Topic 3H - Solids

Types of Solids

Molecular

Discrete Molecules Held by Intermolecular Forces
Ice, "Dry Ice", Sugars

Network

Covalently-Bonded Arrays of Atoms
Diamond, Graphite, Ceramics

Amorphous

No Long-Range Order or Well-Defined Crystal Structure
Glass, Rubber, Plastics

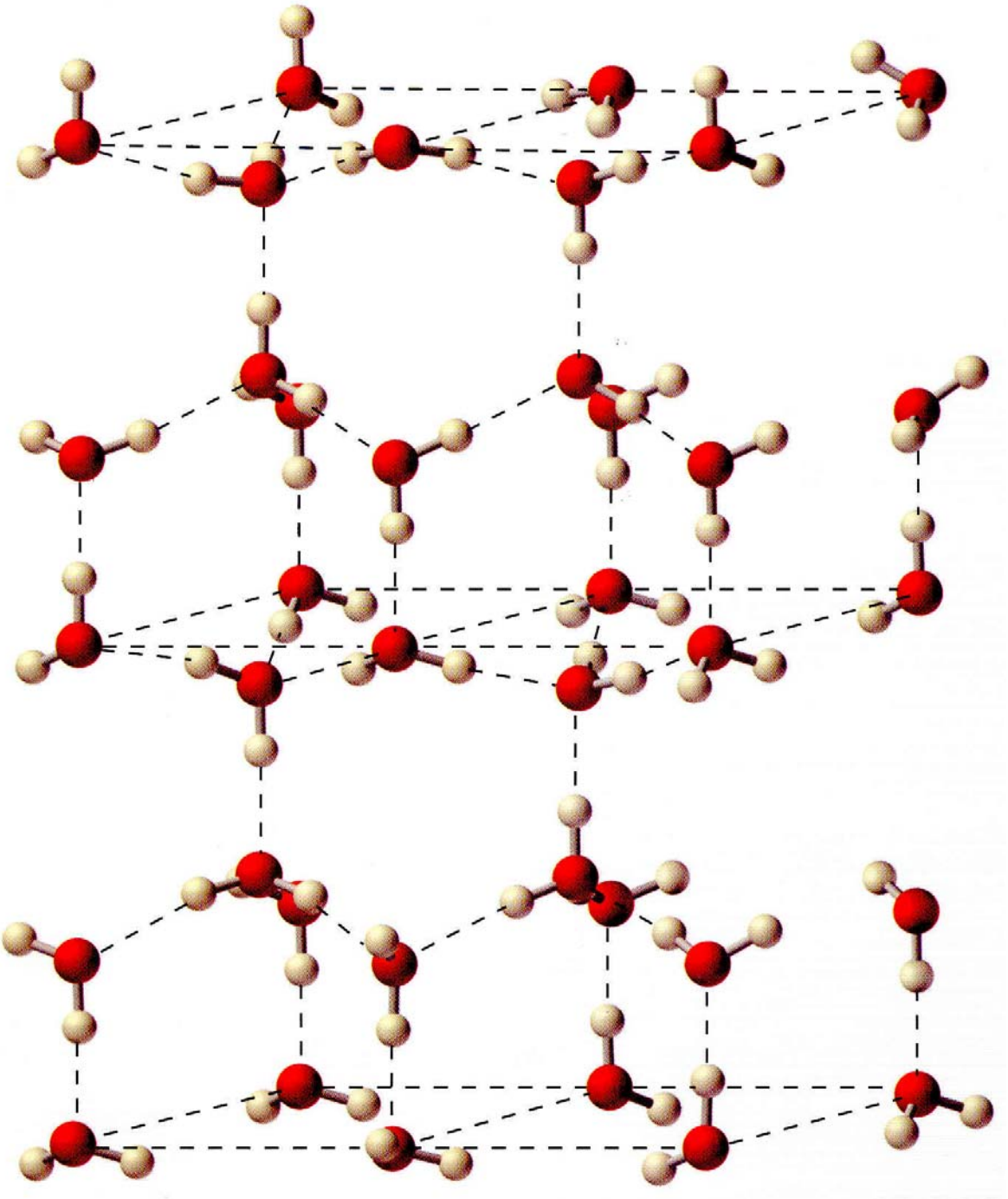
Metallic

Cations in a "Sea of Electrons"
Most metals

Ionic

Cations and Anions
NaCl, ZnS, KBr, etc.

Figure 14.31: The Crystal Structure of Water Ice



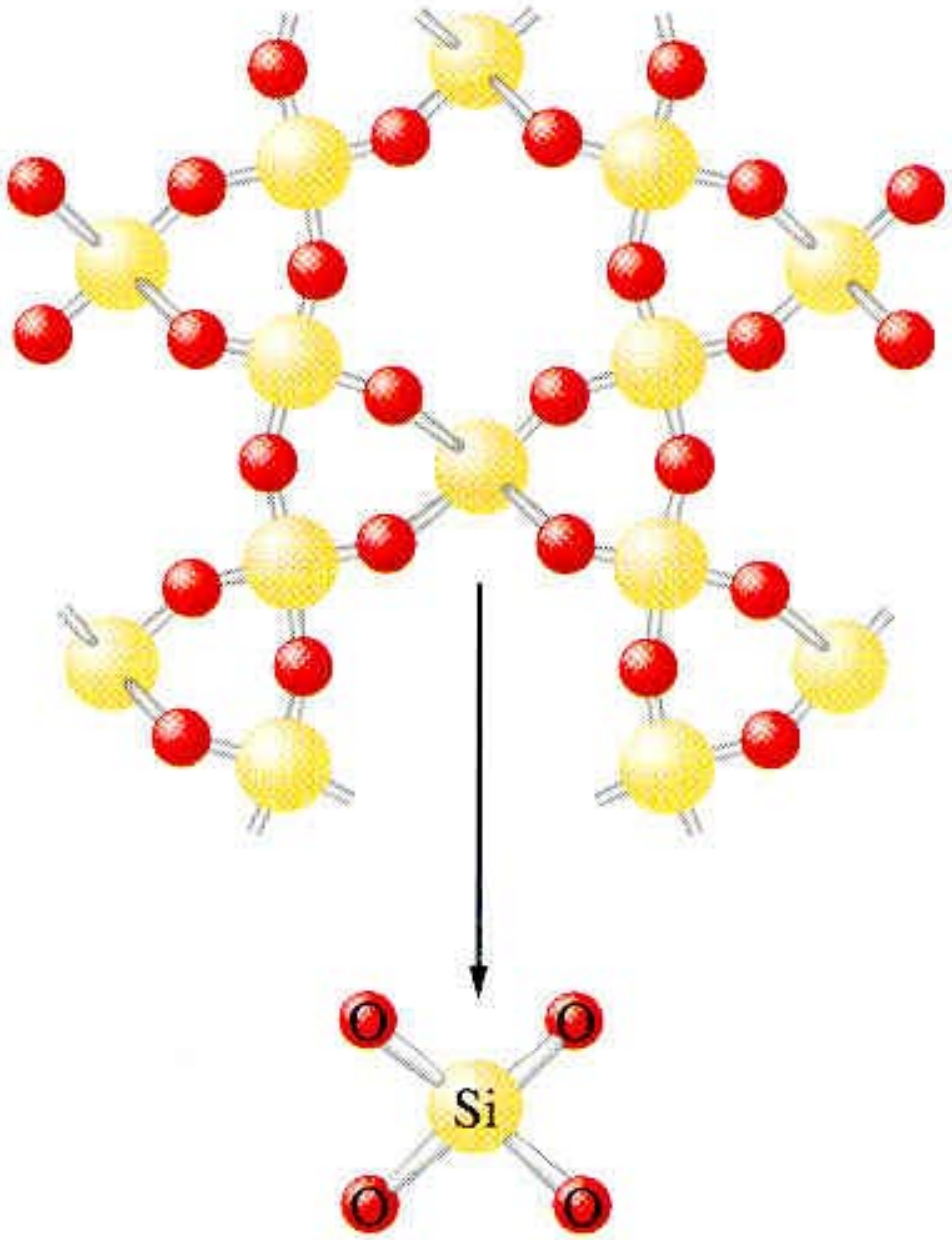
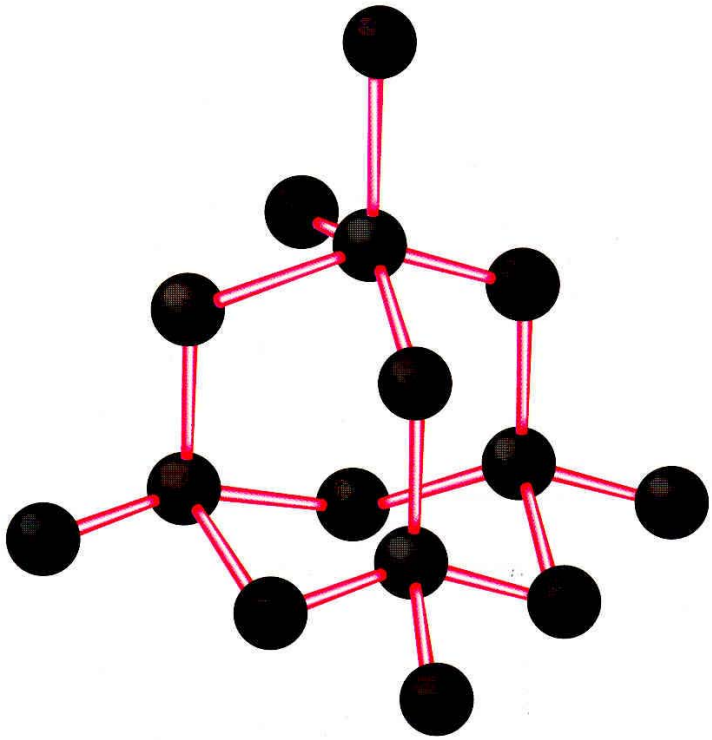
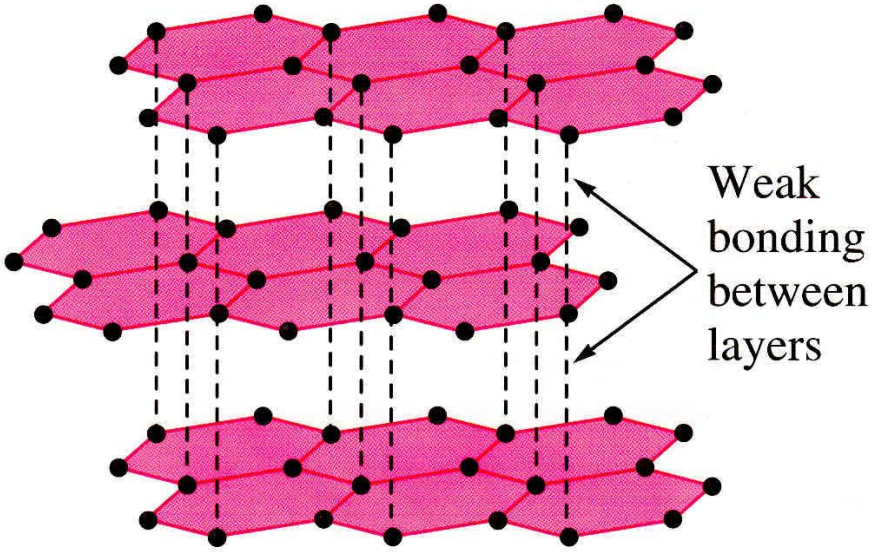


FIGURE 16.29

(Top) The structure of quartz (empirical formula SiO_2). Quartz contains chains of SiO_4 tetrahedra (bottom) that share oxygen atoms.

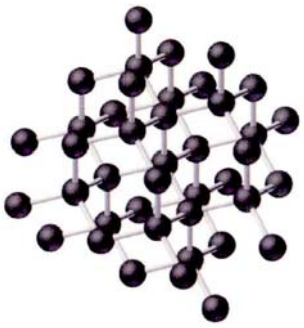


Diamond



Graphite

Figure 10.22
Diamond and graphite structures (ALLOTROPES)



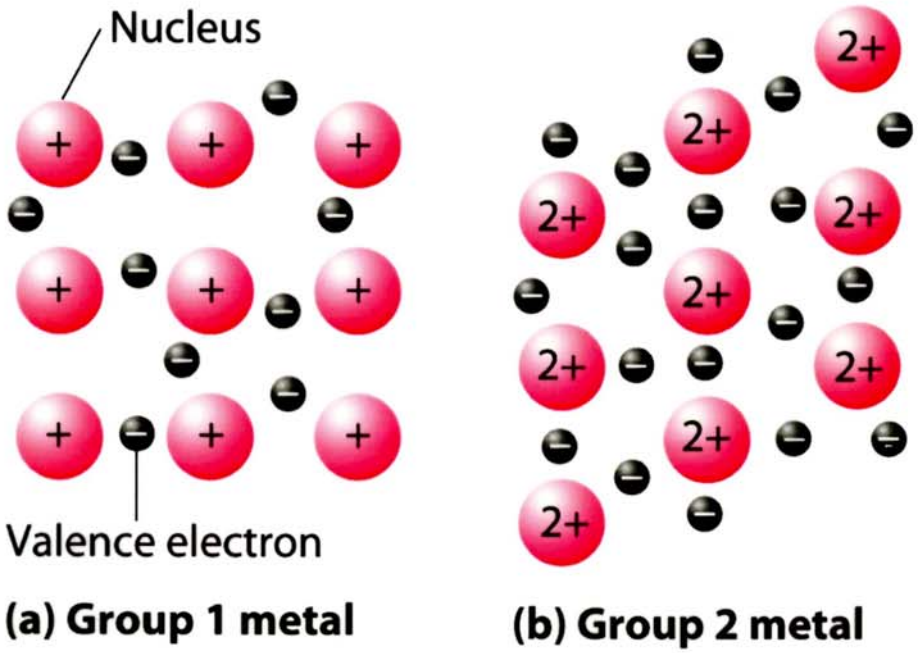
Diamond

Graphite

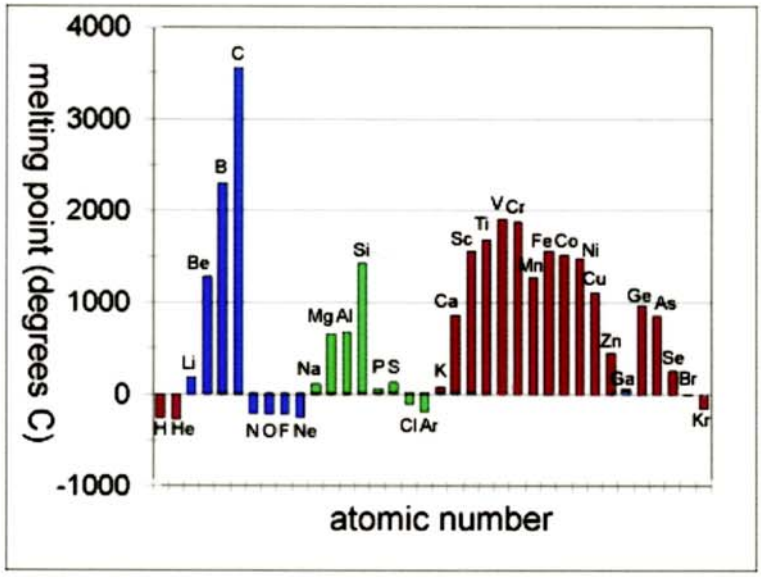
Buckminsterfullerene

Bonding in Metallic Solids

"Sea of Electrons" Model:



The Electron-Sea Model of Bonding in Metals. Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.



Structures of Crystalline Solids

Close-Packed

Coordination No. = 12 (max. possible for identical spheres)
Volume occupied = 74%
Interstices:
Two tetrahedral "holes" per atom
One octahedral "hole" per atom

Cubic Close-Packed:
Layers = A B C A B C A B C . . . .
Slip planes ⇒ malleability, ductility
Examples: Al, Cu, Ag, Au, Ni, Pt, Pb

Hexagonal Close-Packed:
Layers = A B A B A B A B . . . .
No slip planes ⇒ brittle, not malleable
Examples: Zn, Cd, Mg, Co, Be, Ti

Body-Centered Cubic

Coordination No. = 8
Volume occupied = 68%
Fe, Cr, Mn, V, Mo, alkali metals

Simple Cubic

Coordination No. = 6
Volume occupied = 52.4%
Rare

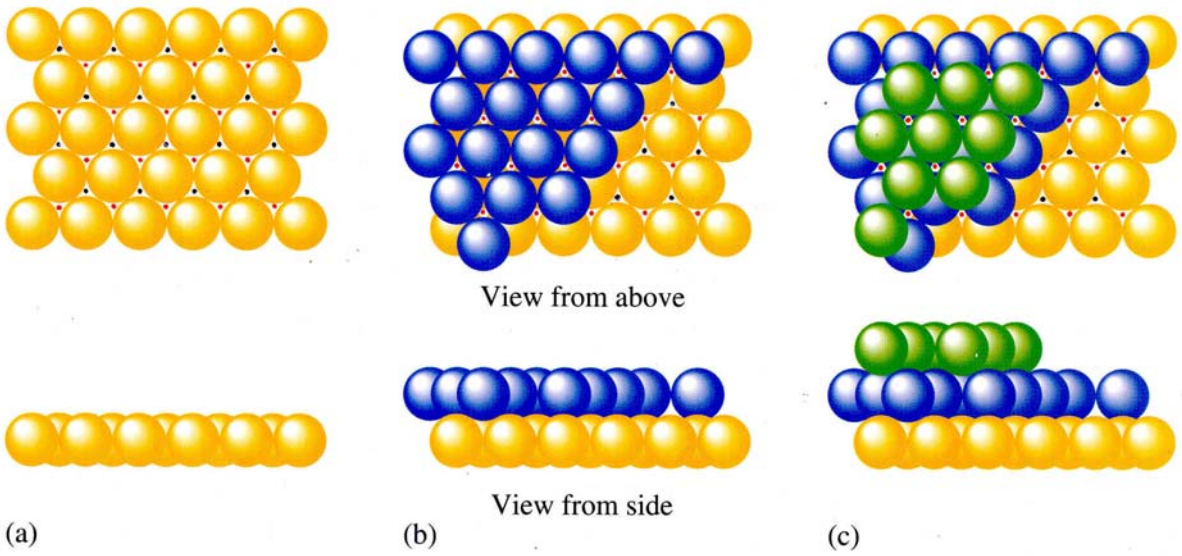
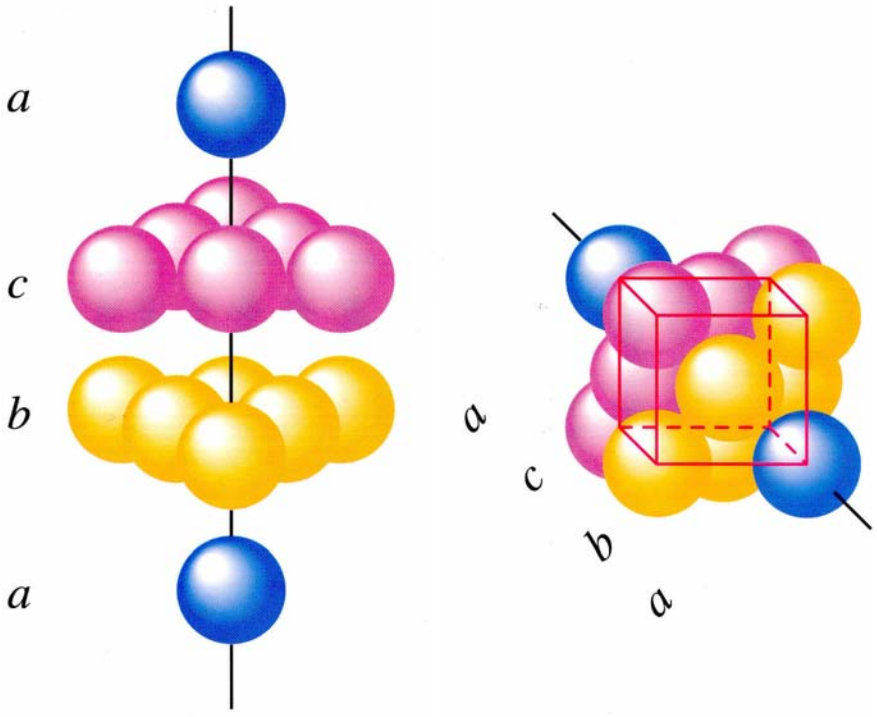


Figure 10.13
The closest packing of spheres



An atom in every fourth layer lies over an atom in the first layer.

Figure 10.15
Cubic closest packing

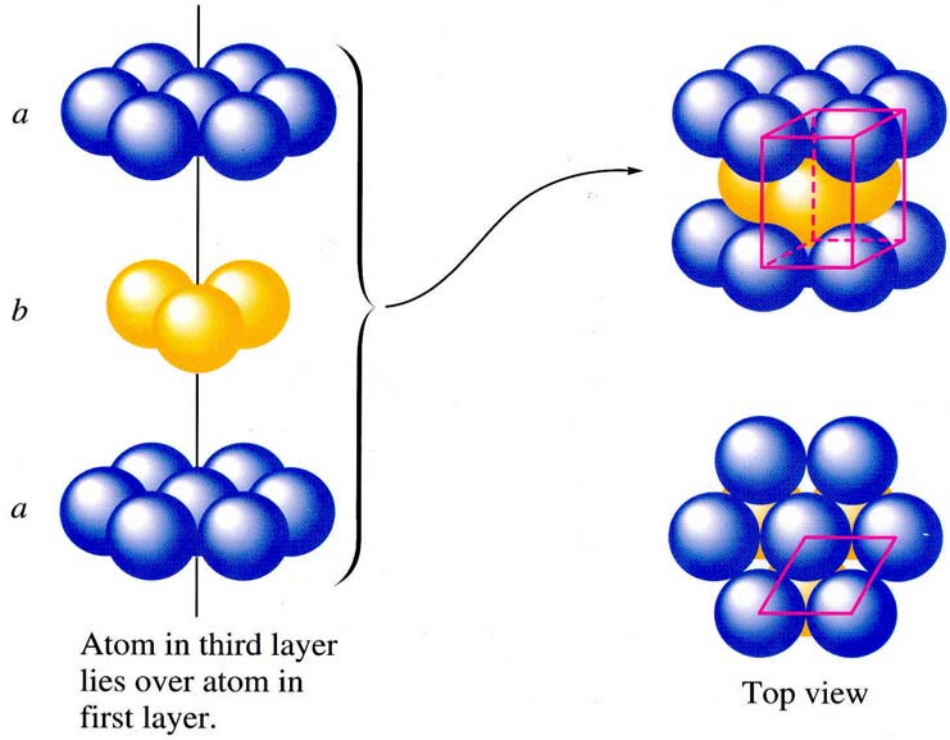


Figure 10.14
Hexagonal closest packing

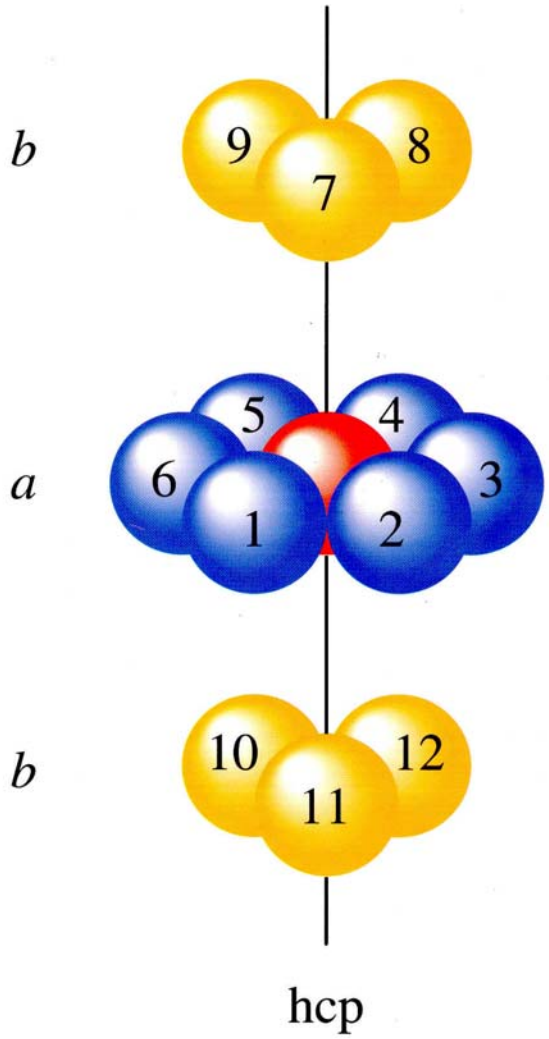


Figure 10.16
Closest neighbors in closest packed spheres

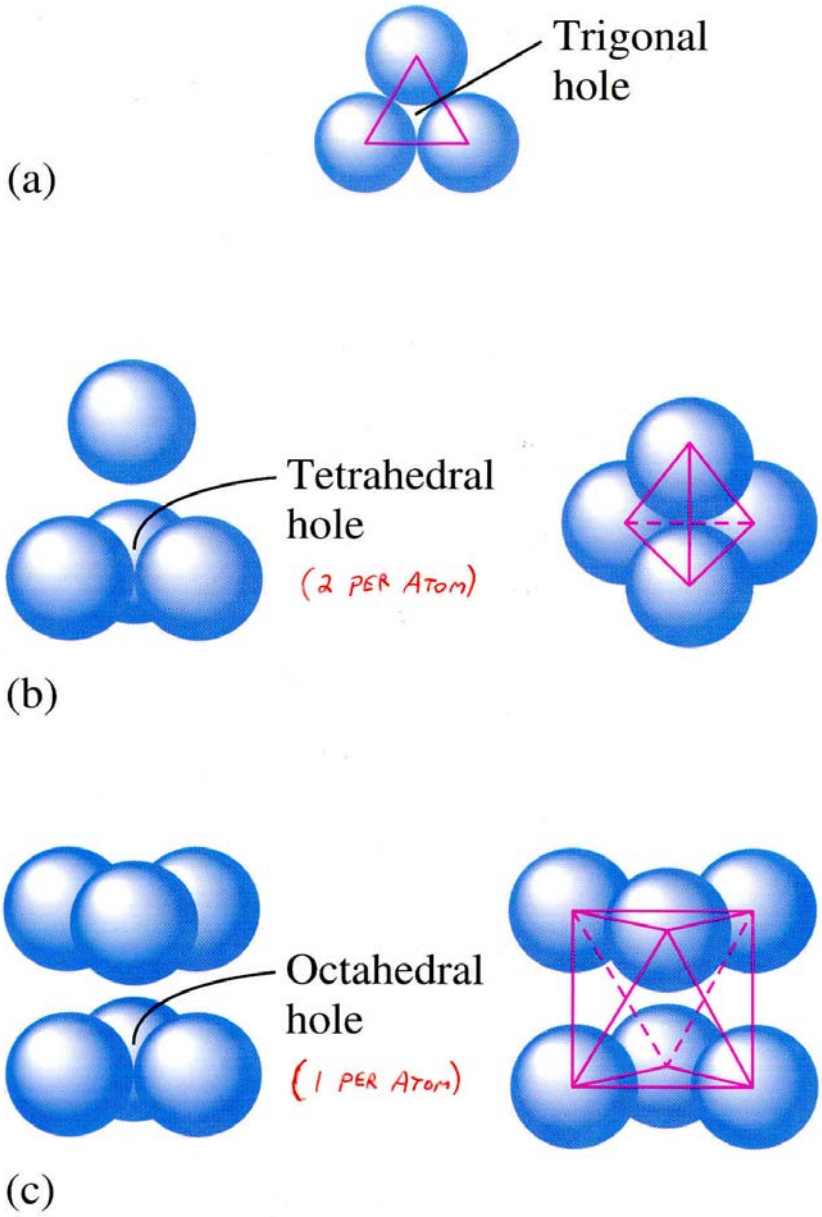


Figure 10.33
Trigonal, tetrahedral, and octahedral holes

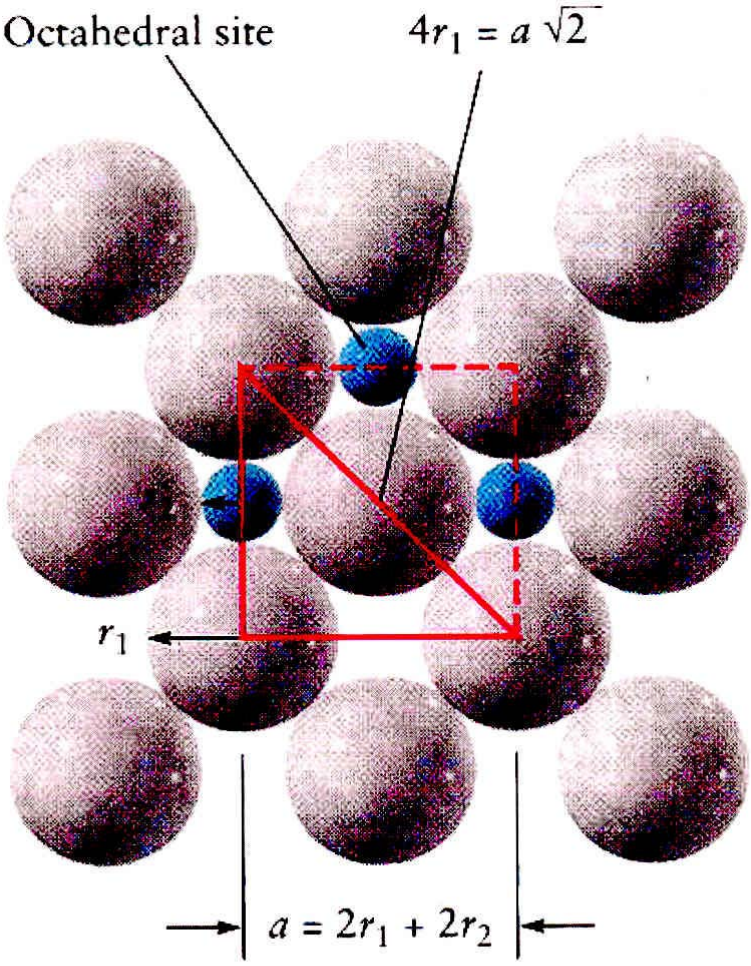


FIGURE 21.15 Octahedral sites in an fcc lattice. The geometric procedure for relating the site radius r_2 to the atom radius r_1 is shown.

From Pythagorean Theorem,

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

$$16r^2 = 2a^2$$

$$a = 8^{1/2}\, r$$

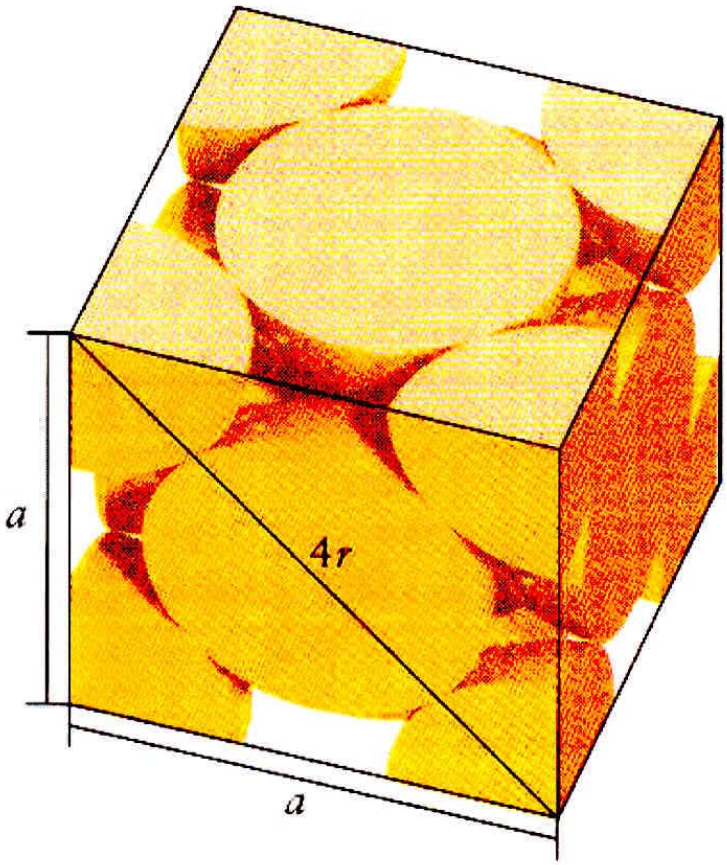
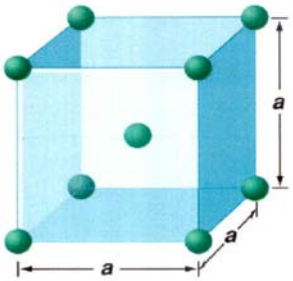
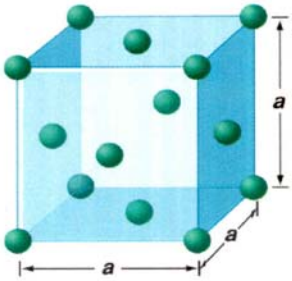
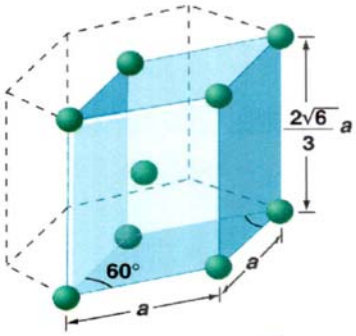
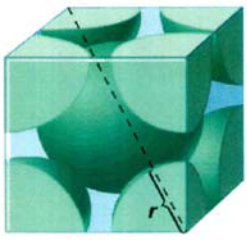
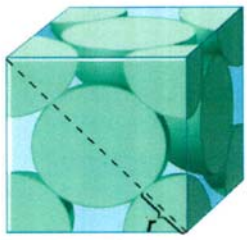
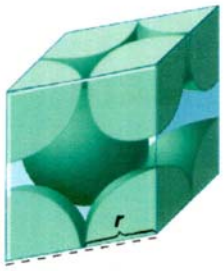
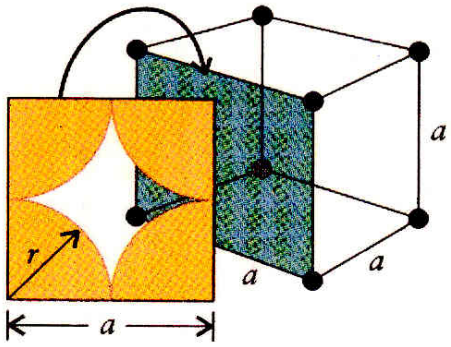
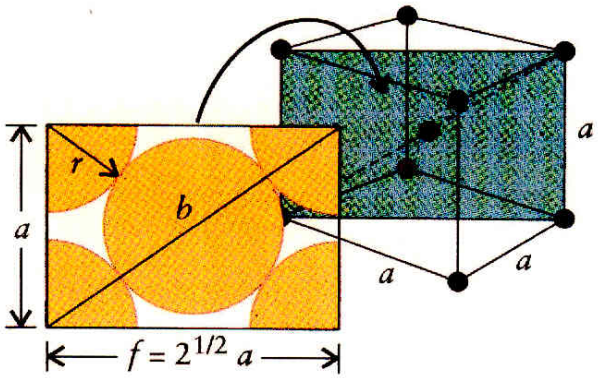


FIGURE 5.31 The relation of the dimensions of a face-centered cubic unit cell to the radius, *r*, of the spheres. The spheres are in contact along the face diagonals.

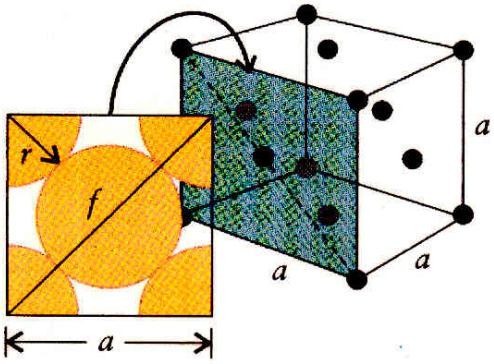
Lattice type	Body-centered cubic	Face-centered cubic	Hexagonal close-packed
Unit cell Ball-and-line			
Unit cell Space-filling			
Atomic radius	$r = \frac{\sqrt{3}}{4} a$	$r = \frac{\sqrt{2}}{4} a$	$r = \frac{1}{2} a$
Cell volume	$V = a^3$	$V = a^3$	$V = \sqrt{2}\, a^3$
Atoms / unit cell	2	4	2
	$a = \frac{4}{\sqrt{3}} r = 2.309\, r$	$a = \frac{4}{\sqrt{2}} r = 2.828\, r$	$a = 2\, r$



(a) Primitive cubic



(b) Body-centered cubic



(c) Face-centered cubic (ccp)

FIGURE 5.33 The geometries of three cubic unit cells, showing the relation of the dimensions of each cell to the radius, *r*, of a sphere representing an atom or ion. The side of a cell is *a*, the diagonal of the body of a cell, *b*, and the diagonal of a face, *f*.

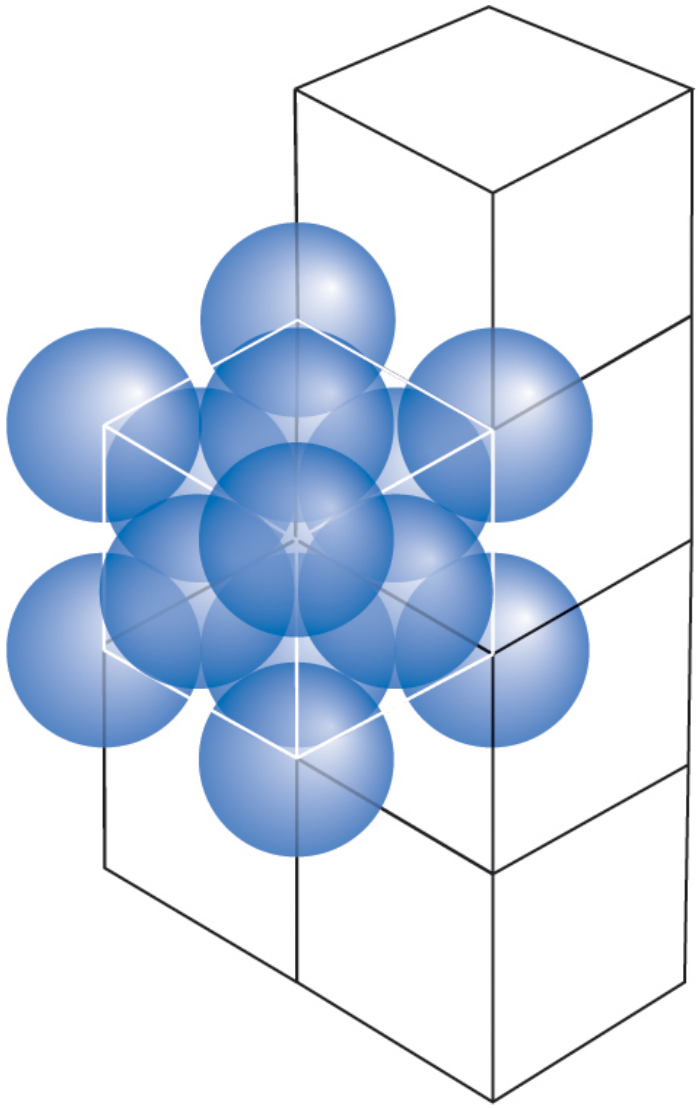


FIGURE 6.33 The entire crystal structure is constructed from a single type of unit cell by stacking the cells together without any gaps.

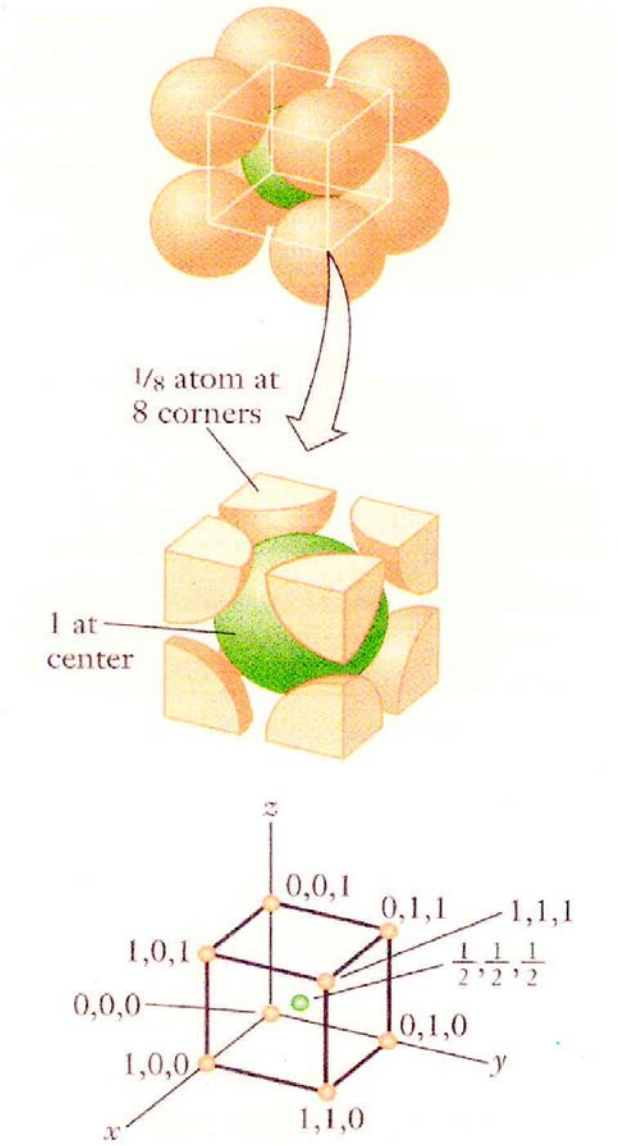


FIGURE 21.12 The b.c.c. structure. An atom is located at the center of each cubic cell (green) as well as at each corner of the cube (orange). The atoms are reduced slightly in size to make positions clear.

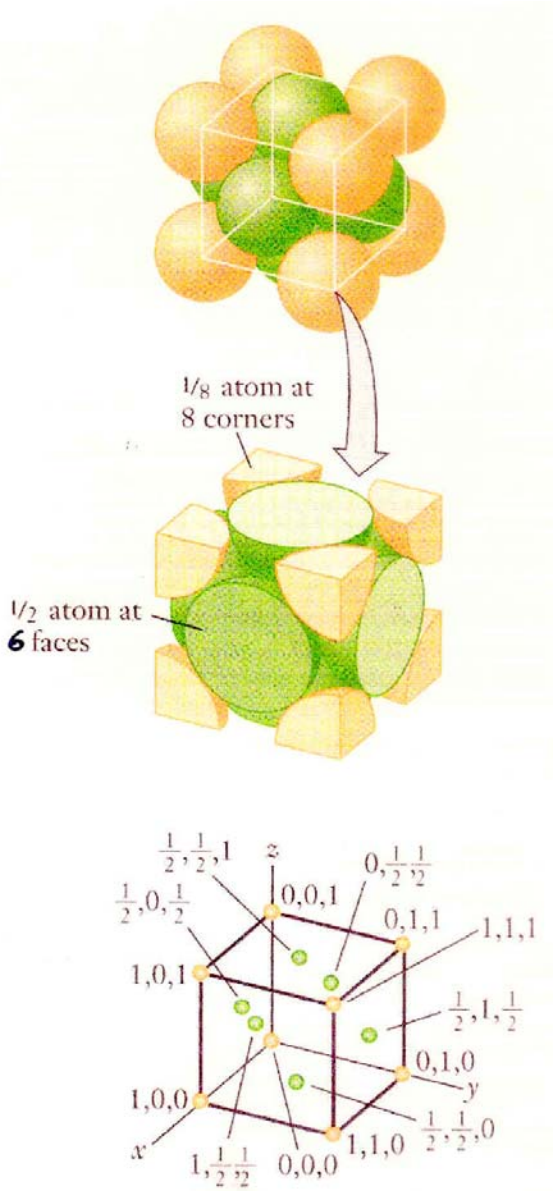


FIGURE 21.13 The f.c.c. structure. Atoms are located at the centers of the faces (green) as well as at the corners of the cube (orange). The atoms are reduced slightly in size to make positions clear.

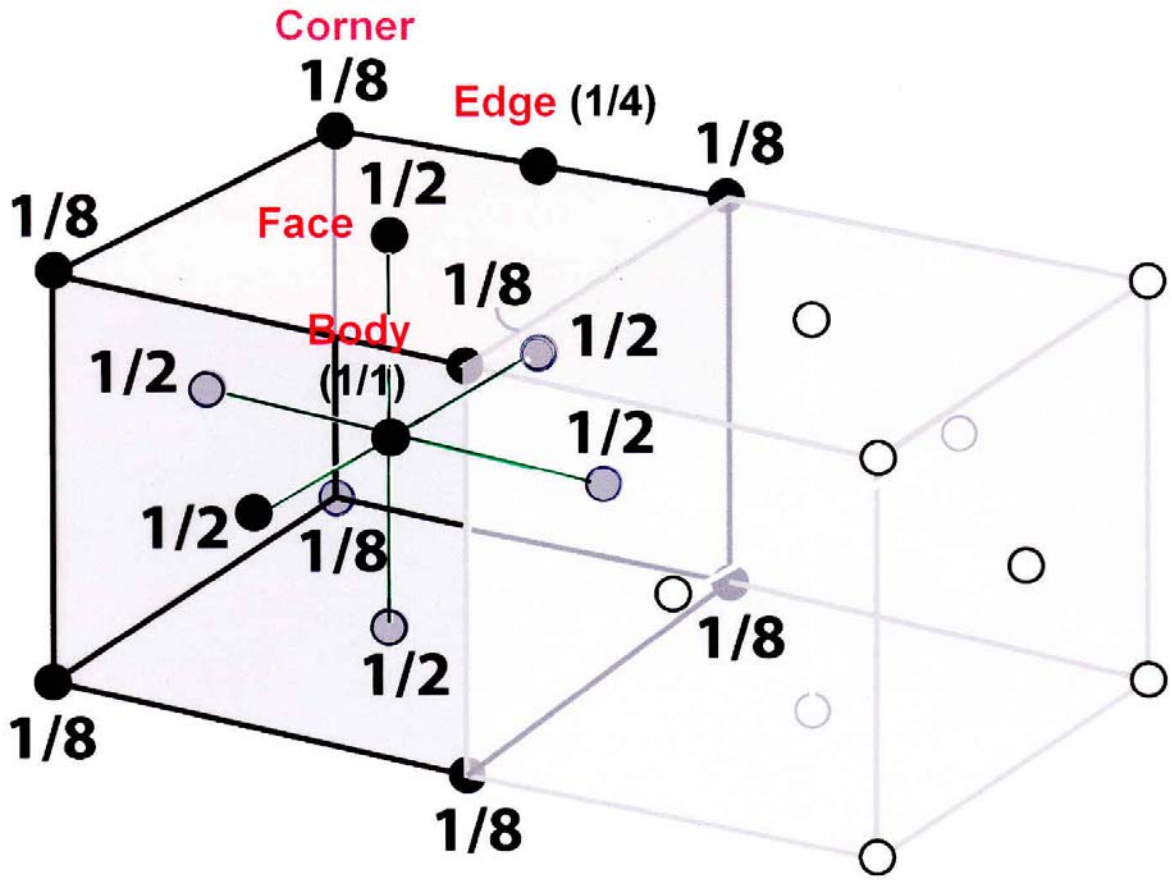


Table 17-2 Structural Properties of Cubic Lattices

	Simple Cubic	Body-Centered Cubic	Face-Centered Cubic
Lattice points per cell	1	2	4
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$a\sqrt{3}/2 = 0.866a$	$a\sqrt{2}/2 = 0.707a$
Atomic radius	$a/2$	$a\sqrt{3}/4 = 0.433a$	$a\sqrt{2}/4 = 0.354a$
Packing fraction	$\frac{\pi}{6} = 0.524$	$\frac{\sqrt{3}\pi}{8} = 0.680$	$\frac{\sqrt{2}\pi}{6} = 0.740$

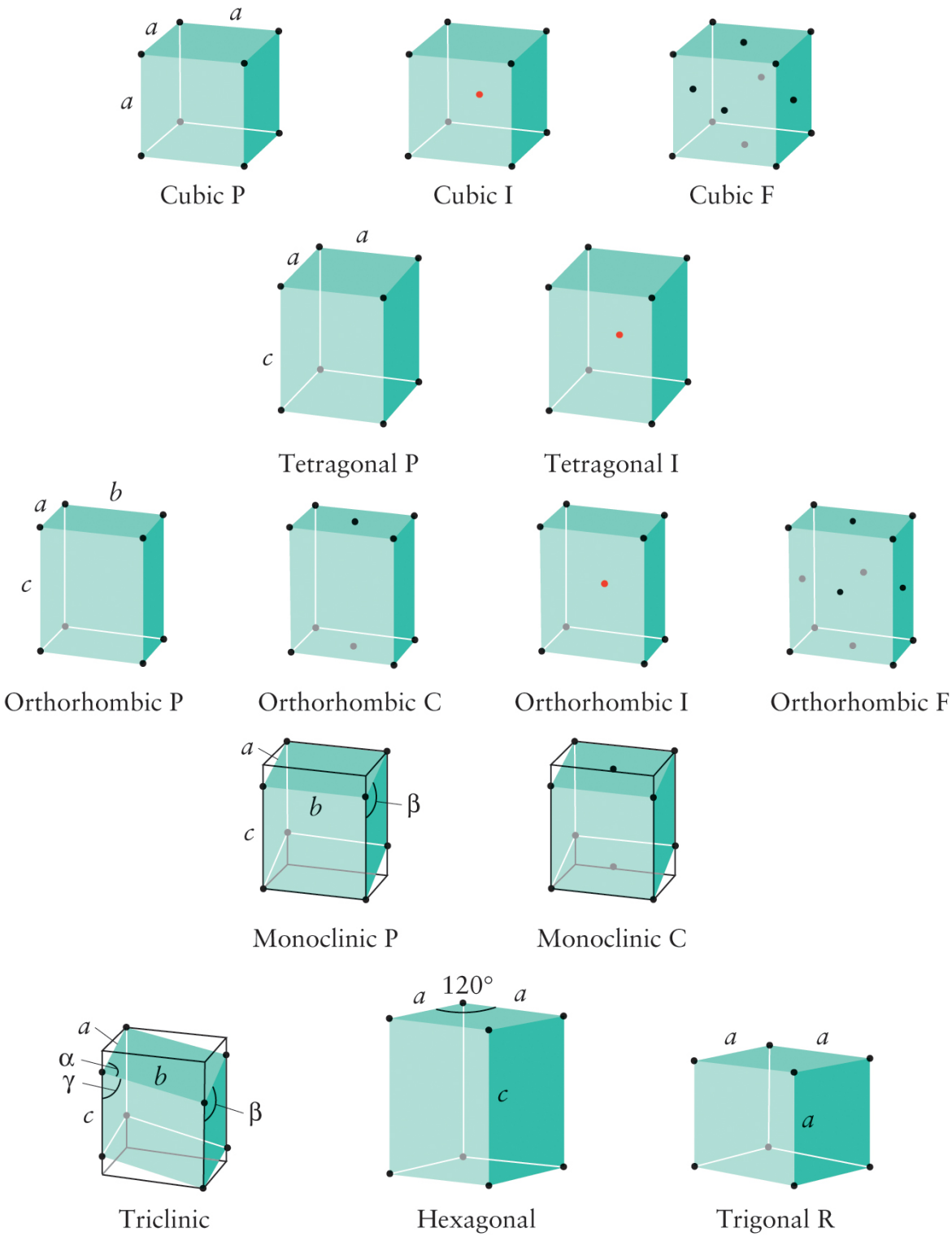
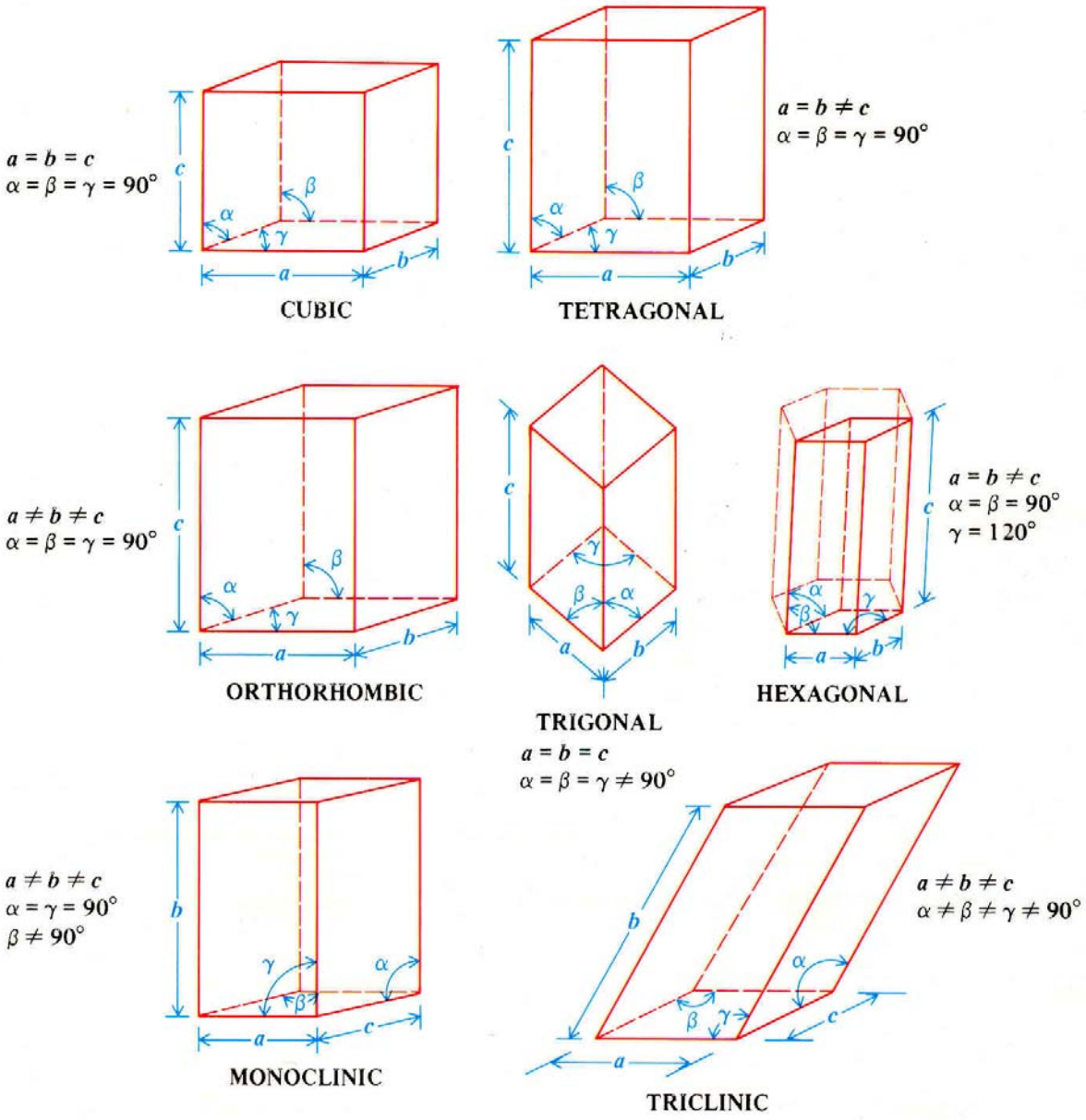


FIGURE 6.37 The 14 Bravais lattices. P denotes primitive; I, body-centered; F, face-centered; C, with a lattice point on two opposite faces; and R, rhombohedral (a rhomb is an oblique equilateral parallelogram).



$$V_{\text{unit cell}} = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

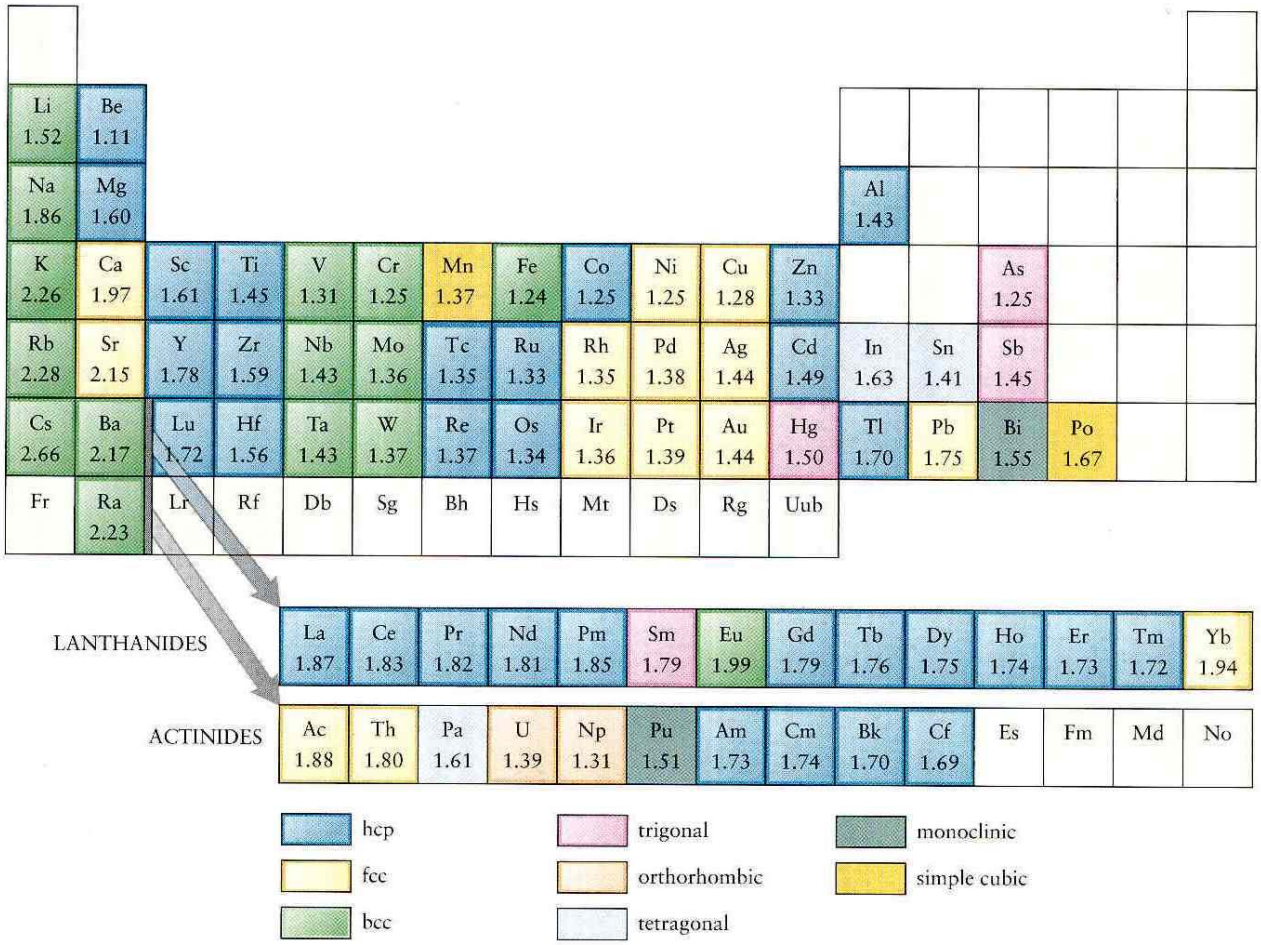


FIGURE 21.20 Crystal structures of the metallic elements at 25°C and 1 atm pressure. Atomic radii (Å) are calculated as one half the closest atom–atom distance in each structure; in most cases this is the same radius as calculated using the hard sphere contact model of Example 21.4. There are no known crystal structures for those elements for which atomic radii are not listed.

Structures of Ionic Solids

Rock-Salt

6,6 Coordination (1 : 1)
c.c.p. Cl^- anions, with Na^+ cations in all octahedral holes
Cation/Anion radius ratio = 0.414 to 0.732 ($R_{Na+}/R_{Cl-} = 0.56$)
R.R. in oct. holes — R.R. in b.c.c.
Examples: NaCl, KBr, MgO, CaO, AgCl

Cesium Chloride

8,8 Coordination (1 : 1)
Interpenetrating primitive cubic structures of cations and anions
Cation/Anion radius ratio > 0.732 ($R_{cs+}/R_{Cl-} = 0.94$)
Examples: CsCl, CsI

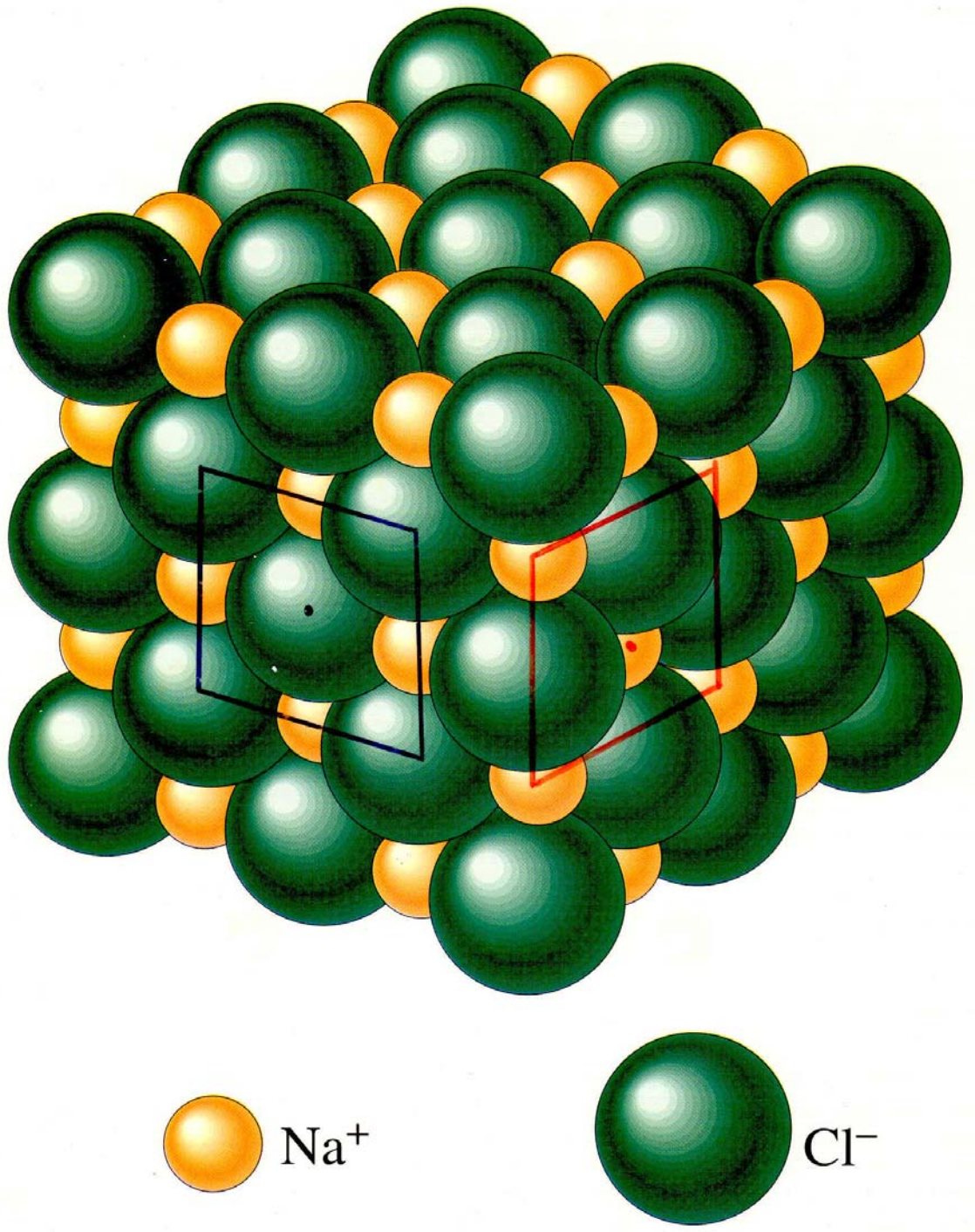
Zinc-Blende

4,4 Coordination (1 : 1)
c.c.p. S^{2-} anions, with Zn^{2+} cations in ½ of the tetrahedral holes
Cation/Anion radius ratio < 0.414 ($R_{Zn2+}/R_{S2-} = 0.33$)
Examples: ZnS, CdS, ZnO

Fluorite

4,2 Coordination (1 : 2)
c.c.p. cations, with anions in all tetrahedral holes
Examples: CaF_2, CeO_2 ($R_{Ca2+}/R_{F-} = 0.75$)

The Arrangement of Ions in Sodium Chloride



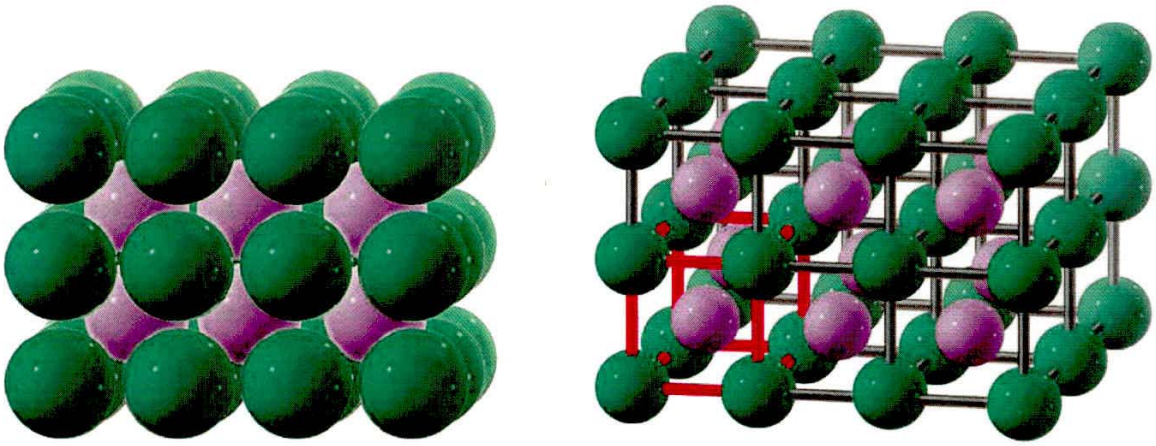
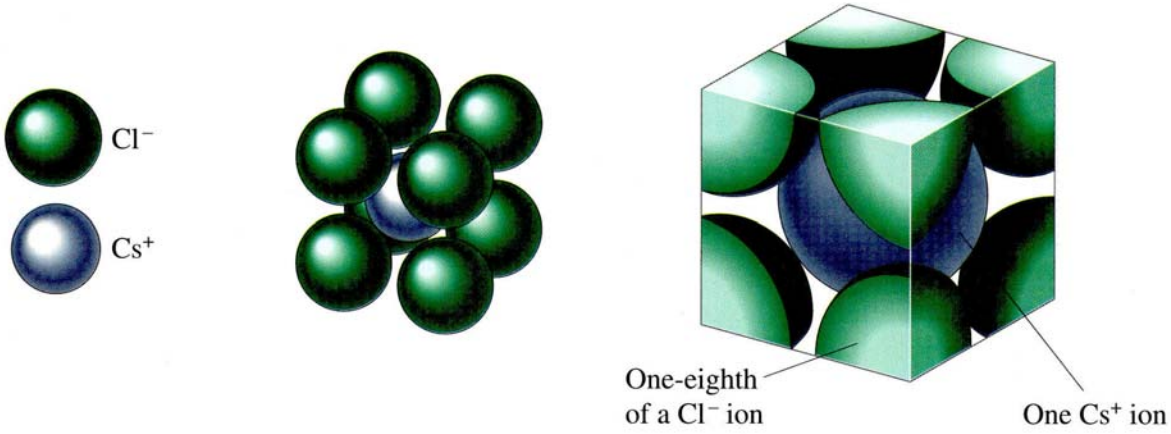


FIGURE 21.17 The structure of cesium chloride. On the left, the sizes of the Cs^+ ions (purplish pink) and the Cl^- ions (green) are drawn to scale. On the right, they are reduced in size to allow a unit cell (shown by red lines) to be outlined clearly. Note that the lattice in this structure is simple cubic, with one Cs^+ ion and one Cl^- ion per unit cell.



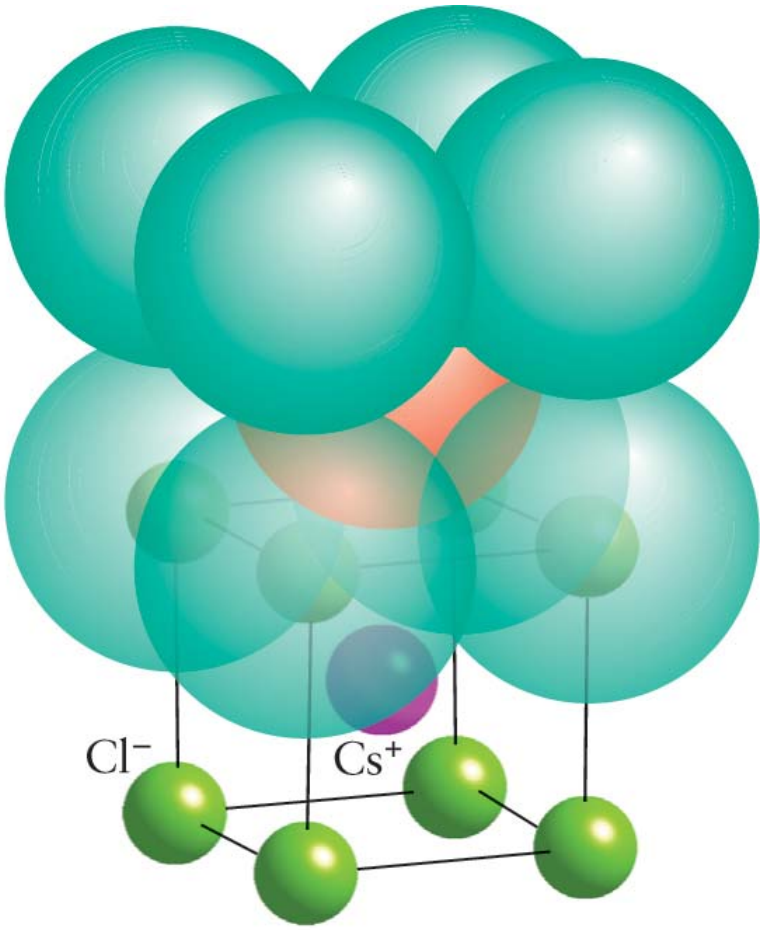
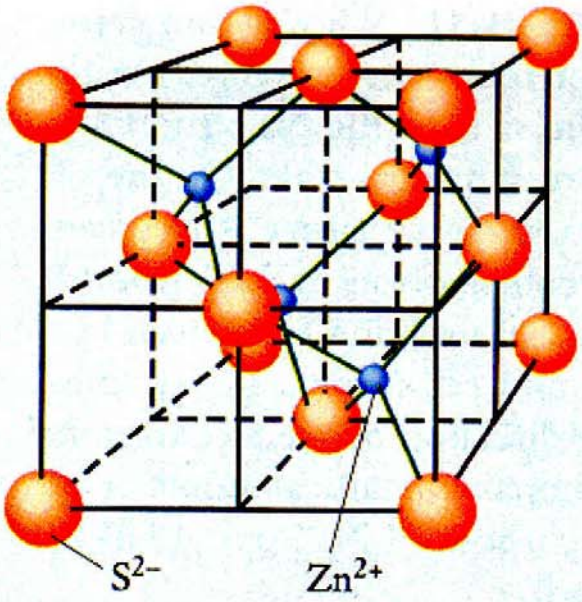
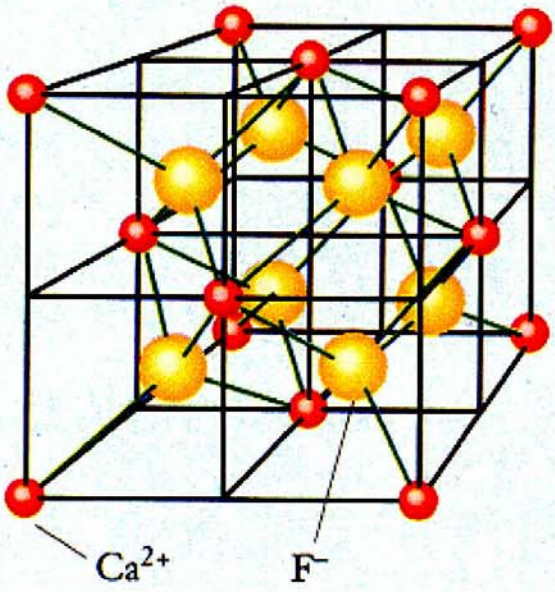


FIGURE 6.43 The cesium chloride structure: above is the unit cell and below a second unit cell showing the location of the centers of the ions.



Sphalerite (ZnS)

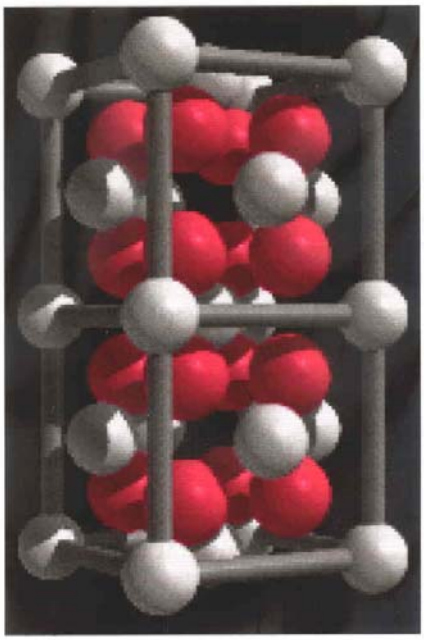


Fluorite (CaF_2)

FIGURE 19.19 Two ionic lattices in the f.c.c. system. A single (nonprimitive) cubic unit cell of each is shown.

CaF_2 (Fluorite structure)

Cubic-close packed Ca^{2+} ions, with F^- ions in all of the tetrahedral holes.



ZnS (Zincblende structure)

Cubic-close packed S^{2-} ions, with Zn^{2+} ions in ½ of the tetrahedral holes.