Crystal Structures

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

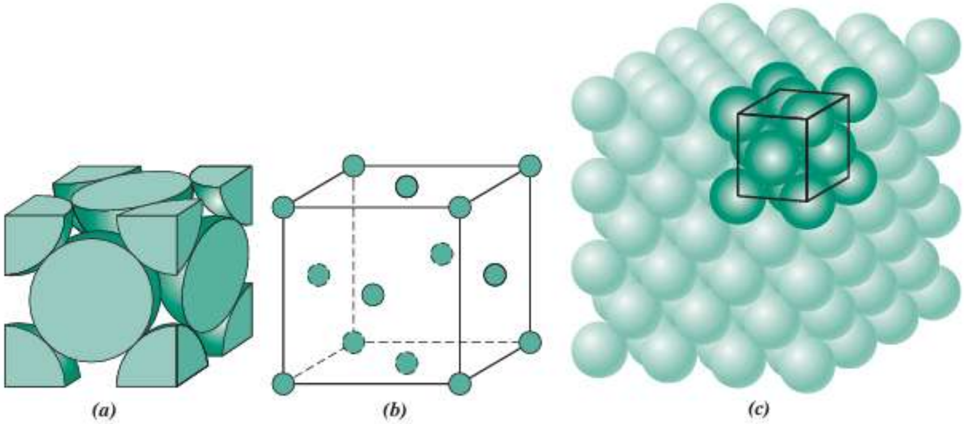

Figure 3.1 For the face-centered cubic crystal structure, (*a*) a hard-sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms.
[Figure (*c*) adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I,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

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 crystal line structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; these noncrystalline or amorphous materials.

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-

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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.

When crystalline structures are described, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the atomic hard-sphere 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 3.1c. 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).

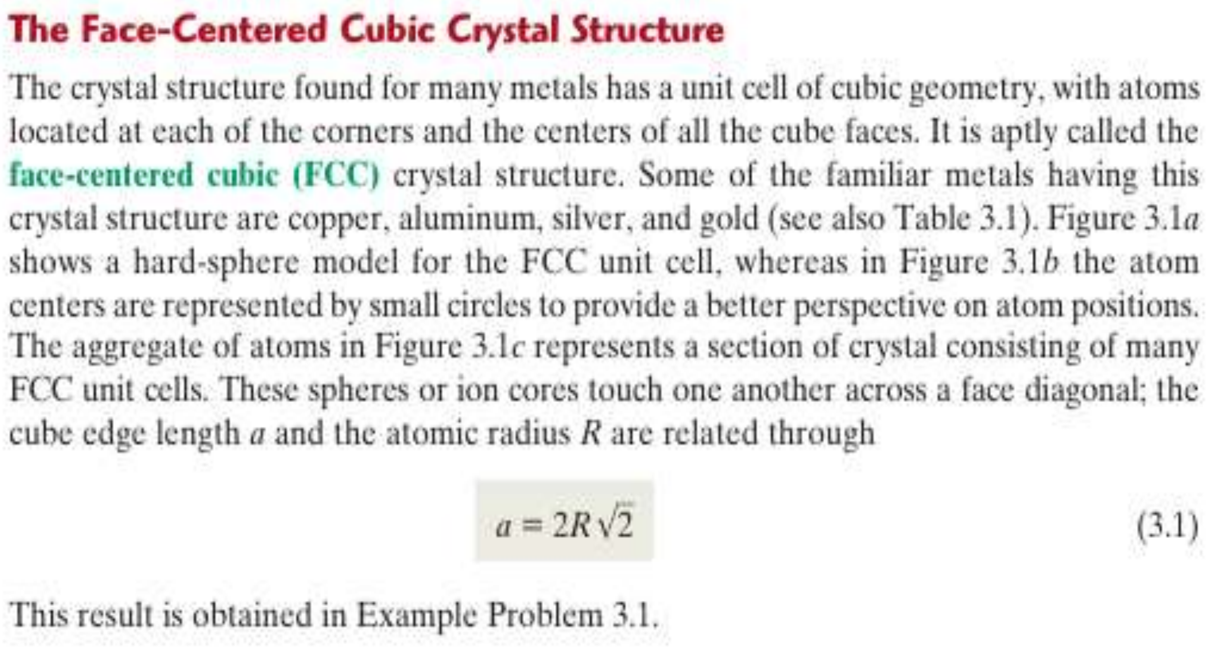
UNIT CELLS

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. 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 3.1c), 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.

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, when we use 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 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 on 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

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

This result is obtained in Example Problem 3.1.

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.

On occasion, we need to determine the number of atoms associated with each unit cell. Depending on an atom's location, it may be considered to be shared with adjacent unit cells—that is, only some fraction of the atom is assigned to a specific cell. For example, for cubic unit cells, an atom completely within the interior "belongs" to that unit cell, one at a cell face is shared with one other cell, and an atom residing at a corner is shared among eight. The number of atoms per unit cell, N, can be computed using the following formula:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \tag{3.2}$$

where

N_i = the number of interior atoms
N_f = the number of face atoms
N_c = the number of corner atoms

For the FCC crystal structure, there are eight corner atoms ($N_c = 8$), six face atoms ($N_f = 6$), and no interior atoms ($N_i = 0$). Thus, from Equation 3.2,

$$N = 0 + \frac{6}{2} + \frac{8}{8} = 4$$

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 is composed of the volume of the cube that 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.

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 (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,

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} \tag{3.3}$$

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

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

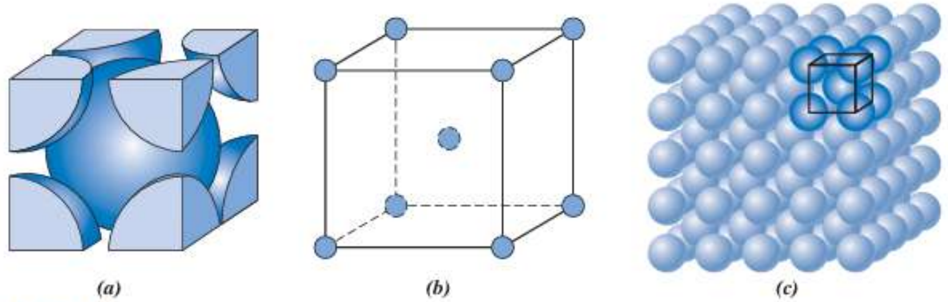


Figure 3.2 For the body-centered cubic crystal structure, (*a*) a hard-sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms.
[Figure (*c*) adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, John Wiley & Sons, 1964. Reproduced with permission of Janet M. Moffatt.]

and corner atoms touch one another along cube diagonals, and unit cell length a and atomic radius R are related through

$$a = \frac{4R}{\sqrt{3}} \tag{3.4}$$

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

Each BCC unit cell has eight corner atoms and a single center atom, which is wholly contained within its cell; therefore, from Equation 3.2, the number of atoms per BCC unit cell is

$$\begin{aligned} N &= N_i + \frac{N_f}{2} + \frac{N_c}{8} \\ &= 1 + 0 + \frac{8}{8} = 2 \end{aligned}$$

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 for FCC, the atomic packing factor is also lower for BCC—0.68 versus 0.74.

It is also possible to have a unit cell that consists of atoms situated only at the corners of a cube. This is called the *simple cubic* (*SC*) *crystal structure*; hard-sphere and reduced-sphere models are shown, respectively, in Figures 3.3*a* and 3.3*b*. None of the metallic elements have this crystal structure because of its relatively low atomic packing factor (see Concept Check 3.1). The only simple-cubic element is polonium, which is considered to be a metalloid (or semi-metal).

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 3.4*a* 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 3.4*b*.[1] The top and bottom

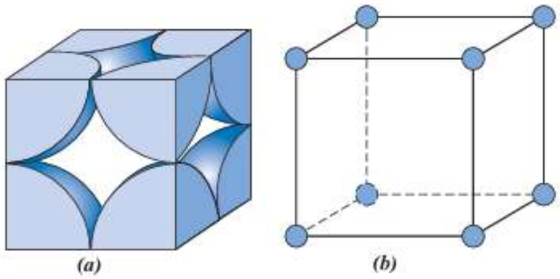


Figure 3.3 For the simple cubic crystal structure, (*a*) a hard-sphere unit cell, and (*b*) a reduced-sphere unit cell.

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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.

In order to compute the number of atoms per unit cell for the HCP crystal structure, Equation 3.2 is modified to read as follows:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{6} \tag{3.5}$$

That is, one-sixth of each corner atom is assigned to a unit cell (instead of 8 as with the cubic structure). Because for HCP there are 6 corner atoms in each of the top and bottom faces (for a total of 12 corner atoms), 2 face center atoms (one from each of the top and bottom faces), and 3 midplane interior atoms, the value of N for HCP is found, using Equation 3.5, to be

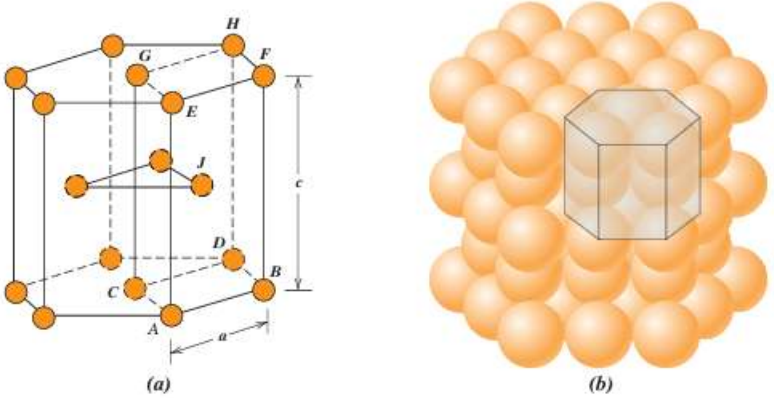

Figure 3.4 For the hexagonal close-packed crystal structure, (*a*) a reduced-sphere unit cell (*a* and *c* represent the short and long edge lengths, respectively), and (*b*) an aggregate of many atoms.

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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,

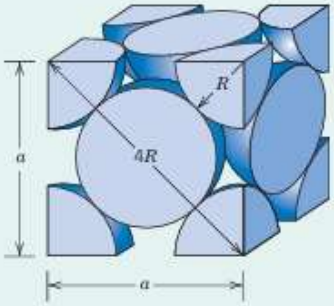
$$a^2 + a^2 = (4R)^2$$

or, solving for a,

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

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \tag{3.6}$$



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

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

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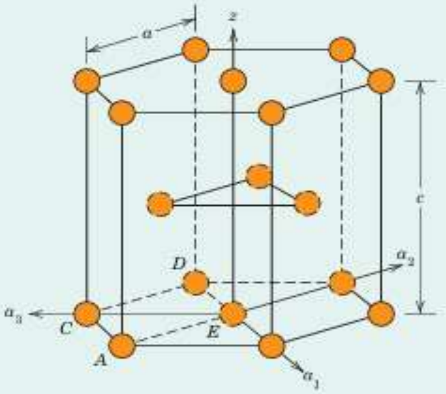
EXAMPLE PROBLEM 3.3

Determination of HCP Unit Cell Volume



(a) Calculate the volume of an HCP unit cell in terms of its a and c lattice parameters.

(b) Now provide an expression for this volume in terms of the atomic radius, R, and the c lattice parameter.

Solution

(a) We use the adjacent reduced-sphere HCP unit cell to solve this problem.

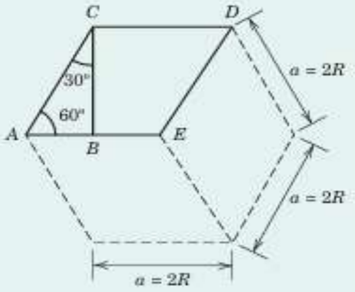
Now, the unit cell volume is just the product of the base area times the cell height, c. This base area is just three times the area of the parallelepiped $ACDE$ shown below. (This $ACDE$ parallelepiped is also labeled in the above unit cell.)

The area of $ACDE$ is just the length of $\overline{CD}$ times the height $\overline{BC}$. But $\overline{CD}$ is just a, and $\overline{BC}$ is equal to

$$\overline{BC} = a\cos(30^\circ) = \frac{a\sqrt{3}}{2}$$

Thus, the base area is just

$$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(a)\left(\frac{a\sqrt{3}}{2}\right) = \frac{3a^2\sqrt{3}}{2}$$



Again, the unit cell volume V_C is just the product of the AREA and c; thus,

$$\begin{aligned} V_C &= \text{AREA}(c) \\ &= \left(\frac{3a^2\sqrt{3}}{2}\right)(c) \\ &= \frac{3a^2c\sqrt{3}}{2} \end{aligned} \tag{3.7a}$$

(b) For this portion of the problem, all we need do is realize that the lattice parameter a is related to the atomic radius R as

$$a = 2R$$

Now making this substitution for a in Equation 3.7a gives

$$\begin{aligned} V_C &= \frac{3(2R)^2c\sqrt{3}}{2} \\ &= 6R^2c\sqrt{3} \end{aligned} \tag{3.7b}$$

DENSITY COMPUTATIONS

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

$$\rho = \frac{nA}{V_C N_A} \tag{3.8}$$

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 3.4

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 3.8 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 3.8 yields

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

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

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