SOLIDS
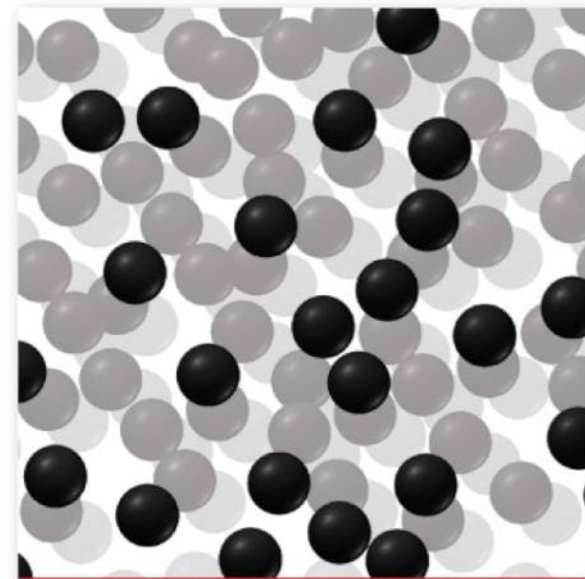
Properties and Structure

Solids -2

- Some solids have their particles arranged in an orderly geometric pattern—we call these **crystalline solids**.

  – salt and diamonds

- Other solids have particles that do not show a regular geometric pattern over a long range—we call these **amorphous solids**.
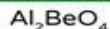
  – plastic and glass

2

Charcoal
C (*s*, amorphous)

3

CHEMICAL COMPOSITION OF GEMSTONES

THE COLOURS OF GEMSTONES ARE AFFECTED BY DIFFERENCES IN CHEMICAL AND ATOMIC STRUCTURE, LEADING TO THE ABSORPTION OF DIFFERENT WAVELENGTHS OF LIGHT. THEIR HARDNESS IS MEASURED ON THE MOHS SCALE, WHICH RUNS FROM 0-10.

ALEXANDRITE
Al_2BeO_4
Hardness: 8.5
Colour caused by chromium ions replacing aluminium in some sites. Colour varies in different light.

AMETHYST
SiO_2
Hardness: 7.0
Their colour is caused by iron 3+ ions replacing silicon in some locations in the structure.

AQUAMARINE
$Be_3Al_2(SiO_3)_6$
Hardness: 7.5-8.0
Colour caused by iron 2+/3+ ions replacing aluminium ions in some locations in the structure.

DIAMOND
C
Hardness: 10
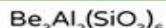Colourless; can be faintly coloured by the trapping of nitrogen atoms in the crystal.

EMERALD
$Be_3Al_2(SiO_3)_6$
Hardness: 7.5-8.0
Colour caused by chromium ions replacing aluminium in some locations in the structure.
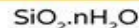
GARNET
$Mg_3Al_2(SiO_4)_3$
Hardness: 6.5-7.5
Colour caused by iron 2+ ions replacing magnesium ions in some locations in the structure.

OPAL
$SiO_2.nH_2O$
Hardness: 5.5-6.0
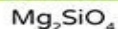Many colours which are caused by interference & diffraction of light passing through the structure.

PEARL
$CaCO_3$
Hardness: 2.5-4.5
Produced in the soft tissue of shelled molluscs. The thinner the layers of the pearl, the finer the lustre.

PERIDOT
Mg_2SiO_4
Hardness: 6.5-7.0
Colour caused by iron 2+ ions replacing magnesium ions in some locations in the structure.

RUBY
Al_2O_3
Hardness: 9.0
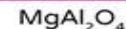Colour caused by chromium ions replacing aluminium ions in some locations in the structure.

SAPPHIRE
Al_2O_3
Hardness: 9.0
Colour caused by titanium and iron ions replacing aluminium ions in some locations in the structure.

SPINEL
$MgAl_2O_4$
Hardness: 7.5-8.0
A variety of colours are possible, caused by impurities such as iron, chromium and nickel.

TOPAZ
$Al_2SiO_4(F,OH)_2$
Hardness: 8.0
Pure topaz gems are colourless & transparent, but tinted by impurities they can have a variety of colours.

TOURMALINE
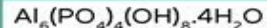$Na_3Li_3Al_6(BO_3)_3(SiO_3)_6F_4$
Hardness: 7.0-7.5
Colour caused by manganese ions replacing lithium and aluminium ions in some sites.
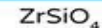
TURQUIOSE
$Al_6(PO_4)_4(OH)_8.4H_2O$
Hardness: 5.0-6.0
Colour caused by the presence of copper ions coordinated to the hydroxide ions and water.

ZIRCON
$ZrSiO_4$
Hardness: 7.5
A range of possible colours that depend on the impurities present. Colourless specimens are popular diamond substitutes.
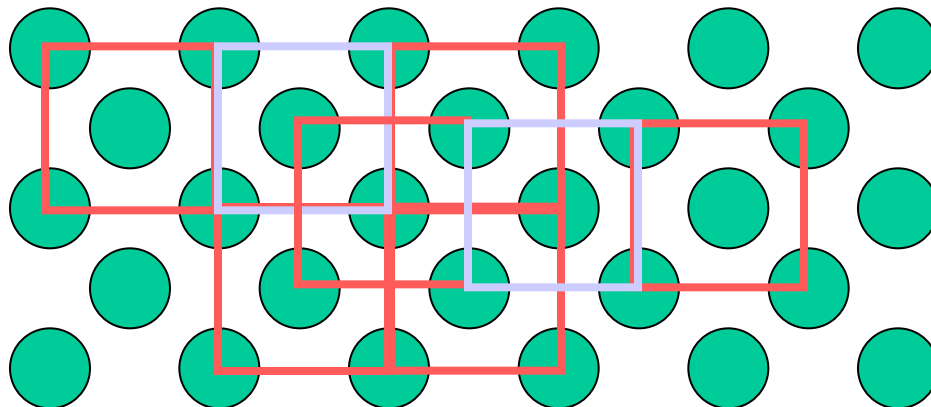
Crystal Lattice

- When allowed to cool slowly, the particles in a liquid will arrange themselves to give the maximum attractive forces.

  – *therefore, minimize the energy*

- The result will generally be a crystalline solid.

- The arrangement of the particles in a crystalline solid is called the *crystal lattice*.

- The smallest unit that shows the pattern of arrangement for all the particles is called the *unit cell*.
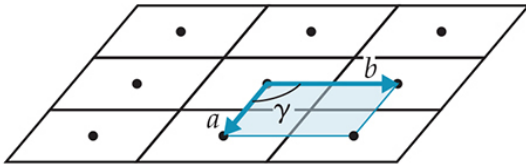
Unit Cells

- Unit cells are three-dimensional.
  - usually containing two or three layers of particles
- Unit cells are repeated over and over to give the macroscopic crystal structure of the solid.
- Starting anywhere within the crystal results in the same unit cell.
- Each particle in the unit cell is called a **lattice point**.
- **Lattice planes** are planes connecting equivalent points in unit cells throughout the lattice.

Lattice Points

- Positions that define the overall structure of the crystalline compound are called **lattice points**.

- Each lattice point has an identical environment.

- **Lattice vectors** connect the points and define the unit cell.

- The next slide shows how this works for five different two-dimensional lattices.
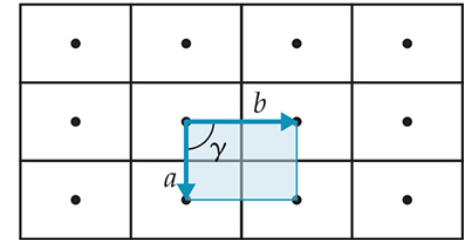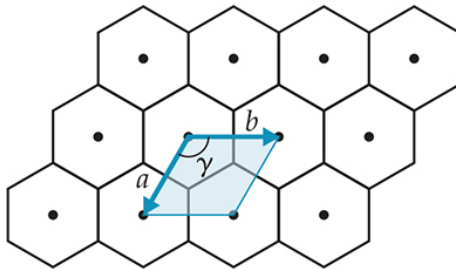
2-D Lattices

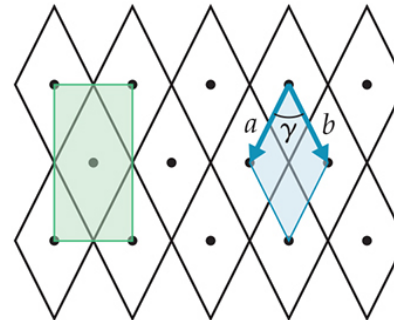**Oblique lattice** ($a \neq b$, γ = arbitrary)
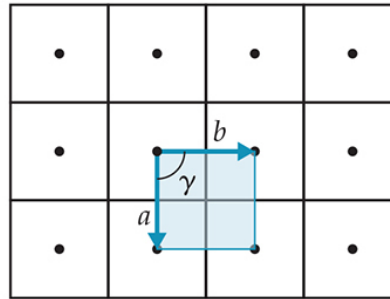
Square lattice ($a = b$, $\gamma = 90°$)
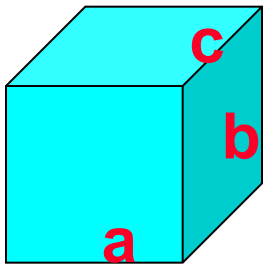
Rectangular lattice ($a \neq b$, $\gamma = 90°$)

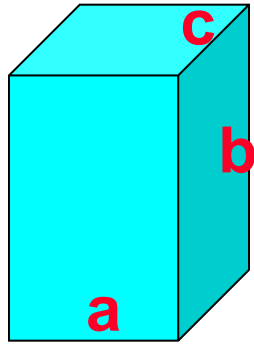**Hexagonal lattice** ($a = b$, $\gamma = 120°$)

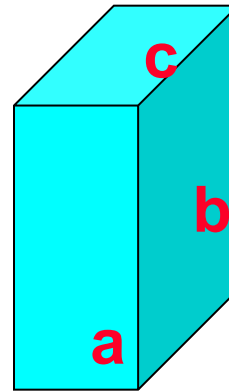**Rhombic lattice** ($a = b$, γ = arbitrary)
Centered rectangular lattice

7 Unit Cells

Cubic
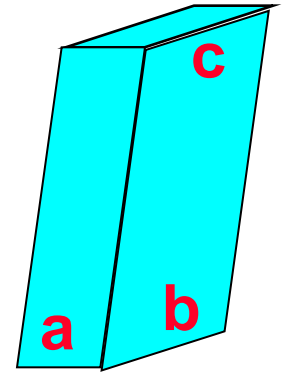a = b = c
all 90°

Tetragonal
a = c < b
all 90°

Orthorhombic
a ≠ b ≠ c
all 90°

Monoclinic
a ≠ b ≠ c
2 faces 90°
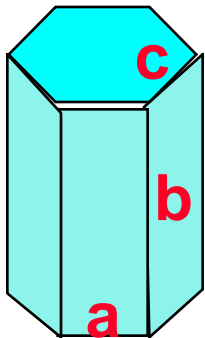
Hexagonal
a = c < b
2 faces 90°
1 face 120°
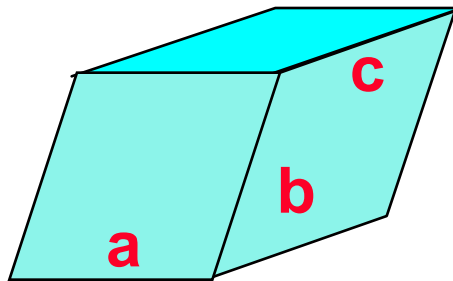
Rhombohedral
a = b = c
no 90°
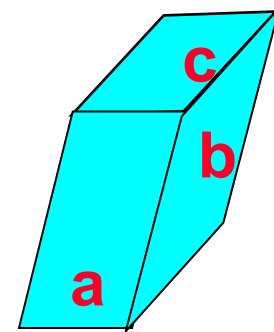
Triclinic
a ≠ b ≠ c
no 90°

Lecture quiz 1

Imagine you generate a three-dimensional lattice by taking *a* and *b* vectors that form a two-dimensional square lattice. Then add a third vector, *c*, that is of different length and perpendicular to the first two. Which of the seven three-dimensional lattices results?

a. **Cubic**

b. **Monoclinic**

c. **Orthorhombic**

d. **Tetragonal**

Primitive vs. Centered Lattices

- **Primitive lattices** have atoms **only** in the lattice points.

- **Centered lattices** have atoms in another regular location, most commonly the **body center** or the **face center**.

Lattice points only at corners
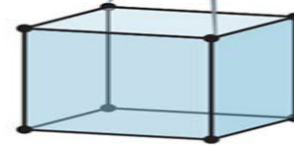
Primitive cubic lattice

Lattice points at corners plus one lattice point in the center of unit cell
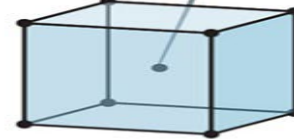
Body-centered cubic lattice

Lattice points at corners plus one lattice point at the center of each face
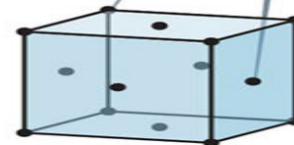
Face-centered cubic lattice

Motifs

Sometimes, the atoms are **not** on the lattice points, but the overall structure follows a particular unit cell. The groups of atoms that define the overall structure is called a **motif**.

Lattice points at corners of unit cell

Motif inside unit cell

No atom falls on a lattice point

Atoms from neighboring unit cells can bond

Begin with a single hexagonal unit cell containing a motif of two carbon atoms.

Tile unit cells together to create the crystal structure.

The interconnected hexagonal rings become apparent when we connect atoms from neighboring unit cells.

Unit Cells -2

- The number of other particles each particle is in contact with is called its **coordination number**.

  – For ions, it is the _number of oppositely charged ions_ an ion is in contact with.

- Higher coordination number means more interaction, therefore, stronger attractive forces holding the crystal together.

- The **packing efficiency** is the percentage of volume in the unit cell occupied by particles.

  – The higher the coordination number, the more efficiently the particles are packing together.

12

Cubic Structures

- Not every part of an atom on a lattice point is completely within that unit cell. One can determine how many atoms are within each unit cell.

- Eight cubes meet at a corner; therefore only $\frac{1}{8}$ of that corner atom is within any one unit cell meeting there.
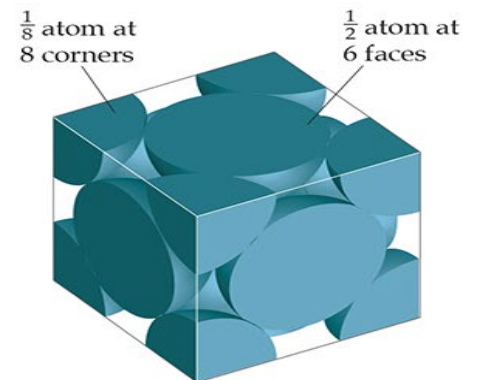
- Two cubes meet at a face; therefore only $\frac{1}{2}$ of that face atom is within any one unit cell meeting there.

- A body-centered atom is entirely within the unit cell.

$\frac{1}{8}$ atom at 8 corners
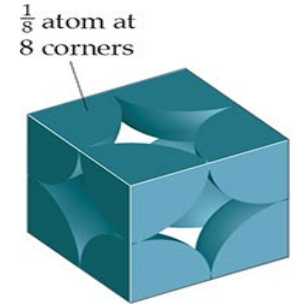
(a) Primitive cubic metal
1 atom per unit cell

$\frac{1}{8}$ atom at 8 corners

1 atom at center
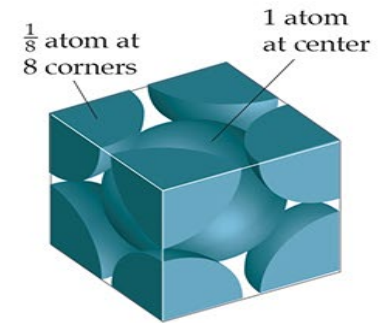
(b) Body-centered cubic metal
2 atoms per unit cell

$\frac{1}{8}$ atom at 8 corners

$\frac{1}{2}$ atom at 6 faces

(c) Face-centered cubic metal
4 atoms per unit cell

Cubic Unit Cells

- all 90° angles between corners of the unit cell
- lengths of all the edges are equal
- if the unit cell is made of spherical particles
  - ⅛ of each corner particle is within the cube
  - ½ of each particle on a face is within the cube
  - ¼ of each particle on an edge is within the cube

- Volume of a Cube $= (\text{edge length})^3$
- Volume of a Sphere $= \dfrac{4}{3}\pi\, r^3$

Cubic Unit Cells— Simple Cubic

- eight particles, one at each corner of a cube

- ⅛ of each particle lies in the unit cell

  - each particle part of eight cells

  - total = 1 particle in each unit cell

    - 8 corners × ⅛

- edge of unit cell = twice the radius

- coordination number of 6

2r
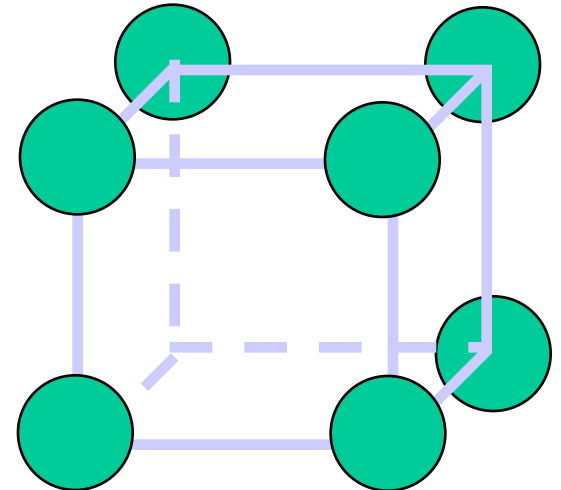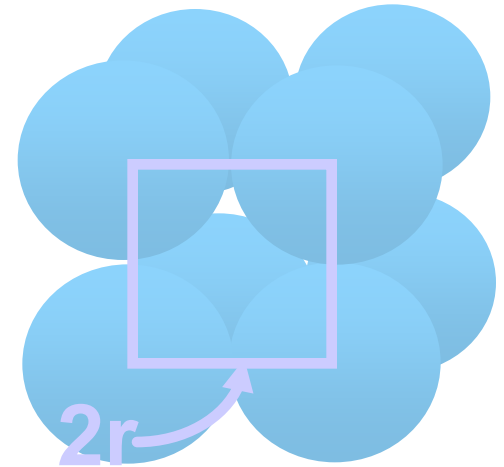
Simple Cubic

Coordination number =
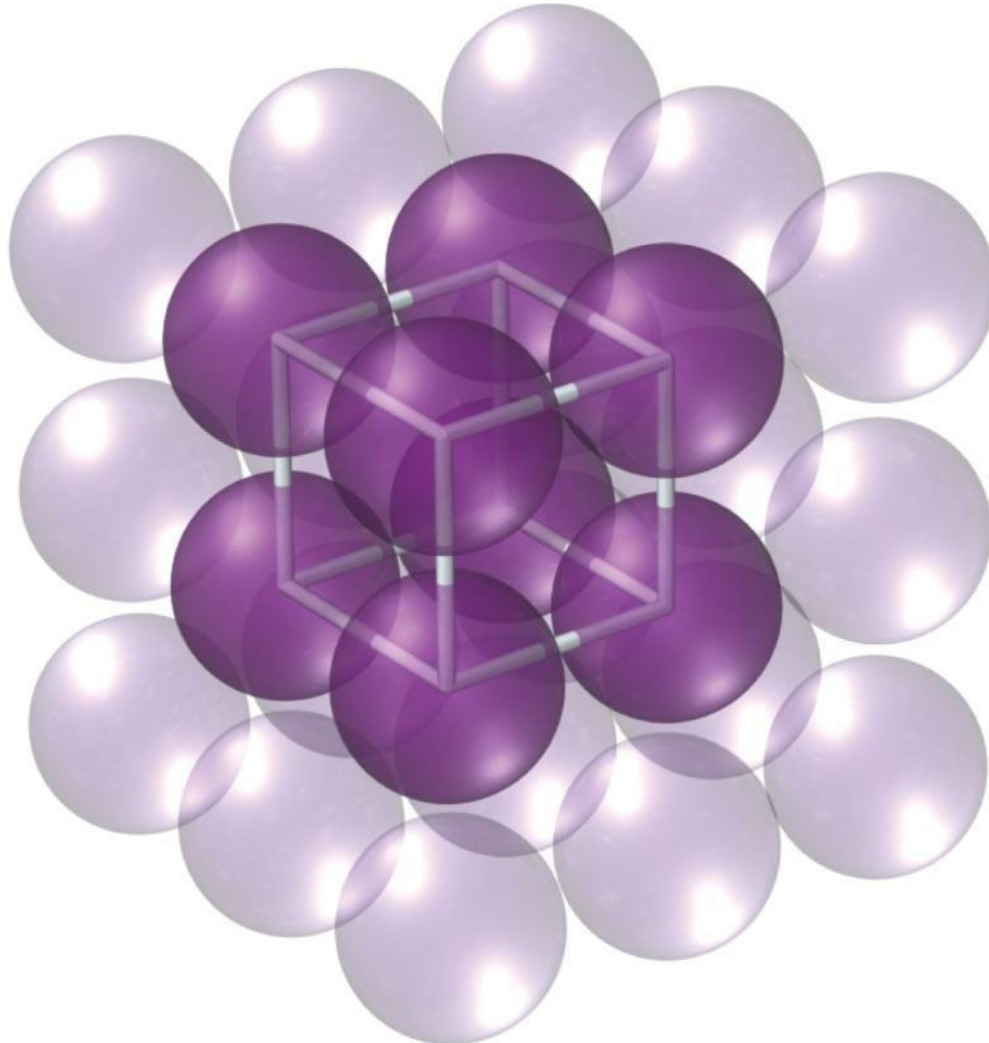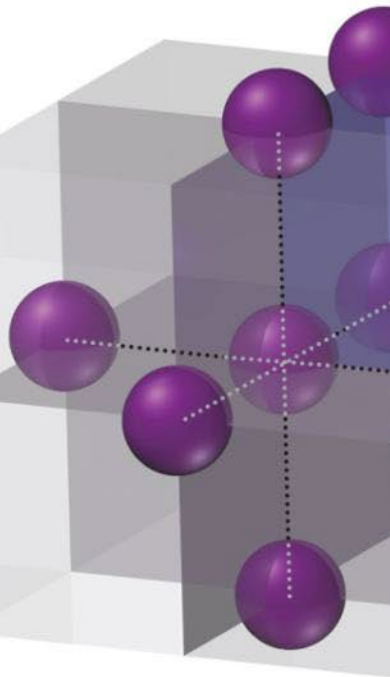
Atoms per unit cell =
$$\frac{1}{8} \times 8 = 1$$

$\frac{1}{8}$ atom at each of 8 corners

16
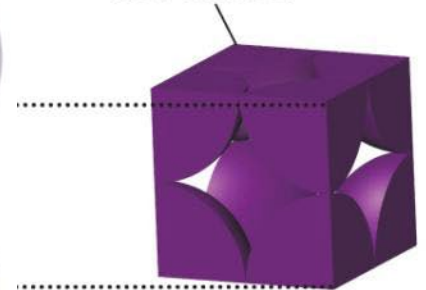
Cubic Unit Cells—Body-Centered Cubic

- nine particles, one at each corner of a cube + one in center

- ⅛ of each corner particle lies in the unit cell

  - two particles in each unit cell

    - 8 corners × ⅛

    - + 1 center

- edge of unit cell = (4/√ 3) times the radius of the particle

- coordination number of 8

$$\frac{4r}{\sqrt{3}}$$
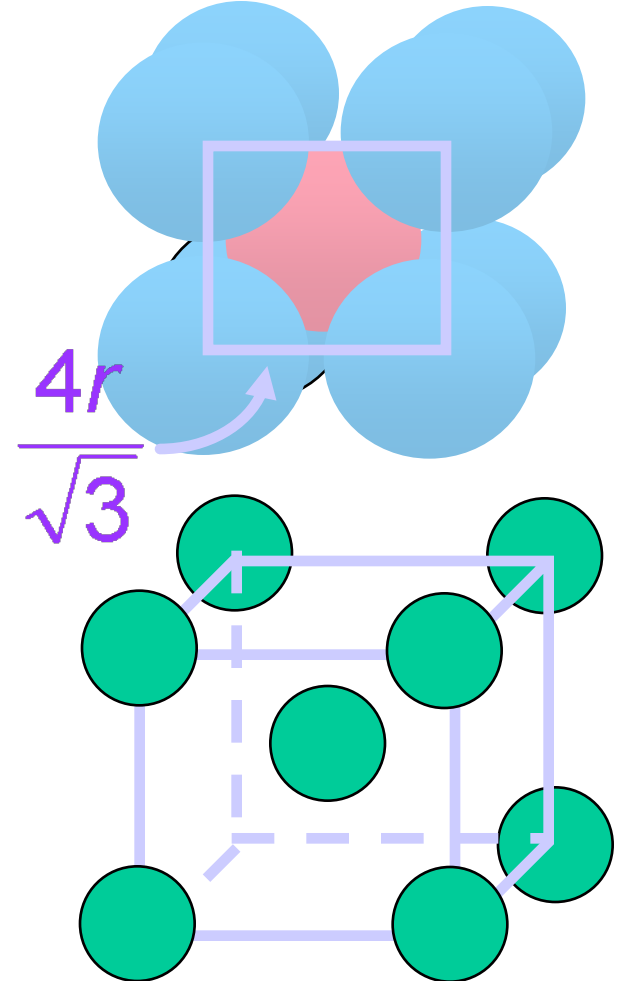
Body-Centered Cubic

Body-Centered Cubic Unit Cell

Coor   Body-centered cubic   cell=
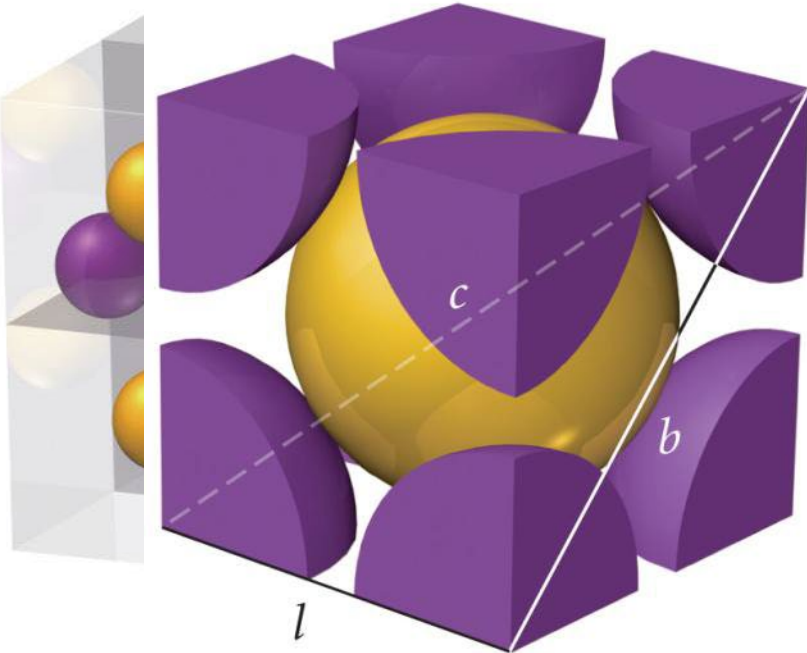
$$c^2 = b^2 + l^2 \qquad b^2 = l^2 + l^2$$
$$c = 4r \qquad\qquad b^2 = 2l^2$$
$$(4r)^2 = 2l^2 + l^2$$
$$(4r)^2 = 3l^2$$
$$l^2 = \frac{(4r)^2}{3}$$
$$l = \frac{4r}{\sqrt{3}}$$

Cubic Unit Cells— Face-Centered Cubic

- 14 particles, one at each corner of a cube + one in center of each face
- ⅛ of each corner particle + ½ of face particle lies in the unit cell
  - four particles in each unit cell
    - 8 corners × ⅛
    - + 6 faces × ½
- edge of unit cell = 2√ 2 times the radius of the particle
- coordination number of 12

$2r\sqrt{2}$

19
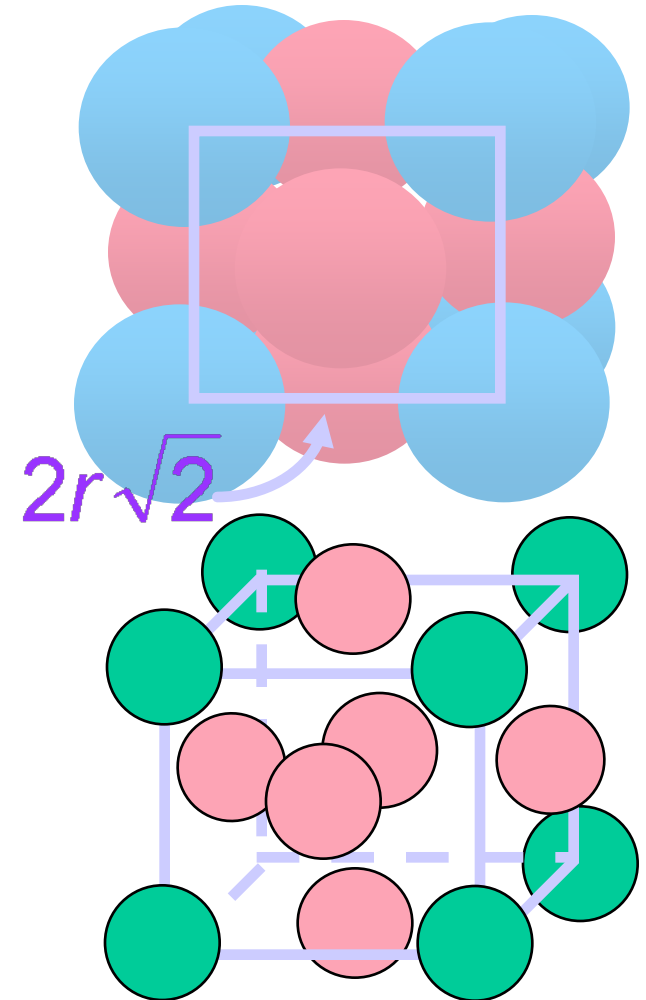
Face-Centered Cubic

Face-centered cubic
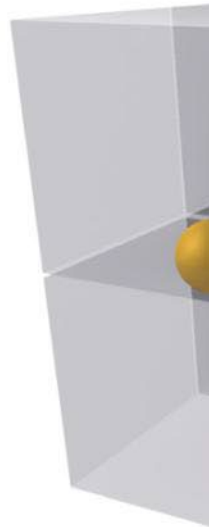
$$b^2 = l^2 + l^2 = 2l^2$$
$$b = 4r$$
$$(4r)^2 = 2l^2$$
$$l^2 = \frac{(4r)^2}{2}$$
$$l = \frac{4r}{\sqrt{2}}$$
$$= 2\sqrt{2}r$$

20
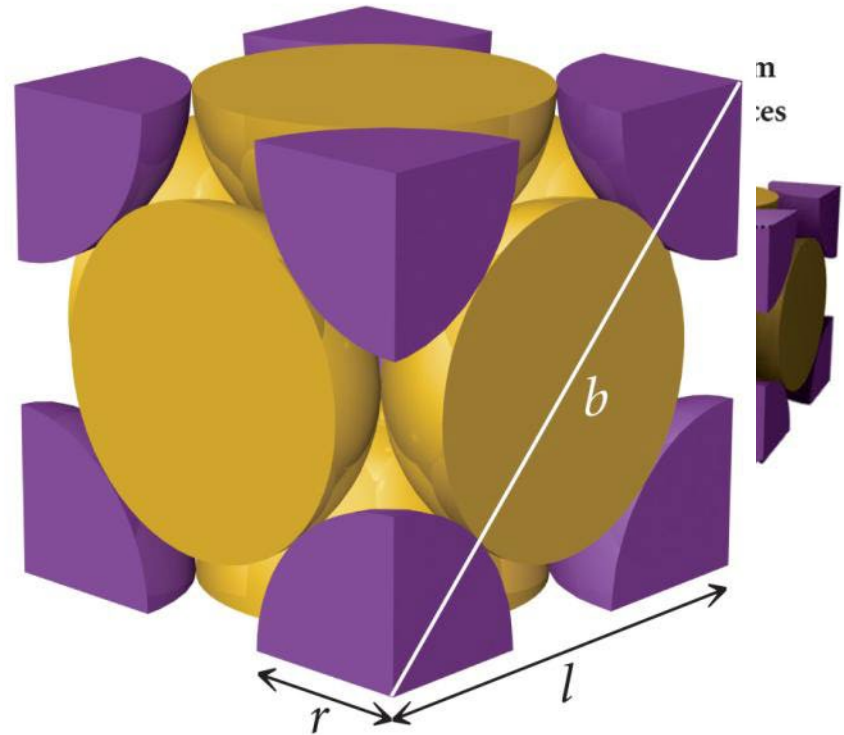
Summary of Cubic Unit Cells

description	CN	length	# of atoms	# of particles
Simple cubic	6	$l = 2r$	1	8
bcc	8	$l = 4r/\sqrt{3}$	2	9
fcc	12	$l = 2r\sqrt{2}$	4	14

- Volume of a Cube $= (\text{edge length})^3$
- Volume of a Sphere $= \dfrac{4}{3}\pi r^3$

Lecture quiz 2

The crystal structure of aluminum is composed of a total of 14 particles. How many atoms are actually in the unit cell?

a. 2

b. 4

c. 6

d. 8

Lecture quiz 3

The crystal structure of lithium is composed of a total of 9 particles. What is the coordination number of lithium?

a. 2

b. 4

c. 6

d. 8

Example : Calculate the density of Al if it crystallizes in a fcc and has a radius of 143 pm.

|	
Given:	face-centered cubic, V = 6.618 × 10⁻²³ cm³, m = 1.792 × 10⁻²² g
Find:	density, g/cm³
Conceptual Plan:	$fcc \longrightarrow mass$ $r \longrightarrow l \longrightarrow V$ # atoms × mass of 1 atom $l = 2r\sqrt{2}$ $V = l^3$ $m, V \longrightarrow d$
Relationships:	d = m/V 1 cm = 10² m, 1 pm = 10⁻¹² m V = l³, l = 2r√2, d = m/V fcc = 4 atoms/uc, Al = 26.982 g/mol, 1 mol = 6.022 × 10²³ atom

Solution:

$$l = 2r\sqrt{2}$$

$$4 \text{ atoms Al} \times \frac{26.982 \text{ g}}{6.022 \times 10^{23} \text{ atoms}} = 1.792 \times 10^{-22} \text{ g}$$

$$143 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{1 \text{ cm}}{10^{-2} \text{ m}} = 1.43 \times 10^{-8} \text{ cm}$$

$$l = 2(1.43 \times 10^{-8} \text{ cm})(1.414) = 4.045 \times 10^{-8} \text{ cm}$$

$$V = l^3 = (4.045 \times 10^{-8} \text{ cm})^3 = 6.618 \times 10^{-23} \text{ cm}^3$$

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

|	
Check:	The accepted density of Al at 20 °C is 2.71 g/cm³, so the answer makes sense.

Closest-Packed Structures
First Layer

- With spheres, it is more efficient to offset each row in the gaps of the previous row than to line up rows and columns.
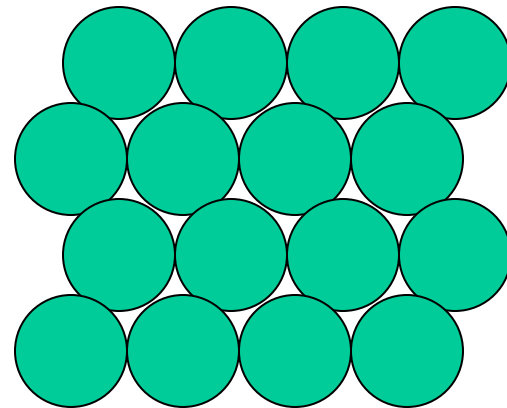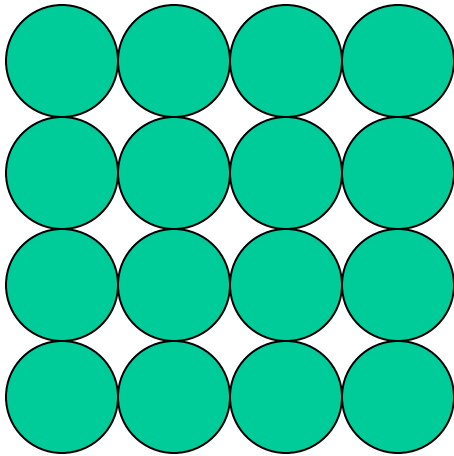
Closest-Packed Structures—Second Layer

- The second-layer atoms can sit directly over the atoms in the first—called an **AA** pattern.

- **Or, the second layer can sit over the holes in the first—called an AB pattern.**
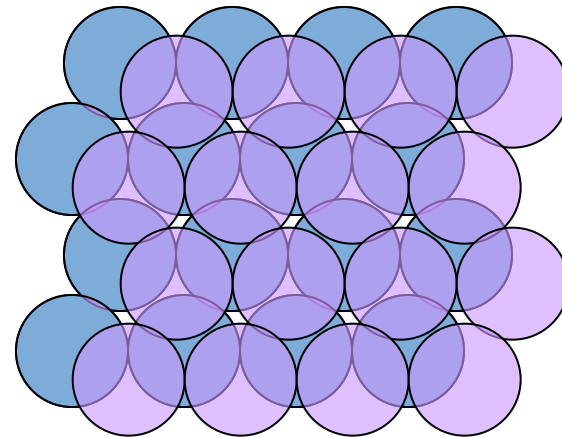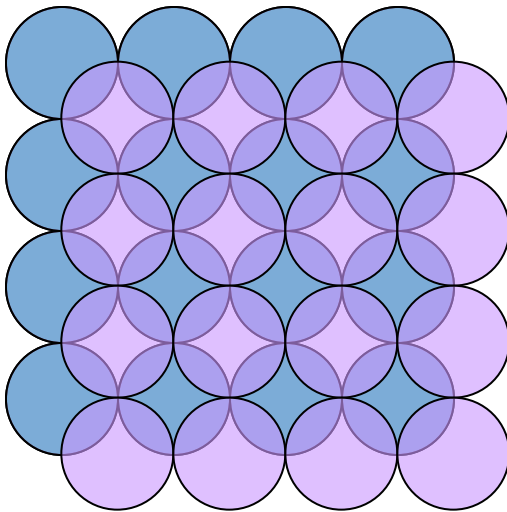
Closest-Packed Structures—
Third Layer, with Offset 2nd Layer

- The third-layer atoms can align directly over the atoms in the first—called an **ABA** pattern.

- **Or, the third layer can sit over the uncovered holes in the first—called an ABC pattern.**
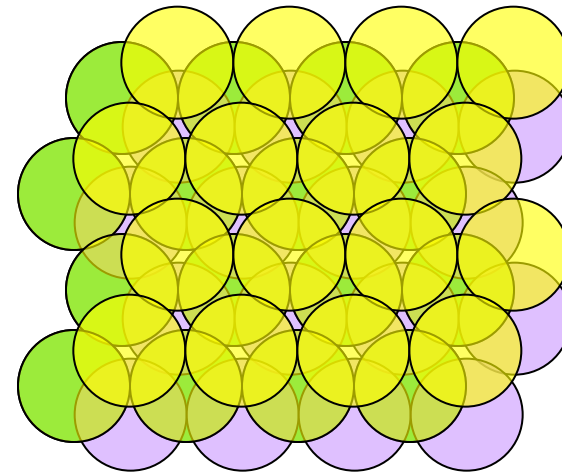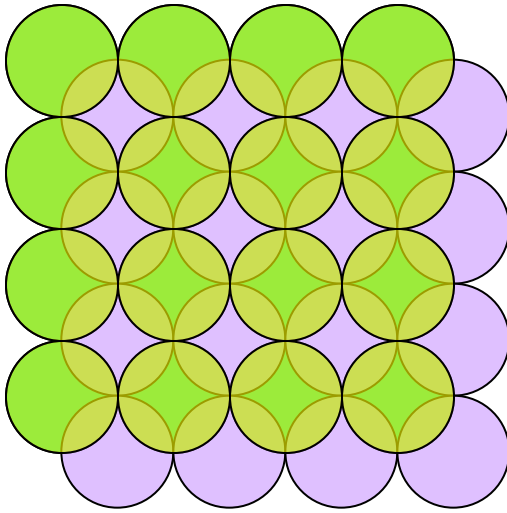
Cubic Closest-Packed
Hexagonal Closest-Packed
Face-Centered Cubic

Hexagonal Closest Packing

60° 120°

Unit cell

Cubic Closest Packed = Face-Centered Cubic

Unit cell

29

Crystalline solids

Molecular solids
- Composite units are molecules
- Low melting points

Ice

Ionic solids
- Composite units are formula units (cations and anions)
- High melting points

Table salt

Atomic solids
- Composite units are atoms

Nonbonding
- Held together by dispersion forces
- Low melting points

Solid xenon

Metallic
- Held together by metallic bonds
- Variable melting points

Gold

Network Covalent
- Held together by covalent bonds
- High melting points

Quartz (silicon dioxide)

Classifying Solids Based on Bonds

- **Metallic solids** are held together by a "sea" of collectively shared electrons.

- **Ionic solids** are sets of cations and anions mutually attracted to one another.

- **Covalent-network solids** are joined by an extensive network of covalent bonds.

- **Molecular solids** are discrete molecules held together by weak forces.
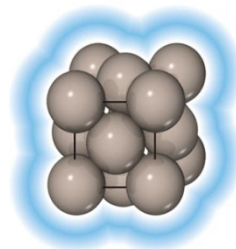
Metallic solids
Extended networks of atoms held together by metallic bonding (Cu, Fe)
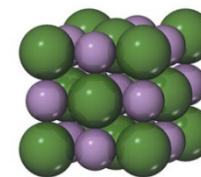
Ionic solids
Extended networks of ions held together by cation–anion interactions (NaCl, MgO)
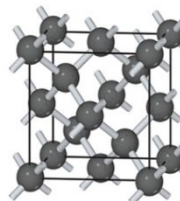
Covalent-network solids
Extended networks of atoms held together by covalent bonds (C, Si)
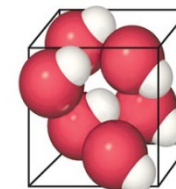
Molecular solids
Discrete molecules held together by intermolecular forces (HBr, H_2O)

Two Other Types of Solids

- **Polymers** contain long chains of atoms connected by covalent bonds; the chains can be connected to other chains by weak forces. These molecules have different properties than small molecules or metallic or ionic compounds.

- **Nanomaterials** are crystalline compounds with the crystals on the order of 1–100 nm; this gives them very different properties than larger crystalline materials.

Metallic Structure

Nickel (Ni)
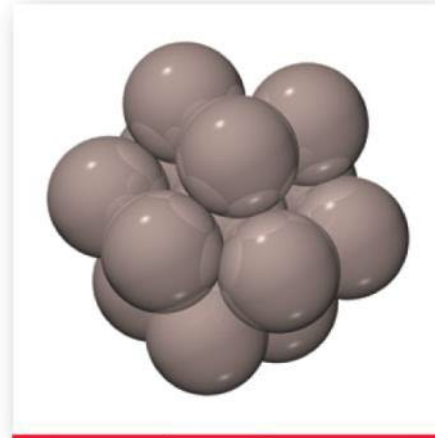
Zinc (Zn)

Metallic Bonding

- One can think of a metal as a group of cations suspended in a sea of electrons (known as the **electron-sea model**).

- The electrical and thermal conductivity, ductility, and malleability of metals is explained by this model.

Metal ion (nucleus + core electrons)

Sea of mobile valence electrons
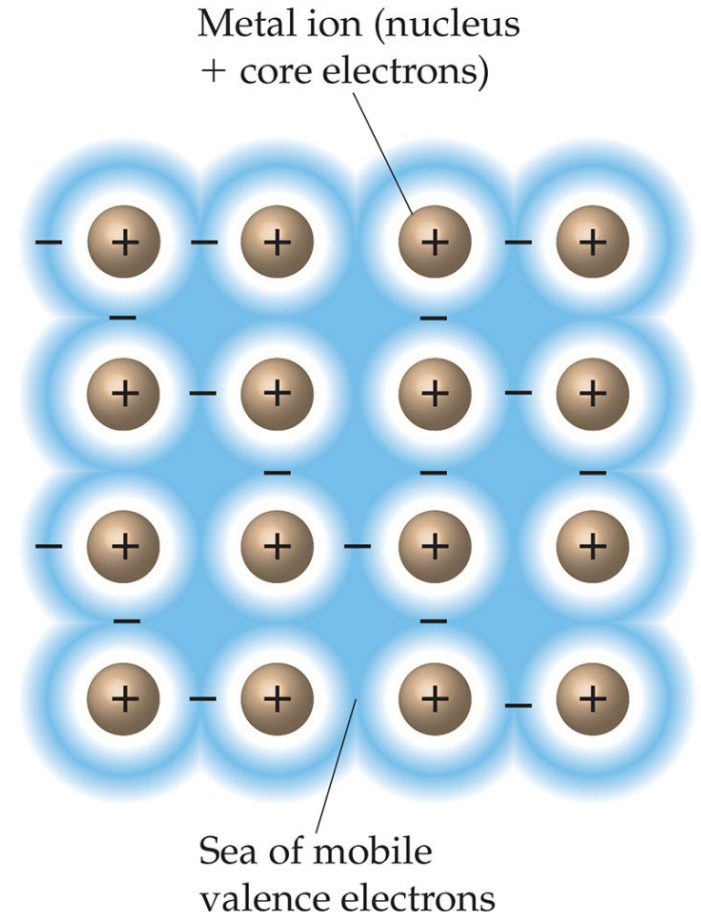
Metallic Structure -2

The structures of many metals conform to one of the cubic unit cells: simple cubic, body-centered cubic, or face-centered cubic.

Motif + Crystal lattice → Crystal structure

Metal atom | Metal atom | Metal atom

Primitive cubic lattice | Body-centered cubic lattice | Face-centered cubic lattice

(a) Primitive cubic metal | (b) Body-centered cubic metal | (c) Face-centered cubic metal | (d) Corner atoms are shared by eight unit cells
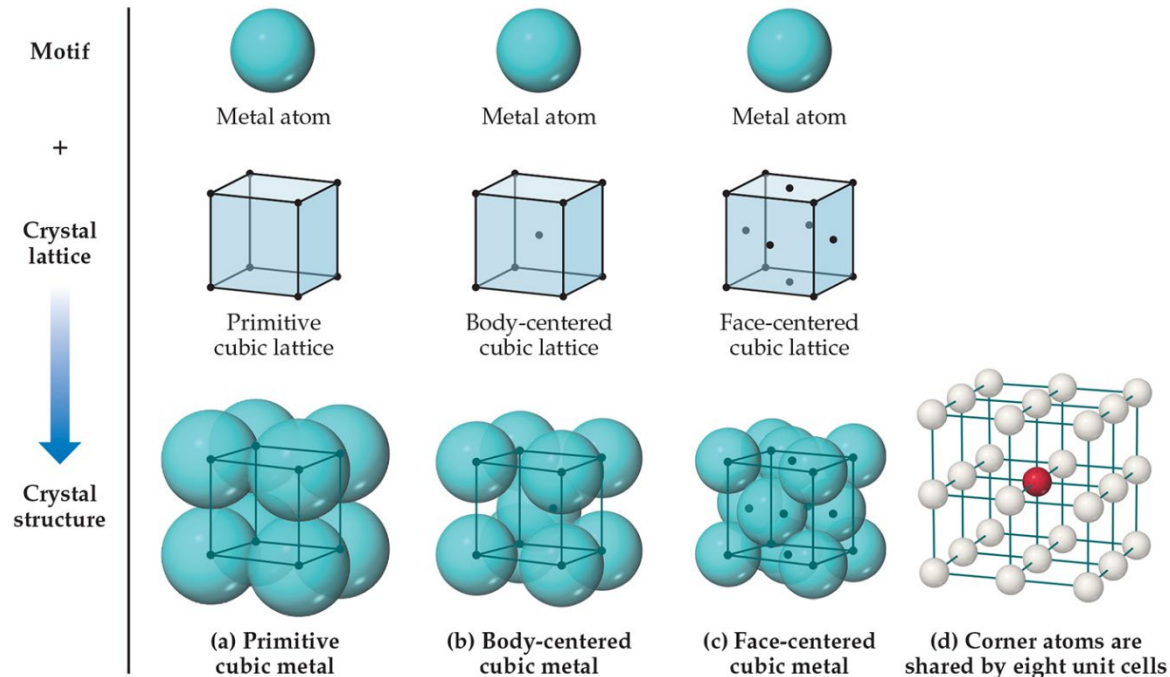
Alloys

- **Alloys** are materials that contain more than one element and have the characteristic properties of metals.

- It is an important means employed to change the properties of certain metals.

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	
Bronze	Copper	88% Cu, 12% Sn	Tough and chemically stable in dry air	Important alloy for early 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

Types of Alloys
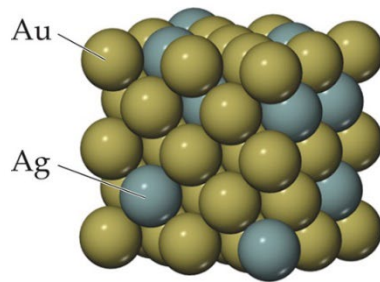
Substitutional alloy
14-karat gold
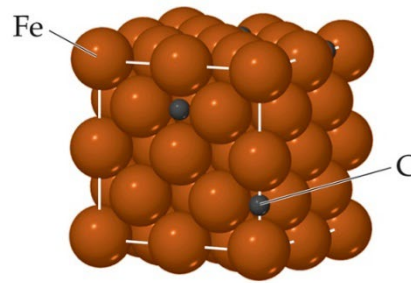
Interstitial alloy
Steel
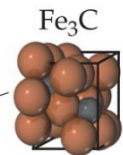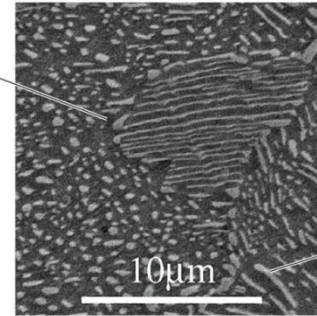
- **Substitutional alloys**: A second element takes the place of a metal atom.

- **Interstitial alloys**: A second element fills a space in the lattice of metal atoms.

- **Heterogeneous alloys**: components not dispersed uniformly

MO Approach Needed

- The electron-sea model would lead to increased attractions for every electron added.

- This would mean that melting points would always increase with added electrons.

Period 6 metals (Cs–Hg)   Period 5 metals (Rb–Cd)

Period 4 metals (K–Zn)
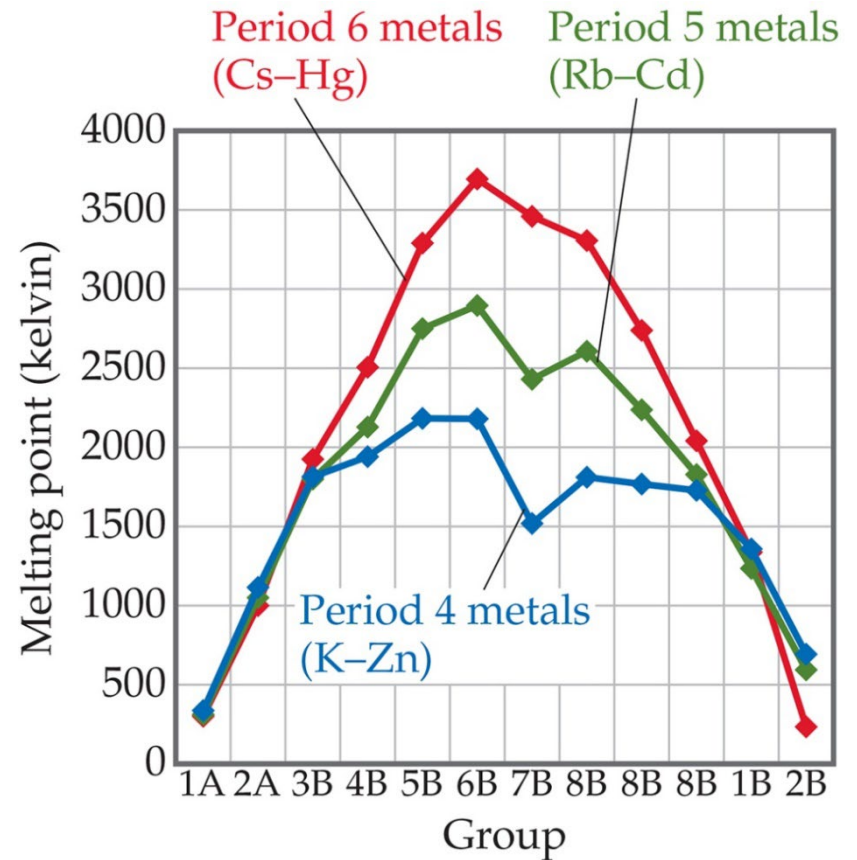
A Molecular-Orbital Approach

As the number of atoms in a chain increases, the energy gap between the bonding orbitals and between the antibonding orbitals disappears, resulting in a continuous **band** of energy. The approach seen here takes into account only *s*-orbital population.
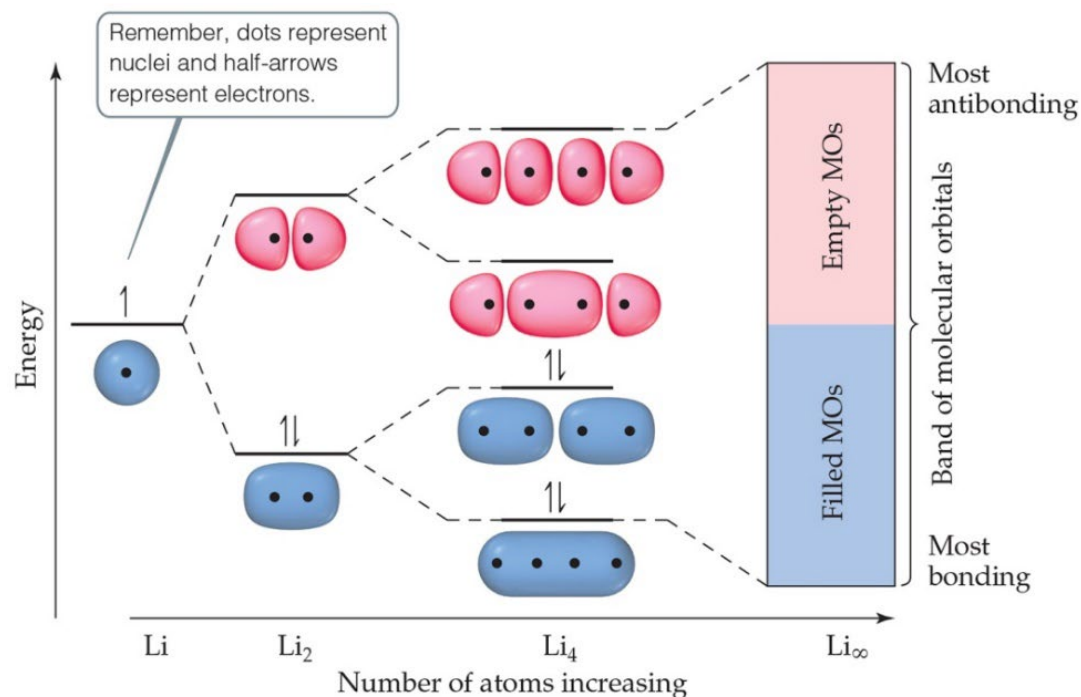
MO Approach with More Orbitals

- Most metals have *d* and *p* orbitals to consider.
- Their MO diagrams lead to more bands that better explain conductivity and other properties of metals.
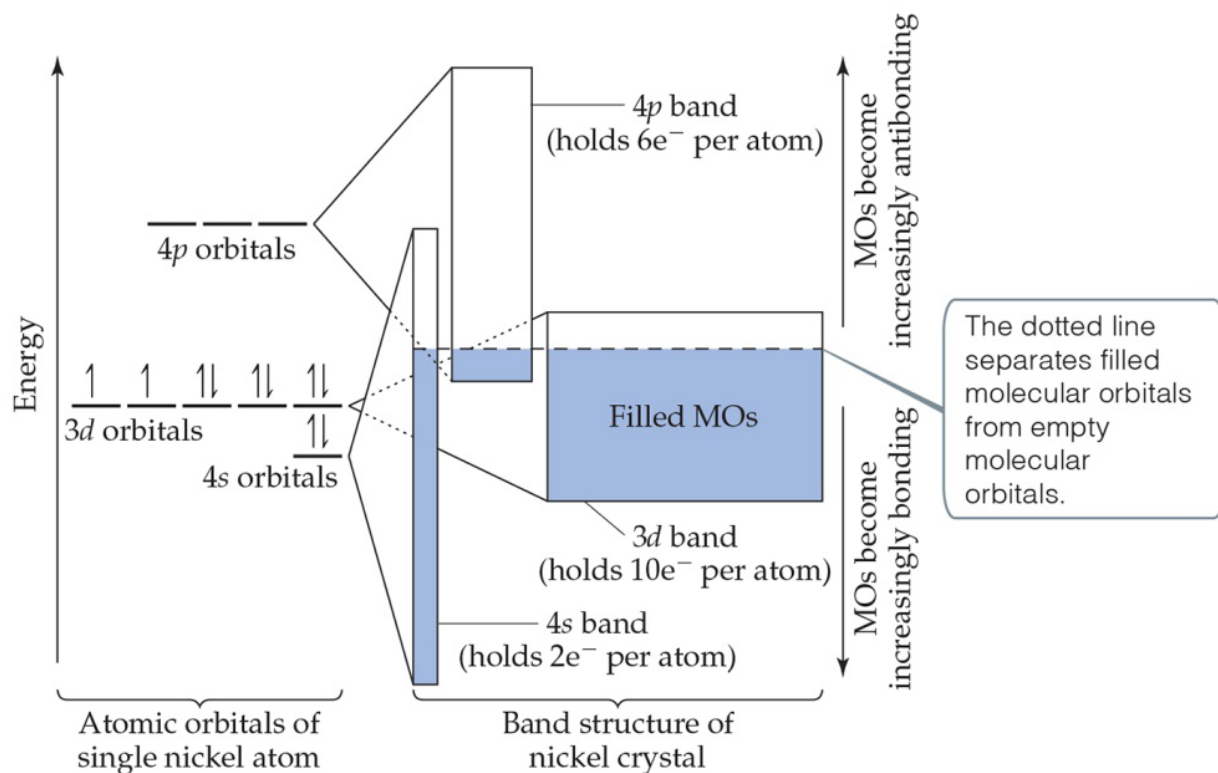
Lecture quiz 5

Which element, W or Au, has the greater number of electrons in antibonding orbitals? Which one would you expect to have the higher melting point?

a. Tungsten (W) has the greater number of electrons in antibonding orbitals, and gold (Au) has the higher melting point.

b. Au has the greater number of electrons in antibonding orbitals, and W has the higher melting point.

c. W has both the greater number of electrons in antibonding orbitals and higher melting point.

Semiconductors

- They have a gap between the occupied MOs (valence band) and the unoccupied ones (conduction band).

- Electrons must enter the conduction band for electron transfer.

- Group IVA elements have gaps between the bands of 0.08 to 3.05 eV (7 to 300 kJ/mol).
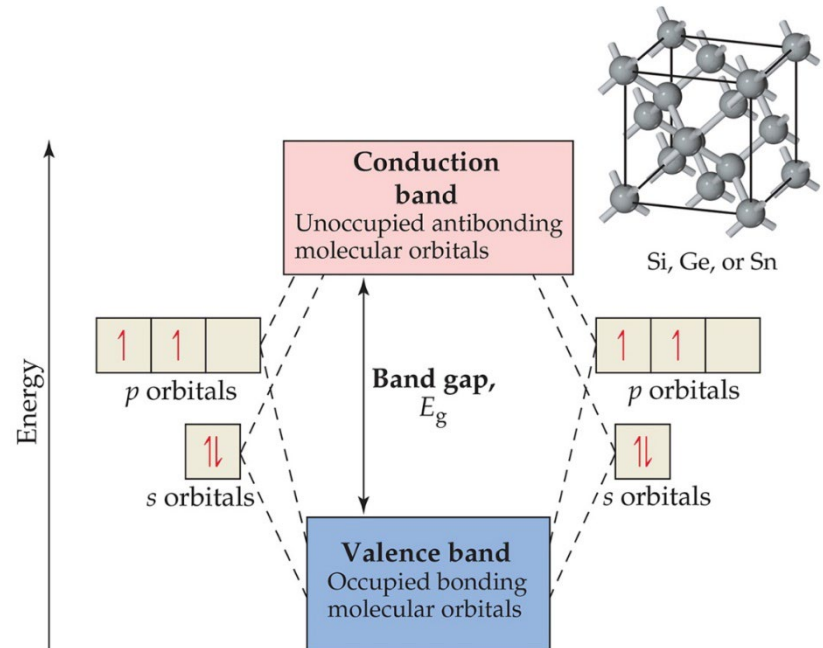
Note: Band gaps over 3.5 eV lead to the material being an insulator.

Doping

- Changing the conductivity of semiconductors by adding impuitity to an element, giving more or fewer electrons.

- **n-type semiconductors** have more electrons, so the negative charge travels in the conductance band.

- **p-type semiconductors** have fewer electrons, so the "hole" travels in the valence band.

Energy

Conduction band

Valence band

Band gap, E_g

Empty MOs

Filled MOs

Undoped semiconductor
(a)

n-type semiconductor
(b)

p-type semiconductor
(c)
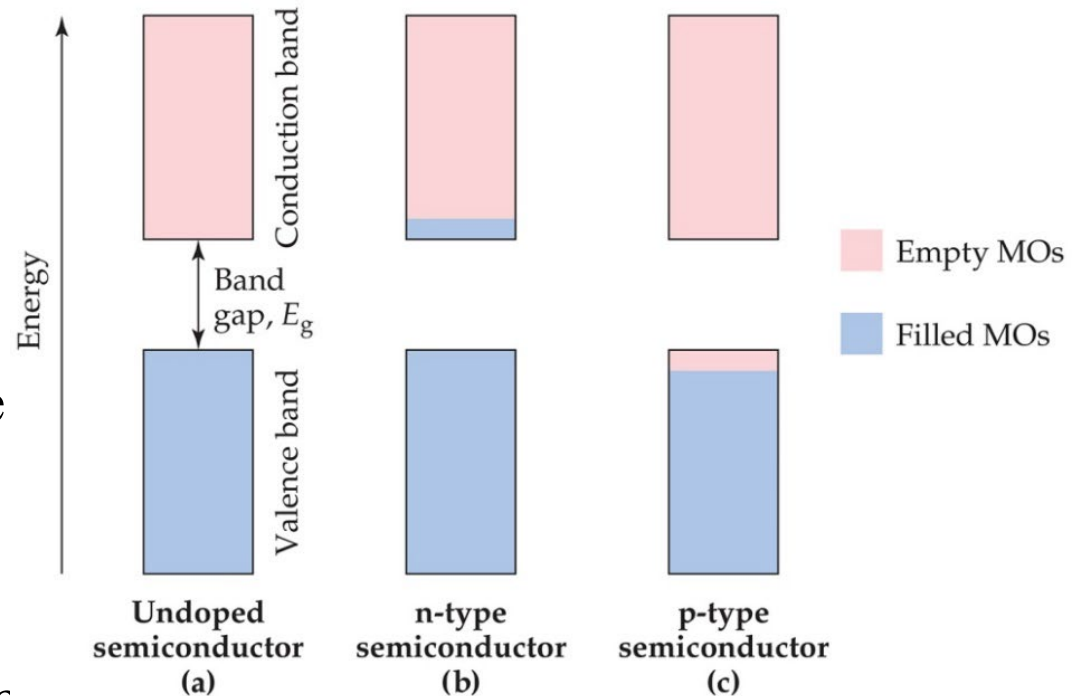
Ionic Solids

- They are held together by electrostatic attractions between cations and anions.

- Ionic solids have very high melting and boiling points and are quintessential crystals.

- Because the charge is centered on the anions, they are electronic insulators.
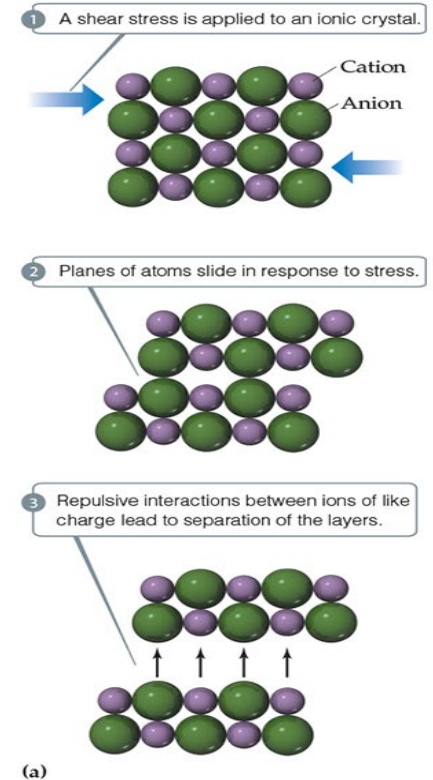
Ionic Solids

- Most favorable structures have cation–anion distances as close as possible, but the anion–anion and cation–cation distances are maximized.

- Three common structures for 1:1 salts:
  - CsCl structure
  - NaCl (rock salt) structure
  - Zinc blende (ZnS) structure
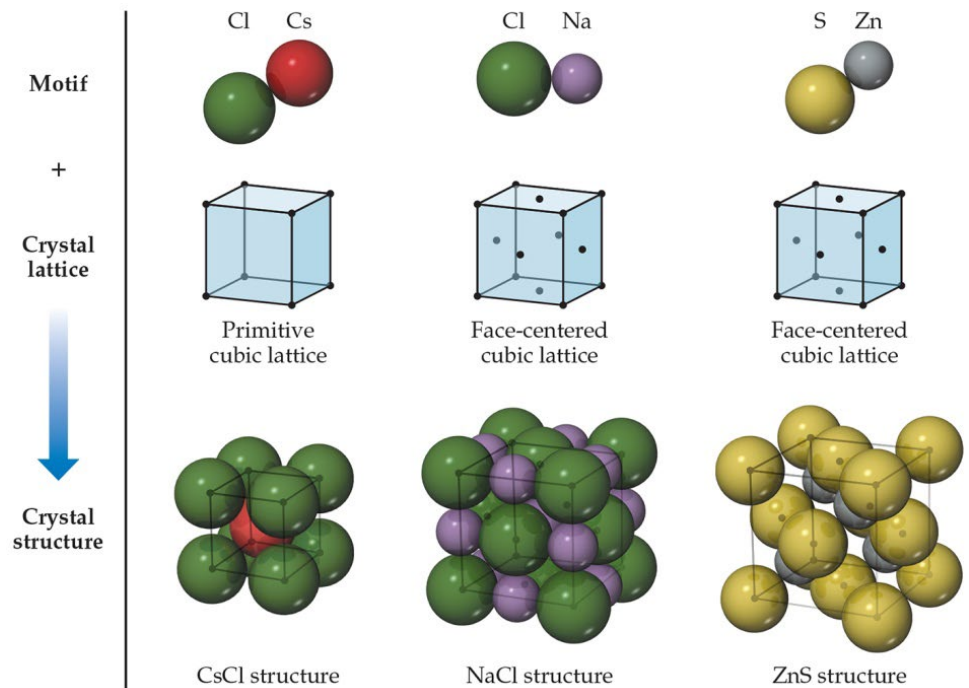
Ionic Crystals

Cesium chloride (CsCl)

Sodium chloride (NaCl)
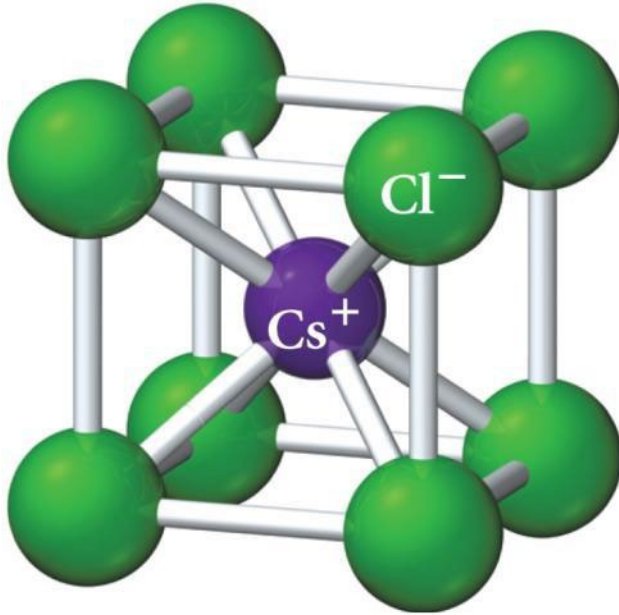
CsCl
coordination number = 8
Cs$^+$ = 167 pm
Cl$^-$ = 181 pm
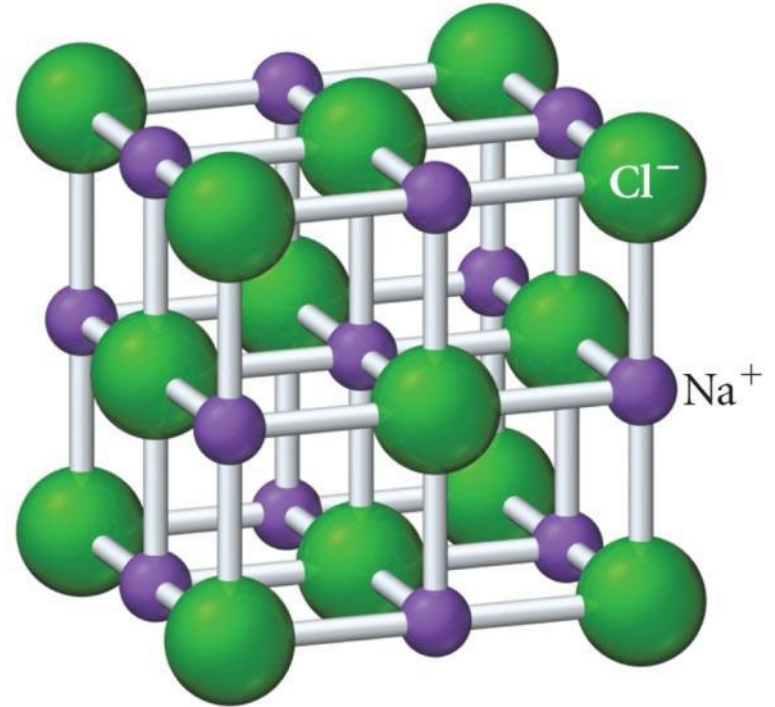
NaCl
coordination number = 6
Na$^+$ = 97 pm
Cl$^-$ = 181 pm

Effect of Ion Size on Structure

The size of the cation compared to the anion (radius ratio) is the major factor in which structure is seen for ionic compounds.
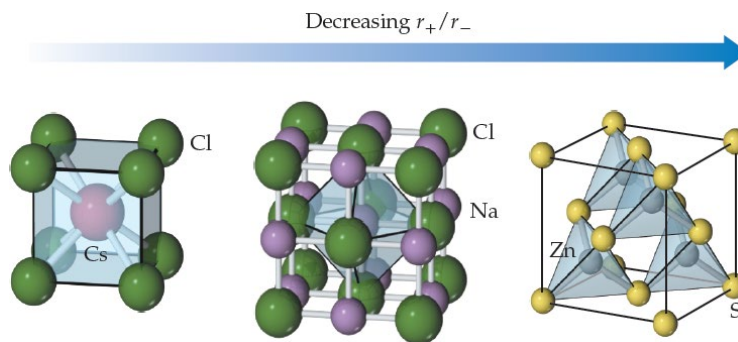
	CsCl	**NaCl**	**ZnS**
Cation radius, r_+ (Å)	1.81	1.16	0.88
Anion radius, r_- (Å)	1.67	1.67	1.70
$\dfrac{r_+}{r_-}$	1.08	0.69	0.52
Cation coordination number	8	6	4
Anion coordination number	8	6	4

Coordination Number and Structure

- Not all ionic compounds have a 1:1 ratio of cation to anion (or vice versa).
- Since other combinations exist, other structures exist.
- The coordination numbers vary to give the expected ratio of ions.

Increasing anion-to-cation ratio

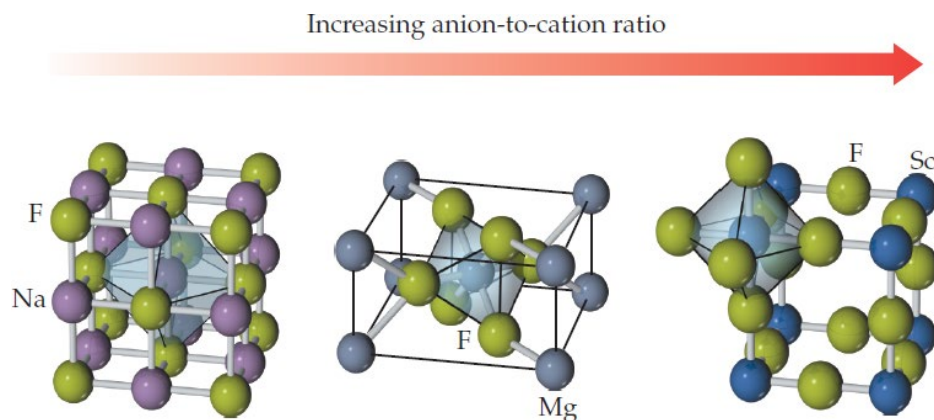|	NaF	MgF$_2$	ScF$_3$
Cation coordination number	6	6	6
Cation coordination geometry	Octahedral	Octahedral	Octahedral
Anion coordination number	6	3	2
Anion coordination geometry	Octahedral	Trigonal planar	Linear

Cesium Chloride Structures

- coordination number = 8
- ⅛ of each Cl^- (184 pm) inside the unit cell
- whole Cs^+ (167 pm) inside the unit cell
  - **cubic hole** = hole in simple cubic arrangement of Cl^- ions
- $Cs:Cl = 1: (8 \times ⅛)$
- Therefore, the formula is CsCl.

Cesium chloride (CsCl)

Cl^-

Cs^+
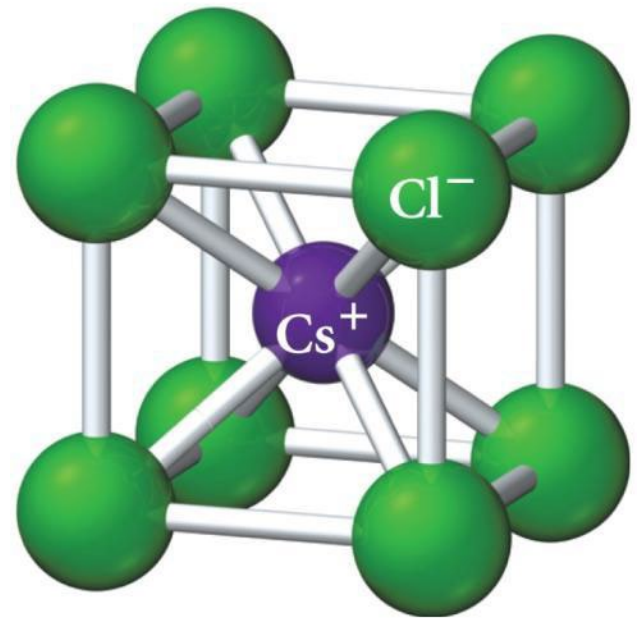
Lattice Holes

- In hexagonal closest-packed or cubic closest-packed lattices, there are eight tetrahedral holes and four octahedral holes per unit cell.
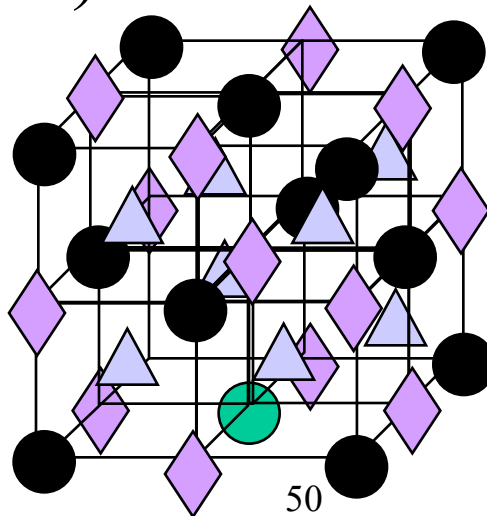
- In a simple cubic lattice, there is 1 cubic hole per unit cell.

- Number and type of holes occupied determine formula (empirical) of the salt.

◇ **= Octahedral**

△ **= Tetrahedral**

Rock Salt Structures

- coordination number = 6
- Cl^- ions (181 pm) in a face-centered cubic arrangement
  - ⅛ of each corner Cl^- inside the unit cell
  - ½ of each face Cl^- inside the unit cell
- each Na^+ (97 pm) in holes between Cl^-
  - **octahedral holes**
  - 1 in center of unit cell
  - ¼ of each edge Na^+ inside the unit cell
- Na:Cl = (¼ × 12) + 1: (⅛ × 8) + (½ × 6) = 4:4 = 1:1
- Therefore, the formula is NaCl.

Sodium chloride (NaCl)

Cl^-

Na^+
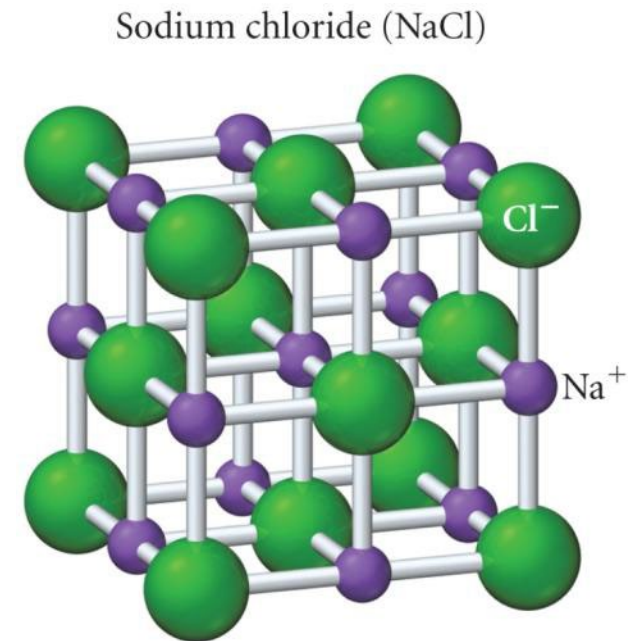
Zinc Blende Structures

- coordination number = 4
- S^{2-} ions (184 pm) in a face-centered cubic arrangement
  - ⅛ of each corner S^{2-} inside the unit cell
  - ½ of each face S^{2-} inside the unit cell
- each Zn^{2+} (74 pm) in holes between S^{2-}
  - **tetrahedral holes**
  - 1 whole in ½ the holes
- Zn:S = (4 × 1) : (⅛ × 8) + (½ × 6) = 4:4 = 1:1
- Therefore, the formula is ZnS.

Zinc blende (ZnS)

S^{2-}

Zn^{2+}
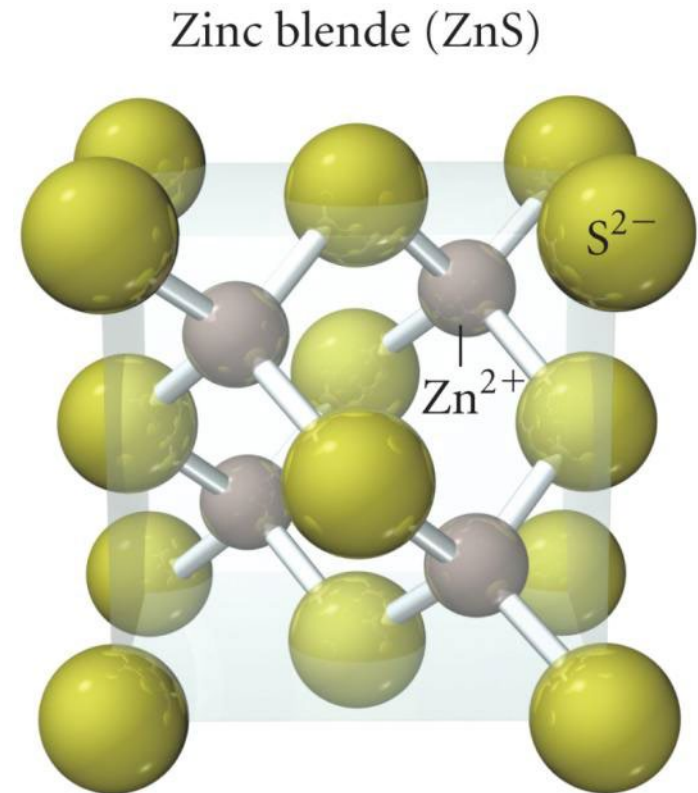
Fluorite Structures

- coordination number = 4
- Ca^{2+} ions (99 pm) in a face-centered cubic arrangement
  - ⅛ of each corner Ca^{2+} inside the unit cell
  - ½ of each face Ca^{2+} inside the unit cell
- each F^- (133 pm) in holes between Ca^{2+}
  - **tetrahedral holes**
  - 1 whole in all the holes
- $Ca:F = (⅛ \times 8) + (½ \times 6): (8 \times 1) = 4:8 = 1:2$
- Therefore, the formula is CaF_2.
  - fluorite structure common for 1:2 ratio

- usually get the **antifluorite** structure when the cation:anion ratio is 2:1
  - The anions occupy the lattice sites and the cations occupy the tetrahedral holes. Like K_2O.

53

Calcium fluoride (CaF_2)

Ca^{2+}

F^-
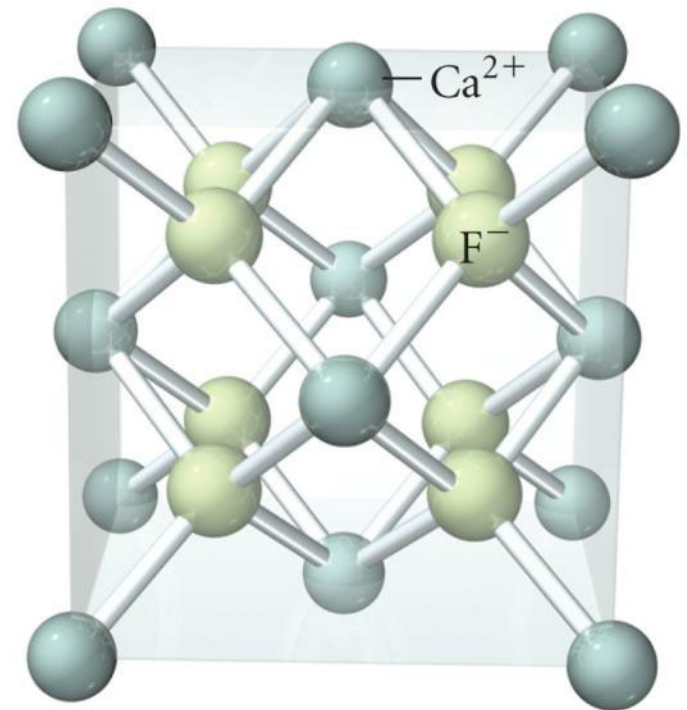
Lecture quiz 6

Atoms in metals easily slip past one another as mechanical force is applied; can you think of why this would not be true for ionic solids?
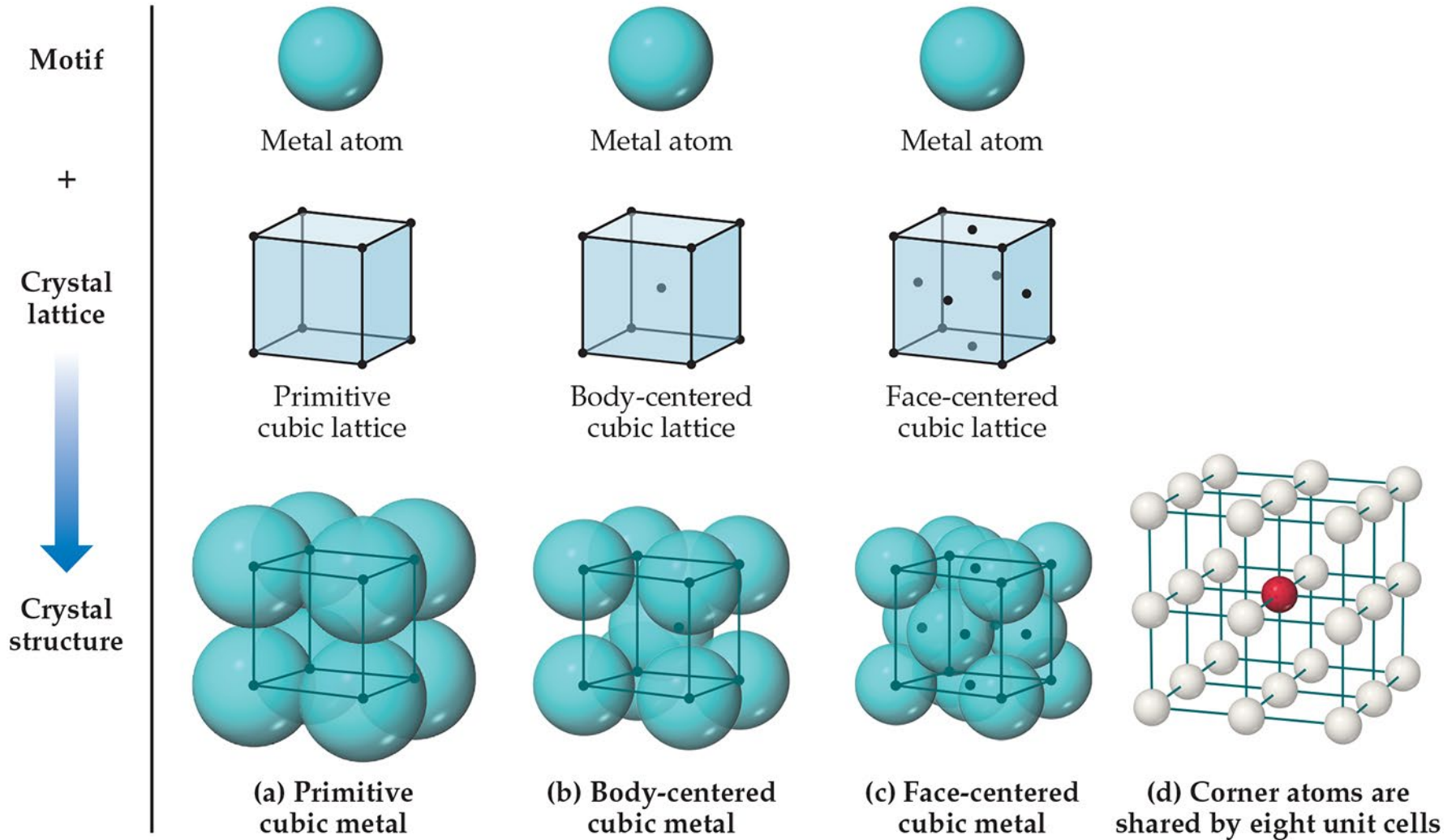
a. **Ionic solids have less efficient packing that makes the slipping motion difficult, causing the solid to be brittle.**

b. **When ions slip past each other, like charges experience repulsions, causing the solid to be brittle.**

Lecture quiz 7

Is it possible for all atoms in an ionic compound to lie on the lattice points as they do in the metallic structures shown in the illustration?

a. Yes, all lattice points are equivalent.

b. Yes, because although an ionic substance has at least two different atoms, the different atoms can lie on the same lattice point.

c. No, the lattice points in the metallic structure are different from those in an ionic one.

d. No, an ionic substance has at least two different atoms, and different atoms cannot lie on the same lattice points.

Factors to consider

Motif

Metal atom | Metal atom | Metal atom

+

Crystal lattice

Primitive cubic lattice | Body-centered cubic lattice | Face-centered cubic lattice

Crystal structure

(a) Primitive cubic metal | **(b) Body-centered cubic metal** | **(c) Face-centered cubic metal** | **(d) Corner atoms are shared by eight unit cells**
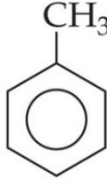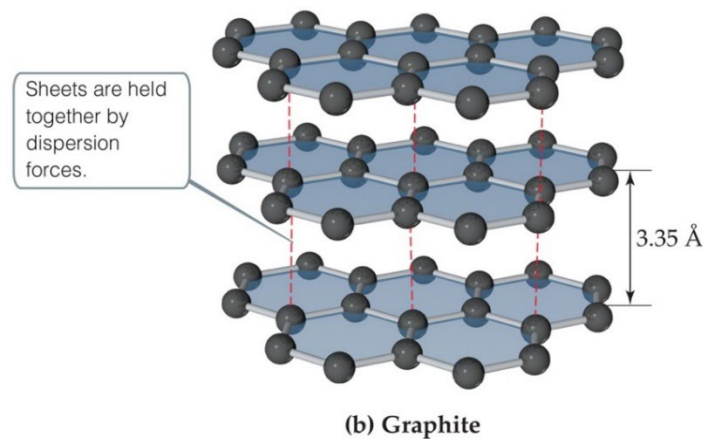
Lecture quiz 8

In the crystal structure of potassium oxide, the oxide ions are coordinated by eight potassium ions. What is the coordination number of potassium?

a. 2

b. 4

c. 6

d. 8

Molecular Solids

- Consist of atoms or molecules held together by weaker forces (dispersion, dipole–dipole, or hydrogen bonds).

- Shape (ability to stack) matters for some physical properties, like boiling point.

- Graphite is an example.

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

Sheets are held together by dispersion forces.

3.35 Å

(b) Graphite

Covalent-Network Solids

- Atoms are covalently bonded over large network distances with regular patterns of atoms.

- Tend to have higher melting and boiling points.

- Diamond is an example.

Each carbon atom is bonded to four other carbon atoms, forming a tedrahedron.
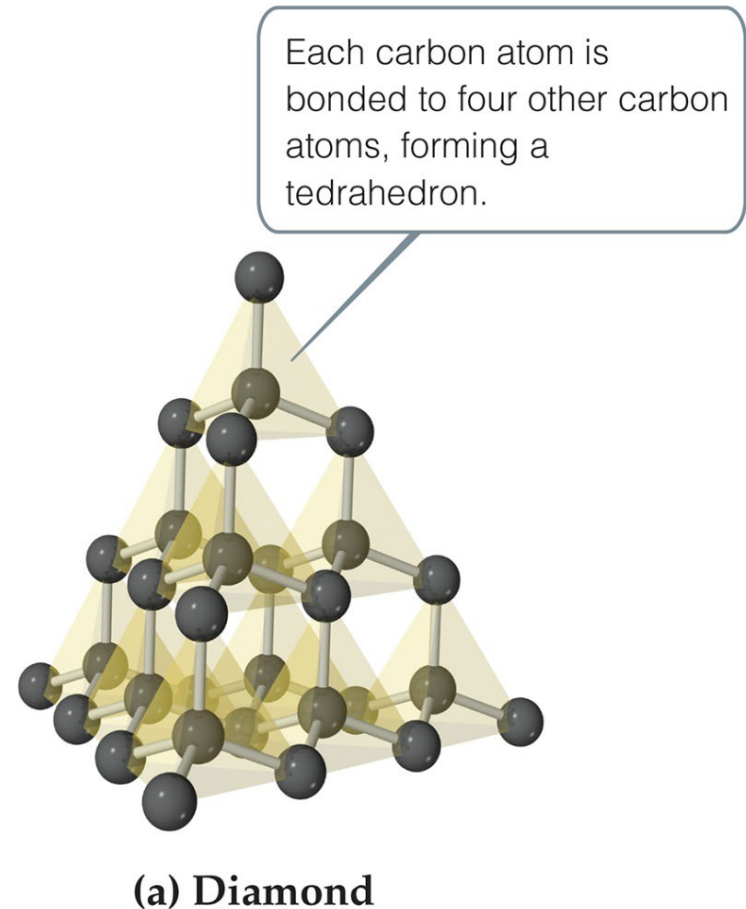
(a) Diamond

Properties of Diamond

- very high melting, ~3800 °C
  - need to overcome some covalent bonds
- very rigid
  - due to the directionality of the covalent bonds
- very hard
  - due to the strong covalent bonds holding the atoms in position
  - used as abrasives
- electrical insulator
- thermal conductor
 - best known
- chemically very nonreactive
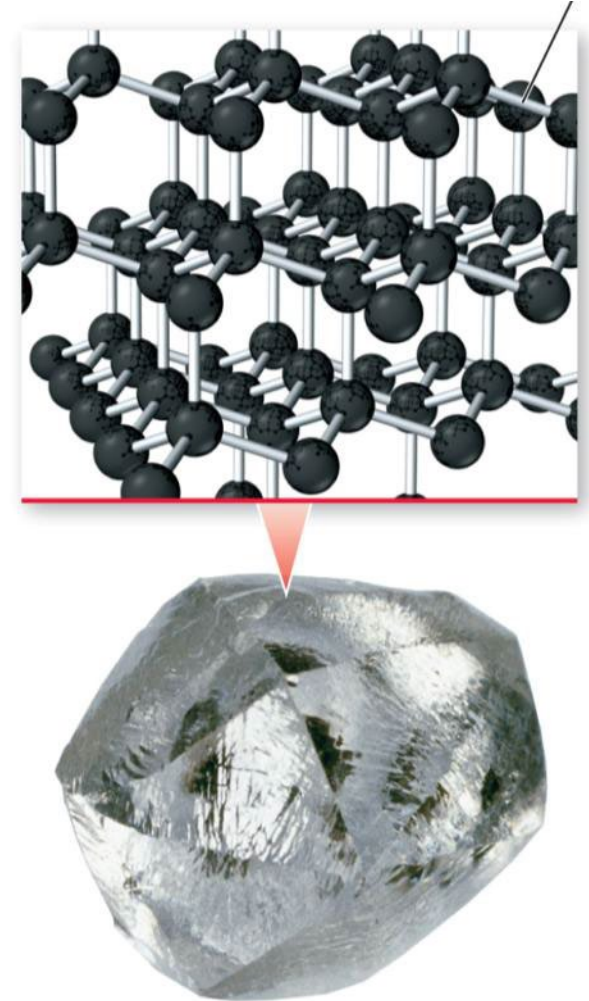
(a) Diamond

The Graphite Structure—
a Two-Dimensional Network

- In graphite, the carbon atoms in a sheet are covalently bonded together.
  - forming six-membered flat rings fused together
    - similar to benzene
    - bond length = 142 pm
  - sp^2
    - Each C has three sigma bonds and one pi bond.
  - trigonal-planar geometry
  - each sheet a giant molecule
- The sheets are then stacked and held together by dispersion forces.
 - Sheets are 341 pm apart.

Properties of Graphite

- hexagonal crystals
- high melting, ~3800 °C
  - need to overcome some covalent bonding
- slippery feel
  - Because there are only dispersion forces holding the sheets together, they can slide past each other.
    - glide planes
  - lubricants
- electrical conductor
  - parallel to sheets
- thermal insulator
- chemically very nonreactive
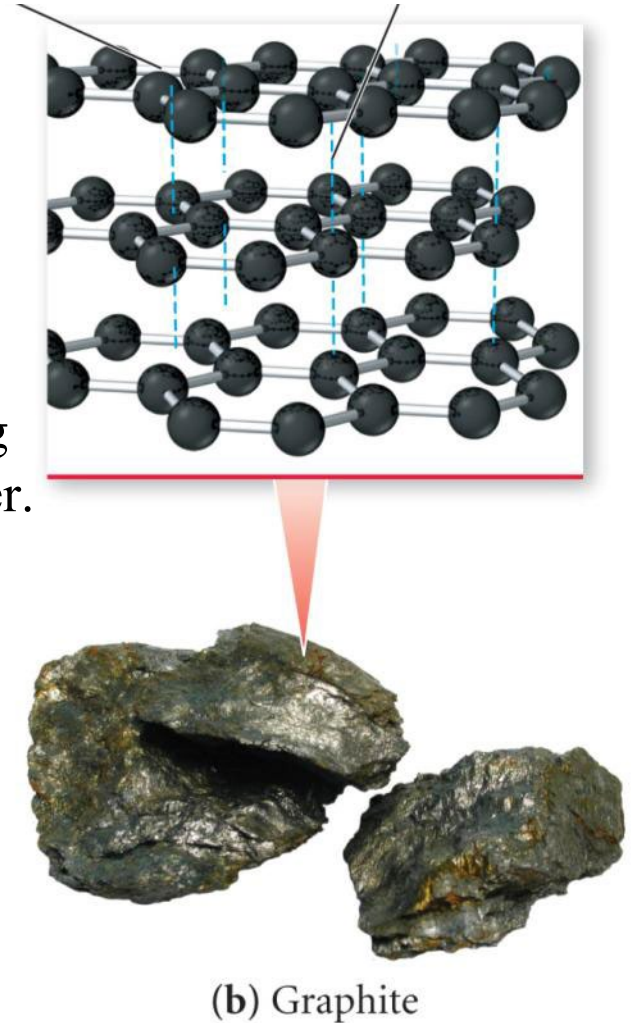
(b) Graphite

A New Form of Carbon

- Until the mid-1980s the only allotropes of carbon known were diamond and graphite.

- A new form of carbon in which discrete C_{60} molecules existed was discovered.

- The shape was like a soccer ball or a geodesic dome. It was called "buckminsterfullerene" or "buckyballs."
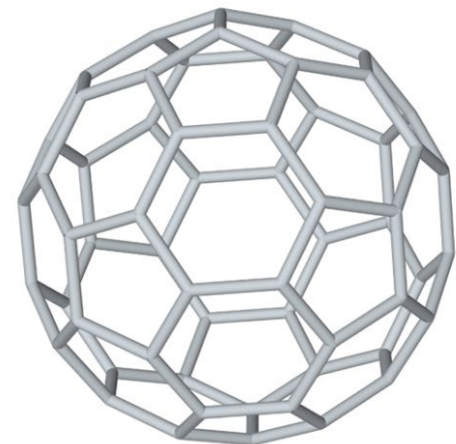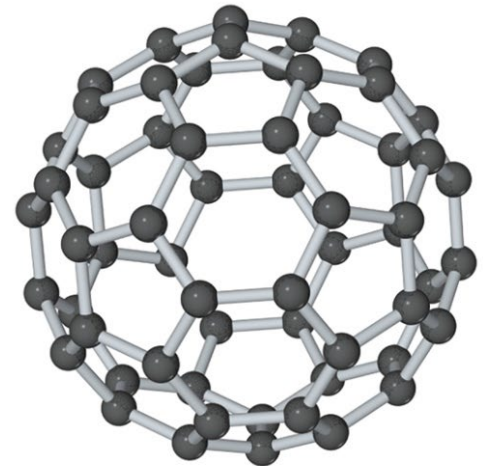
Carbon on the Nanoscale

- The "straightening" of buckyballs led to new materials.

- Carbon nanotubes can be made with metallic or semiconducting properties without doping.

- They are very strong materials.

- Graphene has been discovered: single layers with the structure of graphite.
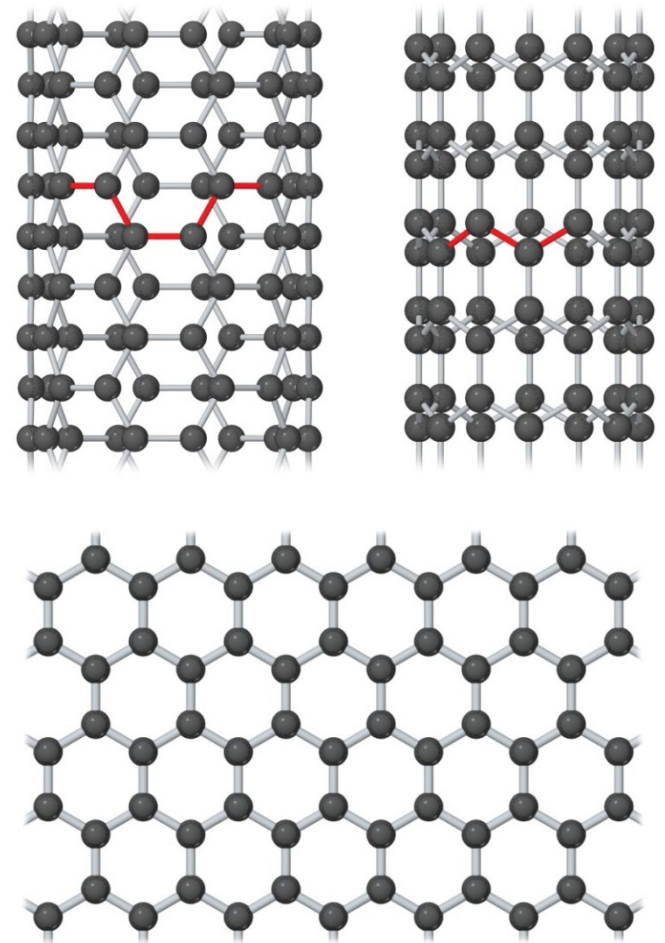
X-RAY DIFFRACTION

- Determining crystal structure
    x-ray diffraction used to obtain structure of
    proteins (1962 Nobel Prize myoglobin) &
    hemoglobin
- Due to order structure - crystals consists of repeating planes
- Planes act as reflecting surfaces
- X-ray reflecting off surface creates diffraction pattern

    constructive interference gives more intense (higher
    amplitude) weaves.

- only at certain angles will x-rays stay in-phase
- creates light and dark areas on photographs
- used to determine type of unit cell and size
- if molecular, then can determine position of each atom

$$n\lambda = 2d \sin \theta \quad \text{Bragg's equation}$$

d=distance between atomic planes θ =angle of reflection