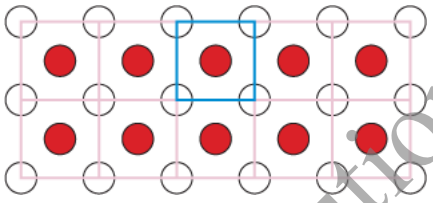
Pearson

12.3: Crystalline Solids: Unit Cells and Basic Structures

Key Concept Video **Unit Cells: Simple Cubic, Body-Centered Cubic, and Face-Centered Cubic**

X-ray crystallography allows us to determine the regular arrangements of atoms within a crystalline solid. This arrangement is called the **crystalline lattice**. The crystalline lattice of any solid is nature's way of aggregating the particles to minimize their energy.



The Unit Cell

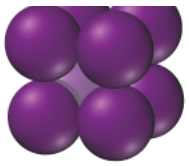
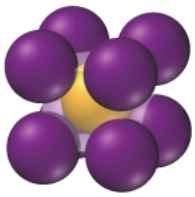
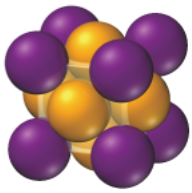
We represent the crystalline lattice with a small collection of atoms, ions, or molecules called the **unit cell**. When the unit cell is repeated over and over—like the tiles of a floor or the pattern in a wallpaper design, but in three dimensions—the entire lattice is reproduced. For example, consider the two-dimensional crystalline lattice shown at left. The unit cell for this lattice is the blue square. Each circle represents an atom, ion, or molecule. Repeating the unit cell pattern throughout the two-dimensional space generates the entire lattice.

Many different unit cells exist, and we often classify unit cells by their symmetry. In this book, we focus primarily on *cubic unit cells* (although we also look at one hexagonal unit cell). Cubic unit cells are characterized by equal edge lengths and 90° angles at their corners. Figure 12.3 presents the three cubic unit cells—simple cubic, body-centered cubic, and face-centered cubic—and some of their basic characteristics. The two colors in this figure help illustrate the different positions of the atoms; the colors *do not* represent different *kinds* of atoms. For these unit cells, *each atom in any one structure is identical to the other atoms in that structure*.

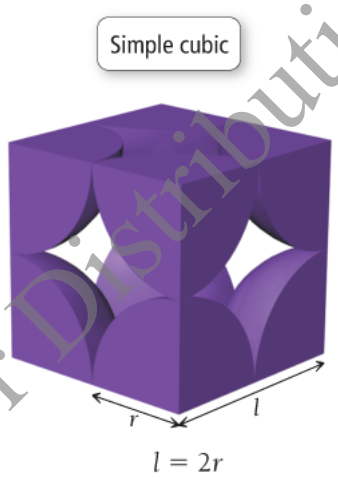
Figure 12.3 **The Cubic Crystalline Lattices**

The different colors used for the atoms in this figure are for clarity only. All atoms within each structure are identical.

Cubic Cell Name	Atoms per Unit Cell	Structure	Coordination Number	Edge Length in Terms of *r*	Packing Efficiency (fraction of volume occupied)
					

Simple Cubic	1		6	$2r$	52%
Body-Centered Cubic	2		8	$\frac{4r}{\sqrt{3}}$	68%
Face-Centered Cubic	4		12	$2\sqrt{2}r$	74%

Unit cells, such as the cubic ones shown here, are customarily portrayed with "whole" atoms, even though only a part of the whole atom may actually be in the unit cell.



In the simple cubic lattice, the atoms touch along each edge so that the edge length is $2r$.

The **simple cubic** unit cell (Figure 12.4) consists of a cube with one atom at each corner. The atoms touch along each edge of the cube, so the edge length is twice the radius of the atoms ($l = 2r$). Even though it may seem like the unit cell contains eight atoms, it actually contains only one. Each corner atom is shared by eight other unit cells. In other words, any one unit cell actually contains only one-eighth of each of the eight atoms at its corners, for a total of just one atom per unit cell.

Figure 12.4 Simple Cubic Crystal Structure

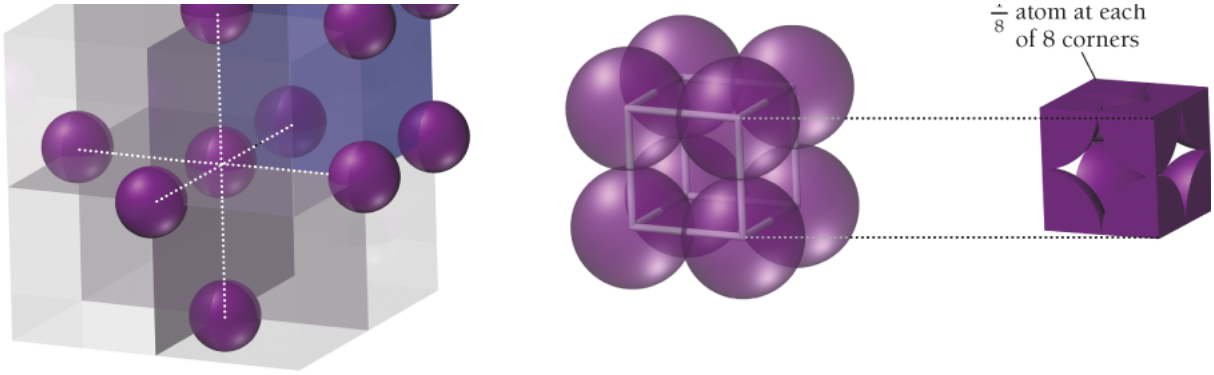
In the leftmost structure, the atoms have been reduced in size for clarity.

Simple Cubic Unit Cell

Coordination number = 6

Atoms per unit cell

$\frac{1}{8} \times 8 = 1$



A characteristic feature of any unit cell is the **coordination number**, the number of atoms with which each atom is in *direct contact*. The coordination number is the number of atoms with which a particular atom can strongly interact. The simple cubic unit cell has a coordination number of 6; any one atom touches six others, as Figure 12.4 illustrates. A quantity closely related to the coordination number is the **packing efficiency**, the percentage of the volume of the unit cell occupied by the spheres. The higher the coordination number, the greater the packing efficiency. The simple cubic unit cell has a packing efficiency of 52%—the simple cubic unit cell contains a lot of empty space.

Example 12.2 Calculating the Packing Efficiency of a Unit Cell

Calculate the packing efficiency of the simple cubic unit cell.

SOLUTION

The packing efficiency is defined as the ratio of the volume of the unit cell occupied by atoms to the volume of the unit cell itself, all multiplied by 100%.

$$\text{packing efficiency} = \frac{V_{\text{atom}}}{V_{\text{unit cell}}} \times 100\%$$

First determine the volume occupied by atoms. Because each unit cell contains one atom, the volume of the unit cell occupied by atoms is simply the volume of one atom.

$$V_{\text{atom}} = \frac{4}{3}\pi r^3$$

Next, calculate the volume of the cube in terms of the radius of the atom. The volume of a cube is its edge length cubed, and the edge length of the simple cubic unit cell is $2r$.

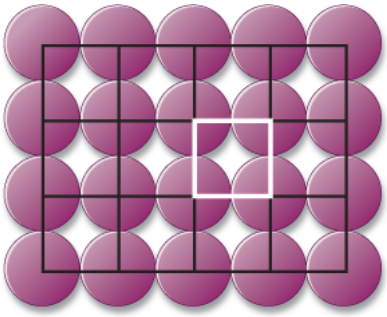
$$\begin{aligned} V_{\text{unit cell}} &= l^3 \\ &= (2r)^3 \\ &= 8r^3 \end{aligned}$$

Calculate the packing efficiency by dividing the volume of the atom by the volume of the unit cell and multiplying by 100%.

$$\begin{aligned} \text{packing efficiency} &= \frac{V_{\text{atom}}}{V_{\text{unit cell}}} \times 100\% \\ &= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\% \\ &= \frac{\frac{4}{3}\pi \cancel{r^3}}{8\,\cancel{r^3}} \times 100\% \end{aligned}$$

$$= \frac{4}{24}\pi \times 100\%$$
$$= 52.36\%$$

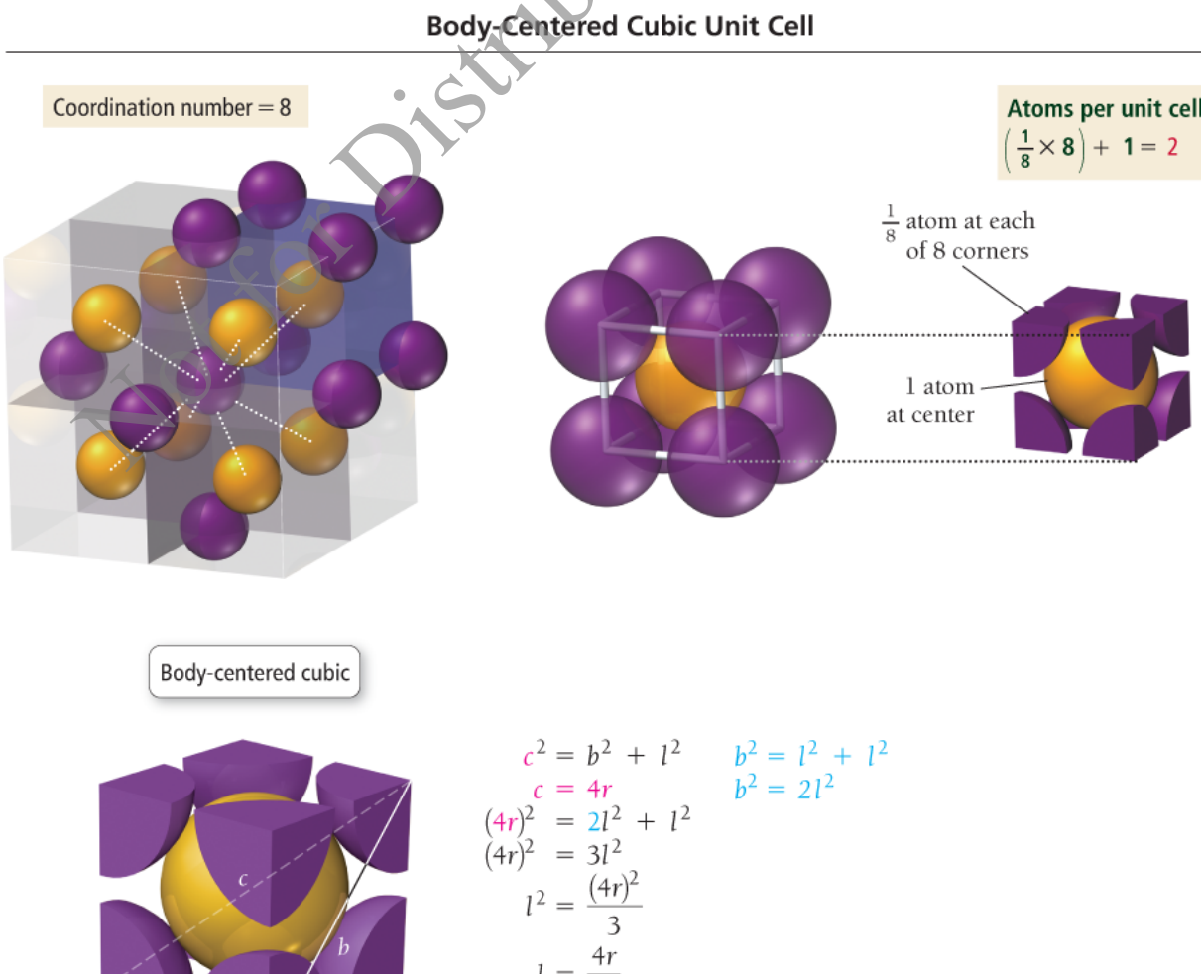
FOR PRACTICE 12.2 Calculate the packing efficiency of the two-dimensional lattice shown here.

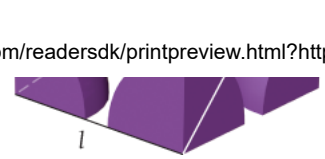


The **body-centered cubic** unit cell (Figure 12.5) consists of a cube with one atom at each corner and one atom (of the same kind) in the very center of the cube. Note that in the body-centered unit cell, the atoms *do not* touch along each edge of the cube, but instead along the diagonal line that runs from one corner, through the middle of the cube, to the opposite corner. The edge length in terms of the atomic radius is therefore $l = 4r/\sqrt{3}$as shown in this diagram:

Figure 12.5 Body-Centered Cubic Crystal Structure

The different colors used for the atoms in this figure are for clarity only. All atoms within the structure are identical. In the leftmost structure, the atoms have been reduced in size for clarity.





In the body-centered cubic lattice, the atoms touch only along the cube diagonal (line labeled c). The edge length is $4r/\sqrt{3}$.

The body-centered cubic unit cell contains two atoms per unit cell because the center atom is not shared with any other neighboring cells. The coordination number of the body-centered cubic unit cell is 8, which we can see by examining the atom in the very center of the cube, which touches eight atoms at the corners. The packing efficiency is 68%, significantly higher than for the simple cubic unit cell. Each atom in this structure strongly interacts with more atoms than each atom in the simple cubic unit cell.

Example 12.3 Relating Unit Cell Volume, Edge Length, and Atomic Radius

A body-centered cubic unit cell has a volume of 4.32×10^{-23} cm^3. Find the radius of the atom in pm.

SORT You are given the volume of a unit cell and asked to find the radius of the atom.

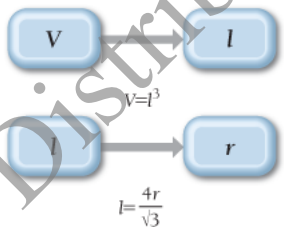
GIVEN: $V = 4.32 \times 10^{-23}$ cm^3

FIND: r (in pm)

STRATEGIZE Use the volume to find the edge length of the unit cell.

Then use the edge length to find the radius of the atom.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$V = l^3 \text{ (volume of a cube)}$$
$$l = \frac{4r}{\sqrt{3}} \text{ (edge lenght of body-centered cubic unit cell)}$$

SOLVE Solve the equation for the volume of a cube for l and substitute in the given value for V to find l.

Solve the equation for the edge length of a body-centered cubic unit cell for r and substitute in the value of l (from the previous step) to find r.

Convert r from cm to m and then to pm.

SOLUTION

$$V = l^3$$
$$l = \sqrt[3]{V} = \sqrt[3]{4.32 \times 10^{-23}\ \text{cm}^3} = 3.5088 \times 10^{-8}\ \text{cm}$$
$$l = \frac{4r}{\sqrt{3}}$$
$$\sqrt{3}l \qquad \sqrt{3}\left(3.5088 \times 10^{-8}\ \text{cm}\right) \qquad 1.5102 \times 10^{-8}\ \text{cm}$$

$$l = \frac{b}{4} = \frac{1.5193 \times 10^{-8}\ \text{cm}}{4} = 3.798 \times 10^{-9}\ \text{cm}$$

$$1.5193 \times 10^{-8}\ \text{cm} \times \frac{0.01\ \text{m}}{1\ \text{cm}} \times \frac{1\ \text{pm}}{10^{-12}\ \text{m}} = 152\ \text{pm}$$

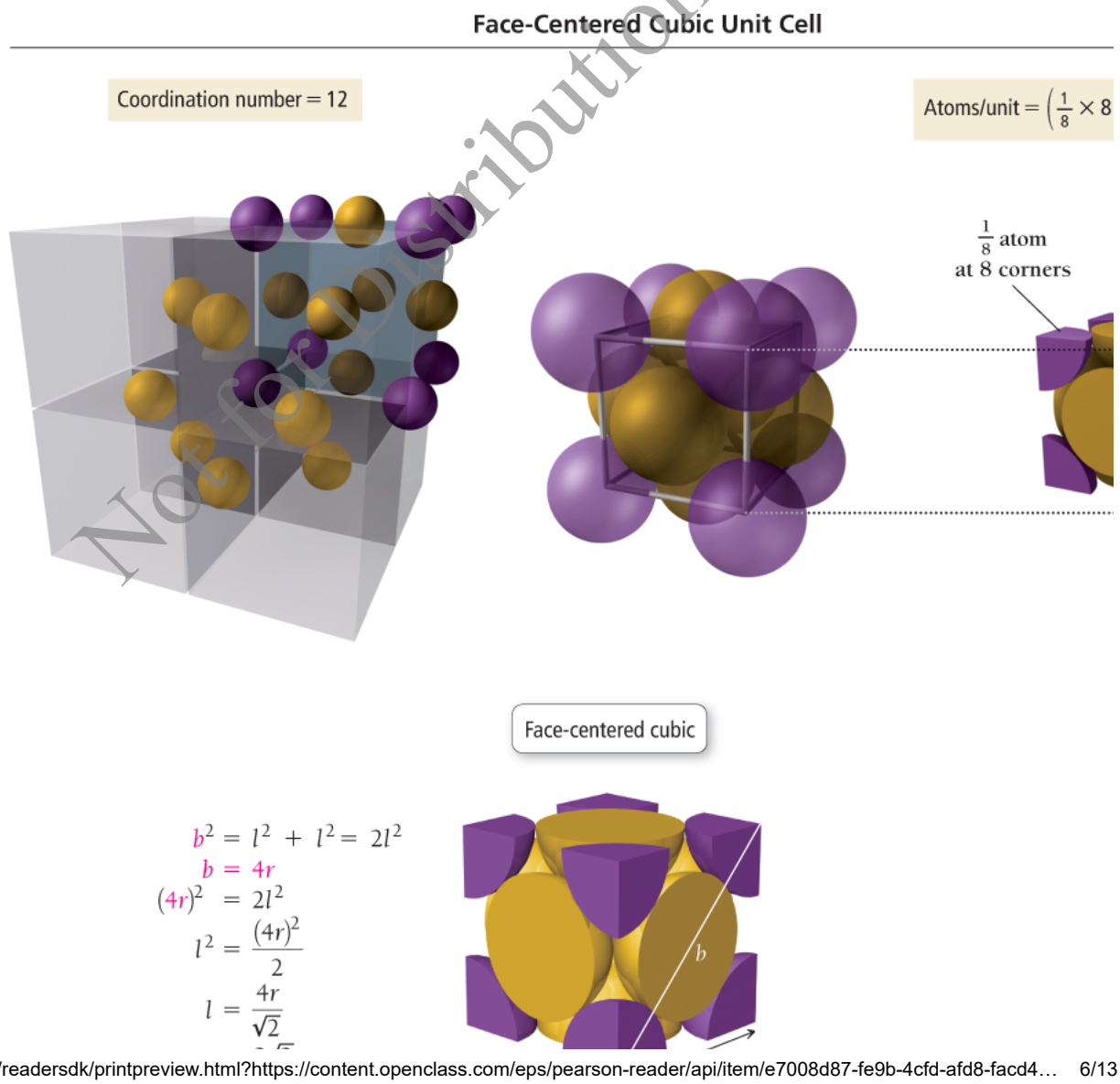
CHECK The units of the answer (pm) are correct. The magnitude is also reasonable since atomic radii range roughly from 50 to 200 pm.

FOR PRACTICE 12.3 An atom has a radius of 138 pm and crystallizes in the body-centered cubic unit cell. What is the volume of the unit cell in cm^3?

The **face-centered cubic** unit cell (Figure 12.6) is a cube with one atom at each corner and one atom (of the same kind) in the center of each cube face. Note that in the face-centered unit cell (like the body-centered unit cell), the atoms *do not* touch along each edge of the cube. Instead, the atoms touch *along the diagonal face.* The edge length in terms of the atomic radius is therefore $l = 2\sqrt{2}r$.

Figure 12.6 Face-Centered Cubic Crystal Structure

The different colors used on the atoms in this figure are for clarity only. All atoms within the structure are identical. In the leftmost structure, the atoms have been reduced in size for clarity.



$= 2\sqrt{2}r$

In the face-centered cubic lattice, the atoms touch along a face diagonal (line labeled b). The edge length is $2\sqrt{2r}$.

The face-centered unit cell contains four atoms per unit cell because the center atoms on each of the six faces are shared between two unit cells. There are $\frac{1}{2} \times 6 = 3$face-centered atoms plus a $\frac{1}{8} \times 8 = 1$corner atom, for a total of four atoms per unit cell. The coordination number of the face-centered cubic unit cell is 12, and its packing efficiency is 74%. In this structure, any one atom strongly interacts with more atoms than in either the simple cubic unit cell or the body-centered cubic unit cell.

Example 12.4 Relating Density to Crystal Structure

Aluminum crystallizes with a face-centered cubic unit cell. The radius of an aluminum atom is 143 pm. Calculate the density of solid crystalline aluminum in $\mathrm{g/cm^3}$.

SORT You are given the radius of an aluminum atom and its crystal structure. You are asked to find the density of solid aluminum.

GIVEN: $r = 143\ \mathrm{pm},$ face-centered cubic

FIND: d

STRATEGIZE The conceptual plan is based on the definition of density. Because the unit cell has the physical properties of the entire crystal, you can find the mass and volume of the unit cell and use these to calculate its density.

CONCEPTUAL PLAN

$$\begin{aligned} d &= m/V \\ m &= \text{mass of unit cell} \\ &= \text{number of atoms in cell} \times \text{mass of each atom} \\ V &= \text{volume of unit cell} \\ &= (\text{edge length})^3 \end{aligned}$$

SOLVE Begin by finding the mass of the unit cell. Determine the mass of an aluminum atom from its molar mass. Because the face-centered cubic unit cell contains four atoms per unit cell, you multiply the mass of aluminum by 4 to find the mass of a unit cell.

SOLUTION

$$\begin{aligned} m\,(\text{Al atom}) &= 26.98 \frac{g}{\cancel{\text{mol}}} \times \frac{1\ \cancel{\text{mol}}}{6.022 \times 10^{23}\ \text{atoms}} \\ &= 4.480 \times 10^{-23} \frac{\text{g}}{\text{atom}} \\ m\,(\text{unit cell}) &= 4\ \cancel{\text{atoms}} \left(4.480 \times 10^{-23} \frac{\text{g}}{\cancel{\text{atom}}} \right) \\ &= 1.792 \times 10^{-22}\ \text{g} \end{aligned}$$

Next, calculate the edge length (l) of the unit cell (in m) from the atomic radius of aluminum. For the face-centered cubic structure, $l = 2\sqrt{2}r$.

$$\begin{aligned} l &= 2\sqrt{2}r \\ &= 2\sqrt{2}\,(143\ \text{pm}) \end{aligned}$$

$$= 2\sqrt{2}\left(143 \times 10^{-12}\ \text{m}\right)$$
$$= 4.045 \times 10^{-10}\ \text{m}$$

Calculate the volume of the unit cell (in cm) by converting the edge length to cm and cubing the edge length. (Use centimeters because you want to report the density in units of g/cm^3.)

$$V = l^3$$
$$= \left(4.045 \times 10^{-10}\ \cancel{\text{m}} \times \frac{1\ \text{cm}}{10^{-2}\ \cancel{\text{m}}}\right)^3$$
$$= 6.618 \times 10^{-23}\ \text{cm}^3$$

Finally, calculate the density by dividing the mass of the unit cell by the volume of the unit cell.

$$d = \frac{m}{V} = \frac{1.792 \times 10^{-22}\text{g}}{6.618 \times 10^{-23}\ \text{cm}^3}$$
$$= 2.71\ \text{g/cm}^3$$

CHECK The units of the answer are correct. The magnitude of the answer is reasonable because the density is greater than $1\ \text{g/cm}^3$ (as you would expect for metals), but still not too high (because aluminum is a low-density metal).

FOR PRACTICE 12.4 Chromium crystallizes with a body-centered cubic unit cell. The radius of a chromium atom is 125 pm. Calculate the density of solid crystalline chromium in g/cm^3.

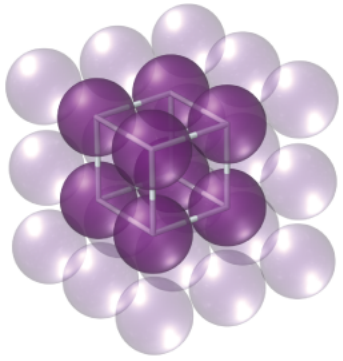
Interactive Worked Example 12.4 Relating Density to Crystal Structure

Conceptual Connection 12.1 Cubic Structures

Closest-Packed Structures

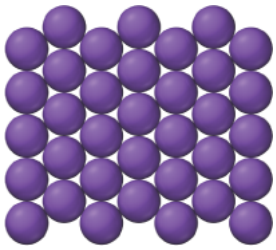
Interactive

Another way to envision crystal structures, which is especially useful in metals where bonds are not usually directional, is to think of the atoms as stacking in layers, much as fruit is stacked at the grocery store. For example, we can envision the simple cubic structure as one layer of atoms arranged in a square pattern with the next layer stacking directly over the first, so that the atoms in one layer align exactly on top of the atoms in the layer beneath it. As we saw previously, this simple cubic unit crystal structure has a great deal of empty space—only 52% of the volume is occupied by the spheres, and the coordination number is 6.

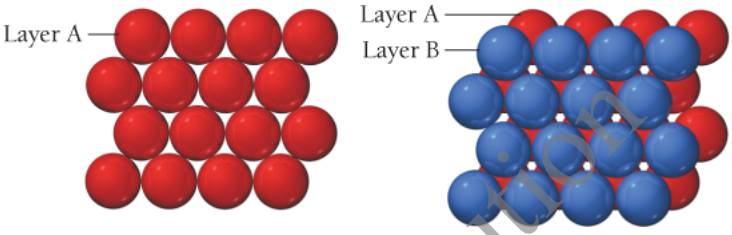


Simple Cubic

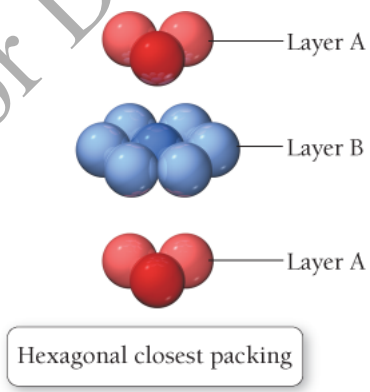
More space-efficient packing can be achieved by aligning neighboring rows of atoms in a pattern with one row offset from the next by one-half a sphere, as shown here:



In this way, the atoms pack more closely to each other in any one layer. We can further increase the packing efficiency by placing the next layer *not directly on top of the first*, but again offset so that any one atom actually sits in the indentation formed by three atoms in the layer beneath it, as shown here:



This kind of packing leads to two different crystal structures called *closest-packed structures*, both of which have a packing efficiency of 74% and a coordination number of 12. In the first of these two closest-packed structures—called **hexagonal closest packing**—the third layer of atoms aligns exactly on top of the first, as shown here:

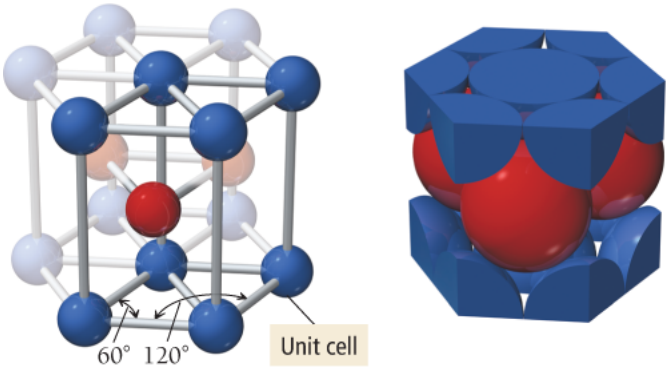


The pattern from one layer to the next is ABAB, with the third layer aligning exactly above the first. Notice that the central atom in layer B of this structure is touching six atoms in its own layer, three atoms in the layer above it, and three atoms in the layer below, for a coordination number of 12. The unit cell for this crystal structure is not a cubic unit cell but a hexagonal one, as shown in Figure 12.7.

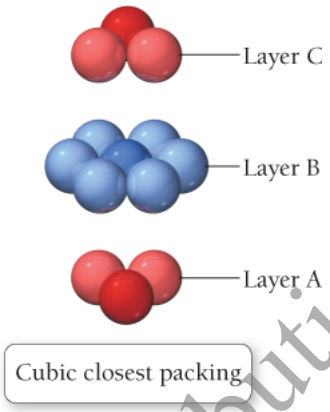
Figure 12.7 Hexagonal Closest Packing Crystal Structure

The unit cell is outlined in bold.

Hexagonal Closest Packing



In the second of the two closest-packed structures—called **cubic closest packing**—the third layer of atoms is offset from the first, as shown here:



The pattern from one layer to the next is ABCABC, with every fourth layer aligning with the first. Although not simple to visualize, the unit cell for cubic closest packing is the face-centered cubic unit cell, as shown in Figure 12.8. The cubic closest-packed structure is identical to the face-centered cubic unit cell structure.

Figure 12.8 Cubic Closest-Packing Crystal Structure

The unit cell of the cubic closest-packed structure is face-centered cubic.