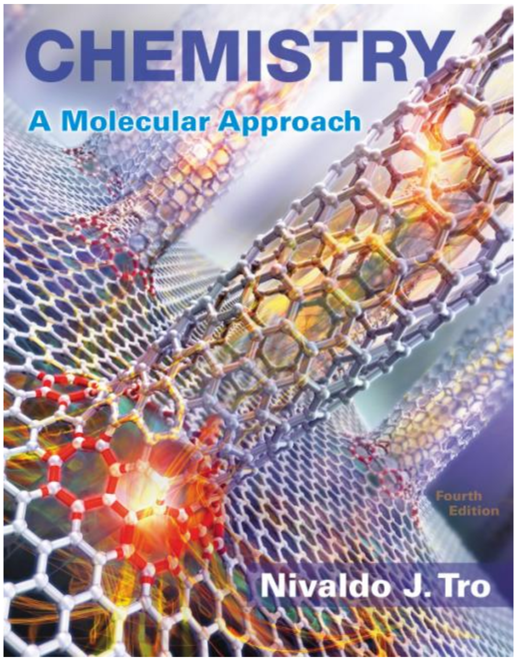


Lecture Presentation

Chapter 12

Solids and Modern Materials

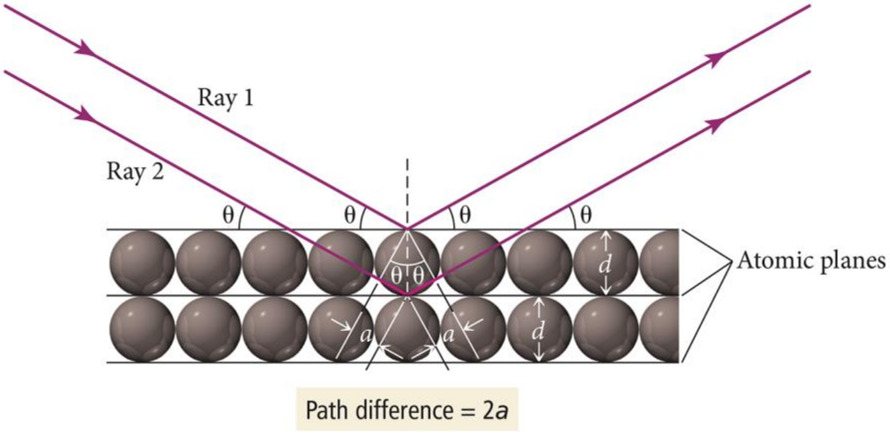
Graphene

- Thinnest, strongest known material; only one atom thick
- Conducts heat and electricity
- Transparent and completely impermeable to all substances
- Potential to be used in making faster computers, foldable touchscreens, ultrathin light panels, super-strong plastics for satellites, airplanes, ships, and cars

X-Ray Crystallography

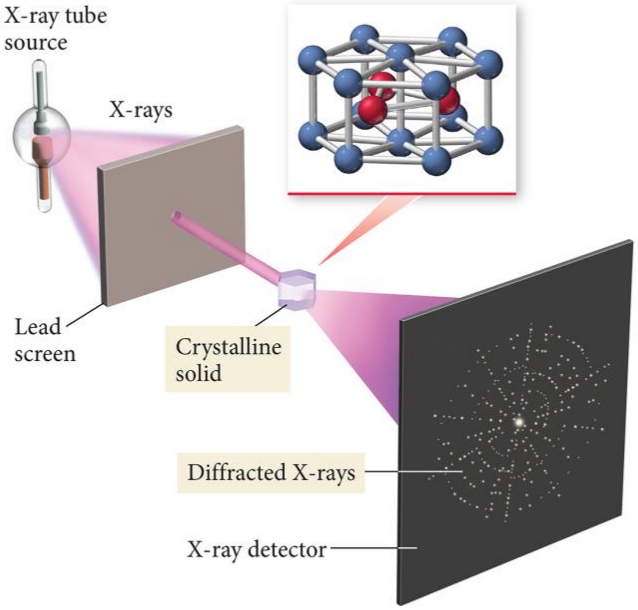
- **X-ray diffraction** is a powerful technique that allows us to look into crystals to determine the arrangement of the atoms and measure the distances between them.
- Atomic planes within crystals are separated by about 10^2 pm.
- X-ray light forms interference patterns or diffraction patterns when it interacts with atoms in the crystal.
- Path length traveled by different rays and angle of reflection tell us the distance between planes of atoms.

Diffraction from a Crystal



$$n\lambda = 2d \sin\theta$$

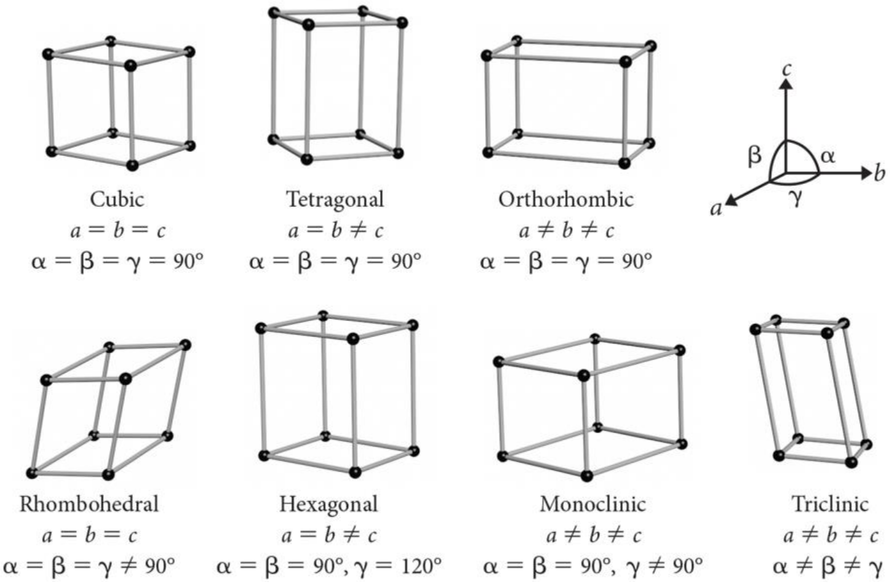
X-Ray Diffraction Analysis



Crystal Lattice

- X-ray crystallography allows us to determine the regular arrangements of atoms within a crystalline solid.
- This arrangement 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 are repeated over and over to give the macroscopic crystal structure of the solid.
- We usually classify unit cells by their symmetry.

Fundamental Types of Unit Cells

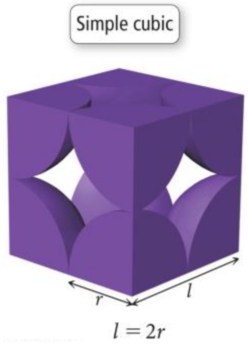


Unit Cells

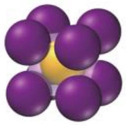
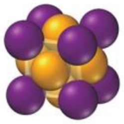
- The number of other particles each particle is in contact with is called its **coordination number**.
  - For ions, it is the number of oppositely charged ions an ion is in contact with.
- A higher coordination number means more interaction; therefore, stronger attractive forces hold the crystal together.
- 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 packed together.

Cubic Unit Cells

- All unit cell corners are 90° angles.
- The length of all the edges is equal.
- Three types: simple cubic, body-centered cubic, and face-centered cubic
- If the unit cell is composed 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.



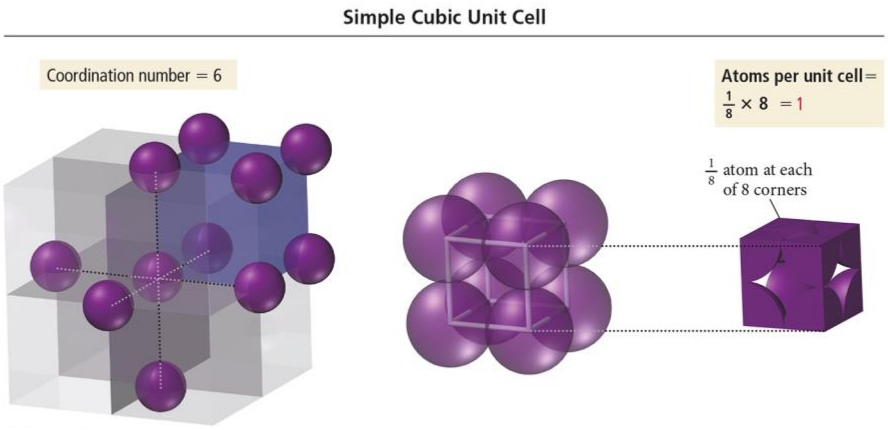
The Cubic Crystalline Lattices

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%

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 = one particle in each unit cell
    - 8 corners × ⅛
- Edge of unit cell = twice the radius
- Coordination number of 6

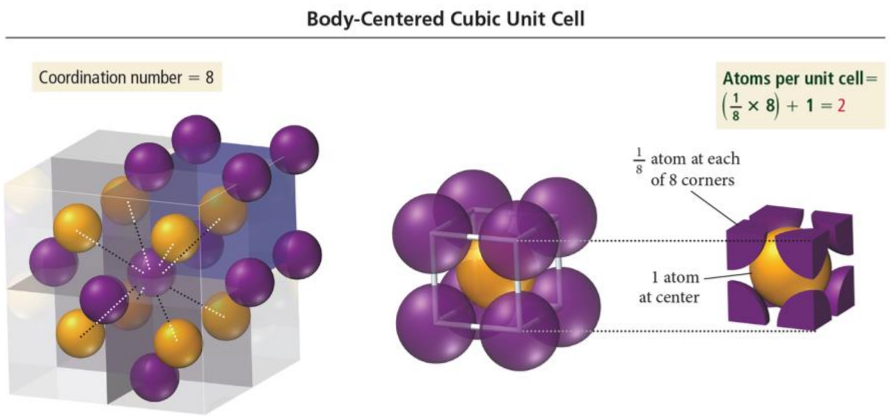
Simple Cubic



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 × 1/8
    - + 1 center
- Edge of unit cell = $(4/\sqrt{3})$ times the radius of the particle
- Coordination number of 8

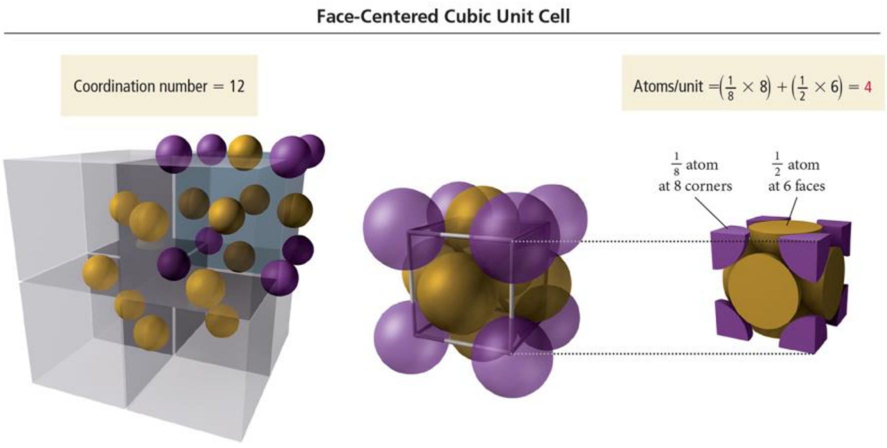
Body-Centered Cubic



Cubic Unit Cells: Face-Centered Cubic

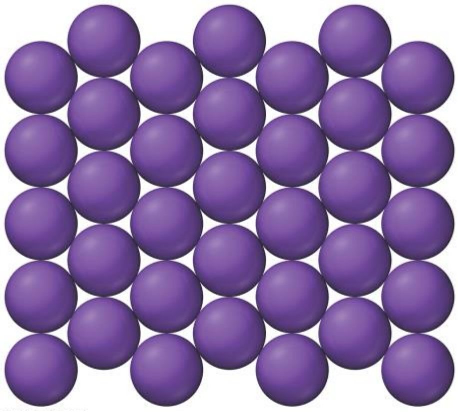
- 14 particles, one at each corner of a cube + one in center of each face
- ⅛ of each corner particle + ½ of face particle lies in the unit cell.
  - 4 particles in each unit cell
    - 8 corners × ⅛
    - + 6 faces × ½
- Edge of unit cell = $2\sqrt{2}$ times the radius of the particle
- Coordination number of 12

Face-Centered Cubic



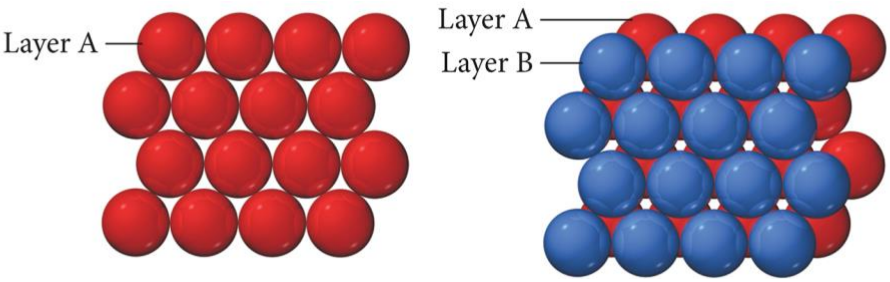
Closest-Packed Structures First Layer

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



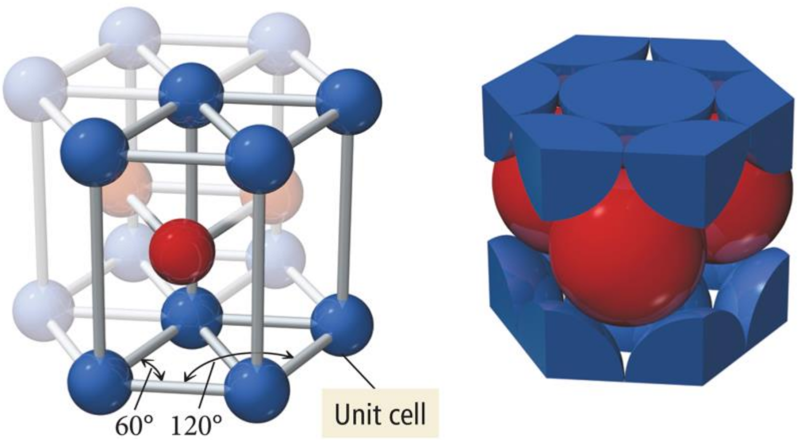
Closest-Packed Structures Second Layer

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



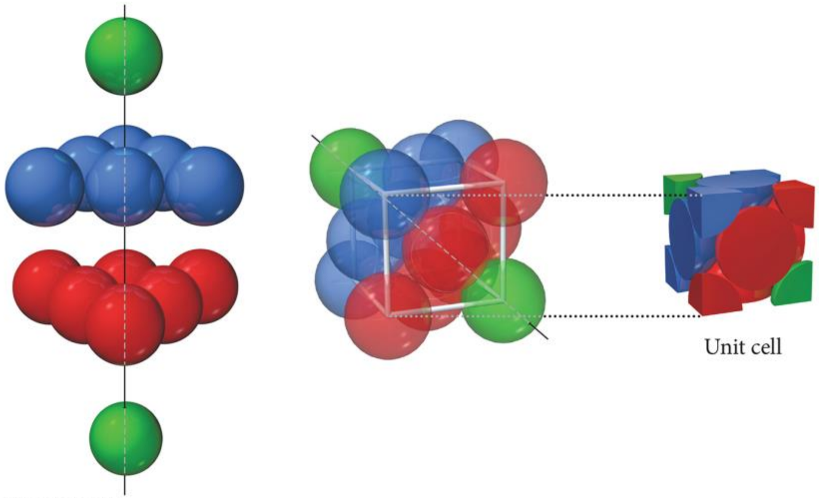
Hexagonal Closest-Packed Structures

Hexagonal Closest Packing



Cubic Closest-Packed Structures

Cubic Closest Packed = Face-Centered Cubic



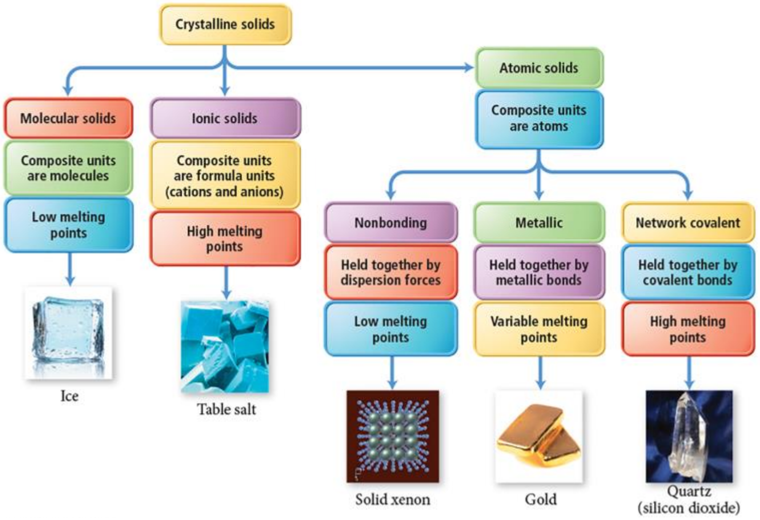
Classifying Crystalline Solids

- Crystalline solids are classified by the individual particles that comprise them: molecular, ionic, and atomic.
- Atomic solids are classified by the kinds of attractive forces holding the particles together: nonbonded, metallic, and network covalent.

Classifying Crystalline Solids

- **Molecular solids** are solids whose composite particles are molecules.
- **Ionic solids** are solids whose composite particles are ions.
- **Atomic solids** are solids whose composite particles are atoms.
  - **Nonbonding atomic solids** are held together by dispersion forces.
  - **Metallic atomic solids** are held together by metallic bonds.
  - **Network covalent atomic solids** are held together by covalent bonds.

Types of Crystalline Solids



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)

Molecular Solids

- The lattice sites are occupied by molecules.
  - CO_2, H_2O, $C_{12}H_{22}O_{11}$
- The molecules are held together by intermolecular attractive forces.
  - Dispersion forces, dipole–dipole attractions, and H bonds
- Weak attractive forces, relatively low melting points
- Some crystallize in different structures, called **polymorphs**.
  - Different properties
  - Important in pharmaceuticals

Polymorphism: Chocolate

TABLE 12.1 Crystalline Forms of Cocoa Butter

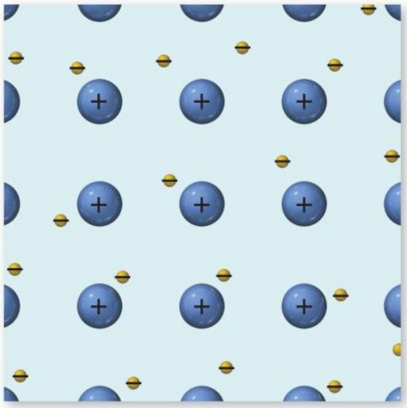
Crystalline Structure Type (Polymorph)	Melting Point (°C)	Description	Increasing Density and Stability
I	17.3	Soft, crumbly, noticeable blooming, melts in the hand.	↓
II	23.3	Soft, crumbly, noticeable blooming, melts in the hand.	
III	25.5	Firm, poor snap, some blooming, melts in the hand.	
IV	27.3	Firm, poor snap, some blooming, melts in the hand.	
V	33.8	Firm, good snap, smooth and shiny surface, melts in the mouth, most desirable.	
VI	36.3	Hard, some blooming, cannot be formed from melt, takes several months to form.	

Ionic Solids

- Lattice sites are occupied by ions.
- They are held together by strong coulombic forces.
- High melting points

Metallic Bonding

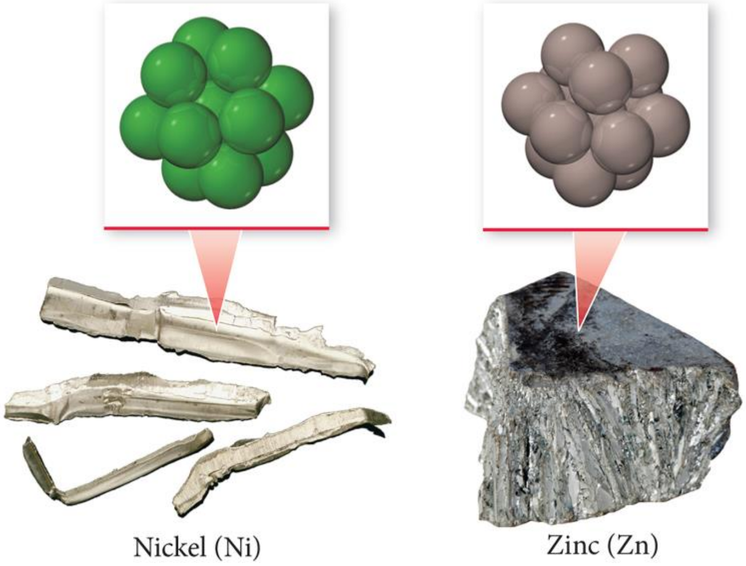
- Metal atoms release their valence electrons.
- Metal cation "islands" fixed in a "sea" of mobile electrons



Atomic Solids

- Nonbonding atomic solids
  - Held together by weak dispersion forces
  - Very low melting points
  - Noble gases in solid form
- Metallic atomic solids
  - Held together by metallic bonding
  - Varying melting points
  - Form closest-packed crystal structures
- Network covalent solids
  - Held together by covalent bonds
  - Structure restricted by geometry of bonds
  - Very high melting points

Closest-Packed Crystal Structures in Metals



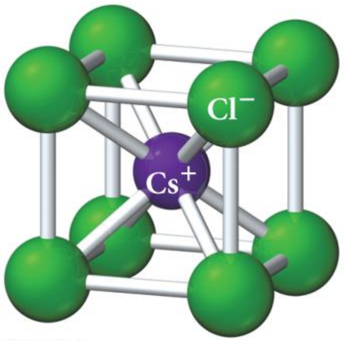
Ionic Solids

- Structure must accommodate both cations and anions.
- The coordination number represents the number of close cation–anion interactions in the crystal.
- The higher the coordination number, the more stable the solid.
  - Lowers the potential energy of the solid
- The coordination number depends on the relative sizes of the cations and anions that maintain charge balance.
  - Generally, anions are larger than cations.
  - The number of anions that can surround the cation is limited by the size of the cation.
  - The closer in size the ions are, the higher the coordination number.

Cesium Chloride Structure

- 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 × ⅛); therefore the formula is CsCl.

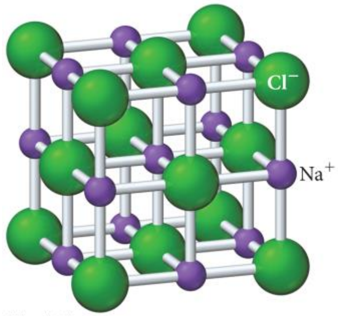
Cesium chloride (CsCl)



Rock Salt Structure

- 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
- Na^+ (97 pm) in holes between Cl^-
  - **Octahedral holes**
  - 1 in center of unit cell
  - 1 whole particle in every octahedral hole
  - 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.

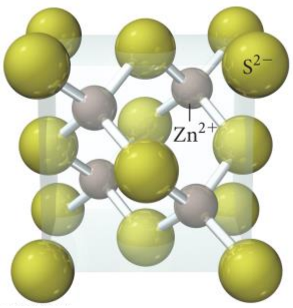
Sodium chloride (NaCl)



Zinc Blende Structure

- 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 particle in ½ the holes
- Zn:S = (4 × 1) : (⅛ × 8) + (½ × 6) = 4:4 = 1:1
- Therefore, the formula is ZnS.

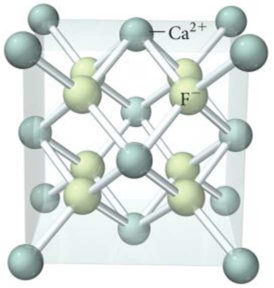
Zinc blende (ZnS)



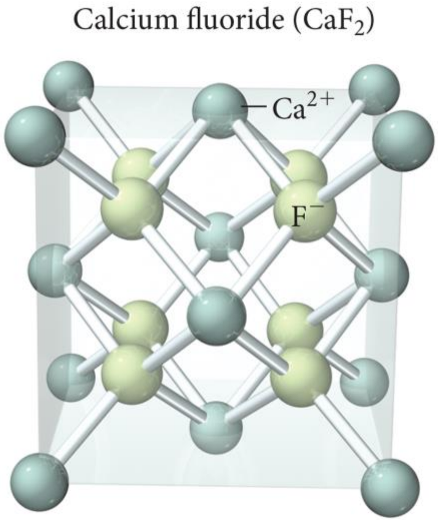
Fluorite Structure

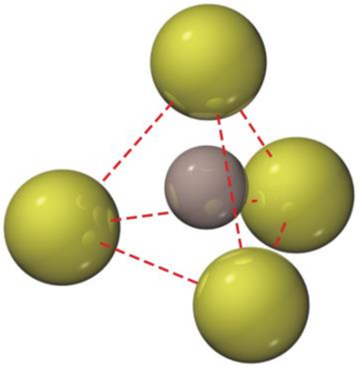
- Coordination number = 4
- Ca^{2+} ions (99 pm) in a face-centered cubic arrangement
  - ⅛ of each corner Ca^{2+} inside the unit cell
  - ½ of each face Ca^{2+} inside the unit cell
- Each F^- (133 pm) in holes between Ca^{2+}
  - **Tetrahedral holes**
  - 1 whole particle in all the holes
- Ca:F = (⅛ × 8) + (½ × 6): (8 × 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.

Calcium fluoride (CaF_2)



Lattice Holes



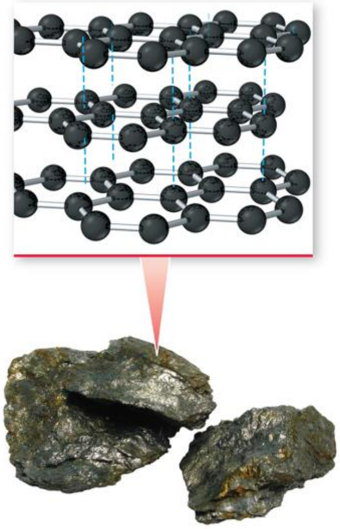


Network Covalent Atomic Solids: Carbon

- Graphite and diamond
- In graphite, the carbon atoms in a sheet are covalently bonded together.
  - Forming six-member 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

- High melting point, ~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



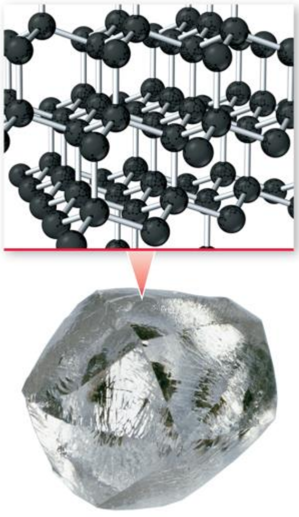
(a) Graphite

Diamond

- The carbon atoms in a diamond each have four covalent bonds to surrounding atoms.
  - *sp*^{3}
  - Tetrahedral geometry
- This effectively makes each crystal one giant molecule held together by covalent bonds.
  - You can follow a path of covalent bonds from any atom to every other atom.

Properties of Diamond

- Very high melting point, ~3800 °C
  - Need to overcome some covalent bonds
- Very rigid
  - Due to the directionality of the covalent bonds
- Very hard
  - Strong covalent bonds holding the atoms in position
  - Used as abrasives
- Electrical insulator
- Thermal conductor
  - Best known
- Chemically very nonreactive



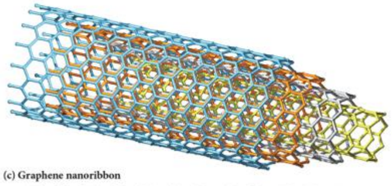
(b) Diamond

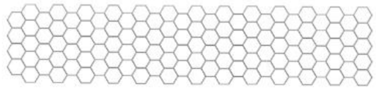
Buckministerfullerenes and Nanotubes

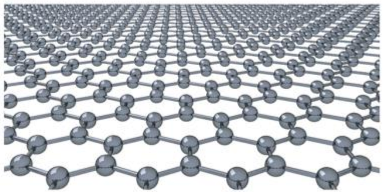
- Form of carbon, discovered in 1980s
- Occurs as soccer-ball-shaped clusters of 60 carbon atoms (C_{60}).
- Called **fullerenes**, or **bucky balls**
- Nanotubes—sheets of interconnected C_6 rings that assume the shape of a cylinder
  - Single-walled tubes—one layer of interconnected rings
  - Multiwalled tubes—concentric layers of interconnected rings

Carbon Structures


(a) Single-walled nanotube (SWNT)


(b) Multiwalled nanotube (MWNT)

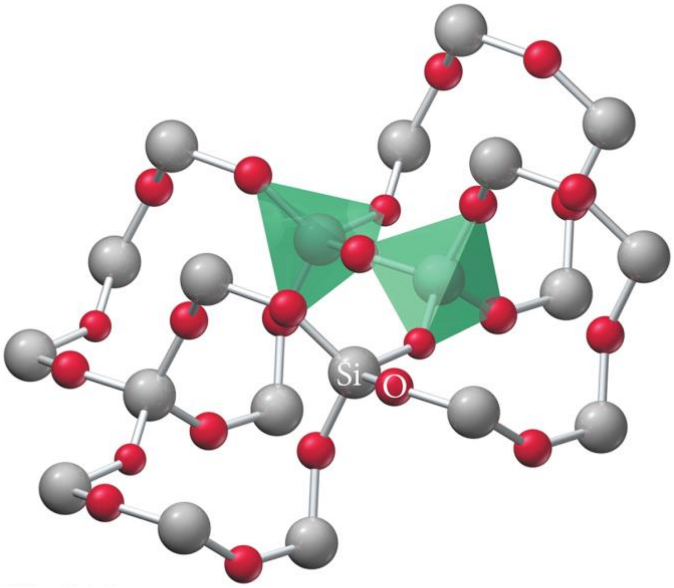

(c) Graphene nanoribbon


(d) Graphene sheet

Silicates

- ~90% of Earth’s crust
- Extended network covalent structure
  - Si atom bonded to four O atoms; each O atom bonded to two Si atoms
  - Tetrahedral
- Quartz

Quartz



Ceramics

- Ceramics—inorganic, nonmetallic solids prepared from powders mixed with water, formed into the desired shape, and then heated
- Extensively used to make bricks, tiles, pottery, dishware, and insulating elements in electrical devices
- Aluminosilicates, clay
  - Kaolinite, $Al_2Si_2O_5(OH)_4$,heated above 1500 ^oC gives a white ceramic.
  - Most important component in porcelain

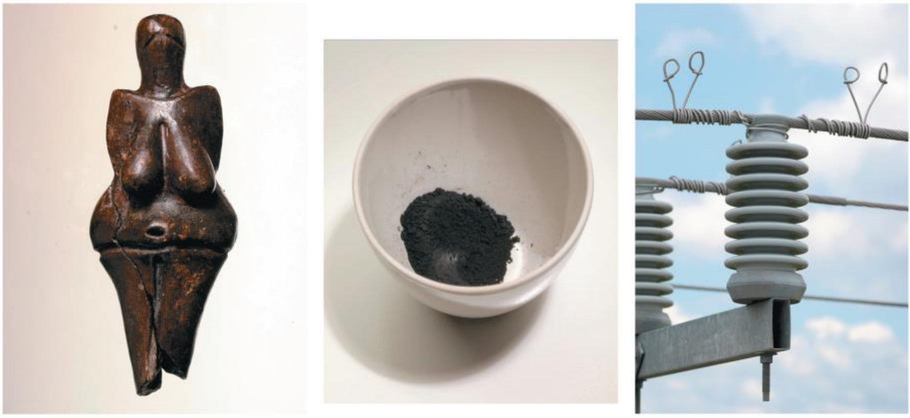
Oxide Ceramics

- Most common: Al_2O_3 and MgO
- Both physically and chemically stable at high temperatures
- Outstanding **refractory materials**—materials that can be used in high-temperature applications
  - Industrial furnaces, high-speed cutting tools, crucibles, heating elements, and fire proofing
  - Tend to be brittle and subject to thermal shock

Nonoxide Ceramics

- Include Si_3N_4, BN, and SiC
- Si_3N_4—network covalent solid with a structure similar to silica
- BN—isoelectronic with C_2 and forms structures similar to carbon
  - Has the diamond structure, which results in a hard, strong substance similar to diamond

Ceramics



Glass

- **Glass**—quickly cooled amorphous silica
- **Vitreous silica** or **fused silica**
  - Hard, high-temperature resistant, low thermal expansion, transparent to visible and UV light
  - Expensive for most applications
- **Soda-lime glass** (window glass)
  - 70% silica, balance of mostly Na_2O and CaO
  - Transparent to visible light but not UV
  - High thermal expansion
  - Less expensive, but cracks under thermal shock

Glass

- **Borosilicate glass** (also known as **Pyrex**)
  - Has added boric acid instead of CaO to glass mixture
  - Withstands heating and cooling cycles
- **Leaded glass** or **crystal**
  - PbO mixed with SiO_2
  - High refractive index; makes ringing sound when tapped
  - Toxicity concerns; lead-free crystal development

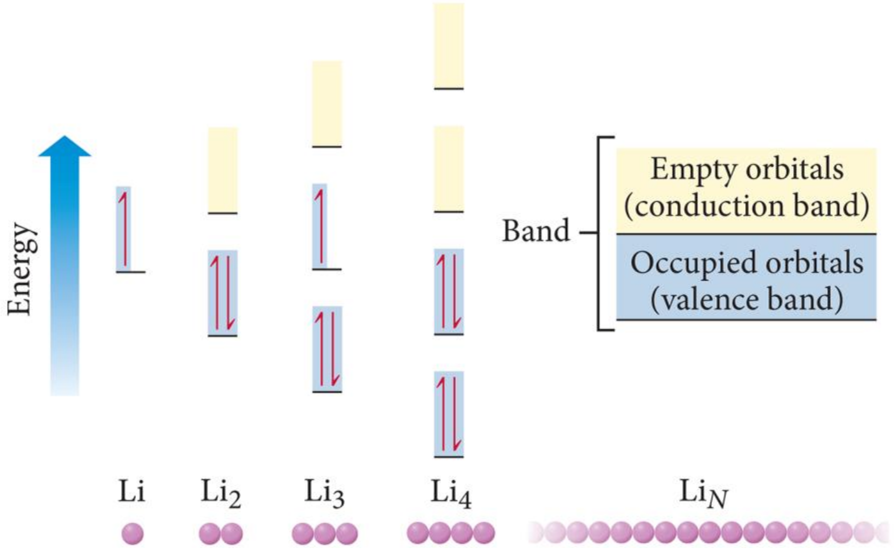
Semiconductors and Band Theory

- The structures of metals and covalent network solids result in every atom’s orbitals being shared by the entire structure—molecular orbitals.
- Molecular orbitals are delocalized over entire molecule.
- **Band theory**—stems from molecular orbital theory, with orbitals delocalized over entire crystal.

Band Theory

- The band of bonding molecular orbitals is called the **valence band**.
- The band of antibonding molecular orbitals is called the **conduction band**.

Molecular Orbitals in Lithium



Band Gap and Conductivity

- **Band gap**—energy gap between valence and conduction bands
- **Conductors**—valence band and conduction band energetically continuous
- **Semiconductors**—have band gap; electrons can be promoted from valence to conduction band.
- **Insulators**—large band gap restricting electron promotion

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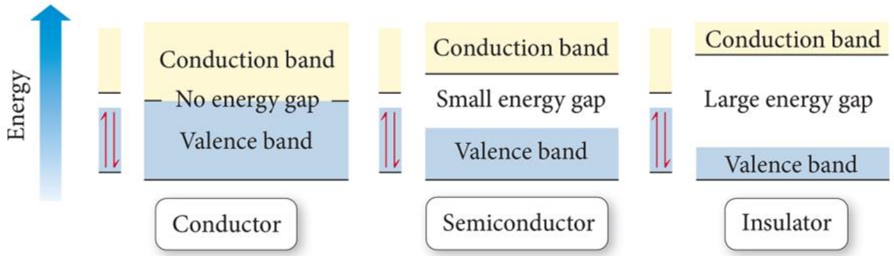
Band Gaps and Conductivity



Band Gap of Group IV Elements

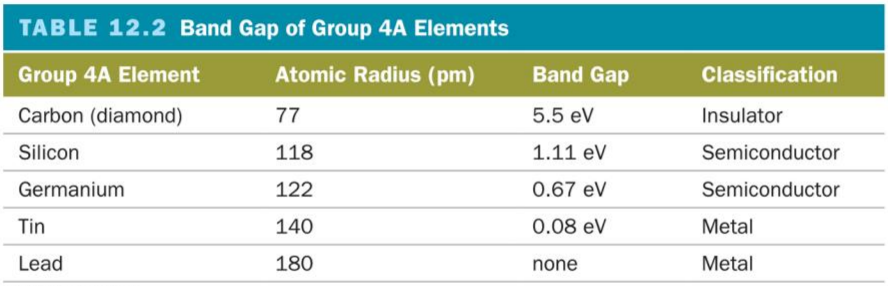


TABLE 12.2 Band Gap of Group 4A Elements

Group 4A Element	Atomic Radius (pm)	Band Gap	Classification
Carbon (diamond)	77	5.5 eV	Insulator
Silicon	118	1.11 eV	Semiconductor
Germanium	122	0.67 eV	Semiconductor
Tin	140	0.08 eV	Metal
Lead	180	none	Metal

Doping Semiconductors

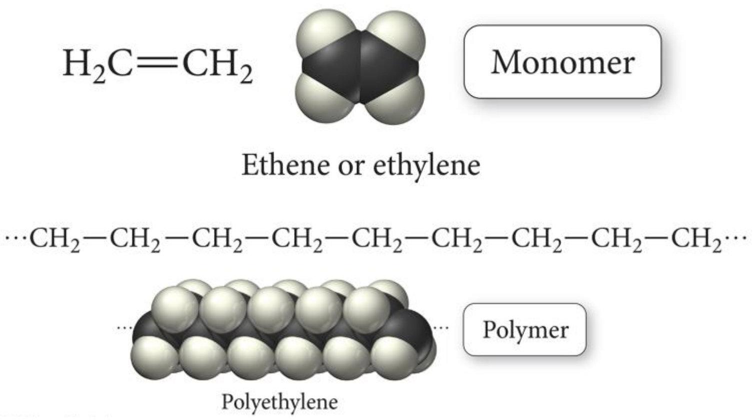
- **Doping**—adding impurities to semiconductor's crystal to increase its conductivity
  - To increase the number of electrons in the conduction band
- **n-type semiconductors**—doped by adding electron-rich impurities; negatively charged electrons in conduction band
- **p-type semiconductors**—doped with an electron-deficient impurity, resulting in electron "holes" in the valence band
  - Electrons can jump between these holes in the valence band, allowing conduction of electricity.

Diodes

- When a p-type semiconductor adjoins an n-type semiconductor, the result is a **p–n junction**.
- Electricity can flow across the p–n junction in only one direction; this is called a **diode**.
- This also allows the accumulation of electrical energy, called an **amplifier**.

Polymers

- Polymers—very large molecules made by repeated linking together of monomers
  - **Monomers**—small molecules



$H_2C{=}CH_2$

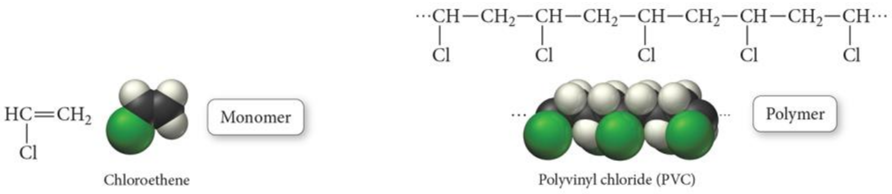
Ethene or ethylene

$\cdots CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2\cdots$

Polyethylene

Polymers

- **Natural polymers—**polymers found in living organisms, like starches, proteins, and DNA
- **Synthetic polymers—**polymers made in a lab
  - Plastics, Styrofoam cups, nylon rope, Plexiglas



$$\underset{\displaystyle \mathrm{Cl}}{\mathrm{HC}}{=}\mathrm{CH_2}$$

$$\cdots\underset{\displaystyle \mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\mathrm{CH}}\cdots$$

Polymerization

- **Polymerization** is the process of linking monomer units together.
- **Addition polymerization**—Monomers link together without the elimination of any atoms.
- **Condensation polymerization**—involves the elimination of an atom or a small group of atoms
- **Copolymer—**consists of two different kinds of monomers
- **Dimer—**product that forms between the reaction of two monomers

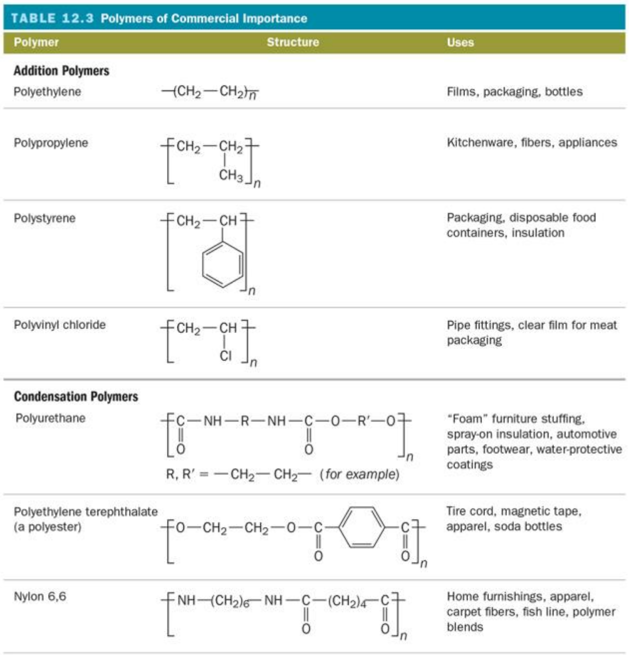


TABLE 12.3 Polymers of Commercial Importance

Polymer	Structure	Uses
Addition Polymers		
Polyethylene	$-(CH_2-CH_2)_n-$	Films, packaging, bottles
Polypropylene	$\left[CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH_2}}\right]_n$	Kitchenware, fibers, appliances
Polystyrene		Packaging, disposable food containers, insulation
Polyvinyl chloride	$\left[CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}\right]_n$	Pipe fittings, clear film for meat packaging
Condensation Polymers		
Polyurethane	$\left[\underset{\displaystyle O}{\underset{\Vert}{C}}-NH-R-NH-\underset{\displaystyle O}{\underset{\Vert}{C}}-O-R'-O\right]_n$ R, R′ = $-CH_2-CH_2-$ (*for example*)	"Foam" furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethylene terephthalate (a polyester)		Tire cord, magnetic tape, apparel, soda bottles
Nylon 6,6	$\left[NH-(CH_2)_6-NH-\underset{\displaystyle O}{\underset{\Vert}{C}}-(CH_2)_4-\underset{\displaystyle O}{\underset{\Vert}{C}}\right]_n$	Home furnishings, apparel, carpet fibers, fish line, polymer blends