GENERAL CHEMISTRY

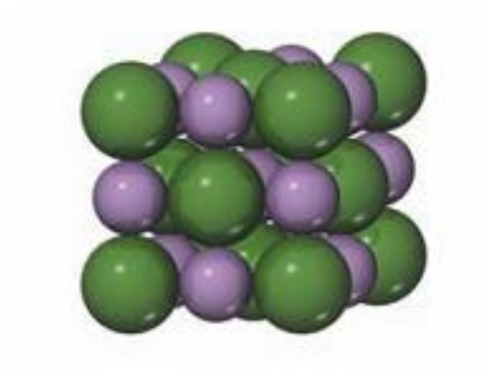
Chapter 12
Solids and Modern Materials

Contents

12-1 Classification of Solids

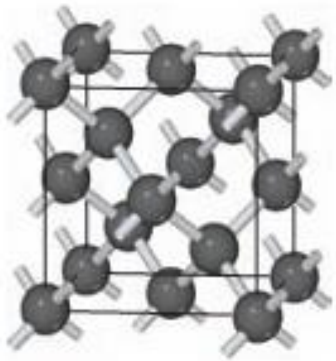
Metallic solids

Extended networks of atoms held together by metallic bonding (Cu, Fe)



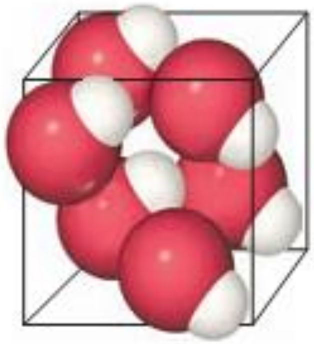
Ionic solids

Extended networks of ions held together by ion–ion interactions (NaCl, MgO)



Covalent-network solids

Extended networks of atoms held together by covalent bonds (C, Si)



Molecular solids

Discrete molecules held together by intermolecular forces (HBr, H_2O)

12-2 Structures of Solids

Crystalline solids are solids in which atoms are arranged in an orderly repeating pattern

- have well-defined faces and shapes

Iron pyrite
(FeS_2)
a crystaline solid

Amorphous solids lack the order found in crystalline solids

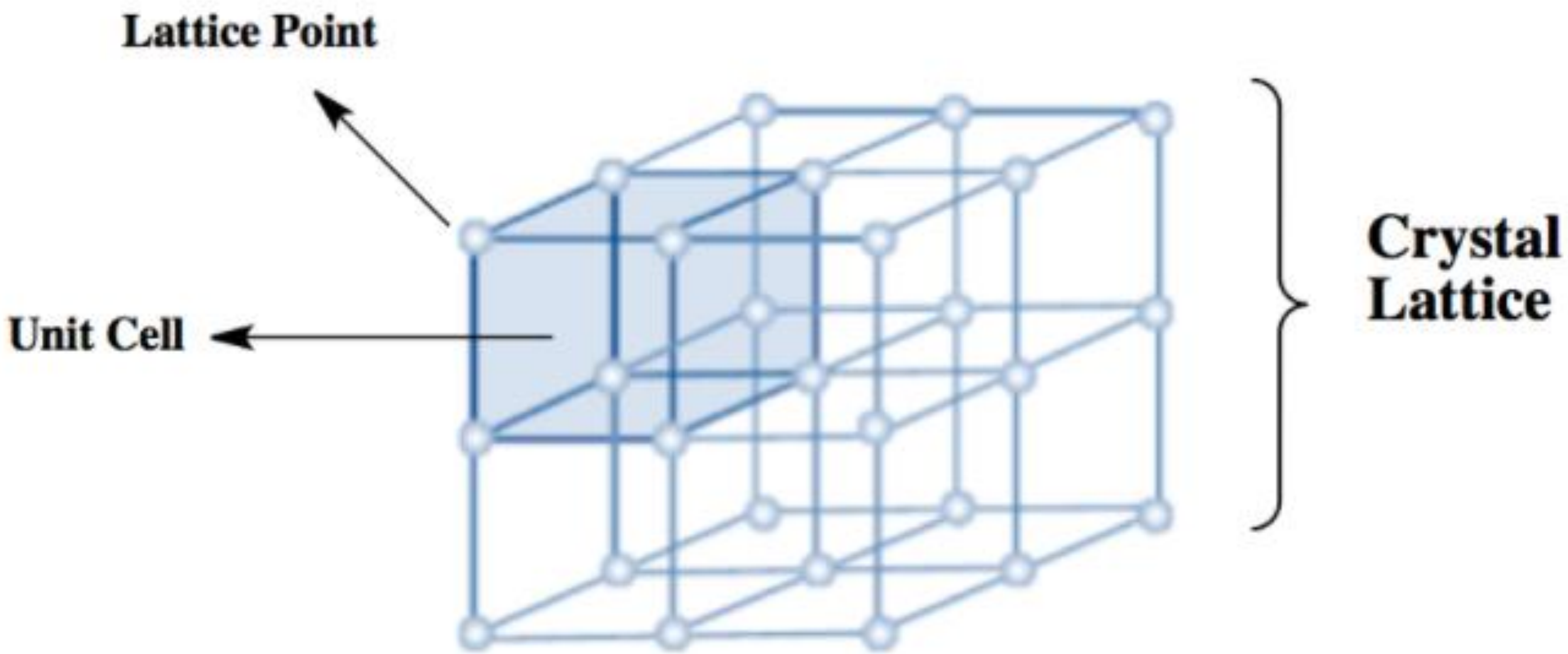
- similar to the structures of liquids at the atomic level, but the molecules, atoms, and/or ions lack the freedom of motion they have in liquids.
- do not have the well-defined faces and shapes

Obsidian
(typically $KAlSi_3O_8$)
an amorphous solid

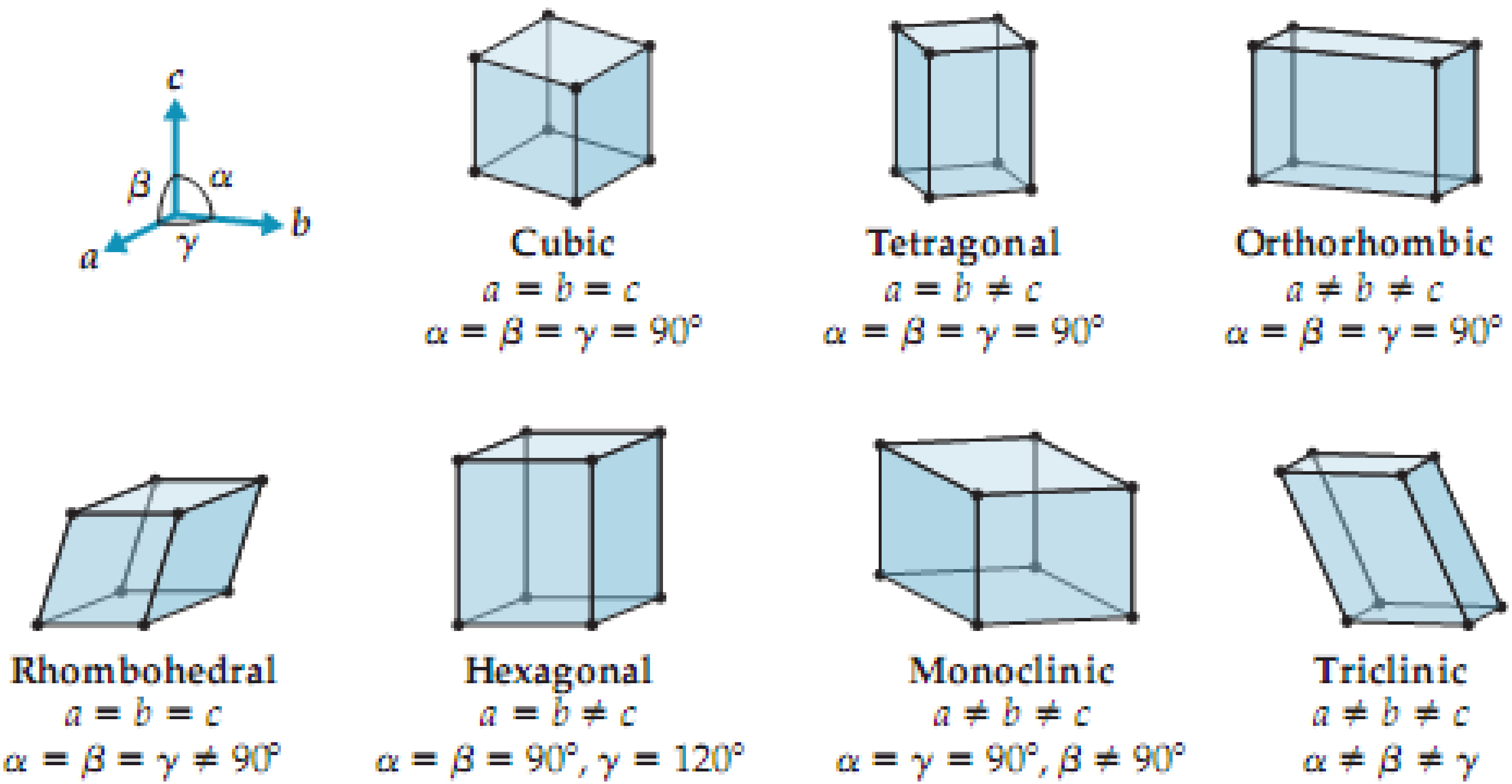
Unit Cells and Crystal Lattices

When examining the particles within a crystal you may observe them tightly packed in an organized pattern.

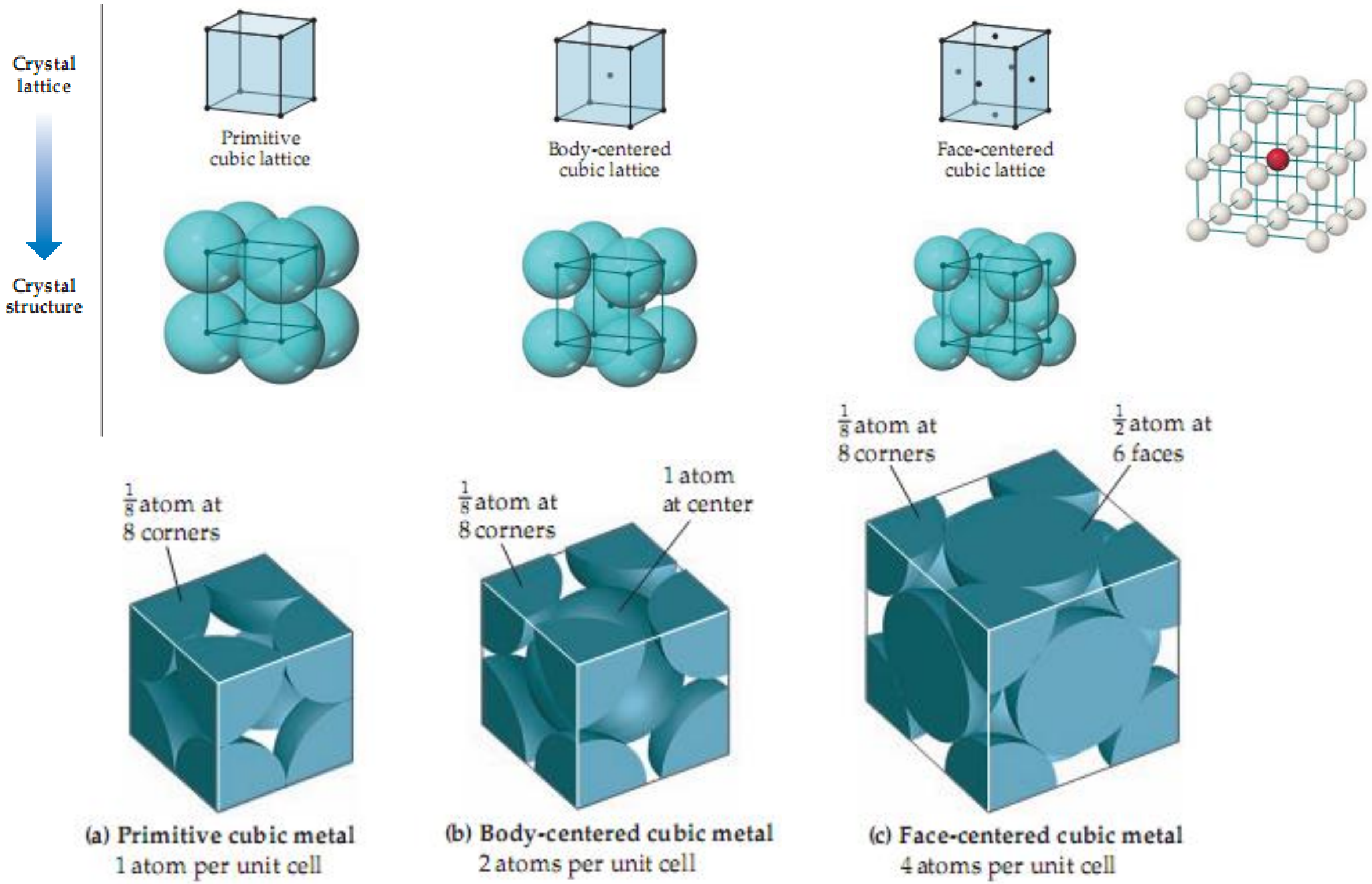
- The **lattice point** represents the area within the crystal that has identical surroundings all around.
- The **unit cell** represents the smallest portion of the crystal that, if reproduced in all three directions, would give the crystal.



The seven 3D primitive lattices



12-3 Metallic solids

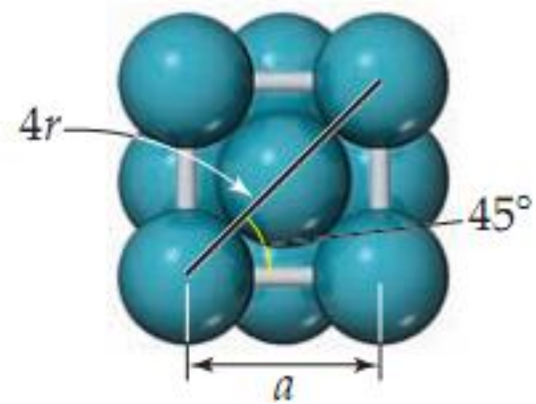


EXAMPLE

It is not possible to pack spheres together without leaving some void spaces between the spheres. Packing efficiency is the fraction of space in a crystal that is actually occupied by atoms. **Determine the packing efficiency of a face-centered cubic metal**.

A face-centered cubic metal has four atoms per unit cell. Therefore, the volume occupied by the atoms is

$$\text{Occupied volume} = 4 \times \left(\frac{4\pi r^3}{3}\right) = \frac{16\pi r^3}{3}$$



A diagonal across a face of the unit cell is equal to four times the atomic radius, r

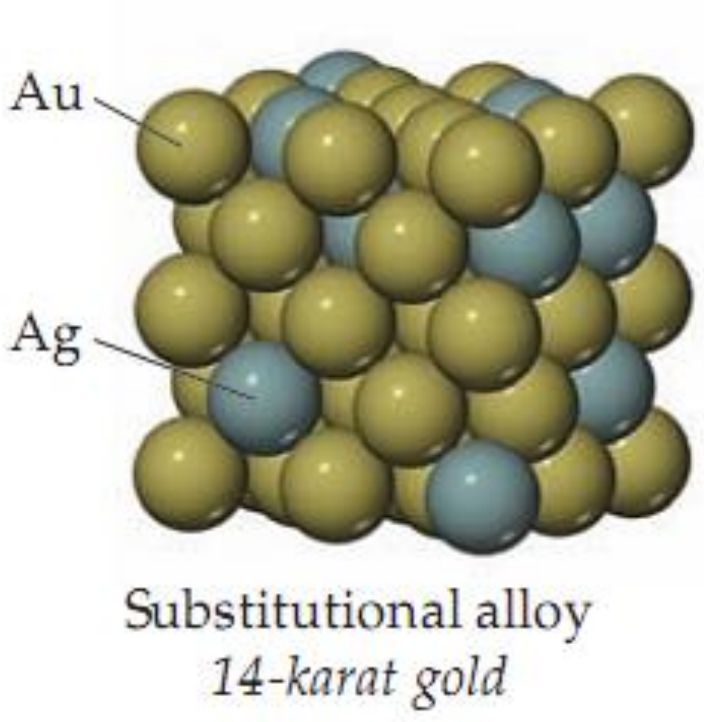
$$a = 4r\cos(45^\circ) = 4r(\sqrt{2}/2) = (2\sqrt{2})r$$

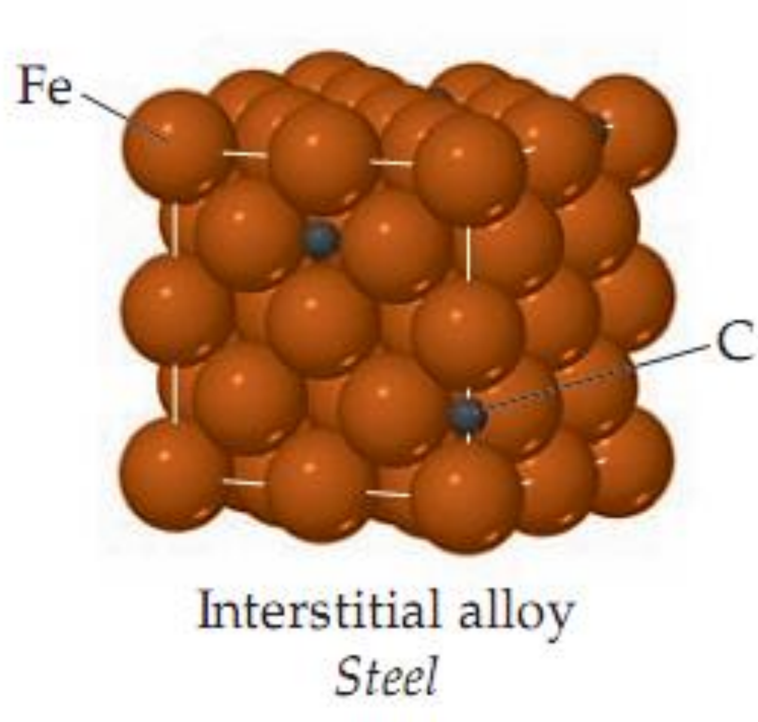
$$\text{Packing efficiency} = \frac{\text{volume of atoms}}{\text{volume of unit cell}} = \frac{\left(\frac{16}{3}\right)\pi r^3}{(2\sqrt{2})^3 r^3} = 0.74 \text{ or } 74\%$$

Alloy

An alloy is a material that contains more than one element and has the characteristic properties of a metal.

Solid solution:





- Solvent: Au
- Solute: Ag

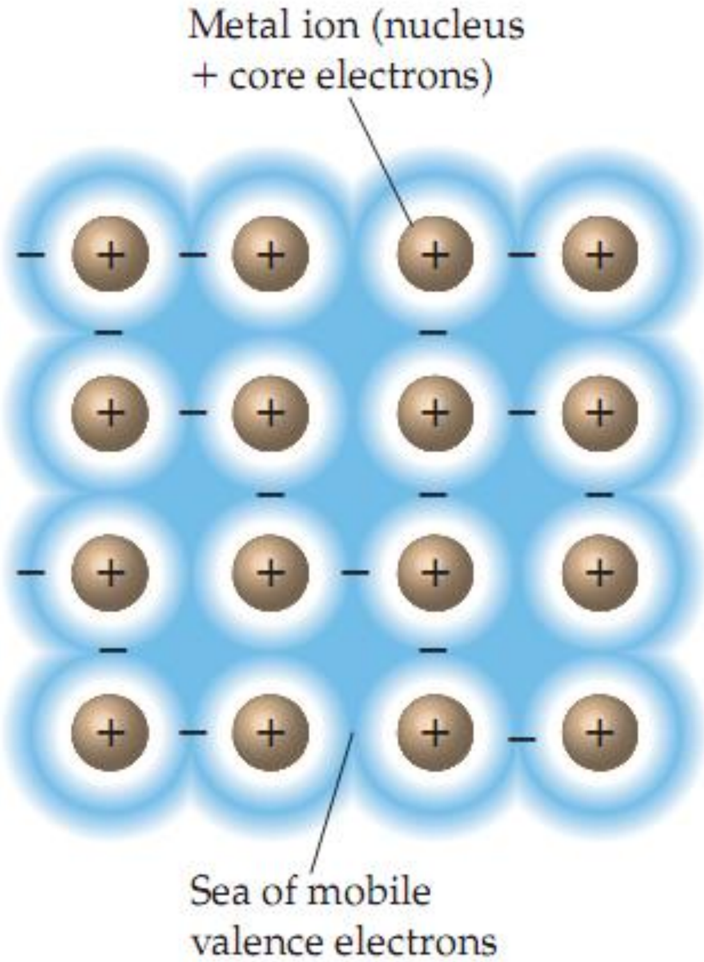
- Solvent: F
- Solute: C

Table 12.2 Some Common Alloys

Name	Primary Element	Typical Composition (by Mass)	Properties	Uses
Wood's metal	Bismuth	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	Low melting point (70 °C)	Fuse plugs, automatic sprinklers
Yellow brass	Copper	67% Cu, 33% Zn	Ductile, takes polish	Hardware items
Bronze	Copper	88% Cu, 12% Sn	Tough and chemically stable in dry air	Important alloy for earl civilizations
Stainless steel	Iron	80.6% Fe, 0.4% C, 18% Cr, 1% Ni	Resists corrosion	Cookware, surgical instruments
Plumber's solder	Lead	67% Pb, 33% Sn	Low melting point (275 °C)	Soldering joints
Sterling silver	Silver	92.5% Ag, 7.5% Cu	Bright surface	Tableware
Dental amalgam	Silver	70% Ag, 18% Sn, 10% Cu, 2% Hg	Easily worked	Dental fillings
Pewter	Tin	92% Sn, 6% Sb, 2% Cu	Low melting point (230 °C)	Dishes, jewelry

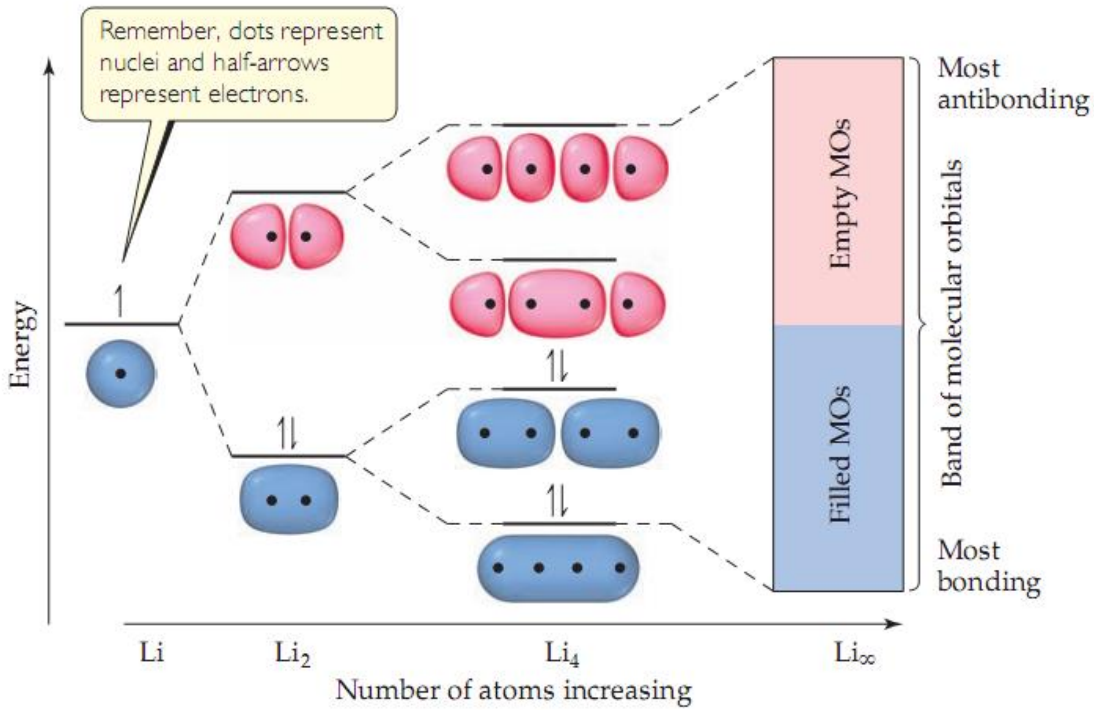
12.4 Metallic Bonding

Electron-Sea Model pictures the metal as an array of metal cations in a “sea” of valence electrons



Molecular–Orbital Model

1. Atomic orbitals combine to make molecular orbitals that can extend over the entire molecule.
2. A molecular orbital can contain zero, one, or two electrons.
3. The number of molecular orbitals in a molecule equals the number of atomic orbitals that combine to form molecular orbitals.
4. Adding electrons to a bonding molecular orbital strengthens bonding, while adding electrons to antibonding molecular orbitals weakens bonding.



12-5 Ionic Solids

Ionic solids are held together by the electrostatic attraction between cations and anions: **ionic bonds**

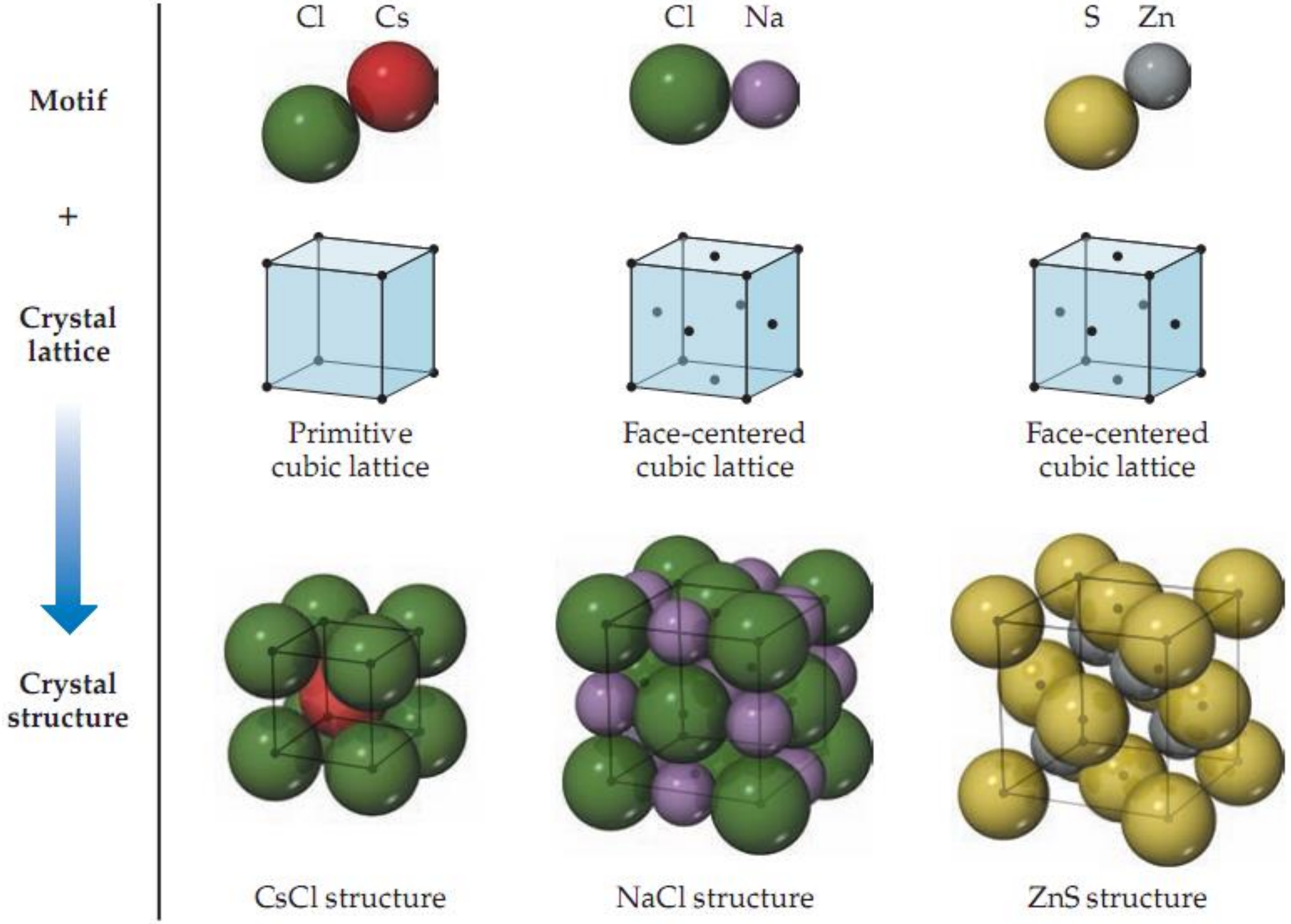
- The high melting and boiling points of ionic compounds are a testament to the strength of the ionic bonds
- The strength of an ionic bond depends on the charges and sizes of the ions

Table 12.3 Properties of the Alkali Metal Halides

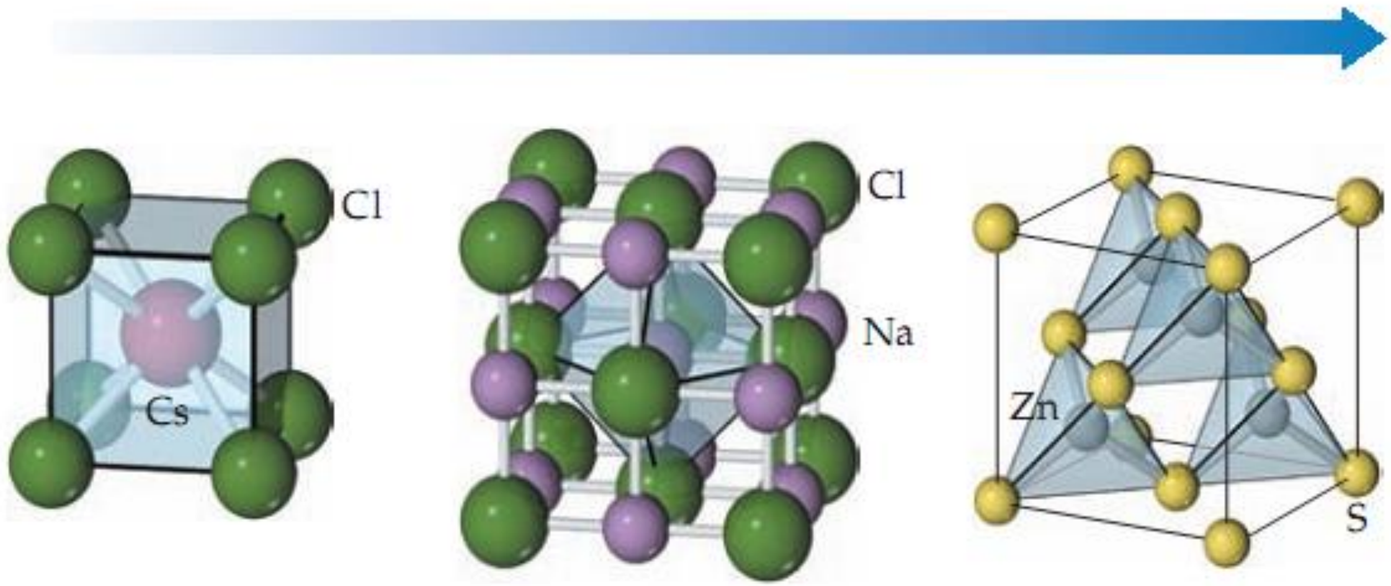
Compound	Cation–Anion Distance (Å)	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	2.01	1030	845
NaCl	2.83	788	801
KBr	3.30	671	734
RbI	3.67	632	674

Structures of Ionic Solids

Because cations are often considerably smaller than anions, the coordination numbers in ionic compounds are smaller than those in close-packed metals

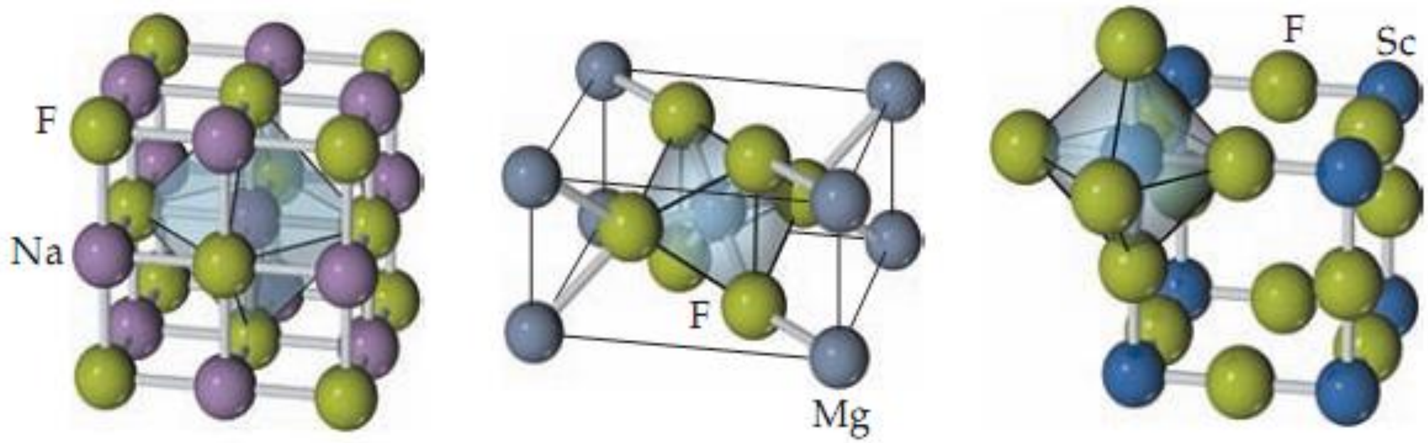


Decreasing r_+/r_-



	CsCl	NaCl	ZnS
Cation radius, r_+ (Å)	1.81	1.16	0.88
Anion radius, r_- (Å)	1.67	1.67	1.70
r_+/r_-	1.08	0.69	0.52
Cation coordination number	8	6	4
Anion coordination number	8	6	4

Increasing anion-to-cation ratio



	NaF	MgF_2	ScF_3
Cation coordination number	6	6	6
Cation coordination geometry	Octahedral	Octahedral	Octahedral
Anion coordination number	6	3	2
Anion coordination geometry	Octahedral	Trigonal planar	Linear

$$\frac{\text{Number of cations per formula unit}}{\text{Number of anions per formula unit}} = \frac{\text{anion coordination number}}{\text{cation coordination number}}$$

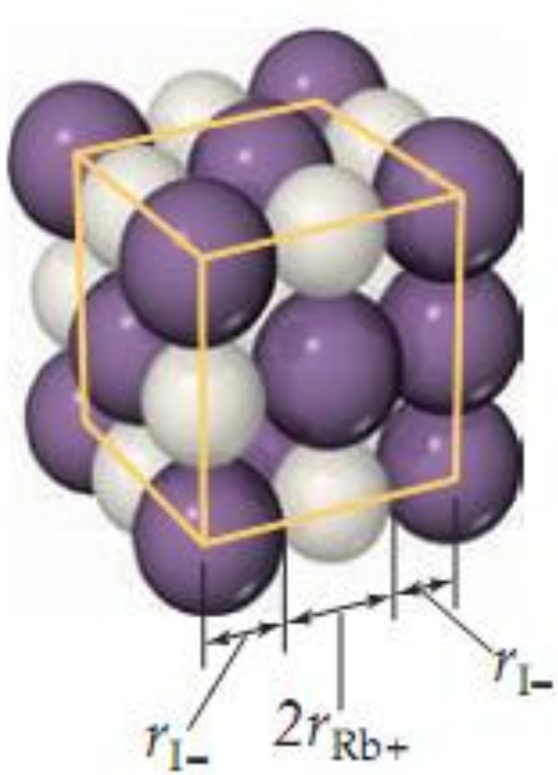
EXAMPLE

Rubidium iodide crystallizes with the same structure as sodium chloride.

(a) How many iodide ions are there per unit cell?

(b) How many rubidium ions are there per unit cell?

(c) Use the ionic radii and molar masses of Rb^+ (1.66 Å), 85.47 g/mol) and I^- (2.06 Å, 126.90 g/mol) to estimate the density of rubidium iodide in g/cm^3



$$r(I^-) + 2r(Rb^+) + r(I^-) = 2r(I^-) + 2r(Rb^+)$$

$$2(2.06\ \text{Å}) + 2(1.66\ \text{Å}) = 7.44\ \text{Å}$$

$$\text{Volume} = (7.44 \times 10^{-8}\ \text{cm})^3 = 4.12 \times 10^{-22}\ \text{cm}^3.$$

$$\text{Mass} = \frac{4(85.47\ \text{g/mol}) + 4(126.90\ \text{g/mol})}{6.022 \times 10^{23}\ \text{mol}^{-1}}$$

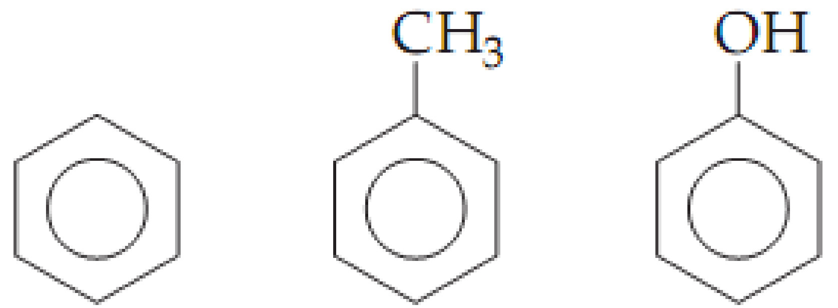
$$= 1.411 \times 10^{-21}\ \text{g}$$

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{1.411 \times 10^{-21}\ \text{g}}{4.12 \times 10^{-22}\ \text{cm}^3} = 3.43\ \text{g/cm}^3$$

12-6 Molecular solids

Molecular solids consist of atoms or neutral molecules held together by dipole–dipole forces, dispersion forces, and/or hydrogen bonds.

- Because these intermolecular forces are weak, molecular solids are soft and have relatively low melting points (usually below 200 °C)

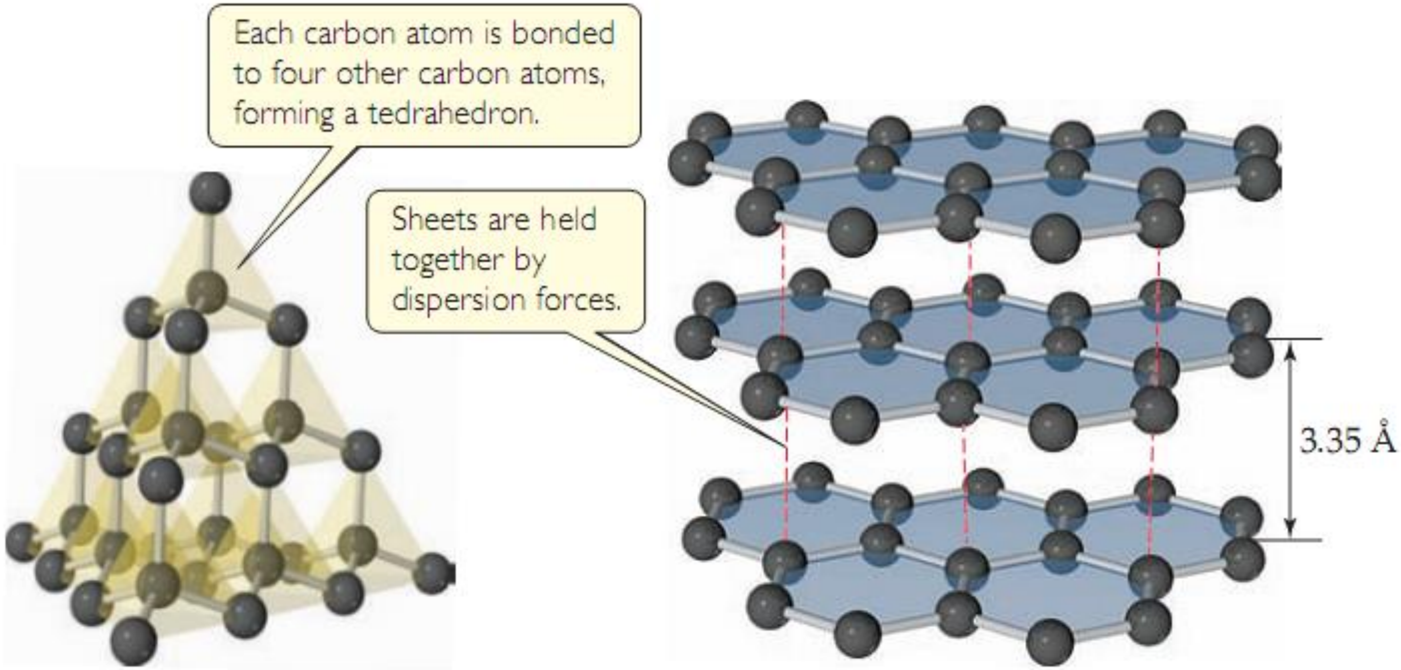


	Benzene	Toluene	Phenol
Melting point (°C)	5	–95	43
Boiling point (°C)	80	111	182

12-7 Covalent-Network solids

Covalent-network solids consist of atoms held together in large networks by covalent bonds.

- Because covalent bonds are much stronger than intermolecular forces, these solids are much harder and have higher melting points than molecular solids



(a) Diamond

(b) Graphite

Homeworks

12.117

12.118

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