

THE STRUCTURE OF METALS

1. Introduction

Metals are usually crystalline when in the solid form. While very large single crystals can be prepared, the normal metallic object consists of an aggregate of many very small crystals. Metals are therefore polycrystalline. The crystals in these materials are normally referred to as its grains. Because of their very small sizes, an optical microscope, operating at magnifications between about 100 and 1000 times, is usually used to examine the structural features associated with the grains in a metal. Structures requiring this range of magnification for their examination fall into the class known as microstructures. Occasionally, metallic objects, such as castings, may have very large crystals that are discernible to the naked eye or are easily resolved under a low-power microscope. Structure in this category is called macrostructure. On the other hand, there are materials whose grains or sizes are much finer and in the nanoscale range. These microstructures are commonly referred to as nanostructure. There is the basic structure inside the grains themselves: that is, the atomic arrangements inside the crystals. This form of structure is logically called the crystal structure.

A crystal is defined as an orderly array of atoms in space. There are many different types of crystal structures, some of which are quite complicated. Fortunately, most metals crystallize in one of three relatively simple structures: the face-centered cubic, the body-centered cubic, and the close-packed hexagonal.

2. UNIT CELLS

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.

3. 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 called the face-centered cubic (FCC) crystal structure. Some of the familiar metals having this crystal structure are copper, aluminum, silver, and gold. Figure 3.1a shows a hard-sphere model for the FCC unit cell, whereas in Figure 3.1b the atom centers are represented by small circles to provide a better perspective of atom positions. The aggregate of atoms in Figure 1c 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

$$a = 2R\sqrt{2} \dots\dots\dots 1$$

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 3.1a; 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,

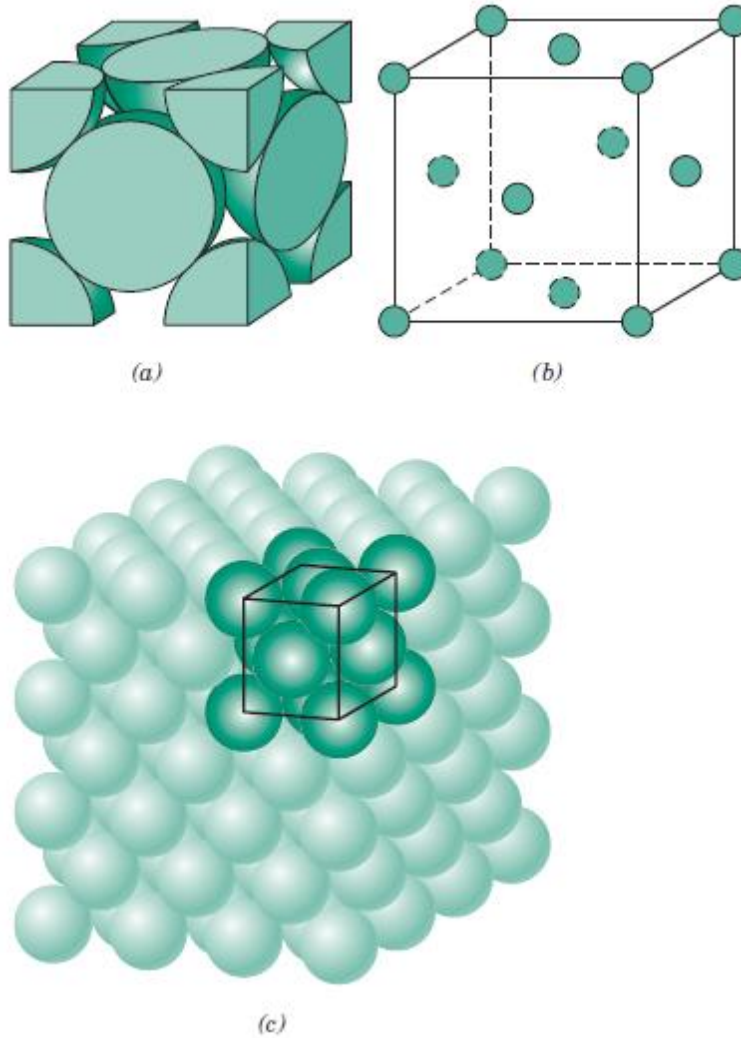


Figure 1 For the face centered cubic crystal structure, (a) a hardsphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms.

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

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For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter.

4. The Body-Centered Cubic Crystal Structure

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 3.2c, whereas Figures 3.2a and 3.2b 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

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

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Chromium, iron, tungsten, as well as several exhibit a BCC structure.

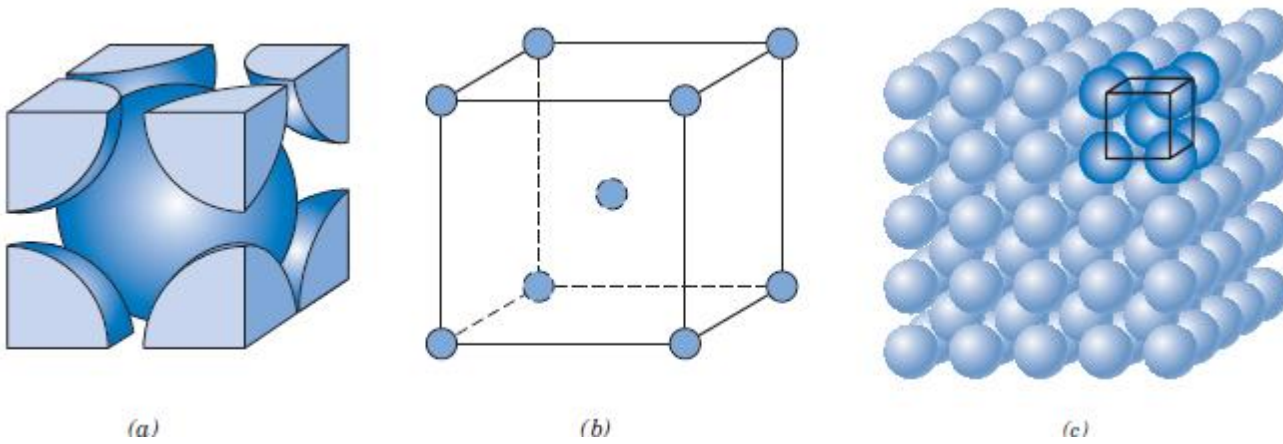


Figure 2 For the body-centered cubic crystal structure, (a) a hard-sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms.

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.

4. The Hexagonal Close-Packed Crystal Structure

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 3a shows a reduced sphere unit cell for this structure, which is termed hexagonal close-packed (HCP); an assemblage of several HCP unit cells is presented in Figure 3b

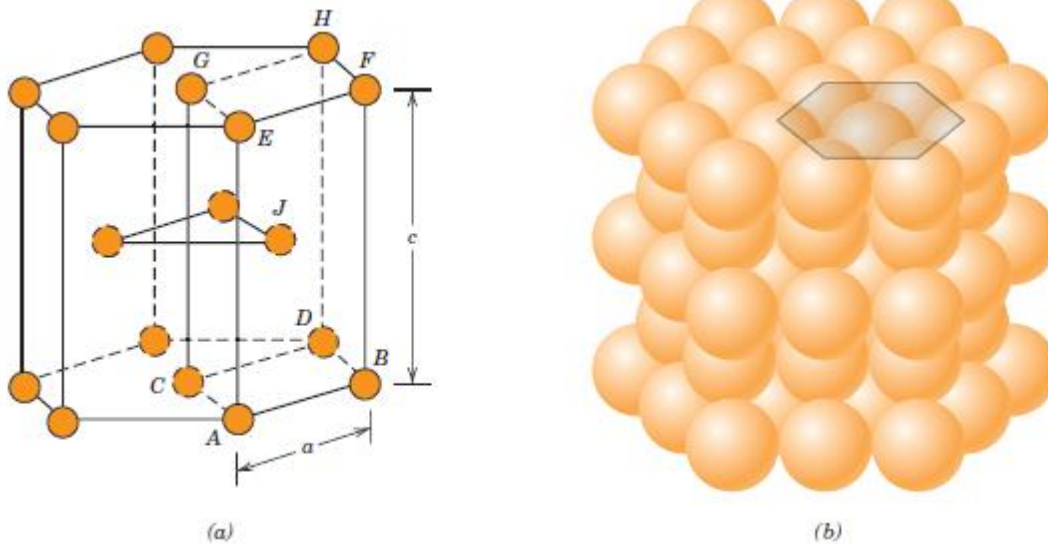


Figure 3 For the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell (a and c represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms.

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 3.3a, the 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.

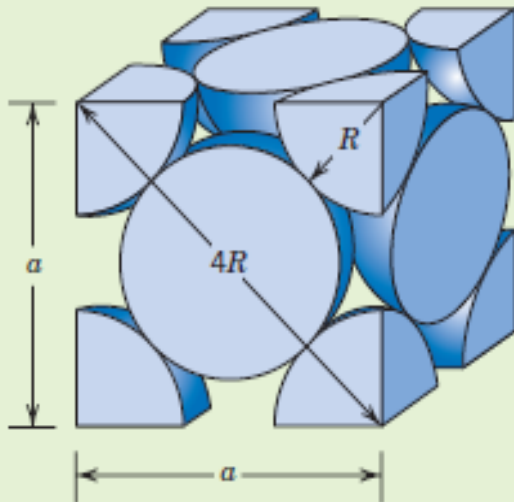
EXAMPLE PROBLEM 3.1

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 ,

$$a = 2R\sqrt{2} \quad (3.1)$$

The FCC unit cell volume V_C may be computed from

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

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

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

From Example Problem 3.1, the total unit cell volume is

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

Therefore, the atomic packing factor is

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

DENSITY COMPUTATIONS

Knowledge of the crystal structure of a metallic solid permits computation of its theoretical density through the relationship

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

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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 16.022×10^{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

$$\begin{aligned}\rho &= \frac{nA_{\text{Cu}}}{V_C N_A} = \frac{nA_{\text{Cu}}}{(16R^3\sqrt{2})N_A} \\ &= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.022 \times 10^{23} \text{ atoms/mol})} \\ &= 8.89 \text{ g/cm}^3\end{aligned}$$

The literature value for the density of copper is 8.94 g/cm³, which is in very close agreement with the foregoing result.

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

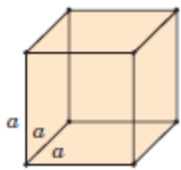
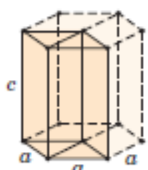
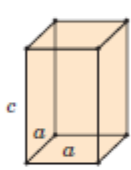

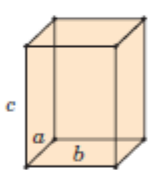
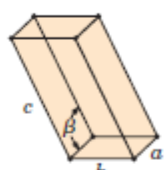
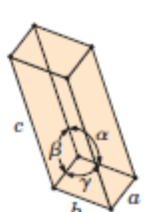
<i>Crystal System</i>	<i>Axial Relationships</i>	<i>Interaxial Angles</i>	<i>Unit Cell Geometr</i>
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b</i> <i>(nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius</i> <i>(nm)</i>
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

^aFCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.