinic—the three axes are *not* mutually perpendicular, as in the familiar Cartesian coordinate scheme.

3.8 POINT COORDINATES

The position of any point located within a unit cell may be specified in terms of its coordinates as fractional multiples of the unit cell edge lengths (i.e., in terms of a, b, and c). To illustrate, consider the unit cell and the point P situated therein as shown in Figure 3.5. We specify the position of P in terms of the generalized coordinates

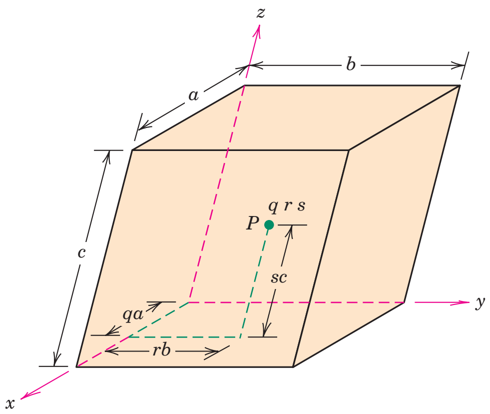


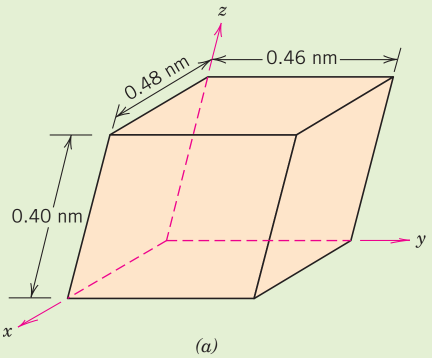
Figure 3.5 The manner in which the q, r, and s coordinates at point P within the unit cell are determined. The q coordinate (which is a fraction) corresponds to the distance qa along the x axis, where a is the unit cell edge length. The respective r and s coordinates for the y and z axes are determined similarly.

q, *r*, and *s* where *q* is some fractional length of *a* along the *x* axis, *r* is some fractional length of *b* along the *y* axis, and similarly for *s*. Thus, the position of *P* is designated using coordinates *q r s* with values that are less than or equal to unity. Furthermore, we have chosen not to separate these coordinates by commas or any other punctuation marks (which is the normal convention).

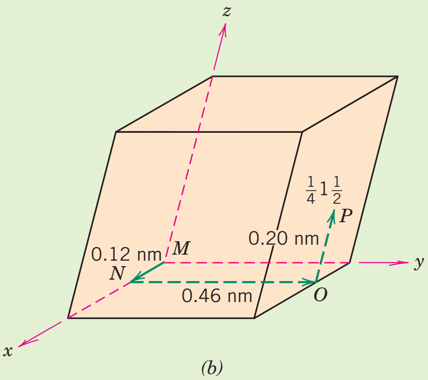
EXAMPLE PROBLEM 3.4

Location of Point Having Specified Coordinates

For the unit cell shown in the accompanying sketch (*a*), locate the point having coordinates $\frac{1}{4}\ 1\ \frac{1}{2}$.



(*a*)



(*b*)

Solution

From sketch (*a*), edge lengths for this unit cell are as follows: $a = 0.48$ nm, $b = 0.46$ nm, and $c = 0.40$ nm. Furthermore, in light of the preceding discussion, fractional lengths are $q = \frac{1}{4}$, $r = 1$, and $s = \frac{1}{2}$. Therefore, first we move from the origin of the unit cell (point *M*) $qa = \frac{1}{4}$ (0.48 nm) = 0.12 nm units along the *x* axis (to point *N*), as shown in the (*b*) sketch. Similarly, we proceed $rb = (1)(0.46$ nm$) = 0.46$ nm parallel to the *y* axis, from point *N* to point *O*. Finally, we move from this position, $sc = \frac{1}{2}$ (0.40 nm) = 0.20 nm units parallel to the *z* axis to point *P* as noted again in sketch (*b*). This point *P* then corresponds to the $\frac{1}{4}\ 1\ \frac{1}{2}$ point coordinates.

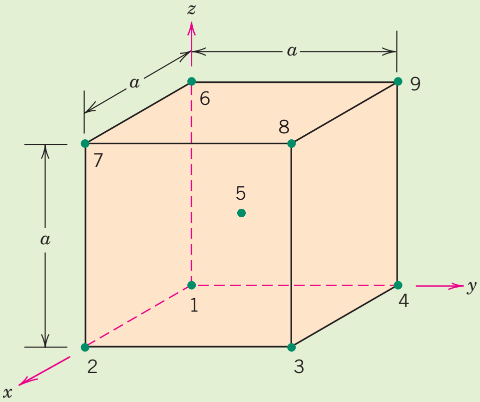
EXAMPLE PROBLEM 3.5

Specification of Point Coordinates

Specify point coordinates for all atom positions for a BCC unit cell.

Solution

For the BCC unit cell of Figure 3.2, atom position coordinates correspond to the locations of the centers of all atoms in the unit cell—that is, the eight corner atoms and single center atom. These positions are noted (and also numbered) in the following figure.



Point coordinates for position number 1 are 0 0 0; this position is located at the origin of the coordinate system, and, therefore, the fractional unit cell edge lengths along the x, y, and z axes are, respectively, $0a$, $0a$, and $0a$. Furthermore, for position number 2, because it lies one unit cell edge length along the x axis, its fractional edge lengths are a, $0a$, and $0a$, respectively, which yield point coordinates of 1 0 0. The following table presents fractional unit cell lengths along the x, y, and z axes, and their corresponding point coordinates for each of the nine points in the preceding figure.

Point Number	*Fractional Lengths*			*Point Coordinates*
	x axis	*y axis*	*z axis*	
1	0	0	0	0 0 0
2	1	0	0	1 0 0
3	1	1	0	1 1 0
4	0	1	0	0 1 0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
6	0	0	1	0 0 1
7	1	0	1	1 0 1
8	1	1	1	1 1 1
9	0	1	1	0 1 1

3.9 CRYSTALLOGRAPHIC DIRECTIONS

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Crystallographic Directions

A crystallographic direction is defined as a line between two points, or a vector. The following steps are used to determine the three directional indices:

1. A vector of convenient length is positioned such that it passes through the origin of the coordinate system. Any vector may be translated throughout the crystal lattice without alteration, if parallelism is maintained.
2. The length of the vector projection on each of the three axes is determined; *these are measured in terms of the unit cell dimensions a, b, and c.*
3. These three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
4. The three indices, not separated by commas, are enclosed in square brackets, thus: $[uvw]$. The u, v, and w integers correspond to the reduced projections along the x, y, and z axes, respectively.

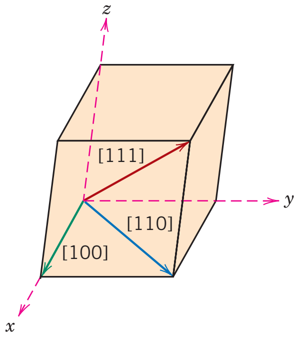


Figure 3.6 The [100], [110], and [111] directions within a unit cell.

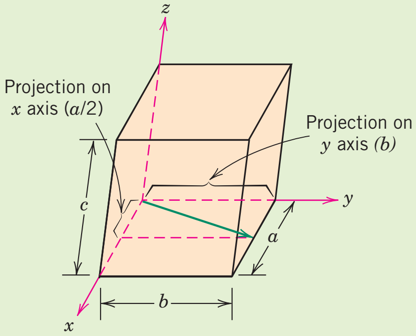
For each of the three axes, there will exist both positive and negative coordinates. Thus negative indices are also possible, which are represented by a bar over the appropriate index. For example, the $[1\bar{1}1]$ direction would have a component in the $-y$ direction. Also, changing the signs of all indices produces an antiparallel direction; that is, $[\bar{1}1\bar{1}]$ is directly opposite to $[1\bar{1}1]$. If more than one direction (or plane) is to be specified for a particular crystal structure, it is imperative for the maintaining of consistency that a positive–negative convention, once established, not be changed.

The [100], [110], and [111] directions are common ones; they are drawn in the unit cell shown in Figure 3.6.

EXAMPLE PROBLEM 3.6

Determination of Directional Indices

Determine the indices for the direction shown in the accompanying figure.



Solution

The vector, as drawn, passes through the origin of the coordinate system, and therefore no translation is necessary. Projections of this vector onto the x, y, and z axes are, respectively, $a/2$, b, and $0c$, which become $\frac{1}{2}$, 1, and 0 in terms of the unit cell parameters (i.e., when the a, b, and c are dropped). Reduction of these numbers to the lowest set of integers is accompanied by multiplication of each by the factor 2. This yields the integers 1, 2, and 0, which are then enclosed in brackets as [120].

This procedure may be summarized as follows:

	x	*y*	*z*
Projections	$a/2$	b	$0c$
Projections (in terms of *a*, *b*, and *c*)	$\frac{1}{2}$	1	0
Reduction	1	2	0
Enclosure		[120]	

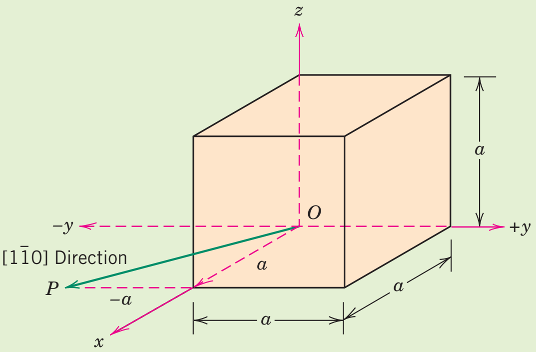
EXAMPLE PROBLEM 3.7

Construction of Specified Crystallographic Direction

Draw a $[1\bar{1}0]$ direction within a cubic unit cell.

Solution

First construct an appropriate unit cell and coordinate axes system. In the accompanying figure the unit cell is cubic, and the origin of the coordinate system, point *O*, is located at one of the cube corners.



This problem is solved by reversing the procedure of the preceding example. For this $[1\bar{1}0]$ direction, the projections along the *x*, *y*, and *z* axes are *a*, −*a*, and 0*a*, respectively. This direction is defined by a vector passing from the origin to point *P*, which is located by first moving along the *x* axis *a* units, and from this position, parallel to the *y* axis −*a* units, as indicated in the figure. There is no *z* component to the vector, because the *z* projection is zero.

For some crystal structures, several nonparallel directions with different indices are crystallographically equivalent; this means that the spacing of atoms along each direction is the same. For example, in cubic crystals, all the directions represented by the following indices are equivalent: [100], $[\bar{1}00]$, [010], $[0\bar{1}0]$, [001], and $[00\bar{1}]$. As a convenience, equivalent directions are grouped together into a *family,* which are enclosed in angle brackets, thus: ⟨100⟩. Furthermore, directions in cubic crystals having the same indices without regard to order or sign—for example, [123] and $[\bar{2}1\bar{3}]$—are equivalent. This is, in general, not true for other crystal systems. For example, for crystals of tetragonal symmetry, [100] and [010] directions are equivalent, whereas [100] and [001] are not.

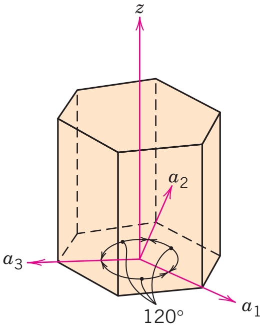


Figure 3.7 Coordinate axis system for a hexagonal unit cell (Miller–Bravais scheme).

Hexagonal Crystals

A problem arises for crystals having hexagonal symmetry in that some crystallographic equivalent directions will not have the same set of indices. This is circumvented by utilizing a four-axis, or *Miller–Bravais,* coordinate system as shown in Figure 3.7. The three a_1, a_2, and a_3 axes are all contained within a single plane (called the basal plane) and are at 120° angles to one another. The z axis is perpendicular to this basal plane. Directional indices, which are obtained as described earlier, will be denoted by four indices, as $[uvtw]$; by convention, the first three indices pertain to projections along the respective a_1, a_2, and a_3 axes in the basal plane.

Conversion from the three-index system to the four-index system,

$$[u'v'w'] \longrightarrow [uvtw]$$

is accomplished by the following formulas:

$$u = \frac{1}{3}(2u' - v') \tag{3.6a}$$

$$v = \frac{1}{3}(2v' - u') \tag{3.6b}$$

$$t = -(u + v) \tag{3.6c}$$

$$w = w' \tag{3.6d}$$

where primed indices are associated with the three-index scheme and unprimed with the new Miller–Bravais four-index system. (Of course, reduction to the lowest set of integers may be necessary, as discussed earlier.) For example, the [010] direction becomes $[\bar{1}2\bar{1}0]$. Several different directions are indicated in the hexagonal unit cell (Figure 3.8*a*).

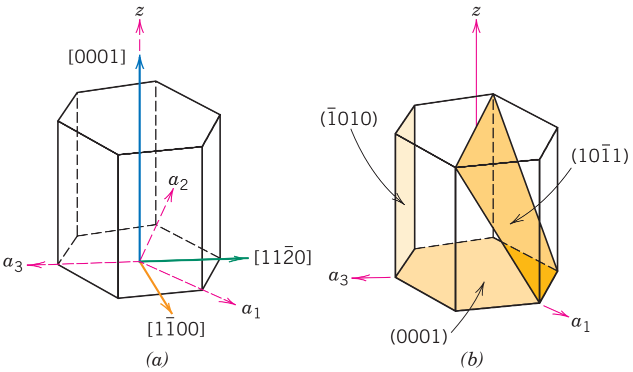


Figure 3.8 For the hexagonal crystal system, (*a*) the $[0001]$, $[1\bar{1}00]$, and $[11\bar{2}0]$ directions, and (*b*) the (0001), $(10\bar{1}1)$, and $(\bar{1}010)$ planes.

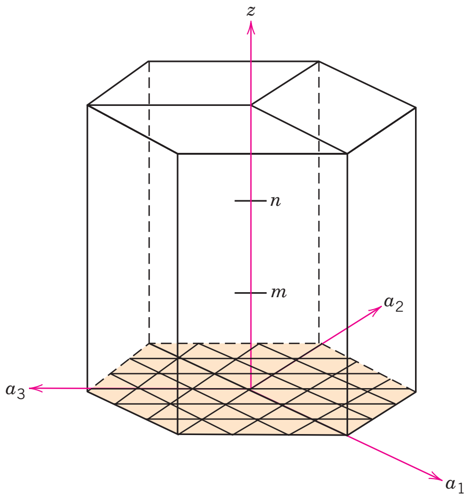


Figure 3.9 Reduced-scale coordinate axis system for hexagonal unit cells that may be used to plot crystallographic directions.

The plotting of crystallographic directions for hexagonal crystals is more complicated than for crystals belonging to the other six systems. For hexagonal it is sometimes more convenient to use the four-axis coordinate system shown in Figure 3.9. As may be noted, a grid has been constructed on the basal plane that consists of sets of lines parallel to each of the a_1, a_2, and a_3 axes. The intersections of two sets of parallel lines (e.g., those for a_2, and a_3) lie on and trisect the other axis (e.g., divide a_1 into thirds) within the hexagonal unit cell. In addition, the z axis of Figure 3.9 is also apportioned into three equal lengths (at trisection points m and n). We will refer to this scheme as a reduced-scale coordinate system.

Construction of a direction specified by four indices is carried out using a procedure similar to that described previously (which involves vector projections along corresponding axes). In this case, rather than taking projections in terms of the lattice parameters a (for a_1, a_2, and a_3,) and c (for the z axis), we employ the reduced-scale scheme of Figure 3.9—i.e., use $\frac{a}{3}$ and $\frac{c}{3}$ instead. This procedure is illustrated in the following example problem.

EXAMPLE PROBLEM 3.8

Conversion and Construction of Directional Indices for a Hexagonal Unit Cell

(a) Convert the [111] direction into the four-index system for hexagonal crystals.
(b) Draw this direction within a reduced-scale coordinate system (per Figure 3.9).
(c) Now draw the [111] direction within a hexagonal unit cell that utilizes a three-axis (a_1, a_2, z) coordinate system.

Solution

(a) This conversion is carried out using Equations 3.6a, 3.6b, 3.6c, and 3.6d, in which

$$u' = 1 \quad v' = 1 \quad w' = 1$$

Thus,

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

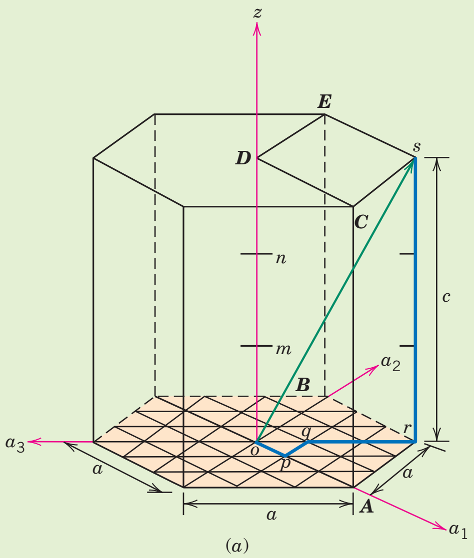
$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$t = -(u + v) = -\left(\frac{1}{3} + \frac{1}{3}\right) = -\frac{2}{3}$$

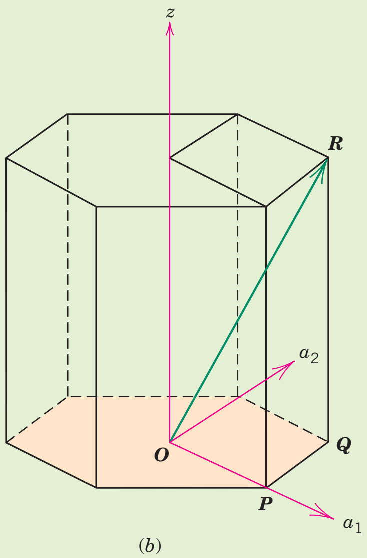
$$w = w' = 1$$

Multiplication of the preceding indices by 3 reduces them to the lowest set, which yields values for u, v, t, and w of 1, 1, −2 and 3, respectively. Hence, the [111] direction becomes $[11\bar{2}3]$.

(b) The following sketch (a) shows a hexagonal unit cell in which the reduced-scale coordinate system has been drawn.



(a)



(b)

Also, one of the three parallelepipeds comprising the hexagonal cell is delineated—its corners are labeled with letters o-A-r-B-C-D-E-s, with the origin of the a_1-a_2-a_3-z axes coordinate system located at the corner labeled o. It is within this unit cell that we draw the $[11\bar{2}3]$ direction. The projections along the a_1, a_2, a_3, and z axes are, respectively $\frac{a}{3}$, $\frac{a}{3}$, $-\frac{2a}{3}$, and $\frac{3c}{3}$ (or c). In constructing this direction vector we begin at the origin (point o), and first proceed $\frac{a}{3}$ units along the a_1 axis to point p, next from this point parallel to the a_2 axis $\frac{a}{3}$ units to point q, then parallel to the a_3 axis $-\frac{2a}{3}$ units to point r, and finally we continue parallel to the z axis c units to point s. Thus, $[11\bar{2}3]$ is represented by the vector that is directed from point o to point s, as noted in the sketch.

(c) Of course, it is possible to draw the equivalent [111] direction using a three-coordinate-axis (a_1-a_2-z) system and the conventional technique. This is represented in sketch (b). In this case, projections on the a_1, a_2, and

z axes are a, a, and c, respectively. First we begin at the origin (point O), then proceed a units along the a_1 axis (to point P), next parallel to the a_2 axis a units (to point Q), and finally parallel to the z axis c units (to point R). Hence, the [111] direction is represented by the vector that passes from O to R as shown.

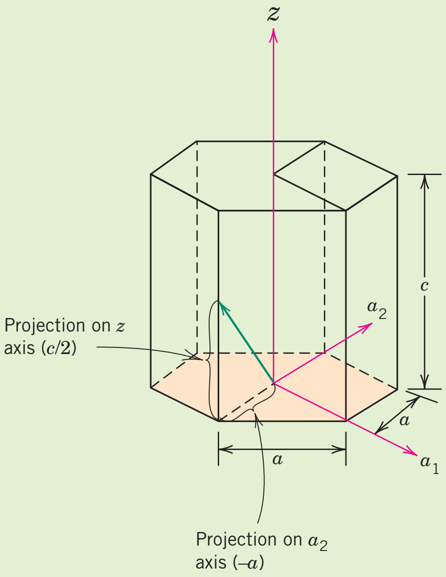
It may be noted that this [111] direction is identical to $[11\overline{2}3]$ from part (b).

The alternative situation is to determine the indices for a direction that has been drawn within a hexagonal unit cell. For this case it is convenient to use the a_1-a_2-z three-coordinate-axis system and then convert these indices into the equivalent set for the four-axis scheme. The following example problem demonstrates this procedure.

EXAMPLE PROBLEM 3.9

Determination of Directional Indices for a Hexagonal Unit Cell

Determine the directional indices (four-index system) for the direction shown in the accompanying figure.



Solution

The first thing we need do is to determine indices for the vector referenced to the three-axis scheme represented in the sketch. Because the direction vector passes through the origin of the coordinate system, no translation is necessary. Projections of this vector onto the a_1, a_2, and z axes are $0a$, $-a$, and $c/2$, respectively, which become 0, -1, and $\frac{1}{2}$ in terms of the unit cell parameters. Reduction of these numbers to the lowest set of integers is possible by multiplying each by the factor 2. This yields 0, -2, and 1, which are then enclosed in brackets as $[0\overline{2}1]$.

Now it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.6a, 3.6b, 3.6c, and 3.6d. For this $[0\bar{2}1]$ direction

$$u' = 0 \qquad v' = -2 \qquad w' = 1$$

and

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(0) - (-2)] = \frac{2}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(-2) - 0] = -\frac{4}{3}$$

$$t = -(u + v) = -\left(\frac{2}{3} - \frac{4}{3}\right) = \frac{2}{3}$$

$$w = w' = 1$$

Multiplication of the preceding indices by 3 reduces them to the lowest set, which yields values for u, v, t, and w of 2, −4, 2, and 3, respectively. Hence, the direction vector shown in the figure is $[2\bar{4}23]$.

3.10 CRYSTALLOGRAPHIC PLANES

Miller indices

The orientations of planes for a crystal structure are represented in a similar manner. Again, the unit cell is the basis, with the three-axis coordinate system as represented in Figure 3.4. In all but the hexagonal crystal system, crystallographic planes are specified by three **Miller indices** as (hkl). Any two planes parallel to each other are equivalent and have identical indices. The procedure used to determine the h, k, and l index numbers is as follows:

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Crystallographic Planes

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.
2. At this point the crystallographic plane either intersects or parallels each of the three axes; the length of the planar intercept for each axis is determined in terms of the lattice parameters a, b, and c.
3. The reciprocals of these numbers are taken. A plane that parallels an axis may be considered to have an infinite intercept, and, therefore, a zero index.
4. If necessary, these three numbers are changed to the set of smallest integers by multiplication or division by a common factor.[3]
5. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (hkl).

An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index. Furthermore, reversing the directions of all indices specifies another plane parallel to, on the opposite side of, and equidistant from the origin. Several low-index planes are represented in Figure 3.10.

---

[3] On occasion, index reduction is not carried out (e.g., for x-ray diffraction studies that are described in Section 3.16); for example, (002) is not reduced to (001). In addition, for ceramic materials, the ionic arrangement for a reduced-index plane may be different from that for a nonreduced one.

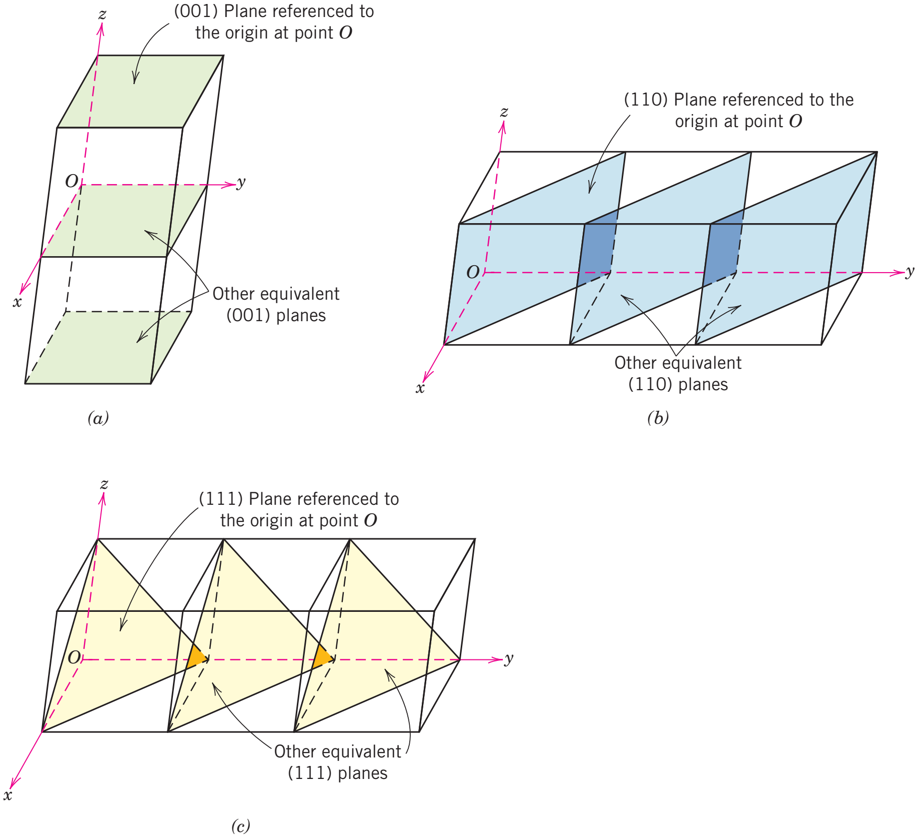


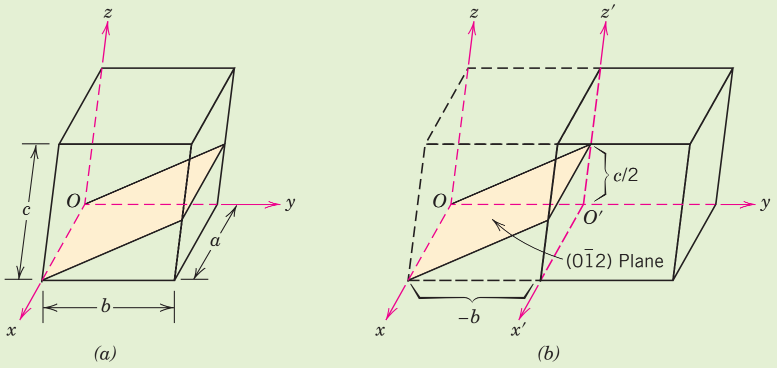
Figure 3.10 Representations of a series each of the (*a*) (001), (*b*) (110), and (*c*) (111) crystallographic planes.

One interesting and unique characteristic of cubic crystals is that planes and directions having the same indices are perpendicular to one another; however, for other crystal systems there are no simple geometrical relationships between planes and directions having the same indices.

EXAMPLE PROBLEM 3.10

Determination of Planar (Miller) Indices

Determine the Miller indices for the plane shown in the accompanying sketch (*a*).



Solution

Because the plane passes through the selected origin O, a new origin must be chosen at the corner of an adjacent unit cell, taken as O' and shown in sketch (*b*). This plane is parallel to the x axis, and the intercept may be taken as ∞a. The y and z axes' intersections, referenced to the new origin O', are $-b$ and $c/2$, respectively. Thus, in terms of the lattice parameters a, b, and c, these intersections are ∞, -1, and $\frac{1}{2}$. The reciprocals of these numbers are 0, -1, and 2; because all are integers, no further reduction is necessary. Finally, enclosure in parentheses yields $(0\bar{1}2)$.

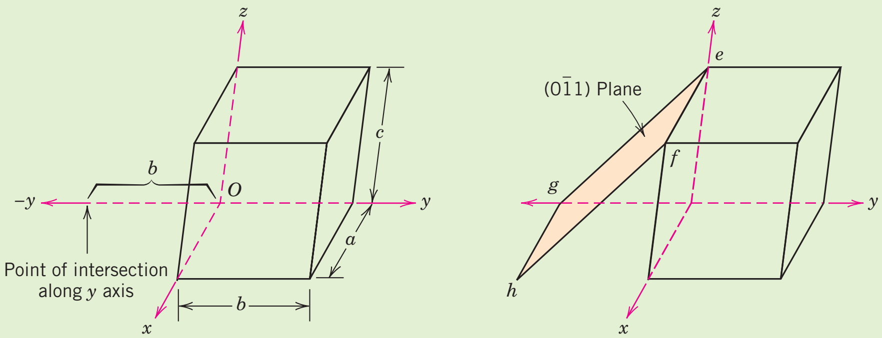
These steps are briefly summarized here:

	x	y	z
Intercepts	∞a	$-b$	$c/2$
Intercepts (in terms of lattice parameters)	∞	-1	$\frac{1}{2}$
Reciprocals	0	-1	2
Reductions (unnecessary)			
Enclosure		$(0\bar{1}2)$	

EXAMPLE PROBLEM 3.11

Construction of Specified Crystallographic Plane

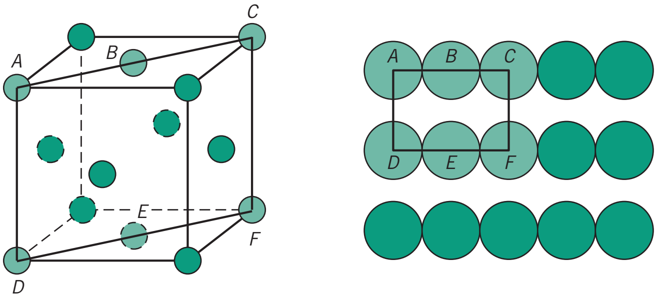
Construct a $(0\bar{1}1)$ plane within a cubic unit cell.



(*a*) (*b*)

Solution

To solve this problem, carry out the procedure used in the preceding example in reverse order. To begin, the indices are removed from the parentheses, and reciprocals are taken, which yields ∞, -1, and 1. This means that the particular plane parallels the x axis while intersecting the y and z axes at $-b$ and c, respectively, as indicated in the accompanying sketch (*a*). This plane has been drawn in sketch (*b*). A plane is indicated by lines representing its intersections with the planes that constitute the faces of the unit cell or their extensions. For example, in this figure, line *ef* is the intersection between the $(0\bar{1}1)$ plane and the top face of the unit cell; also, line *gh* represents the intersection between this same $(0\bar{1}1)$ plane and the plane of the bottom unit cell face extended. Similarly, lines *eg* and *fh* are the intersections between $(0\bar{1}1)$ and back and front cell faces, respectively.



(a) (b)

Figure 3.11 (*a*) Reduced-sphere FCC unit cell with the (110) plane. (*b*) Atomic packing of an FCC (110) plane. Corresponding atom positions from (*a*) are indicated.

Atomic Arrangements

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Planar Atomic Arrangements

The atomic arrangement for a crystallographic plane, which is often of interest, depends on the crystal structure. The (110) atomic planes for FCC and BCC crystal structures are represented in Figures 3.11 and 3.12; reduced-sphere unit cells are also included. Note that the atomic packing is different for each case. The circles represent atoms lying in the crystallographic planes as would be obtained from a slice taken through the centers of the full-sized hard spheres.

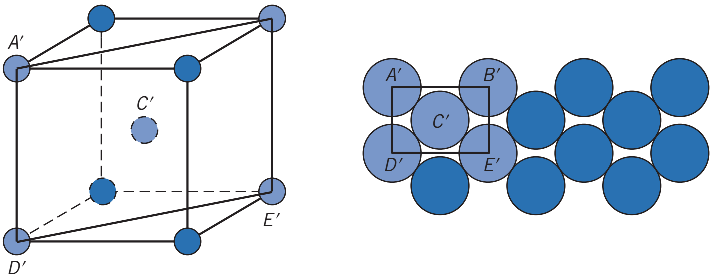
A "family" of planes contains all planes that are crystallographically equivalent—that is, having the same atomic packing; a family is designated by indices that are enclosed in braces—such as {100}. For example, in cubic crystals the (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, $(1\bar{1}\bar{1})$, $(11\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, and $(1\bar{1}1)$ planes all belong to the {111} family. On the other hand, for tetragonal crystal structures, the {100} family would contain only the (100), $(\bar{1}00)$, (010), and $(0\bar{1}0)$ because the (001) and $(00\bar{1})$ planes are not crystallographically equivalent. Also, in the cubic system only, planes having the same indices, irrespective of order and sign, are equivalent. For example, both $(1\bar{2}3)$ and $(3\bar{1}2)$ belong to the {123} family.

Hexagonal Crystals

For crystals having hexagonal symmetry, it is desirable that equivalent planes have the same indices; as with directions, this is accomplished by the Miller–Bravais system shown in Figure 3.7. This convention leads to the four-index (*hkil*) scheme, which is favored in most instances because it more clearly identifies the orientation of a plane in a hexagonal crystal. There is some redundancy in that i is determined by the sum of h and k through

$$i = -(h + k) \tag{3.7}$$

Otherwise the three h, k, and l indices are identical for both indexing systems. Figure 3.8*b* presents several of the common planes that are found for crystals having hexagonal symmetry.



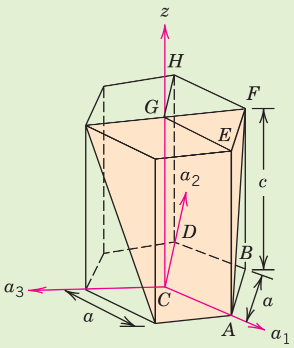
(a) (b)

Figure 3.12 (*a*) Reduced-sphere BCC unit cell with the (110) plane. (*b*) Atomic packing of a BCC (110) plane. Corresponding atom positions from (*a*) are indicated.

EXAMPLE PROBLEM 3.12

Determination of Miller–Bravais Indices for a Plane within a Hexagonal Unit Cell

Determine the Miller–Bravais indices for the plane shown in the hexagonal unit cell.



Solution

To determine these Miller–Bravais indices, consider the plane in the figure referenced to the parallelepiped labeled with the letters A through H at its corners. This plane intersects the a_1 axis at a distance a from the origin of the a_1-a_2-a_3-z coordinate axis system (point C). Furthermore, its intersections with the a_2 and z axes are $-a$ and c, respectively. Therefore, in terms of the lattice parameters, these intersections are 1, −1, and 1. Furthermore, the reciprocals of these numbers are also 1, −1, and 1. Hence

$$h = 1$$
$$k = -1$$
$$l = 1$$

and, from Equation 3.7,

$$\begin{aligned} i &= -(h + k) \\ &= -(1 - 1) = 0 \end{aligned}$$

Therefore the ($hkil$) indices are $(1\bar{1}01)$.

Notice that the third index is zero (i.e., its reciprocal = ∞), which means that this plane parallels the a_3 axis. Inspection of the preceding figure shows that this is indeed the case.

3.11 LINEAR AND PLANAR DENSITIES

The two previous sections discussed the equivalency of nonparallel crystallographic directions and planes. Directional equivalency is related to *linear density* in the sense that, for a particular material, equivalent directions have identical linear densities. The corresponding parameter for crystallographic planes is *planar density,* and planes having the same planar density values are also equivalent.

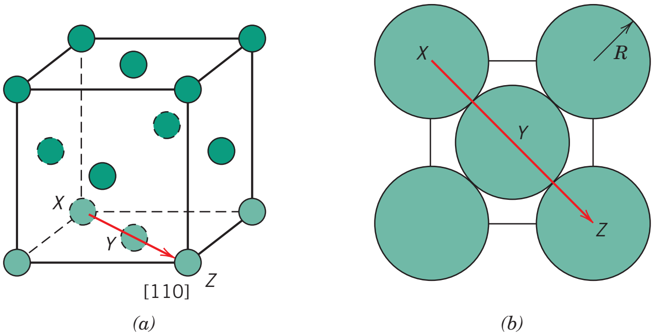


Figure 3.13 (*a*) Reduced-sphere FCC unit cell with the [110] direction indicated. (*b*) The bottom face-plane of the FCC unit cell in (*a*) on which is shown the atomic spacing in the [110] direction, through atoms labeled *X*, *Y*, and *Z*.

Linear density (LD) is defined as the number of atoms per unit length whose centers lie on the direction vector for a specific crystallographic direction; that is,

$$\mathrm{LD} = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}} \tag{3.8}$$

Of course, the units of linear density are reciprocal length (e.g., nm^{-1}, m^{-1}).

For example, let us determine the linear density of the [110] direction for the FCC crystal structure. An FCC unit cell (reduced sphere) and the [110] direction therein are shown in Figure 3.13*a*. Represented in Figure 3.13*b* are the five atoms that lie on the bottom face of this unit cell; here the [110] direction vector passes from the center of atom *X*, through atom *Y*, and finally to the center of atom *Z*. With regard to the numbers of atoms, it is necessary to take into account the sharing of atoms with adjacent unit cells (as discussed in Section 3.4 relative to atomic packing factor computations). Each of the *X* and *Z* corner atoms is also shared with one other adjacent unit cell along this [110] direction (i.e., one-half of each of these atoms belongs to the unit cell being considered), while atom *Y* lies entirely within the unit cell. Thus, there is an equivalence of two atoms along the [110] direction vector in the unit cell. Now, the direction vector length is equal to $4R$ (Figure 3.13*b*); thus, from Equation 3.8, the [110] linear density for FCC is

$$\mathrm{LD}_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R} \tag{3.9}$$

In an analogous manner, planar density (PD) is taken as the number of atoms per unit area that are centered on a particular crystallographic plane, or

$$\mathrm{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}} \tag{3.10}$$

The units for planar density are reciprocal area (e.g., nm^{-2}, m^{-2}).

For example, consider the section of a (110) plane within an FCC unit cell as represented in Figures 3.11*a* and 3.11*b*. Although six atoms have centers that lie on this plane (Figure 3.11*b*), only one-quarter of each of atoms *A*, *C*, *D*, and *F*, and one-half of atoms *B* and *E*, for a total equivalence of just 2 atoms, are on that plane. Furthermore, the area of this rectangular section is equal to the product of its length and width. From Figure 3.11*b*, the length (horizontal dimension) is equal to $4R$, whereas the width (vertical dimension) is equal to $2R\sqrt{2}$, because it corresponds to the FCC unit cell edge length (Equation 3.1). Thus, the area of this planar region is $(4R)(2R\sqrt{2}) = 8R^2\sqrt{2}$, and the planar density is determined as follows:

$$PD_{110} = \frac{2 \text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}} \qquad (3.11)$$

Linear and planar densities are important considerations relative to the process of slip—that is, the mechanism by which metals plastically deform (Section 7.4). Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing.

3.12 CLOSE-PACKED CRYSTAL STRUCTURES

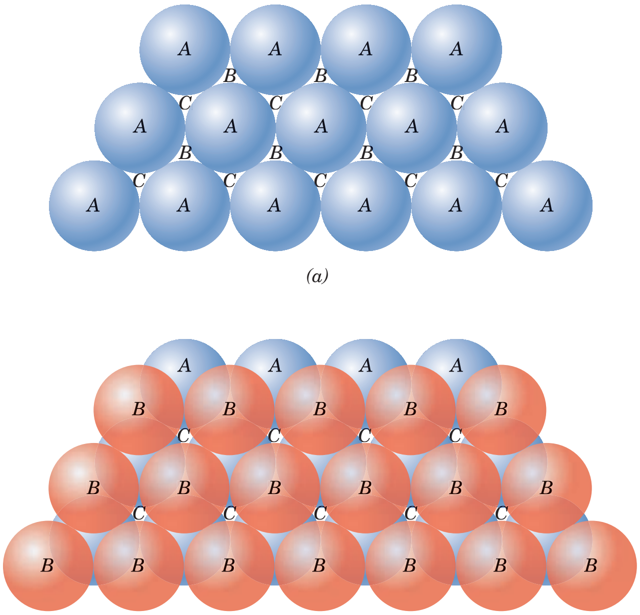
VMSE

Close-Packed Structures (Metals)

You may remember from the discussion on metallic crystal structures that both face-centered cubic and hexagonal close-packed crystal structures have atomic packing factors of 0.74, which is the most efficient packing of equal-sized spheres or atoms. In addition to unit cell representations, these two crystal structures may be described in terms of close-packed planes of atoms (i.e., planes having a maximum atom or sphere-packing density); a portion of one such plane is illustrated in Figure 3.14*a*. Both crystal structures may be generated by the stacking of these close-packed planes on top of one another; the difference between the two structures lies in the stacking sequence.

Let the centers of all the atoms in one close-packed plane be labeled *A*. Associated with this plane are two sets of equivalent triangular depressions formed by three adjacent atoms, into which the next close-packed plane of atoms may rest. Those having the triangle vertex pointing up are arbitrarily designated as *B* positions, while the remaining depressions are those with the down vertices, which are marked *C* in Figure 3.14*a*.

A second close-packed plane may be positioned with the centers of its atoms over either *B* or *C* sites; at this point both are equivalent. Suppose that the *B* positions are arbitrarily chosen; the stacking sequence is termed *AB*, which is



(*a*)

(*b*)

Figure 3.14 (*a*) A portion of a close-packed plane of atoms; *A*, *B*, and *C* positions are indicated. (*b*) The *AB* stacking sequence for close-packed atomic planes. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 50. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

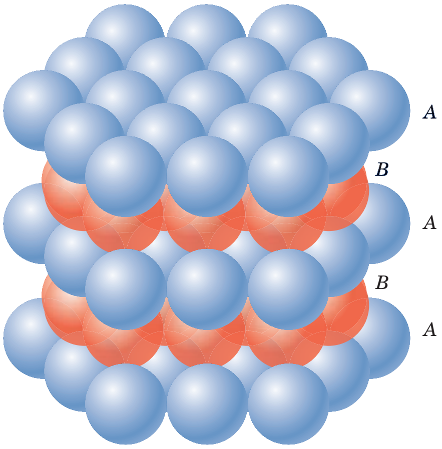


Figure 3.15 Close-packed plane stacking sequence for hexagonal close-packed. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

illustrated in Figure 3.14*b*. The real distinction between FCC and HCP lies in where the third close-packed layer is positioned. For HCP, the centers of this layer are aligned directly above the original *A* positions. This stacking sequence, *ABABAB* . . . , is repeated over and over. Of course, the *ACACAC* . . . arrangement would be equivalent. These close-packed planes for HCP are (0001)-type planes, and the correspondence between this and the unit cell representation is shown in Figure 3.15.

For the face-centered crystal structure, the centers of the third plane are situated over the *C* sites of the first plane (Figure 3.16*a*). This yields an *ABCABCABC* . . . stacking sequence; that is, the atomic alignment repeats every third plane. It is more difficult to correlate the stacking of close-packed planes to the FCC unit cell. However, this relationship is demonstrated in Figure 3.16*b*. These planes are of the (111) type; an FCC unit cell is outlined on the upper left-hand front face of Figure 3.16*b*,

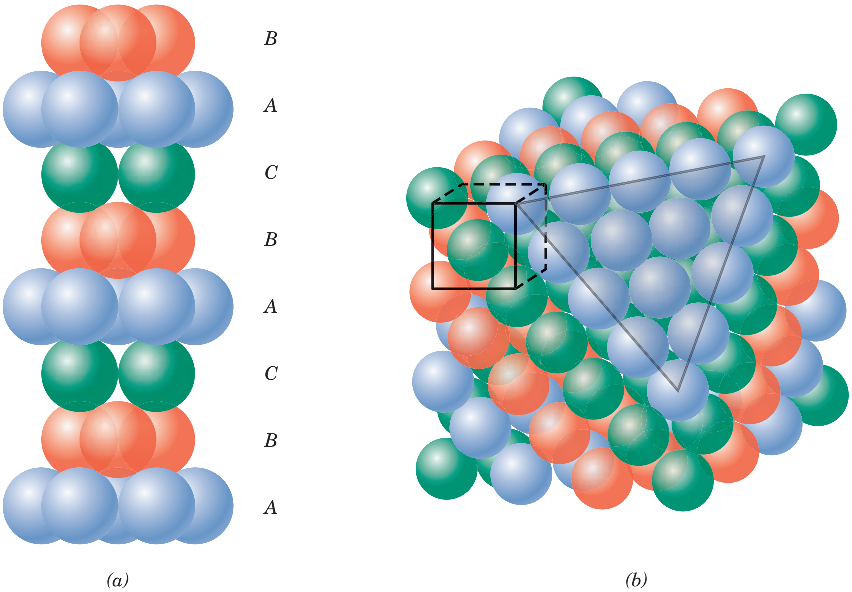


Figure 3.16 (*a*) Close-packed stacking sequence for face-centered cubic. (*b*) A corner has been removed to show the relation between the stacking of close-packed planes of atoms and the FCC crystal structure; the heavy triangle outlines a (111) plane. [Figure (*b*) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

in order to provide a perspective. The significance of these FCC and HCP close-packed planes will become apparent in Chapter 7.

The concepts detailed in the previous four sections also relate to crystalline ceramic and polymeric materials, which are discussed in Chapters 12 and 14. We may specify crystallographic planes and directions in terms of directional and Miller indices; furthermore, on occasion it is important to ascertain the atomic and ionic arrangements of particular crystallographic planes. Also, the crystal structures of a number of ceramic materials may be generated by the stacking of close-packed planes of ions (Section 12.2).

Crystalline and Noncrystalline Materials

3.13 SINGLE CRYSTALS

single crystal

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a **single crystal.** All unit cells interlock in the same way and have the same orientation. Single crystals exist in nature, but they may also be produced artificially. They are ordinarily difficult to grow, because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces, as with some of the gemstones; the shape is indicative of the crystal structure. A photograph of a garnet single crystal is shown in Figure 3.17. Within the past few years, single crystals have become extremely important in many of our modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

3.14 POLYCRYSTALLINE MATERIALS

grain

polycrystalline

Most crystalline solids are composed of a collection of many small crystals or **grains;** such materials are termed **polycrystalline.** Various stages in the solidification of a polycrystalline specimen are represented schematically in Figure 3.18. Initially, small crystals or nuclei form at various positions. These have random crystallographic

Figure 3.17 Photograph of a garnet single crystal that was found in Tongbei, Fujian Province, China. (Photograph courtesy of Irocks.com, Megan Foreman photo.)

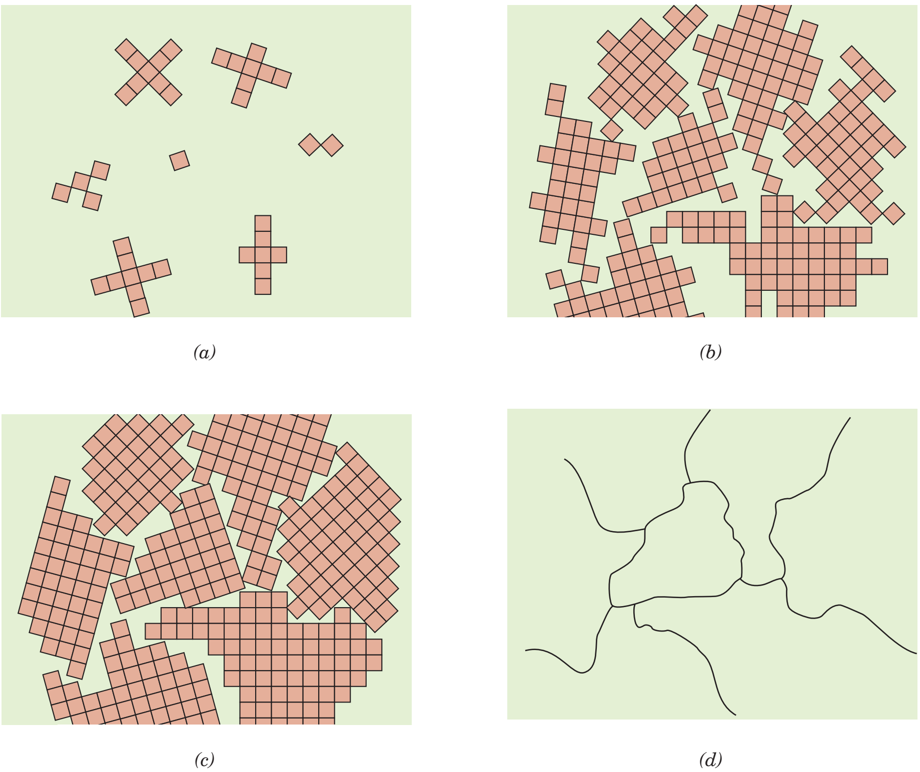


Figure 3.18 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy,* 2nd edition, Constable & Company Ltd., London, 1915.)

orientations, as indicated by the square grids. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremities of adjacent grains impinge on one another as the solidification process approaches completion. As indicated in Figure 3.18, the crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary,** is discussed in more detail in Section 4.6.

grain boundary

3.15 ANISOTROPY

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. This directionality of properties is termed **anisotropy,** and it is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of measurement are **isotropic.** The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry—triclinic structures normally are highly anisotropic. The modulus of elasticity values at [100], [110], and [111] orientations for several materials are presented in Table 3.3.

anisotropy

isotropic

Table 3.3 Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

	Modulus of Elasticity (GPa)		
Metal	**[*100*]**	**[*110*]**	**[*111*]**
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials,* 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

For many polycrystalline materials, the crystallographic orientations of the individual grains are totally random. Under these circumstances, even though each grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically. Also, the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation, in which case the material is said to have a "texture."

The magnetic properties of some iron alloys used in transformer cores are anisotropic—that is, grains (or single crystals) magnetize in a $\langle 100 \rangle$-type direction easier than any other crystallographic direction. Energy losses in transformer cores are minimized by utilizing polycrystalline sheets of these alloys into which have been introduced a "magnetic texture": most of the grains in each sheet have a $\langle 100 \rangle$-type crystallographic direction that is aligned (or almost aligned) in the same direction, which is oriented parallel to the direction of the applied magnetic field. Magnetic textures for iron alloys are discussed in detail in the Material of Importance box in Chapter 20 following Section 20.9.

3.16 X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

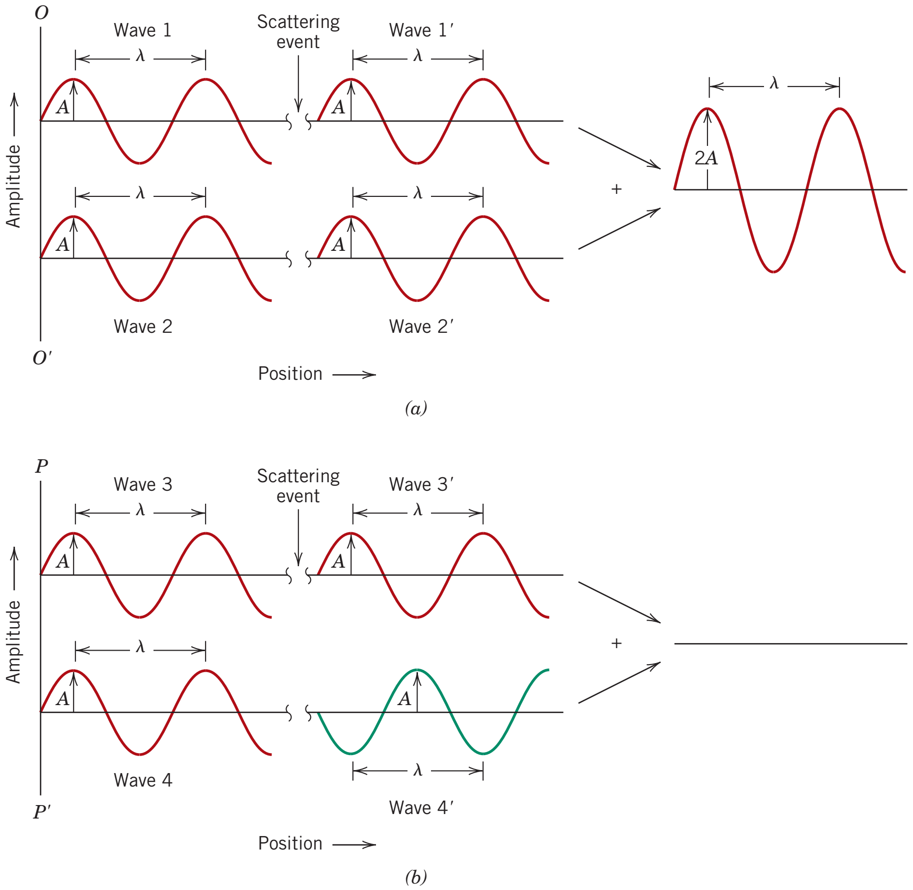
Historically, much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials. We will now give a brief overview of the diffraction phenomenon and how, using x-rays, atomic interplanar distances and crystal structures are deduced.

The Diffraction Phenomenon

Diffraction occurs when a wave encounters a series of regularly spaced obstacles that (1) are capable of scattering the wave, and (2) have spacings that are comparable in magnitude to the wavelength. Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles.

Consider waves 1 and 2 in Figure 3.19*a*, which have the same wavelength (λ) and are in phase at point O–O'. Now let us suppose that both waves are scattered in such a way that they traverse different paths. The phase relationship between the scattered waves, which will depend upon the difference in path length, is important. One possibility results when this path length difference is an integral number of wavelengths. As noted in Figure 3.19*a*, these scattered waves (now labeled 1′ and 2′)

Figure 3.19 (*a*) Demonstration of how two waves (labeled 1 and 2) that have the same wavelength λ and remain in phase after a scattering event (waves 1′ and 2′) constructively interfere with one another. The amplitudes of the scattered waves add together in the resultant wave. (*b*) Demonstration of how two waves (labeled 3 and 4) that have the same wavelength and become out of phase after a scattering event (waves 3′ and 4′) destructively interfere with one another. The amplitudes of the two scattered waves cancel one another.



are still in phase. They are said to mutually reinforce (or constructively interfere with) one another; and, when amplitudes are added, the wave shown on the right side of the figure results. This is a manifestation of **diffraction,** and we refer to a diffracted beam as one composed of a large number of scattered waves that mutually reinforce one another.

diffraction

Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement. The other extreme is that demonstrated in Figure 3.19*b*, wherein the path length difference after scattering is some integral number of *half*-wavelengths. The scattered waves are out of phase—that is, corresponding amplitudes cancel or annul one another, or destructively interfere (i.e., the resultant wave has zero amplitude), as indicated on the right side of the figure. Of course, phase relationships intermediate between these two extremes exist, resulting in only partial reinforcement.

X-Ray Diffraction and Bragg's Law

X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids. When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Let us now examine the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

Consider the two parallel planes of atoms A–A' and B–B' in Figure 3.20, which have the same h, k, and l Miller indices and are separated by the interplanar spacing d_{hkl}. Now assume that a parallel, monochromatic, and coherent (in-phase)

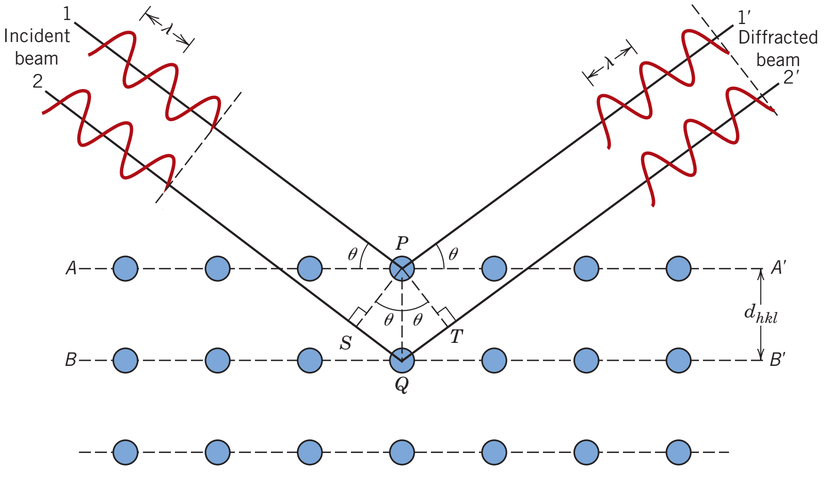


Figure 3.20 Diffraction of x-rays by planes of atoms (A–A' and B–B').

beam of x-rays of wavelength λ is incident on these two planes at an angle θ. Two rays in this beam, labeled 1 and 2, are scattered by atoms P and Q. Constructive interference of the scattered rays 1′ and 2′ occurs also at an angle θ to the planes, if the path length difference between $1-P-1'$ and 2–Q–$2'$ (i.e., $\overline{SQ} + \overline{QT}$) is equal to a whole number, n, of wavelengths. That is, the condition for diffraction is

Bragg's law—relationship among x-ray wavelength, interatomic spacing, and angle of diffraction for constructive interference

$$n\lambda = \overline{SQ} + \overline{QT} \tag{3.12}$$

or

$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta$$

$$= 2d_{hkl}\sin\theta \tag{3.13}$$

Bragg's law

Equation 3.13 is known as **Bragg's law;** also, n is the order of reflection, which may be any integer (1, 2, 3, . . .) consistent with sin θ not exceeding unity. Thus, we have a simple expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam. If Bragg's law is not satisfied, then the interference will be nonconstructive in nature so as to yield a very low-intensity diffracted beam.

The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing d_{hkl}) is a function of the Miller indices (h, k, and l) as well as the lattice parameter(s). For example, for crystal structures that have cubic symmetry,

Interplanar spacing for a plane having indices h, k, and l

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{3.14}$$

in which a is the lattice parameter (unit cell edge length). Relationships similar to Equation 3.14, but more complex, exist for the other six crystal systems noted in Table 3.2.

Bragg's law, Equation 3.13, is a necessary but not sufficient condition for diffraction by real crystals. It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners. However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centers, which can produce out-of-phase scattering at certain Bragg angles. The net result is the absence of some diffracted beams that, according to Equation 3.13, should be present. For example, for the BCC crystal structure, $h + k + l$ must be even if diffraction is to occur, whereas for FCC, h, k, and l must all be either odd or even.

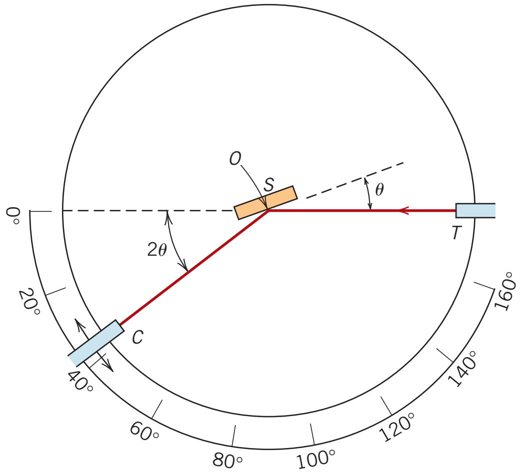


Figure 3.21 Schematic diagram of an x-ray diffractometer; T = x-ray source, S = specimen, C = detector, and O = the axis around which the specimen and detector rotate.

Concept Check 3.2

For cubic crystals, as values of the planar indices h, k, and l increase, does the distance between adjacent and parallel planes (i.e., the interplanar spacing) increase or decrease? Why?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

Diffraction Techniques

One common diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to monochromatic x-radiation. Each powder particle (or grain) is a crystal, and having a large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

The *diffractometer* is an apparatus used to determine the angles at which diffraction occurs for powdered specimens; its features are represented schematically in Figure 3.21. A specimen S in the form of a flat plate is supported so that rotations about the axis labeled O are possible; this axis is perpendicular to the plane of the page. The monochromatic x-ray beam is generated at point T, and the intensities of diffracted beams are detected with a counter labeled C in the figure. The specimen, x-ray source, and counter are all coplanar.

The counter is mounted on a movable carriage that may also be rotated about the O axis; its angular position in terms of 2θ is marked on a graduated scale.[4] Carriage and specimen are mechanically coupled such that a rotation of the specimen through θ is accompanied by a 2θ rotation of the counter; this ensures that the incident and reflection angles are maintained equal to one another (Figure 3.21). Collimators are incorporated within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam.

As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of 2θ; 2θ is

---

[4] Note that the symbol θ has been used in two different contexts for this discussion. Here, θ represents the angular locations of both x-ray source and counter relative to the specimen surface. Previously (e.g., Equation 3.13), it denoted the angle at which the Bragg criterion for diffraction is satisfied.

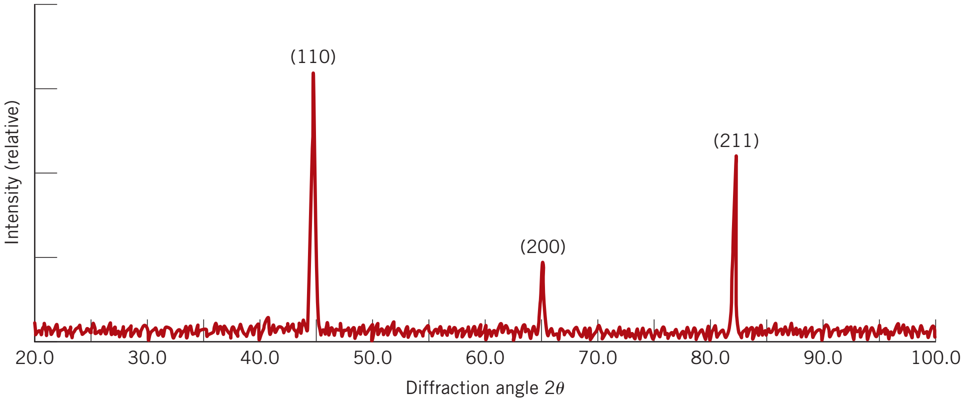


Figure 3.22 Diffraction pattern for polycrystalline α-iron.

termed the *diffraction angle,* which is measured experimentally. Figure 3.22 shows a diffraction pattern for a polycrystalline specimen of α-iron. The high-intensity peaks result when the Bragg diffraction condition is satisfied by some set of crystallographic planes. These peaks are plane-indexed in the figure.

Other powder techniques have been devised wherein diffracted beam intensity and position are recorded on a photographic film instead of being measured by a counter.

One of the primary uses of x-ray diffractometry is for the determination of crystal structure. The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks, whereas arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

X-rays, as well as electron and neutron beams, are also used in other types of material investigations. For example, crystallographic orientations of single crystals are possible using x-ray diffraction (or Laue) photographs. The (*a*) chapter-opening photograph for this chapter was generated using an incident x-ray beam that was directed on a magnesium crystal; each spot (with the exception of the darkest one near the center) resulted from an x-ray beam that was diffracted by a specific set of crystallographic planes. Other uses of x-rays include qualitative and quantitative chemical identifications and the determination of residual stresses and crystal size.

EXAMPLE PROBLEM 3.13

Interplanar Spacing and Diffraction Angle Computations

For BCC iron, compute (a) the interplanar spacing and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Also, assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Solution

(a) The value of the interplanar spacing d_{hkl} is determined using Equation 3.14, with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$, because we are considering the (220) planes. Therefore,

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

$$= \frac{0.2866\text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013\text{ nm}$$

(b) The value of θ may now be computed using Equation 3.13, with $n = 1$, because this is a first-order reflection:

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790\,\text{nm})}{(2)(0.1013\,\text{nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13°$$

The diffraction angle is 2θ, or

$$2\theta = (2)(62.13°) = 124.26°$$

3.17 NONCRYSTALLINE SOLIDS

noncrystalline

amorphous

It has been mentioned that **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called **amorphous** (meaning literally "without form"), or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.

An amorphous condition may be illustrated by comparison of the crystalline and noncrystalline structures of the ceramic compound silicon dioxide (SiO_2), which may exist in both states. Figures 3.23*a* and 3.23*b* present two-dimensional schematic diagrams for both structures of SiO_2. Even though each silicon ion bonds to three oxygen ions for both states, beyond this, the structure is much more disordered and irregular for the noncrystalline structure.

Whether a crystalline or amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. Amorphous materials, therefore, are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty. Furthermore, rapidly cooling through the freezing temperature favors the formation of a noncrystalline solid, because little time is allowed for the ordering process.

Metals normally form crystalline solids, but some ceramic materials are crystalline, whereas others, the inorganic glasses, are amorphous. Polymers may be completely noncrystalline and semicrystalline consisting of varying degrees of crystallinity.

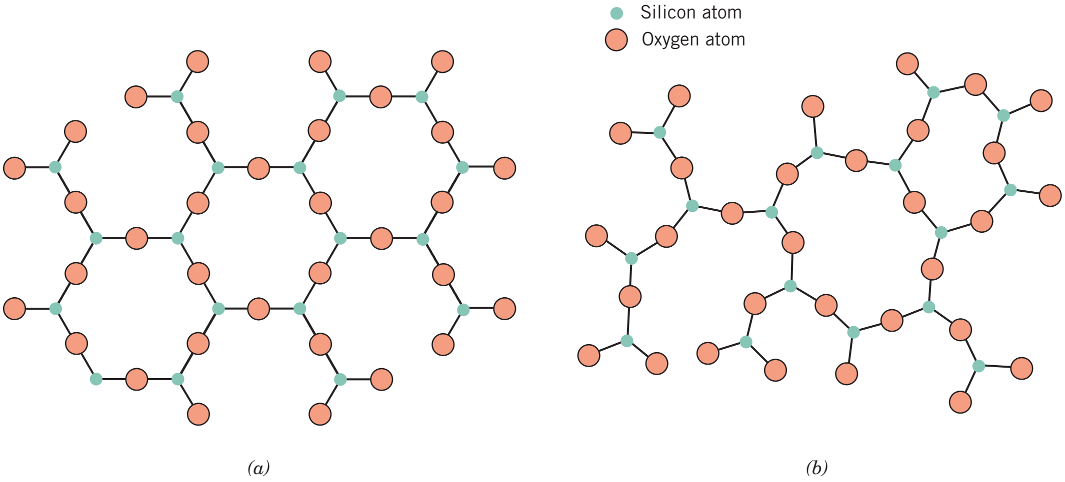


Figure 3.23 Two-dimensional schemes of the structure of (*a*) crystalline silicon dioxide and (*b*) noncrystalline silicon dioxide.

More about the structure and properties of amorphous ceramics and polymers is contained in Chapters 12 and 14.

Concept Check 3.3

Do noncrystalline materials display the phenomenon of allotropy (or polymorphism)? Why or why not?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

SUMMARY

Fundamental Concepts

- Atoms in crystalline solids are positioned in orderly and repeated patterns that are in contrast to the random and disordered atomic distribution found in noncrystalline or amorphous materials.

Unit Cells

- Crystal structures are specified in terms of parallelepiped unit cells, which are characterized by geometry and atom positions within.

Metallic Crystal Structures

- Most common metals exist in at least one of three relatively simple crystal structures:
  - Face-centered cubic (FCC), which has a cubic unit cell (Figure 3.1).
  - Body-centered cubic (BCC), which also has a cubic unit cell (Figure 3.2).
  - Hexagonal close-packed, which has a unit cell of hexagonal symmetry, [Figure 3.3(*a*)].
- Unit cell edge length (a) and atomic radius (R) are related according to
  - Equation 3.1 for face-centered cubic, and
  - Equation 3.3 for body-centered cubic.
- Two features of a crystal structure are
  - Coordination number—the number of nearest-neighbor atoms, and
  - Atomic packing factor—the fraction of solid sphere volume in the unit cell.

Density Computations

- The theoretical density of a metal (ρ) is a function of the number of equivalent atoms per unit cell, the atomic weight, unit cell volume, and Avogadro's number (Equation 3.5).

Polymorphism and Allotropy

- Polymorphism is when a specific material can have more than one crystal structure. Allotropy is polymorphism for elemental solids.

Crystal Systems

- The concept of crystal system is used to classify crystal structures on the basis of unit cell geometry—that is, unit cell edge lengths and interaxial angles. There are seven crystal systems: cubic, tetragonal, hexagonal, orthorhombic, rhombohedral (trigonal), monoclinic, and triclinic.

Point Coordinates
Crystallographic Directions
Crystallographic Planes

- Crystallographic points, directions, and planes are specified in terms of indexing schemes. The basis for the determination of each index is a coordinate axis system defined by the unit cell for the particular crystal structure.
    - The location of a point within a unit cell is specified using coordinates that are fractional multiples of the cell edge lengths.
    - Directional indices are computed in terms of the vector projection on each of the coordinate axes.
    - Planar (or Miller) indices are determined from the reciprocals of axial intercepts.
- For hexagonal unit cells, a four-index scheme for both directions and planes is found to be more convenient.

Linear and Planar Densities

- Crystallographic directional and planar equivalencies are related to atomic linear and planar densities, respectively.
    - Linear density (for a specific crystallographic direction) is defined as the number of atoms per unit length whose centers lie on the vector for this direction (Equation 3.8).
    - Planar density (for a specific crystallographic plane) is taken as the number of atoms per unit area that are centered on the particular plane (Equation 3.10).
- For a given crystal structure, planes having identical atomic packing yet different Miller indices belong to the same family.

Close-Packed Crystal Structures

- Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes of atoms on top of one another. With this scheme A, B, and C denote possible atom positions on a close-packed plane.
    - The stacking sequence for HCP is $ABABAB$. . . .
    - For FCC the stacking sequence is $ABCABCABC$. . . .
- Close-packed planes for FCC and HCP are {111} and {0001}, respectively.

Single Crystals
Polycrystalline Materials

- Single crystals are materials in which the atomic order extends uninterrupted over the entirety of the specimen; under some circumstances, single crystals may have flat faces and regular geometric shapes.
- The vast majority of crystalline solids, however, are polycrystalline, being composed of many small crystals or grains having different crystallographic orientations.
- A grain boundary is the boundary region separating two grains, wherein there is some atomic mismatch.

Anisotropy

- Anisotropy is the directionality dependence of properties. For isotropic materials, properties are independent of the direction of measurement.

X-Ray Diffraction: Determination of Crystal Structures

- X-ray diffractometry is used for crystal structure and interplanar spacing determinations. A beam of x-rays directed on a crystalline material may experience diffraction (constructive interference) as a result of its interaction with a series of parallel atomic planes.

- Bragg's law specifies the condition for diffraction of x-rays—Equation 3.13.

Noncrystalline Solids

- Noncrystalline solid materials lack a systematic and regular arrangement of atoms or ions over relatively large distances (on an atomic scale). Sometimes the term *amorphous* is also used to describe these materials.

Equation Summary

Equation Number	*Equation*	*Solving for*	*Page Number*
3.1	$a = 2R\sqrt{2}$	Unit cell edge length, FCC	48
3.2	$\text{APF} = \dfrac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \dfrac{V_S}{V_C}$	Atomic packing factor	48
3.3	$a = \dfrac{4R}{\sqrt{3}}$	Unit cell edge length, BCC	48
3.5	$\rho = \dfrac{nA}{V_C N_A}$	Theoretical density of a metal	51
3.8	$\text{LD} = \dfrac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$	Linear density	68
3.10	$\text{PD} = \dfrac{\text{number of atoms centered on a plane}}{\text{area of plane}}$	Planar density	69
3.13	$n\lambda = 2d_{hkl}\sin\theta$	Bragg's law; wavelength–interplanar spacing–angle of diffracted beam	76
3.14	$d_{hkl} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$	Interplanar spacing for crystals having cubic symmetry	76

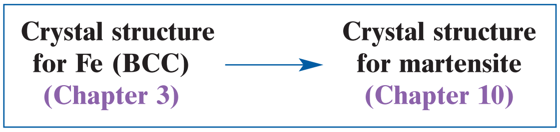
List of Symbols

Symbol	*Meaning*
a	Unit cell edge length for cubic; unit cell x-axial length
A	Atomic weight
d_{hkl}	Interplanar spacing for crystallographic planes having indices h, k, and l
n	Order of reflection for x-ray diffraction
n	Number of atoms associated with a unit cell
N_A	Avogadro's number (6.022×10^{23} atoms/mol)
R	Atomic radius
V_C	Unit cell volume
λ	X-ray wavelength
ρ	Density; theoretical density

Processing/Structure/Properties/Performance Summary

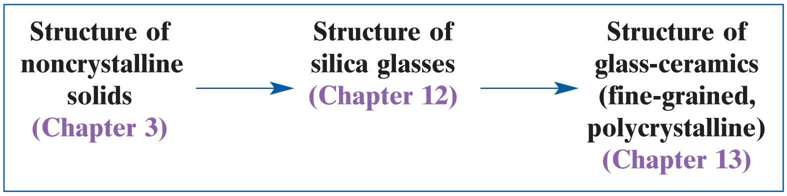
In this chapter we discussed crystal structure, the body-centered cubic crystal structure, and the ability of a metal to experience a change in its crystal structure (polymorphism). A knowledge of these concepts helps us understand the transformation of BCC iron to martensite (which has another crystal structure) in Chapter 10. This relationship is represented by the following diagram:

Iron (Steels)
(Structure)



Also discussed was the notion of a noncrystalline material. Glass-ceramics (Chapter 13) are formed as noncrystalline silica glasses (Chapter 12), which are then heat-treated so as to become crystalline in nature. The following diagram notes this relationship.

Glass-Ceramics
(Structure)



Important Terms and Concepts

allotropy
amorphous
anisotropy
atomic packing factor (APF)
body-centered cubic (BCC)
Bragg's law
coordination number
crystalline
crystal structure
crystal system
diffraction
face-centered cubic (FCC)
grain
grain boundary
hexagonal close-packed (HCP)
isotropic
lattice
lattice parameters
Miller indices
noncrystalline
polycrystalline
polymorphism
single crystal
unit cell

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QUESTIONS AND PROBLEMS

Fundamental Concepts

3.1 What is the difference between atomic structure and crystal structure?

Unit Cells

Metallic Crystal Structures

3.2 If the atomic radius of aluminum is 0.143 nm, calculate the volume of its unit cell in cubic meters.

3.3 Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius R are related through $a = 4R/\sqrt{3}$.

3.4 For the HCP crystal structure, show that the ideal c/a ratio is 1.633.

3.5 Show that the atomic packing factor for BCC is 0.68.

3.6 Show that the atomic packing factor for HCP is 0.74.

Density Computations

3.7 Iron has a BCC crystal structure, an atomic radius of 0.124 nm, and an atomic weight of 55.85 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover.

3.8 Calculate the radius of an iridium atom, given that Ir has an FCC crystal structure, a density of 22.4 g/cm^3, and an atomic weight of 192.2 g/mol.

3.9 Calculate the radius of a vanadium atom, given that V has a BCC crystal structure, a density of 5.96 g/cm^3, and an atomic weight of 50.9 g/mol.

3.10 A hypothetical metal has the simple cubic crystal structure shown in Figure 3.24. If its atomic weight is 70.4 g/mol and the atomic radius is 0.126 nm, compute its density.

3.11 Zirconium has an HCP crystal structure and a density of 6.51 g/cm^3.

(a) What is the volume of its unit cell in cubic meters?

(b) If the c/a ratio is 1.593, compute the values of c and a.

3.12 Using atomic weight, crystal structure, and atomic radius data tabulated inside the front cover, compute the theoretical densities of lead, chromium, copper, and cobalt, and then compare these values with the measured densities listed in this same table. The c/a ratio for cobalt is 1.623.

3.13 Rhodium has an atomic radius of 0.1345 nm and a density of 12.41 g/cm^3. Determine whether it has an FCC or BCC crystal structure.

3.14 The atomic weight, density, and atomic radius for three hypothetical alloys are listed in the following table. For each, determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination. A simple cubic unit cell is shown in Figure 3.24.

Alloy	*Atomic Weight (g/mol)*	*Density (g/cm^3)*	*Atomic Radius (nm)*
A	77.4	8.22	0.125
B	107.6	13.42	0.133
C	127.3	9.23	0.142

3.15 The unit cell for tin has tetragonal symmetry, with a and b lattice parameters of 0.583 and 0.318 nm, respectively. If its density, atomic weight, and atomic radius are 7.27 g/cm^3,

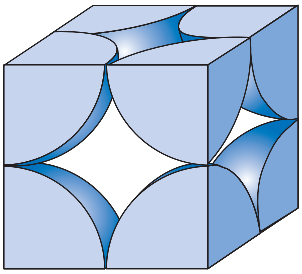
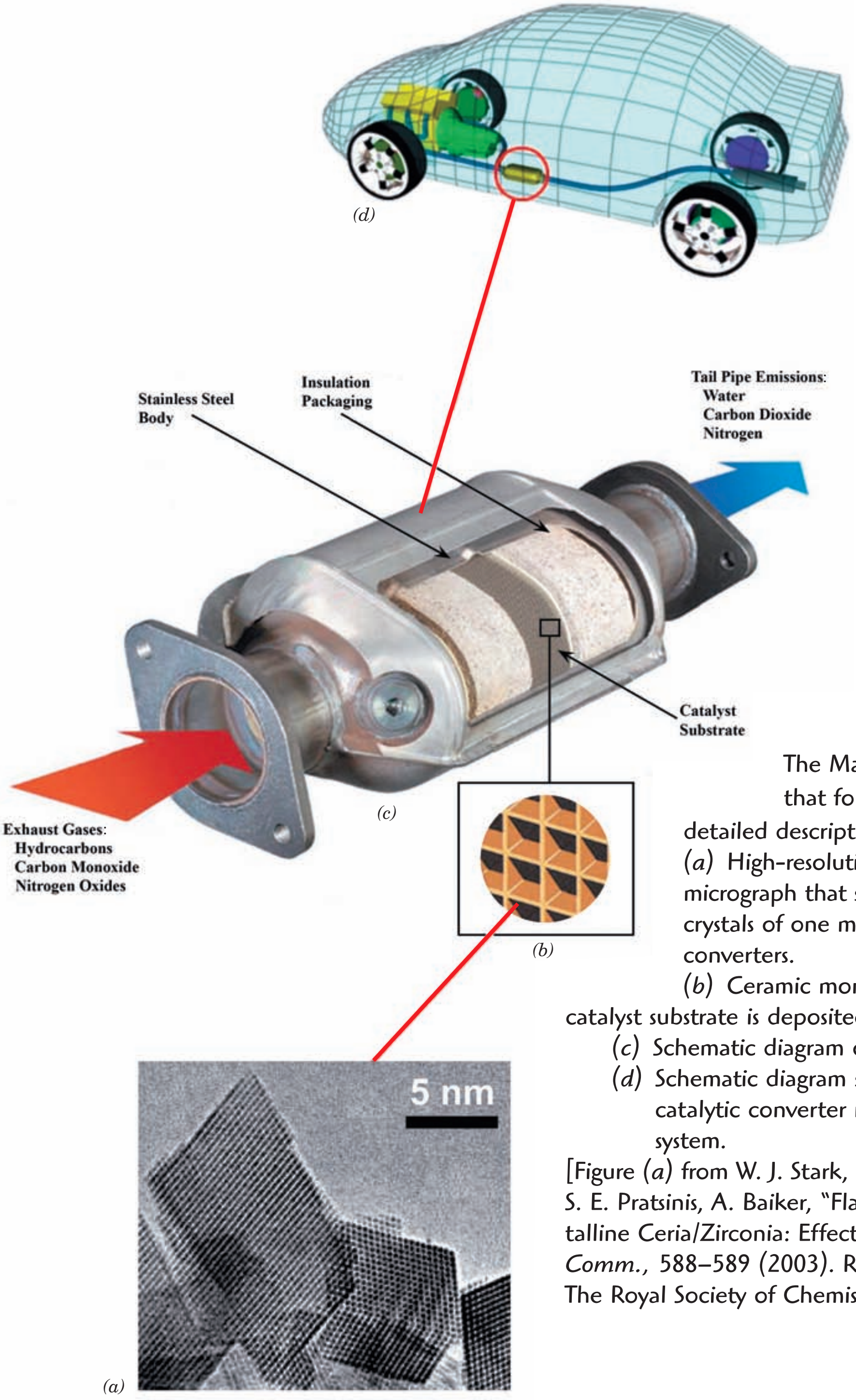


Figure 3.24 Hard-sphere unit cell representation of the simple cubic crystal structure.

Chapter 4 Imperfections in Solids



Atomic defects are responsible for reductions of gas pollutant emissions from today's automobile engines. A catalytic converter is the pollutant-reducing device that is located in the automobile's exhaust system. Molecules of pollutant gases become attached to surface defects of crystalline metallic materials found in the catalytic converter. While attached to these sites, the molecules experience chemical reactions that convert them into other non- or less-polluting substances. The Materials of Importance box that follows Section 4.6 contains a detailed description of this process.

(*a*) High-resolution transmission electron micrograph that shows surface defects on single crystals of one material that is used in catalytic converters.

(*b*) Ceramic monolith on which the metallic catalyst substrate is deposited.

(*c*) Schematic diagram of a catalytic converter.

(*d*) Schematic diagram showing the location of the catalytic converter in an automobile's exhaust system.

[Figure (*a*) from W. J. Stark, L. Mädler, M. Maciejewski, S. E. Pratsinis, A. Baiker, "Flame-Synthesis of Nanocrystalline Ceria/Zirconia: Effect of Carrier Liquid," *Chem. Comm.*, 588–589 (2003). Reproduced by permission of The Royal Society of Chemistry.]

WHY STUDY *Imperfections in Solids?*

The properties of some materials are profoundly influenced by the presence of imperfections. Consequently, it is important to have a knowledge about the types of imperfections that exist and the roles they play in affecting the behavior of materials. For example, the mechanical properties of pure metals experience significant alterations when alloyed (i.e., when impurity atoms are added)—for example, brass (70% copper/30% zinc) is much harder and stronger than pure copper (Section 7.9).

Also, integrated-circuit microelectronic devices found in our computers, calculators, and home appliances function because of highly controlled concentrations of specific impurities that are incorporated into small, localized regions of semiconducting materials (Sections 18.11 and 18.15).

In the processing/structure/properties/performance scheme, reasons for studying imperfections in solids are as follows:

- For the processing of silicon as a semiconducting material, it is important to specify impurity concentration in appropriate units.
- Development of the desirable mechanical properties for steel alloys relies on the presence of specific impurities, some of which form solid solutions. Thus, an understanding of the concept of a solid solution is important.
- The mechanisms of hardening and strengthening for steel alloys involve a crystalline defect called a dislocation. In this chapter we discuss the dislocation concept and the different types.

Learning Objectives

After studying this chapter you should be able to do the following:

1. **Describe both vacancy and self-interstitial crystalline defects.**
2. **Calculate the equilibrium number of vacancies in a material at some specified temperature, given the relevant constants.**
3. **Name the two types of solid solutions and provide a brief written definition and/or schematic sketch of each.**
4. **Given the masses and atomic weights of two or more elements in a metal alloy, calculate the weight percent and atom percent for each element.**
5. **For each of edge, screw, and mixed dislocations:**
   - **(a) describe and make a drawing of the dislocation,**
   - **(b) note the location of the dislocation line, and**
   - **(c) indicate the direction along which the dislocation line extends.**
6. **Describe the atomic structure within the vicinity of (a) a grain boundary and (b) a twin boundary.**

4.1 INTRODUCTION

imperfection

Thus far it has been tacitly assumed that perfect order exists throughout crystalline materials on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various defects or **imperfections.** As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection; the influence is not always adverse, and often specific characteristics are deliberately fashioned by the introduction of controlled amounts or numbers of particular defects, as detailed in succeeding chapters.

Crystalline defect refers to a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to geometry or dimensionality of the defect.

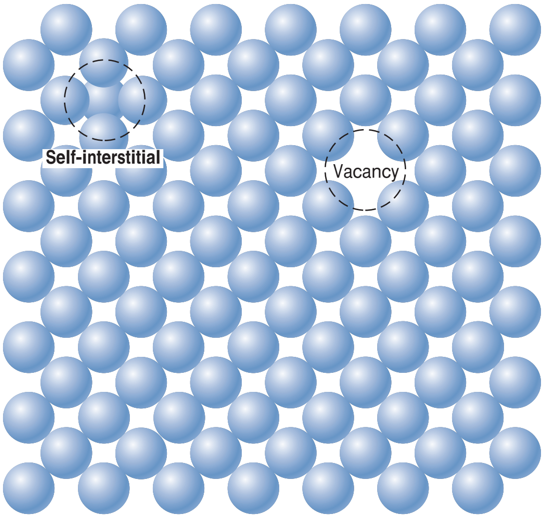


Figure 4.1 Two-dimensional representations of a vacancy and a self-interstitial. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

point defect

Several different imperfections are discussed in this chapter, including **point defects** (those associated with one or two atomic positions), linear (or one-dimensional) defects, and interfacial defects, or boundaries, which are two-dimensional. Impurities in solids are also discussed, because impurity atoms may exist as point defects. Finally, techniques for the microscopic examination of defects and the structure of materials are briefly described.

Point Defects

4.2 VACANCIES AND SELF-INTERSTITIALS

vacancy

The simplest of the point defects is a **vacancy,** or vacant lattice site, one normally occupied from which an atom is missing (Figure 4.1). All crystalline solids contain vacancies and, in fact, it is not possible to create such a material that is free of these defects. The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal.

The equilibrium number of vacancies N_v for a given quantity of material depends on and increases with temperature according to

Temperature dependence of the equilibrium number of vacancies

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) \tag{4.1}$$

Boltzmann's constant

In this expression, N is the total number of atomic sites, Q_v is the energy required for the formation of a vacancy, T is the absolute temperature[1] in kelvins, and k is the gas or **Boltzmann's constant.** The value of k is 1.38×10^{-23} J/atom · K, or 8.62×10^{-5} eV/atom · K, depending on the units of Q_v.[2] Thus, the number of vacancies

---

[1] Absolute temperature in kelvins (K) is equal to °C + 273.

[2] Boltzmann's constant per mole of atoms becomes the gas constant R; in such a case R = 8.31 J/mol·K.

increases exponentially with temperature; that is, as T in Equation 4.1 increases, so also does the expression exp $-(Q_v/kT)$. For most metals, the fraction of vacancies N_v/N just below the melting temperature is on the order of 10^{-4}; that is, one lattice site out of 10,000 will be empty. As ensuing discussions indicate, a number of other material parameters have an exponential dependence on temperature similar to that of Equation 4.1.

self-interstitial

A **self-interstitial** is an atom from the crystal that is crowded into an interstitial site, a small void space that under ordinary circumstances is not occupied. This kind of defect is also represented in Figure 4.1. In metals, a self-interstitial introduces relatively large distortions in the surrounding lattice because the atom is substantially larger than the interstitial position in which it is situated. Consequently, the formation of this defect is not highly probable, and it exists in very small concentrations, which are significantly lower than for vacancies.

EXAMPLE PROBLEM 4.1

Number-of-Vacancies Computation at a Specified Temperature

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.4 g/cm^3, respectively.

Solution

This problem may be solved by using Equation 4.1; it is first necessary, however, to determine the value of N, the number of atomic sites per cubic meter for copper, from its atomic weight A_{Cu}, its density ρ, and Avogadro's number N_{A}, according to

Number of atoms per unit volume for a metal

$$N = \frac{N_{\mathrm{A}}\rho}{A_{\mathrm{Cu}}} \tag{4.2}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(8.4\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{63.5\ \text{g/mol}}$$

$$= 8.0 \times 10^{28}\ \text{atoms/m}^3$$

Thus, the number of vacancies at 1000°C (1273 K) is equal to

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right)$$

$$= (8.0 \times 10^{28}\ \text{atoms/m}^3)\exp\left[-\frac{(0.9\ \text{eV})}{(8.62 \times 10^{-5}\ \text{eV/K})(1273\ \text{K})}\right]$$

$$= 2.2 \times 10^{25}\ \text{vacancies/m}^3$$

4.3 IMPURITIES IN SOLIDS

A pure metal consisting of only one type of atom just isn't possible; impurity or foreign atoms will always be present, and some will exist as crystalline point defects. In fact, even with relatively sophisticated techniques, it is difficult to refine metals to a purity in excess of 99.9999%. At this level, on the order of 10^{22} to 10^{23} impurity atoms will be present in one cubic meter of material. Most familiar metals are

alloy

not highly pure; rather, they are **alloys,** in which impurity atoms have been added intentionally to impart specific characteristics to the material. Ordinarily, alloying is used in metals to improve mechanical strength and corrosion resistance. For example, sterling silver is a 92.5% silver/7.5% copper alloy. In normal ambient environments, pure silver is highly corrosion resistant, but also very soft. Alloying with copper significantly enhances the mechanical strength without depreciating the corrosion resistance appreciably.

solid solution

The addition of impurity atoms to a metal will result in the formation of a **solid solution** and/or a new *second phase,* depending on the kinds of impurity, their concentrations, and the temperature of the alloy. The present discussion is concerned with the notion of a solid solution; treatment of the formation of a new phase is deferred to Chapter 9.

solute, solvent

Several terms relating to impurities and solid solutions deserve mention. With regard to alloys, **solute** and **solvent** are terms that are commonly employed. *Solvent* represents the element or compound that is present in the greatest amount; on occasion, solvent atoms are also called *host atoms*. Solute is used to denote an element or compound present in a minor concentration.

Solid Solutions

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained and no new structures are formed. Perhaps it is useful to draw an analogy with a liquid solution. If two liquids, soluble in each other (such as water and alcohol) are combined, a liquid solution is produced as the molecules intermix, and its composition is homogeneous throughout. A solid solution is also compositionally homogeneous; the impurity atoms are randomly and uniformly dispersed within the solid.

substitutional solid solution

interstitial solid solution

Impurity point defects are found in solid solutions, of which there are two types: **substitutional** and **interstitial.** For the substitutional type, solute or impurity atoms replace or substitute for the host atoms (Figure 4.2). Several features of the solute and solvent atoms determine the degree to which the former dissolves in the latter, as follows:

1. *Atomic size factor*. Appreciable quantities of a solute may be accommodated in this type of solid solution only when the difference in atomic radii between the two atom types is less than about ±15% Otherwise the solute atoms will create substantial lattice distortions and a new phase will form.

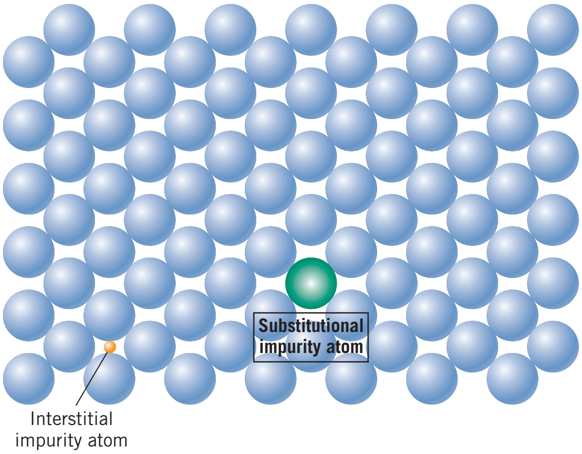


Figure 4.2 Two-dimensional schematic representations of substitutional and interstitial impurity atoms. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

2. *Crystal structure*. For appreciable solid solubility the crystal structures for metals of both atom types must be the same.
3. *Electronegativity*. The more electropositive one element and the more electronegative the other, the greater the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
4. *Valences*. Other factors being equal, a metal will have more of a tendency to dissolve another metal of higher valency than one of a lower valency.

An example of a substitutional solid solution is found for copper and nickel. These two elements are completely soluble in one another at all proportions. With regard to the aforementioned rules that govern degree of solubility, the atomic radii for copper and nickel are 0.128 and 0.125 nm, respectively; both have the FCC crystal structure; and their electronegativities are 1.9 and 1.8 (Figure 2.7); finally, the most common valences are +1 for copper (although it sometimes can be +2) and +2 for nickel.

For interstitial solid solutions, impurity atoms fill the voids or interstices among the host atoms (see Figure 4.2). For metallic materials that have relatively high atomic packing factors, these interstitial positions are relatively small. Consequently, the atomic diameter of an interstitial impurity must be substantially smaller than that of the host atoms. Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%). Even very small impurity atoms are ordinarily larger than the interstitial sites, and as a consequence they introduce some lattice strains on the adjacent host atoms. Problem 4.5 calls for determination of the radii of impurity atoms (in terms of R, the host atom radius) that will just fit into interstitial positions without introducing any lattice strains for both FCC and BCC crystal structures.

Carbon forms an interstitial solid solution when added to iron; the maximum concentration of carbon is about 2%. The atomic radius of the carbon atom is much less than that for iron: 0.071 nm versus 0.124 nm. Solid solutions are also possible for ceramic materials, as discussed in Section 12.5.

4.4 SPECIFICATION OF COMPOSITION

composition

weight percent

It is often necessary to express the **composition** (or *concentration*)[3] of an alloy in terms of its constituent elements. The two most common ways to specify composition are weight (or mass) percent and atom percent. The basis for **weight percent** (wt%) is the weight of a particular element relative to the total alloy weight. For an alloy that contains two hypothetical atoms denoted by 1 and 2, the concentration of 1 in wt%, C_1, is defined as

Computation of weight percent (for a two-element alloy)

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \qquad (4.3)$$

where m_1 and m_2 represent the weight (or mass) of elements 1 and 2, respectively. The concentration of 2 would be computed in an analogous manner.

atom percent

The basis for **atom percent** (at%) calculations is the number of moles of an element in relation to the total moles of the elements in the alloy. The number of

---

[3] The terms *composition* and *concentration* will be assumed to have the same meaning in this book (i.e., the relative content of a specific element or constituent in an alloy) and will be used interchangeably.

moles in some specified mass of a hypothetical element 1, n_{m1}, may be computed as follows:

$$n_{m1} = \frac{m_1'}{A_1} \tag{4.4}$$

Here, m_1' and A_1 denote the mass (in grams) and atomic weight, respectively, for element 1.

Concentration in terms of atom percent of element 1 in an alloy containing element 1 and element 2 atoms, C_1' is defined by[4]

Computation of atom percent (for a two-element alloy)

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \tag{4.5}$$

In like manner, the atom percent of element 2 may be determined.

Atom percent computations also can be carried out on the basis of the number of atoms instead of moles, because one mole of all substances contains the same number of atoms.

Composition Conversions

Sometimes it is necessary to convert from one composition scheme to another—for example, from weight percent to atom percent. We will now present equations for making these conversions in terms of the two hypothetical elements 1 and 2. Using the convention of the previous section (i.e., weight percents denoted by C_1 and C_2, atom percents by C_1' and C_2', and atomic weights as A_1 and A_2), these conversion expressions are as follows:

Conversion of weight percent to atom percent (for a two-element alloy)

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \tag{4.6a}$$

$$C_2' = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100 \tag{4.6b}$$

Conversion of atom percent to weight percent (for a two-element alloy)

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100 \tag{4.7a}$$

$$C_2 = \frac{C_2' A_2}{C_1' A_1 + C_2' A_2} \times 100 \tag{4.7b}$$

Because we are considering only two elements, computations involving the preceding equations are simplified when it is realized that

$$C_1 + C_2 = 100 \tag{4.8a}$$

$$C_1' + C_2' = 100 \tag{4.8b}$$

In addition, it sometimes becomes necessary to convert concentration from weight percent to mass of one component per unit volume of material (i.e., from units of wt% to kg/m^3); this latter composition scheme is often used in diffusion

---

[4] In order to avoid confusion in notations and symbols that are being used in this section, we should point out that the prime (as in C_1' and m_1') is used to designate both composition, in atom percent, and mass of material in units of grams.

computations (Section 5.3). Concentrations in terms of this basis will be denoted using a double prime (i.e., C_1'' and C_2''), and the relevant equations are as follows:

Conversion of weight percent to mass per unit volume (for a two-element alloy)

$$C_1'' = \left(\frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \right) \times 10^3 \tag{4.9a}$$

$$C_2'' = \left(\frac{C_2}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \right) \times 10^3 \tag{4.9b}$$

For density ρ in units of g/cm^3, these expressions yield C_1'' and C_2'' in kg/m^3.

Furthermore, on occasion we desire to determine the density and atomic weight of a binary alloy given the composition in terms of either weight percent or atom percent. If we represent alloy density and atomic weight by ρ_{ave} and A_{ave}, respectively, then

Computation of density (for a two-element metal alloy)

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \tag{4.10a}$$

$$\rho_{\text{ave}} = \frac{C_1' A_1 + C_2' A_2}{\dfrac{C_1' A_1}{\rho_1} + \dfrac{C_2' A_2}{\rho_2}} \tag{4.10b}$$

Computation of atomic weight (for a two-element metal alloy)

$$A_{\text{ave}} = \frac{100}{\dfrac{C_1}{A_1} + \dfrac{C_2}{A_2}} \tag{4.11a}$$

$$A_{\text{ave}} = \frac{C_1' A_1 + C_2' A_2}{100} \tag{4.11b}$$

It should be noted that Equations 4.9 and 4.11 are not always exact. In their derivations, it is assumed that total alloy volume is exactly equal to the sum of the volumes of the individual elements. This normally is not the case for most alloys; however, it is a reasonably valid assumption and does not lead to significant errors for dilute solutions and over composition ranges where solid solutions exist.

EXAMPLE PROBLEM 4.2

Derivation of Composition-Conversion Equation

Derive Equation 4.6a.

Solution

To simplify this derivation, we will assume that masses are expressed in units of grams and denoted with a prime (e.g., m_1'). Furthermore, the total alloy mass (in grams) M' is

$$M' = m_1' + m_2' \tag{4.12}$$

Using the definition of C_1' (Equation 4.5) and incorporating the expression for n_{m1}, Equation 4.4, and the analogous expression for n_{m2} yields

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

$$= \frac{\dfrac{m_1'}{A_1}}{\dfrac{m_1'}{A_1} + \dfrac{m_2'}{A_2}} \times 100 \tag{4.13}$$

Rearrangement of the mass-in-grams equivalent of Equation 4.3 leads to

$$m_1' = \frac{C_1 M'}{100} \tag{4.14}$$

Substitution of this expression and its m_2' equivalent into Equation 4.13 gives

$$C_1' = \frac{\dfrac{C_1 M'}{100 A_1}}{\dfrac{C_1 M'}{100 A_1} + \dfrac{C_2 M'}{100 A_2}} \times 100 \tag{4.15}$$

Upon simplification we have

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

which is identical to Equation 4.6a.

EXAMPLE PROBLEM 4.3

Composition Conversion—From Weight Percent to Atom Percent

Determine the composition, in atom percent, of an alloy that consists of 97 wt% aluminum and 3 wt% copper.

Solution

If we denote the respective weight percent compositions as $C_{\text{Al}} = 97$ and $C_{\text{Cu}} = 3$, substitution into Equations 4.6a and 4.6b yields

$$C_{\text{Al}}' = \frac{C_{\text{Al}} A_{\text{Cu}}}{C_{\text{Al}} A_{\text{Cu}} + C_{\text{Cu}} A_{\text{Al}}} \times 100$$

$$= \frac{(97)(63.55 \text{ g/mol})}{(97)(63.55 \text{ g/mol}) + (3)(26.98 \text{ g/mol})} \times 100$$

$$= 98.7 \text{ at\%}$$

and

$$C'_{\mathrm{Cu}} = \frac{C_{\mathrm{Cu}}A_{\mathrm{Al}}}{C_{\mathrm{Cu}}A_{\mathrm{Al}} + C_{\mathrm{Al}}A_{\mathrm{Cu}}} \times 100$$

$$= \frac{(3)(26.98\ \mathrm{g/mol})}{(3)(26.98\ \mathrm{g/mol}) + (97)(63.55\ \mathrm{g/mol})} \times 100$$

$$= 1.30\ \mathrm{at\%}$$

Miscellaneous Imperfections

4.5 DISLOCATIONS—LINEAR DEFECTS

edge dislocation

dislocation line

VMSE Edge

A *dislocation* is a linear or one-dimensional defect around which some of the atoms are misaligned. One type of dislocation is represented in Figure 4.3: an extra portion of a plane of atoms, or half-plane, the edge of which terminates within the crystal. This is termed an **edge dislocation;** it is a linear defect that centers on the line that is defined along the end of the extra half-plane of atoms. This is sometimes termed the **dislocation line,** which, for the edge dislocation in Figure 4.3, is perpendicular to the plane of the page. Within the region around the dislocation line there is some localized lattice distortion. The atoms above the dislocation line in Figure 4.3 are squeezed together, and those below are pulled apart; this is reflected in the slight curvature for the vertical planes of atoms as they bend around this extra half-plane. The magnitude of this distortion decreases with distance away from the dislocation line; at positions far removed, the crystal lattice is virtually perfect. Sometimes the edge dislocation in Figure 4.3 is represented by the symbol ⊥, which also indicates the position of the dislocation line. An edge dislocation may also be formed by an extra half-plane of atoms that is included in the bottom portion of the crystal; its designation is a ⊤.

screw dislocation

VMSE Screw

Another type of dislocation, called a **screw dislocation,** may be thought of as being formed by a shear stress that is applied to produce the distortion shown in Figure 4.4*a*: the upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion. The atomic distortion associated with a screw dislocation is also linear and along a dislocation line, line *AB* in Figure 4.4*b*. The screw dislocation derives its name from the spiral or helical path or ramp that is traced around the dislocation line by the atomic planes of atoms. Sometimes the symbol ↻ is used to designate a screw dislocation.

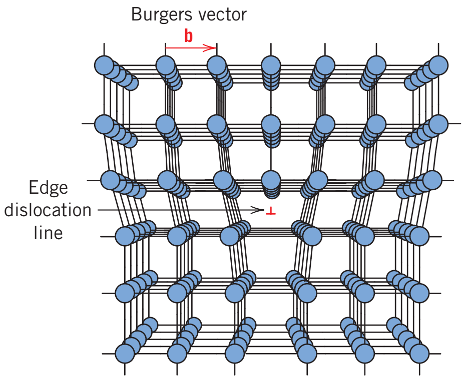
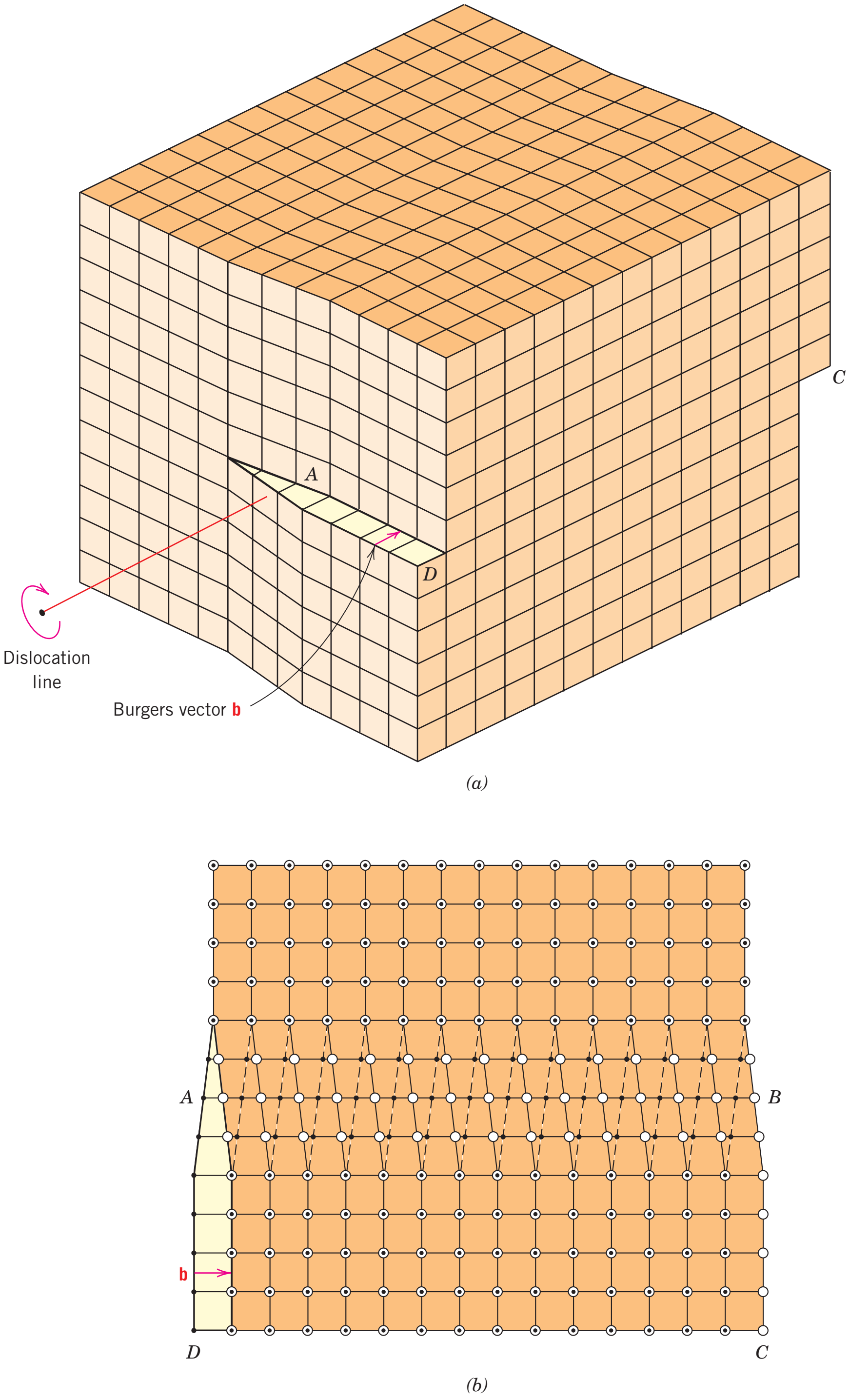


Figure 4.3 The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science,* McGraw-Hill Book Company, New York, 1976, p. 153.)

Figure 4.4 (*a*) A screw dislocation within a crystal. (*b*) The screw dislocation in (*a*) as viewed from above. The dislocation line extends along line *AB*. Atom positions above the slip plane are designated by open circles, those below by solid circles. [Figure (*b*) from W. T. Read, Jr., *Dislocations in Crystals,* McGraw-Hill Book Company, New York, 1953.]



(*a*)

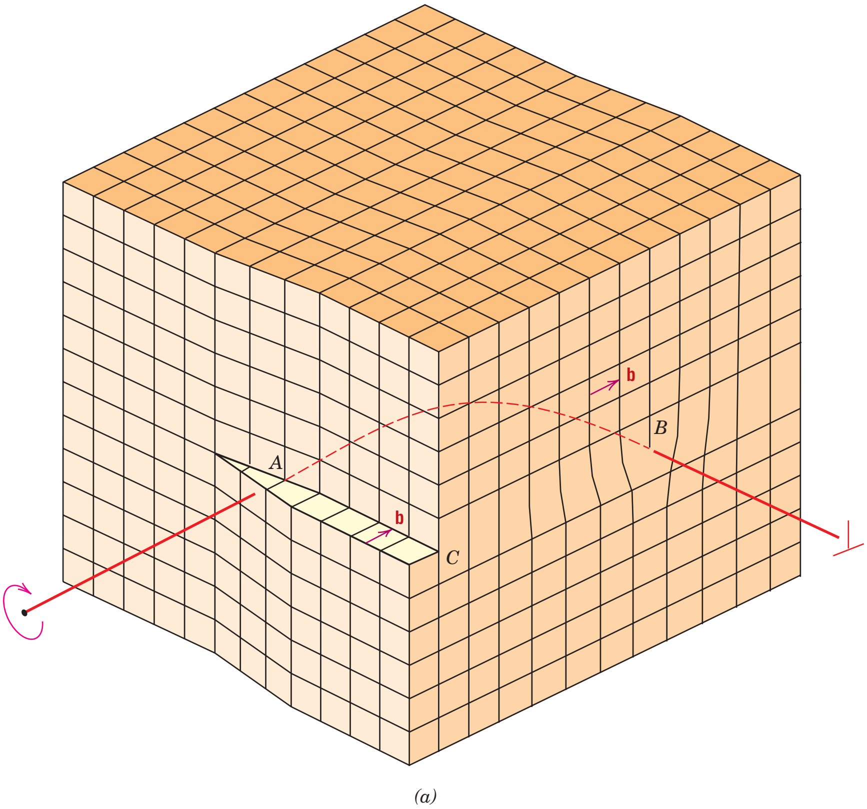
(*b*)

mixed dislocation

VMSE

Mixed

Most dislocations found in crystalline materials are probably neither pure edge nor pure screw, but exhibit components of both types; these are termed **mixed dislocations.** All three dislocation types are represented schematically in Figure 4.5; the lattice distortion that is produced away from the two faces is mixed, having varying degrees of screw and edge character.



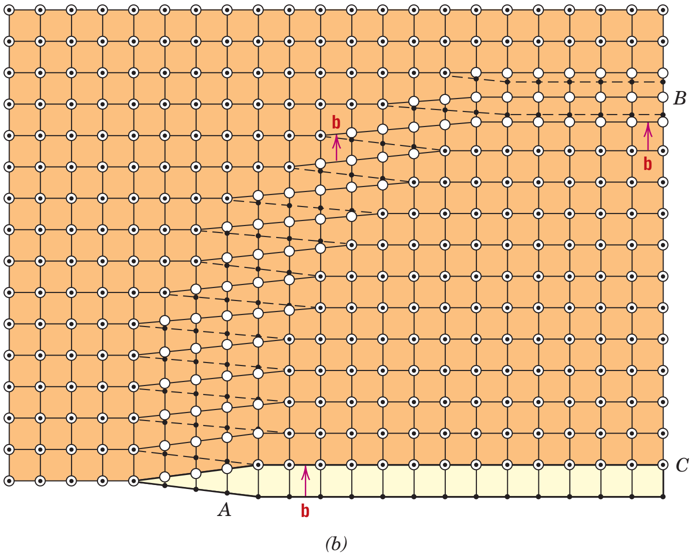


Figure 4.5 (*a*) Schematic representation of a dislocation that has edge, screw, and mixed character. (*b*) Top view, where open circles denote atom positions above the slip plane, and solid circles, atom positions below. At point *A*, the dislocation is pure screw, while at point *B*, it is pure edge. For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw. [Figure (*b*) from W. T. Read, Jr., *Dislocations in Crystals,* McGraw-Hill Book Company, New York, 1953.]

Burgers vector

The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a **Burgers vector,** denoted by a **b.** Burgers vectors are indicated in Figures 4.3 and 4.4 for edge and screw dislocations, respectively. Furthermore, the nature of a dislocation (i.e., edge, screw, or mixed) is defined by the relative orientations of dislocation line and Burgers vector. For an edge, they are perpendicular

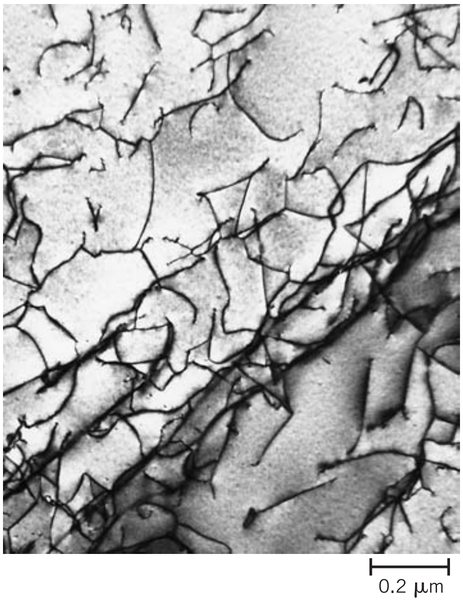


Figure 4.6 A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations. 51,450×. (Courtesy of M. R. Plichta, Michigan Technological University.)

(Figure 4.3), whereas for a screw, they are parallel (Figure 4.4); they are neither perpendicular nor parallel for a mixed dislocation. Also, even though a dislocation changes direction and nature within a crystal (e.g., from edge to mixed to screw), the Burgers vector will be the same at all points along its line. For example, all positions of the curved dislocation in Figure 4.5 will have the Burgers vector shown. For metallic materials, the Burgers vector for a dislocation will point in a close-packed crystallographic direction and will be of magnitude equal to the interatomic spacing.

As we note in Section 7.2, the permanent deformation of most crystalline materials is by the motion of dislocations. In addition, the Burgers vector is an element of the theory that has been developed to explain this type of deformation.

Dislocations can be observed in crystalline materials using electron-microscopic techniques. In Figure 4.6, a high-magnification transmission electron micrograph, the dark lines are the dislocations.

Virtually all crystalline materials contain some dislocations that were introduced during solidification, during plastic deformation, and as a consequence of thermal stresses that result from rapid cooling. Dislocations are involved in the plastic deformation of crystalline materials, both metals and ceramics, as discussed in Chapters 7 and 12. They have also been observed in polymeric materials and are discussed in Section 14.13.

4.6 INTERFACIAL DEFECTS

Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and/or crystallographic orientations. These imperfections include external surfaces, grain boundaries, phase boundaries, twin boundaries, and stacking faults.

External Surfaces

One of the most obvious boundaries is the external surface, along which the crystal structure terminates. Surface atoms are not bonded to the maximum number of nearest neighbors, and are therefore in a higher energy state than the atoms at interior positions. The bonds of these surface atoms that are not satisfied give rise to a surface energy, expressed in units of energy per unit area (J/m^2 or erg/cm^2). To reduce

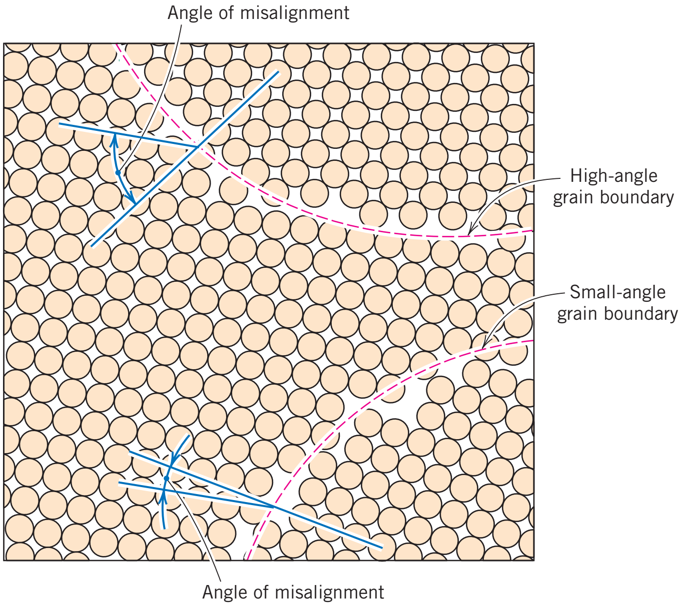


Figure 4.7 Schematic diagram showing small- and high-angle grain boundaries and the adjacent atom positions.

this energy, materials tend to minimize, if at all possible, the total surface area. For example, liquids assume a shape having a minimum area—the droplets become spherical. Of course, this is not possible with solids, which are mechanically rigid.

Grain Boundaries

Another interfacial defect, the grain boundary, was introduced in Section 3.14 as the boundary separating two small grains or crystals having different crystallographic orientations in polycrystalline materials. A grain boundary is represented schematically from an atomic perspective in Figure 4.7. Within the boundary region, which is probably just several atom distances wide, there is some atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one.

Various degrees of crystallographic misalignment between adjacent grains are possible (Figure 4.7). When this orientation mismatch is slight, on the order of a few degrees, then the term *small-* (or *low-*) *angle grain boundary* is used. These boundaries can be described in terms of dislocation arrays. One simple small-angle grain boundary is formed when edge dislocations are aligned in the manner of Figure 4.8. This type is called a *tilt boundary;* the angle of misorientation, θ, is also indicated in the figure. When the angle of misorientation is parallel to the boundary, a *twist boundary* results, which can be described by an array of screw dislocations.

The atoms are bonded less regularly along a grain boundary (e.g., bond angles are longer), and consequently, there is an interfacial or grain boundary energy similar to the surface energy just described. The magnitude of this energy is a function of the degree of misorientation, being larger for high-angle boundaries. Grain boundaries are more chemically reactive than the grains themselves as a consequence of this boundary energy. Furthermore, impurity atoms often preferentially segregate along these boundaries because of their higher energy state. The total interfacial energy is lower in large or coarse-grained materials than in fine-grained ones, because there is less total boundary area in the former. Grains grow at elevated temperatures to reduce the total boundary energy, a phenomenon explained in Section 7.13.

In spite of this disordered arrangement of atoms and lack of regular bonding along grain boundaries, a polycrystalline material is still very strong; cohesive forces

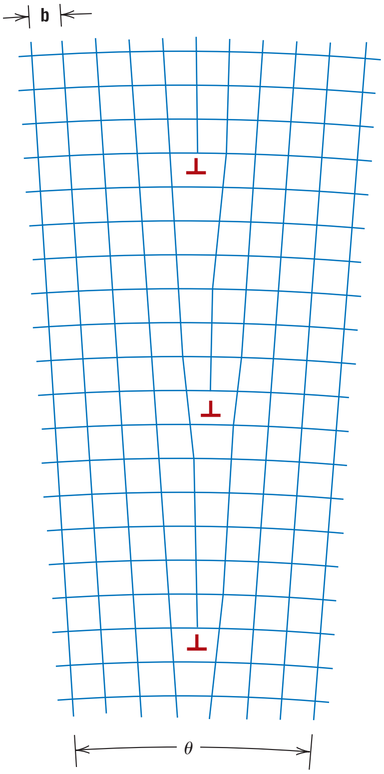


Figure 4.8 Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.

within and across the boundary are present. Furthermore, the density of a polycrystalline specimen is virtually identical to that of a single crystal of the same material.

Phase Boundaries

Phase boundaries exist in multiphase materials (Section 9.3), wherein a different phase exists on each side of the boundary; furthermore, each of the constituent phases has its own distinctive physical and/or chemical characteristics. As we shall see in subsequent chapters, phase boundaries play an important role in determining the mechanical characteristics of some multiphase metal alloys.

Twin Boundaries

A *twin boundary* is a special type of grain boundary across which there is a specific mirror lattice symmetry; that is, atoms on one side of the boundary are located in mirror-image positions of the atoms on the other side (Figure 4.9). The region of

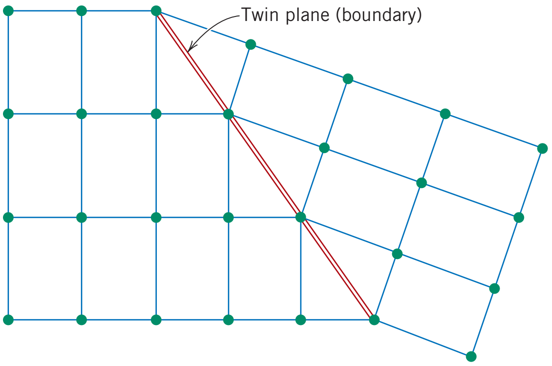


Figure 4.9 Schematic diagram showing a twin plane or boundary and the adjacent atom positions (colored circles).

MATERIALS OF IMPORTANCE

Catalysts (and Surface Defects)

A *catalyst* is a substance that speeds up the rate of a chemical reaction without participating in the reaction itself (i.e., it is not consumed). One type of catalyst exists as a solid; reactant molecules in a gas or liquid phase are adsorbed[5] onto the catalytic surface, at which point some type of interaction occurs that promotes an increase in their chemical reactivity rate.

Adsorption sites on a catalyst are normally surface defects associated with planes of atoms; an interatomic/intermolecular bond is formed between a defect site and an adsorbed molecular species. Several types of surface defects, represented schematically in Figure 4.10, include ledges, kinks, terraces, vacancies, and individual adatoms (i.e., atoms adsorbed on the surface).

One important use of catalysts is in catalytic converters on automobiles, which reduce the emission of exhaust gas pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x, where x is variable), and unburned hydrocarbons. (See the chapter-opening diagrams and photograph for this chapter.) Air is introduced into the exhaust emissions from the automobile engine; this mixture of gases then passes over the catalyst, which adsorbs on its surface molecules of CO, NO_x, and O_2. The NO_x dissociates into N and O atoms, whereas the O_2 dissociates into its atomic species. Pairs of nitrogen atoms combine to form N_2 molecules, and carbon monoxide is oxidized to form carbon dioxide (CO_2). Furthermore, any unburned hydrocarbons are also oxidized to CO_2 and H_2O.

One of the materials used as a catalyst in this application is $(Ce_{0.5}Zr_{0.5})O_2$. Figure 4.11 is a high-resolution transmission electron micrograph that shows several single crystals of this material. Individual atoms are resolved in this micrograph as well as some of the defects presented in Figure 4.10. These surface defects act as adsorption sites for the atomic and molecular species noted in the previous paragraph. Consequently, dissociation, combination, and oxidation reactions involving these species are facilitated, such that the content of pollutant species (CO, NO_x, and unburned hydrocarbons) in the exhaust gas stream is reduced significantly.

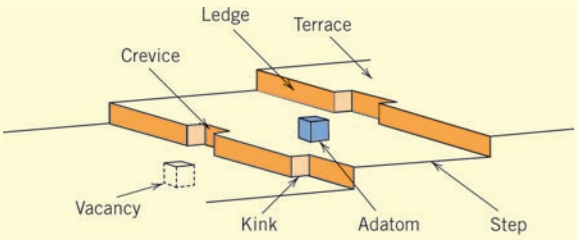


Figure 4.10 Schematic representations of surface defects that are potential adsorption sites for catalysis. Individual atom sites are represented as cubes.

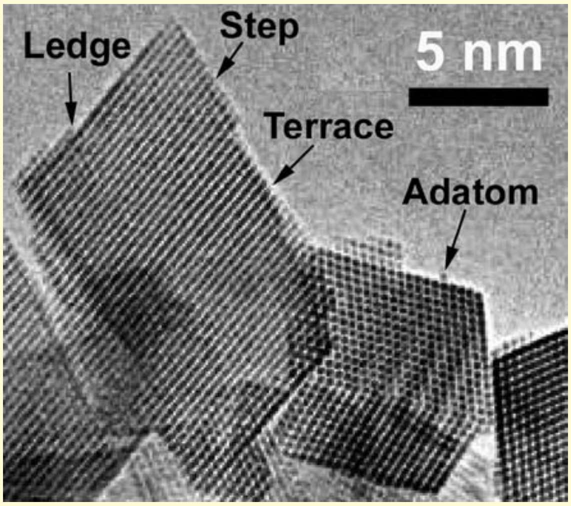


Figure 4.11 High-resolution transmission electron micrograph that shows single crystals of $(Ce_{0.5}Zr_{0.5})O_2$; this material is used in catalytic converters for automobiles. Surface defects represented schematically in Figure 4.10 are noted on the crystals. [From W. J. Stark, L. Mädler, M. Maciejewski, S. E. Pratsinis, A. Baiker, "Flame-Synthesis of Nanocrystalline Ceria/Zirconia: Effect of Carrier Liquid," *Chem. Comm.*, 588–589 (2003). Reproduced by permission of The Royal Society of Chemistry.]

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[5] ***Ad**sorption* is the adhesion of molecules of a gas or liquid to a solid surface. It should not be confused with ***ab**sorption,* which is the assimilation of molecules into a solid or liquid.

material between these boundaries is appropriately termed a *twin*. Twins result from atomic displacements that are produced from applied mechanical shear forces (mechanical twins), and also during annealing heat treatments following deformation (annealing twins). Twinning occurs on a definite crystallographic plane and in a specific direction, both of which depend on the crystal structure. Annealing twins are typically found in metals that have the FCC crystal structure, whereas mechanical twins are observed in BCC and HCP metals. The role of mechanical twins in the deformation process is discussed in Section 7.7. Annealing twins may be observed in the photomicrograph of the polycrystalline brass specimen shown in Figure 4.13*c*. The twins correspond to those regions having relatively straight and parallel sides and a different visual contrast than the untwinned regions of the grains within which they reside. An explanation for the variety of textural contrasts in this photomicrograph is provided in Section 4.10.

Miscellaneous Interfacial Defects

Other possible interfacial defects include stacking faults and ferromagnetic domain walls. Stacking faults are found in FCC metals when there is an interruption in the *ABCABCABC* . . . stacking sequence of close-packed planes (Section 3.12). For ferromagnetic and ferrimagnetic materials, the boundary that separates regions having different directions of magnetization is termed a *domain wall,* which is discussed in Section 20.7.

Associated with each of the defects discussed in this section is an interfacial energy, the magnitude of which depends on boundary type, and which will vary from material to material. Normally, the interfacial energy will be greatest for external surfaces and least for domain walls.

Concept Check 4.1

The surface energy of a single crystal depends on crystallographic orientation. Does this surface energy increase or decrease with an increase in planar density? Why?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

4.7 BULK OR VOLUME DEFECTS

Other defects exist in all solid materials that are much larger than those heretofore discussed. These include pores, cracks, foreign inclusions, and other phases. They are normally introduced during processing and fabrication steps. Some of these defects and their effects on the properties of materials are discussed in subsequent chapters.

4.8 ATOMIC VIBRATIONS

atomic vibration

Every atom in a solid material is vibrating very rapidly about its lattice position within the crystal. In a sense, these **atomic vibrations** may be thought of as imperfections or defects. At any instant of time not all atoms vibrate at the same frequency and amplitude, nor with the same energy. At a given temperature there will exist a distribution of energies for the constituent atoms about an average energy. Over time the vibrational energy of any specific atom will also vary in a random manner. With rising temperature, this average energy increases, and, in fact, the temperature of a solid is really just a measure of the average vibrational activity of atoms and molecules. At room temperature, a typical vibrational frequency is on the order of 10^{13} vibrations per second, whereas the amplitude is a few thousandths of a nanometer.

Many properties and processes in solids are manifestations of this vibrational atomic motion. For example, melting occurs when the vibrations are vigorous enough to rupture large numbers of atomic bonds. A more detailed discussion of atomic vibrations and their influence on the properties of materials is presented in Chapter 19.

Microscopic Examination

4.9 BASIC CONCEPTS OF MICROSCOPY

On occasion it is necessary or desirable to examine the structural elements and defects that influence the properties of materials. Some structural elements are of *macroscopic* dimensions; that is, they are large enough to be observed with the unaided eye. For example, the shape and average size or diameter of the grains for a polycrystalline specimen are important structural characteristics. Macroscopic grains are often evident on aluminum streetlight posts and also on highway guardrails. Relatively large grains having different textures are clearly visible on the surface of the sectioned copper ingot shown in Figure 4.12. However, in most materials the constituent grains are of *microscopic* dimensions, having diameters that may be on the order of microns,[6] and their details must be investigated using some

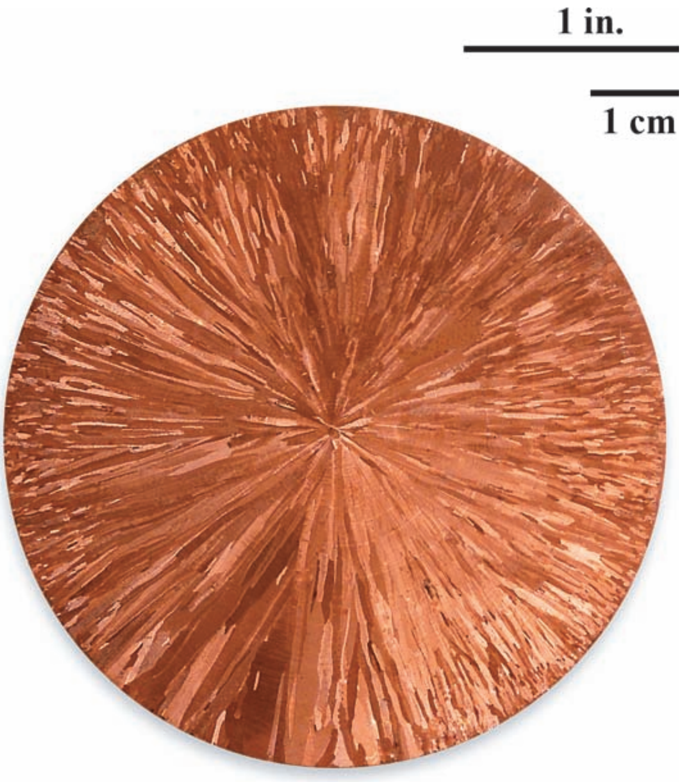

Figure 4.12 Cross-section of a cylindrical copper ingot. The small needle-shaped grains may be observed, which extend from the center radially outward.

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[6] A micron (μm), sometimes called a micrometer, is 10^{-6} m.