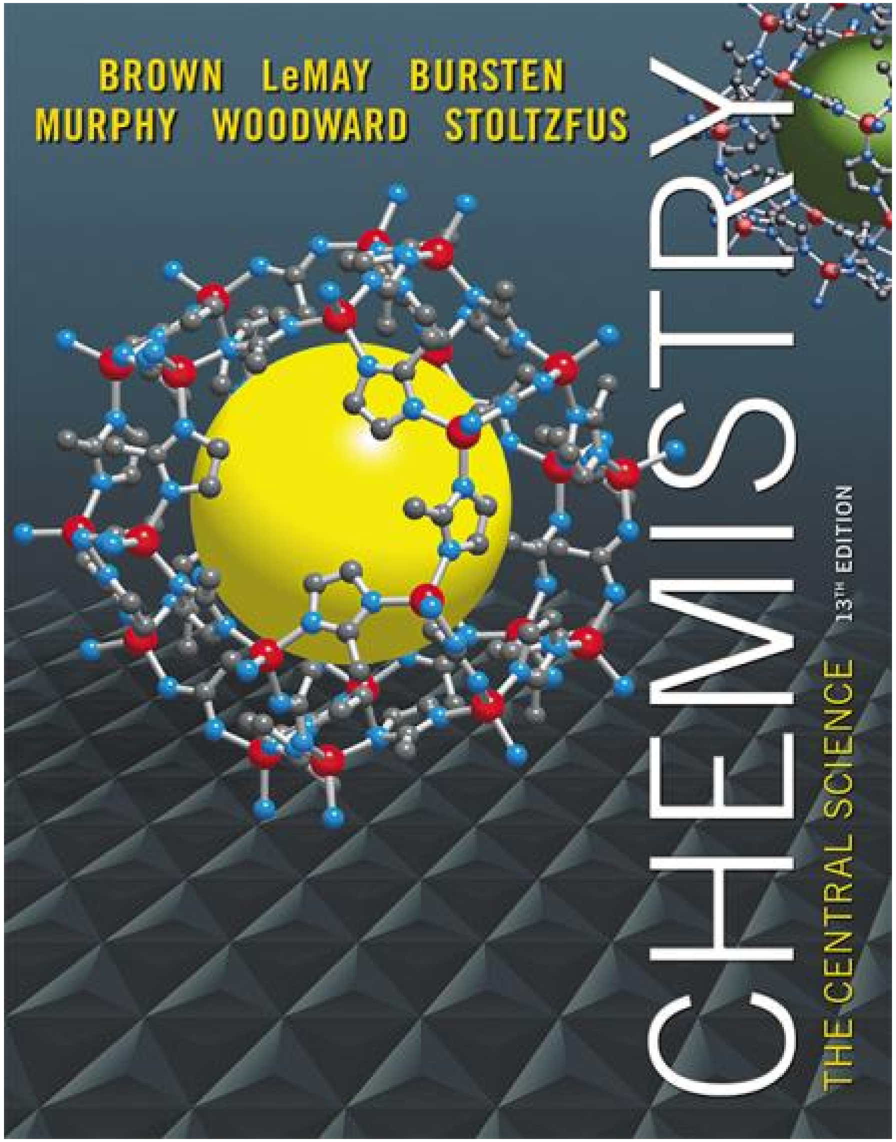

Lecture Presentation

Chapter 12

Solids and Modern Materials

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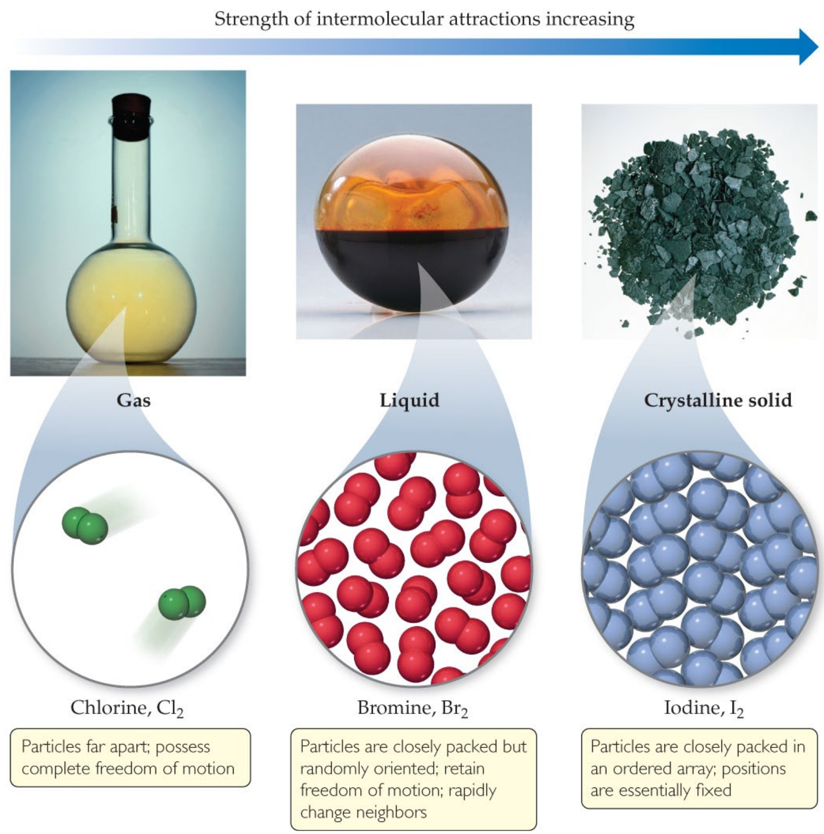
States of Matter

- The fundamental difference between states of matter is the strength of the intermolecular forces of attraction.
- Stronger forces bring molecules closer together.
- Solids and liquids are referred to as the *condensed phases*.



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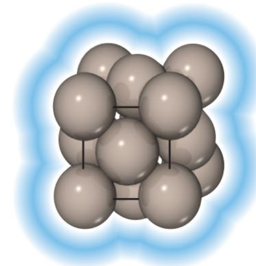
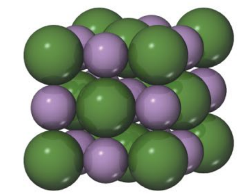
Classifying Solids Based on Bonds

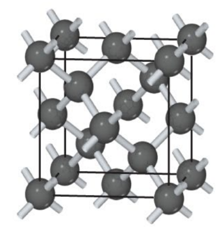
- **Metallic solids** are held together by a “sea” of collectively shared electrons.
- **Ionic solids** are sets of cations and anions mutually attracted to one another.
- **Covalent-network solids** are joined by an extensive network of covalent bonds.
- **Molecular solids** are discrete molecules held together by weak forces.



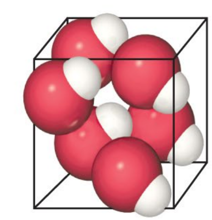
Metallic solids
Extended networks of atoms held together by metallic bonding (Cu, Fe)



Ionic solids
Extended networks of ions held together by 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)

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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.

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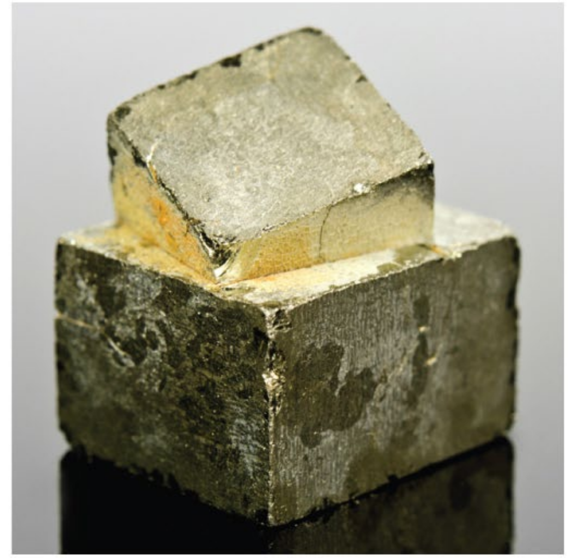
One Organization of Solids

- Solids with a regular repeating pattern of atoms are **crystalline**.
- **Amorphous** solids are characterized by a distinct lack of order in the arrangement of atoms.
- Since crystalline solids have a regular pattern, they are of more interest to most chemists.



Iron pyrite (FeS_2), a crystaline solid

Obsidian (typically $KAlSi_3O_8$), an amorphous solid

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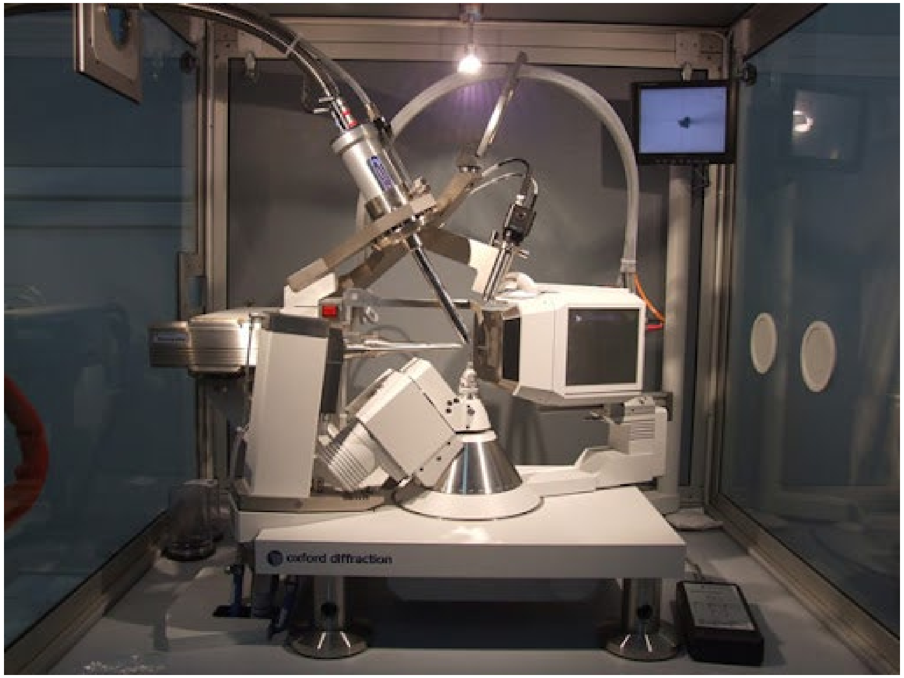
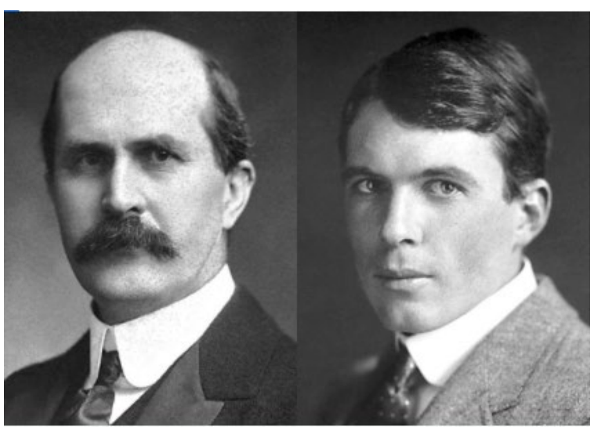
Singe crystal XRD diffraction



1915 Nobel prize



William Henry Bragg   William Lawrence Bragg

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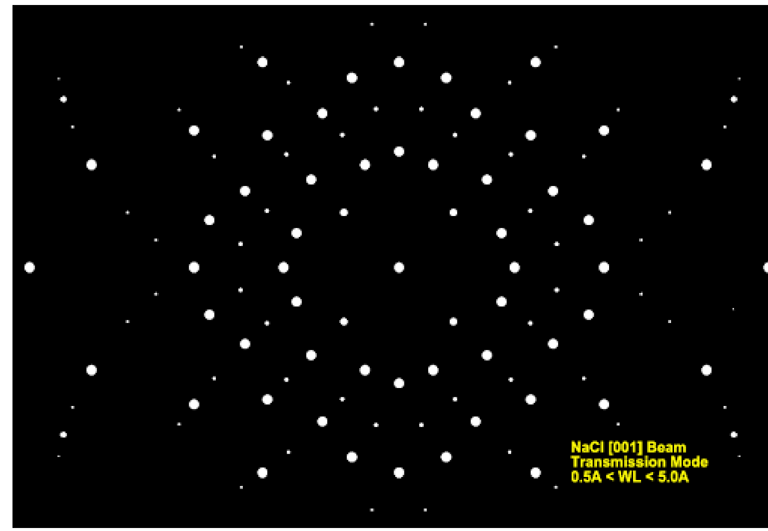
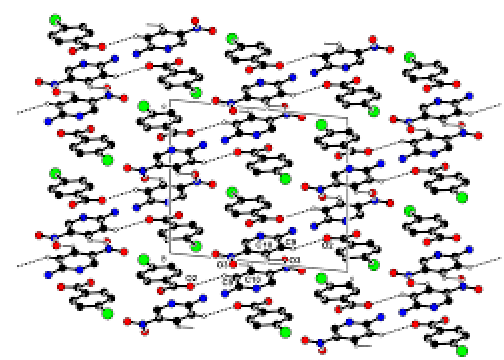
XRD data





Molecular arrangement

Unit Cell

- The basis of a repeating pattern is the unit cell.
- The structure of a crystalline solid is defined by
  - the size and shape of the unit cell.
  - the locations of atoms within the unit cell.

Crystal (晶体结构) = lattice(点阵) +motif (基元)

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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.

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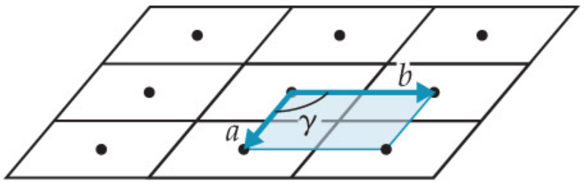
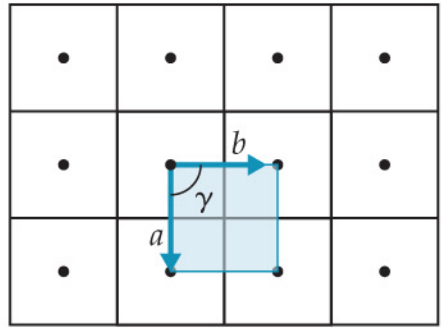
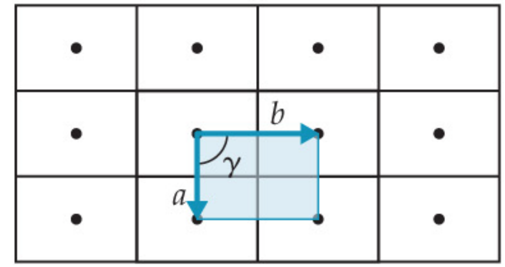
2-D Lattices



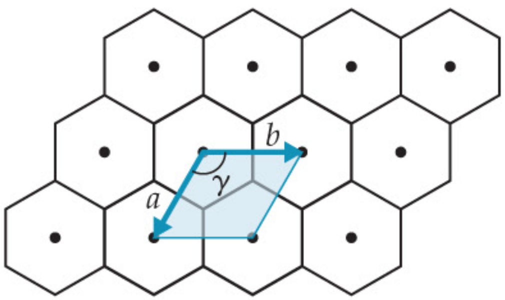
Oblique lattice ($a \neq b$, γ = arbitrary)



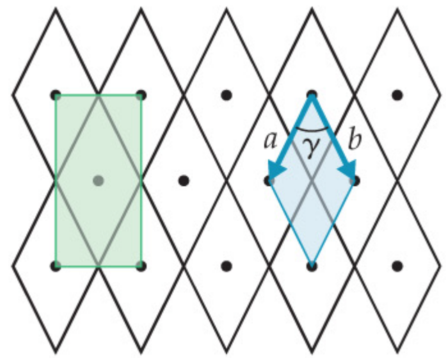
Square lattice ($a = b$, $\gamma = 90°$)



Rectangular lattice ($a \neq b$, $\gamma = 90°$)



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



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

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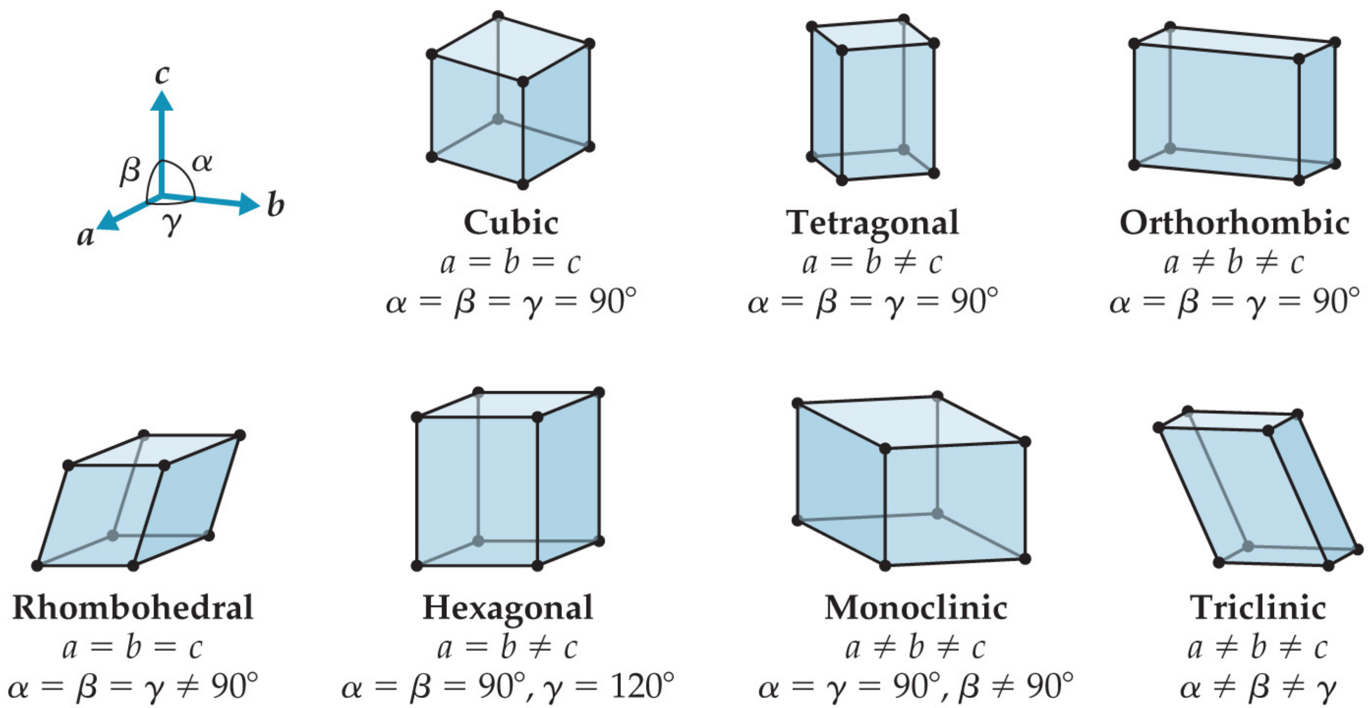
3-D Crystal Lattices

- There are seven basic three-dimensional lattices: cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic, and triclinic.



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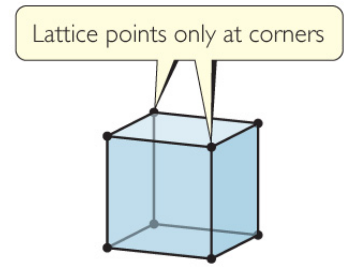
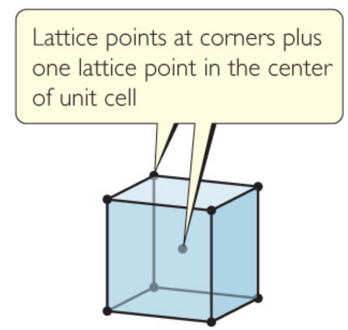
Primitive vs. Centered Lattices

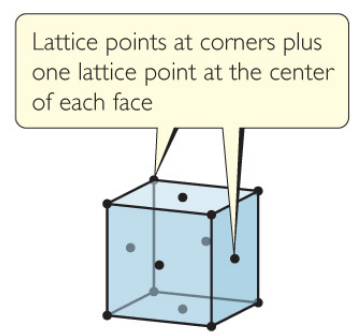
- **Primitive lattices** lattice points at each corner.
- **Centered lattices** has one lattice point at the center (**body-center),** or has one lattice point at each face (**face-center)**.



Primitive cubic lattice



Body-centered cubic lattice



Face-centered cubic lattice

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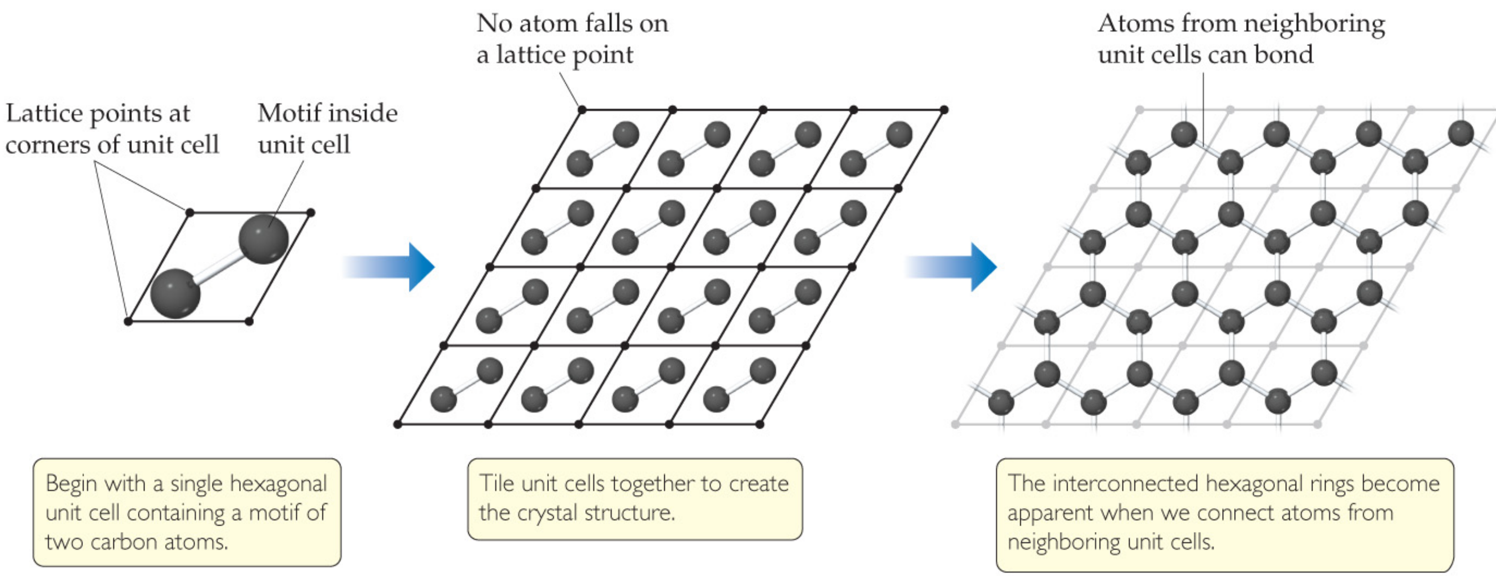
Motifs

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**.



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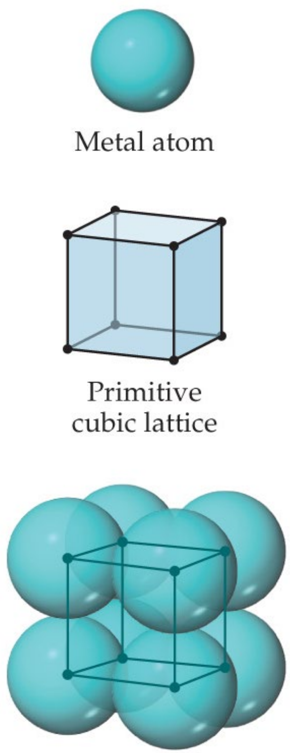
Metallic Structure

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



(a) Primitive cubic metal **(b) Body-centered cubic metal** **(c) Face-centered cubic metal**

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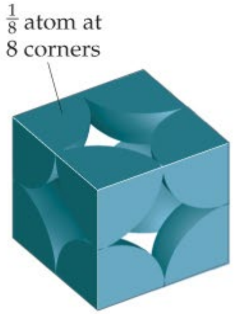
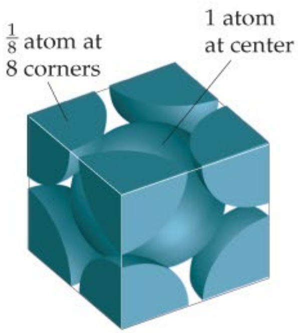
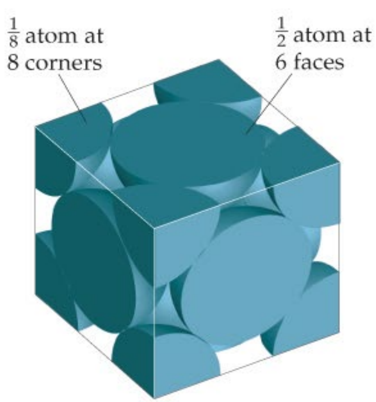
Cubic Structures



(a) Primitive cubic metal
1 atom per unit cell



(b) Body-centered cubic metal
2 atoms per unit cell



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

- 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 1/8 of that corner atom is within any one unit cell meeting there.
- Two cubes meet at a face, therefore only 1/2 of that face atom is within any one unit cell meeting there.
- A body-centered atom is entirely within the unit cell.

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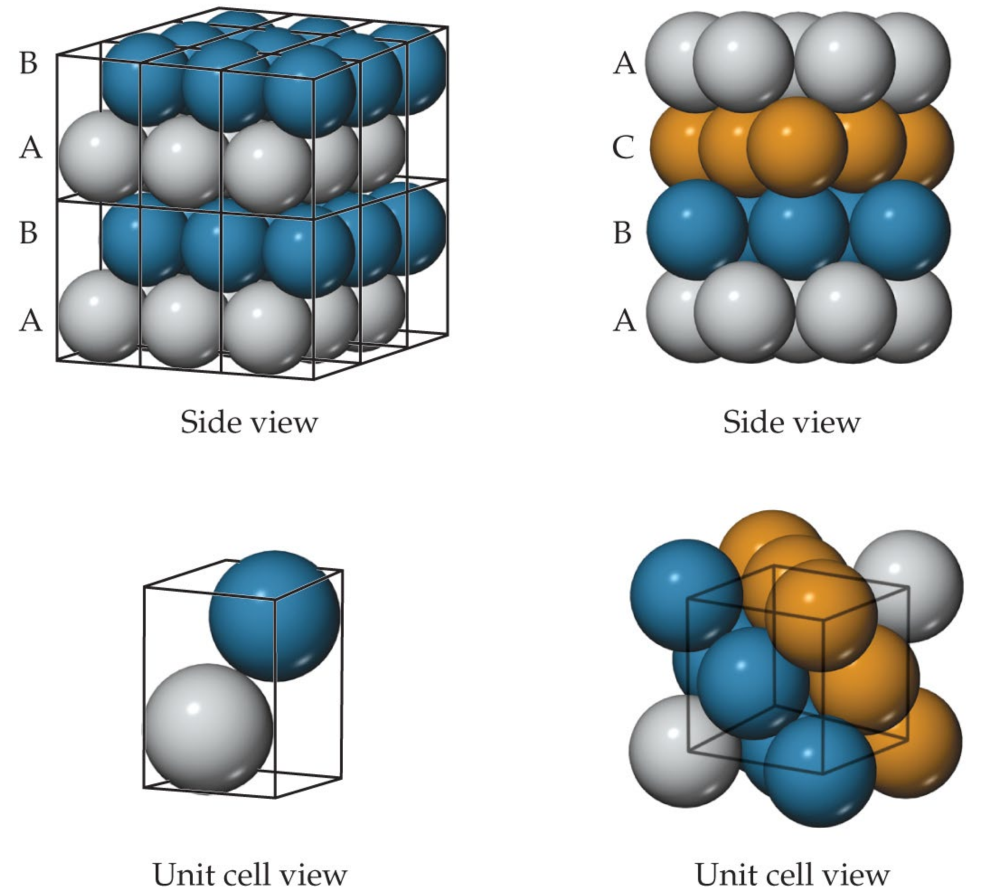
Close Packing



(a) Hexagonal close-packed metal

(b) Cubic close-packed metal

- Nature does not like empty space!
- The atoms in a crystal pack as close together as they can.
- The two common types of packing seen are
  - cubic close-packed.
  - hexagonal close-packed.

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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	Hardware items
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

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Alloys, the quest to make good materials even better

高端合金材料主要应用于高端制造领域

高端合金材料主要应用于高端制造领域

主要下游	主要位置/部件
航空航天	航空发动机燃气室、导向室、涡轮叶片、涡轮盘等
核电	蒸汽发生器、燃料包壳材料、结构材料、燃料棒定位格架、 高温气体炉热交换器等
燃气轮机	涡轮叶片、叶轮等
汽车	涡轮增压器的涡轮叶轮；内燃机的阀座、镶块、进气阀等
其他领域	玻璃制造、冶金、医疗器械等

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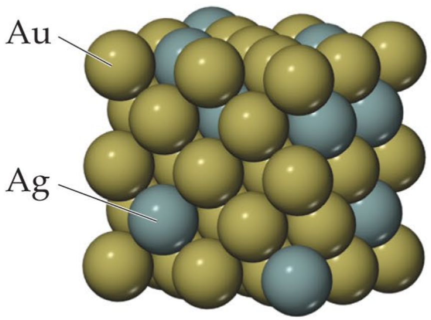
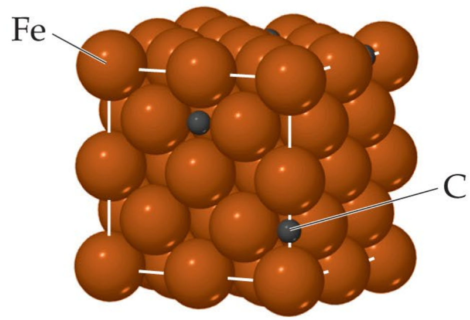
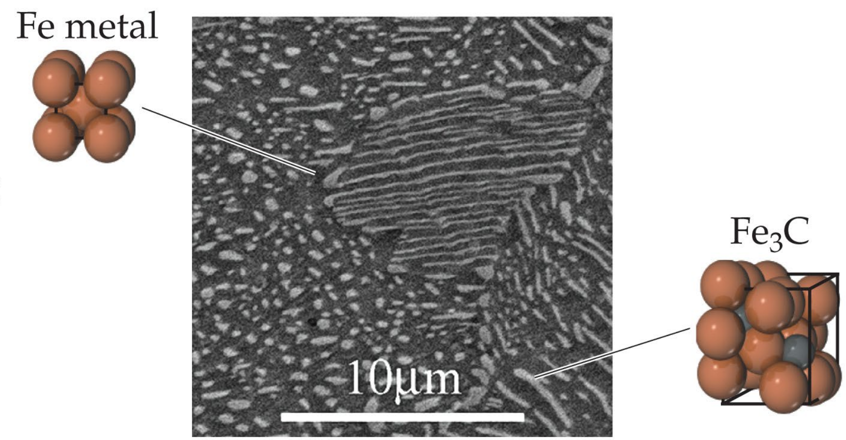
Types of Alloys



Substitutional alloy
14-karat gold



Interstitial alloy
Steel



- **Substitutional alloys**: A second element takes the place of a metal atom. (Homogeneous alloys)
- **Interstitial alloys**: A second element fills a space in the lattice of metal atoms.
- **Heterogeneous alloys**: components not dispersed uniformly

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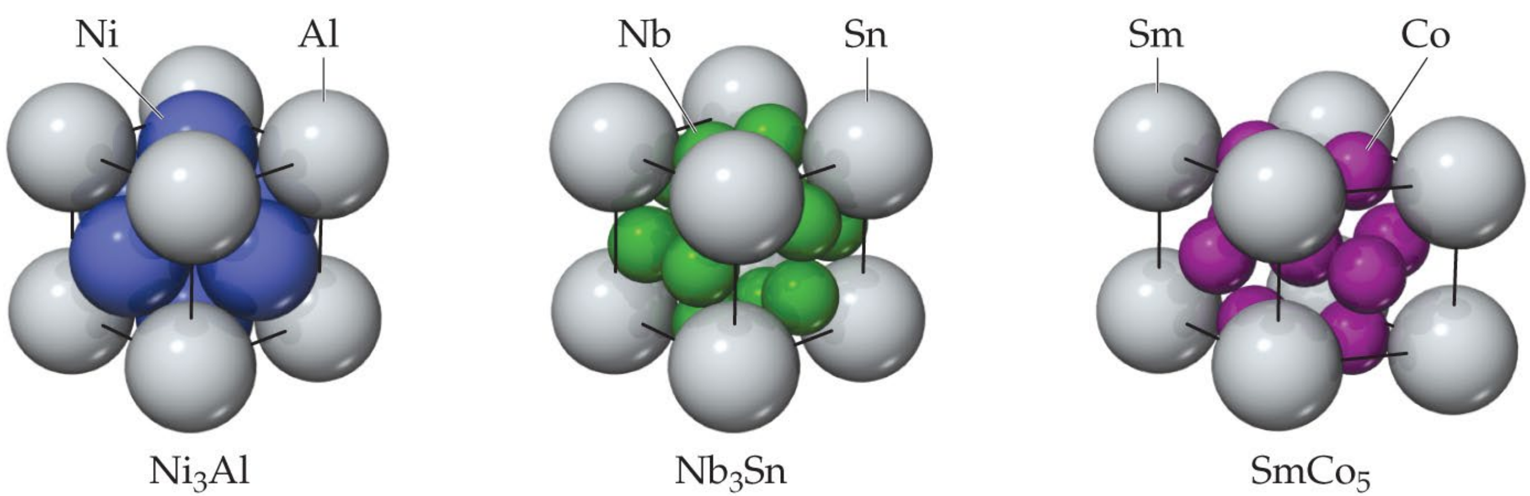
Intermetallic Compounds

- compounds, *not* mixtures
- distinct properties, definite composition (since they are compounds)
- ordered, rather than randomly distributed



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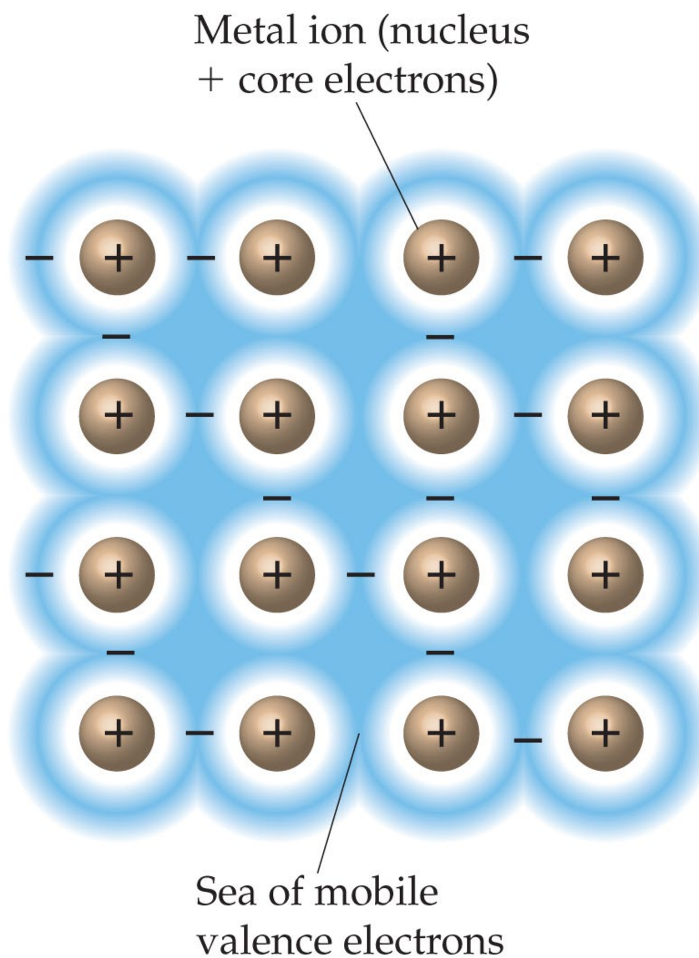
Metallic Bonding

- One can think of a metal as a group of cations suspended in a sea of electrons.
- The electrical and thermal conductivity, ductility, and malleability of metals is explained by this model.



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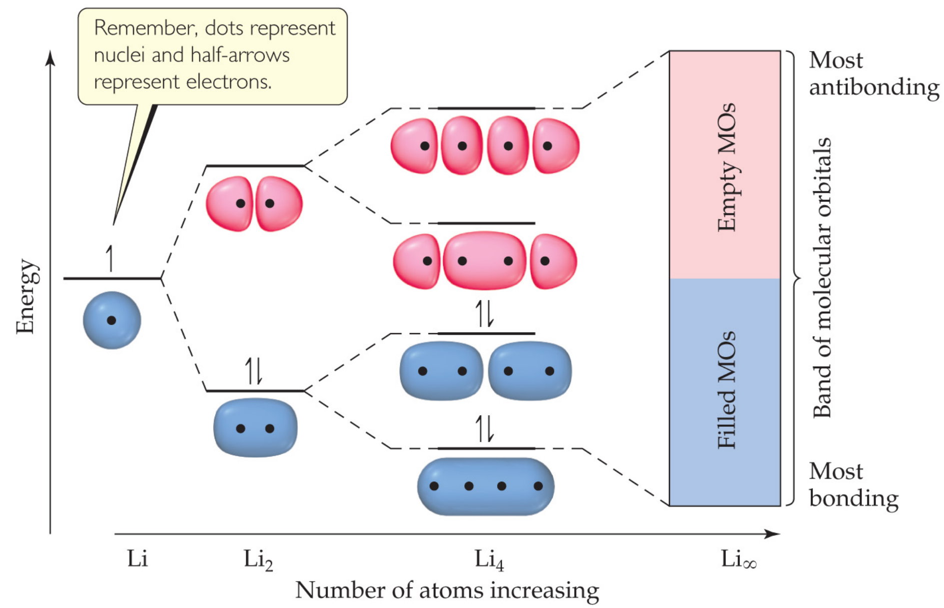
A Molecular-Orbital Approach

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 only takes into account *s*-orbital population.



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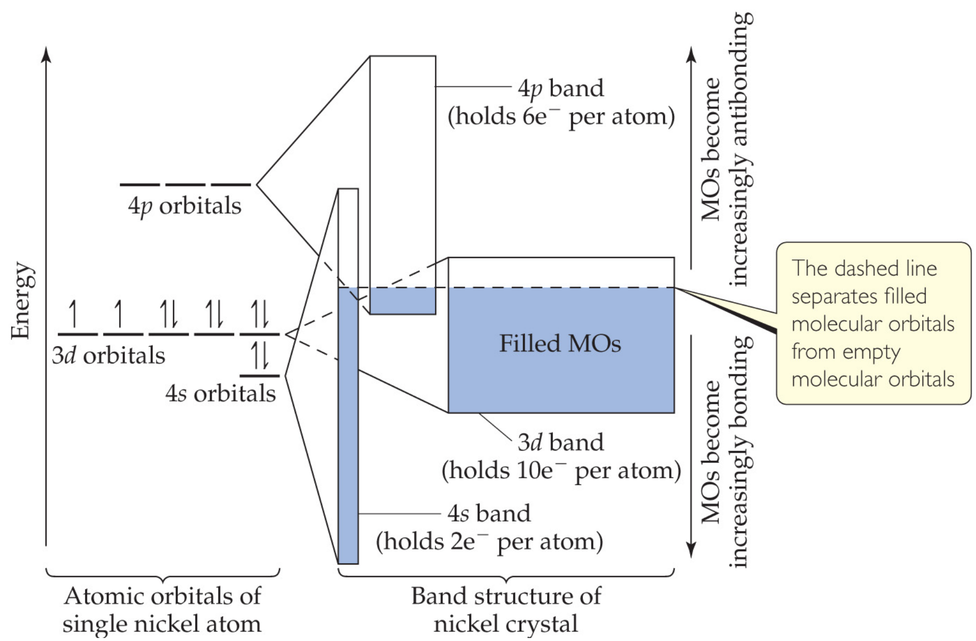
MO Approach with More Orbitals

- 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.



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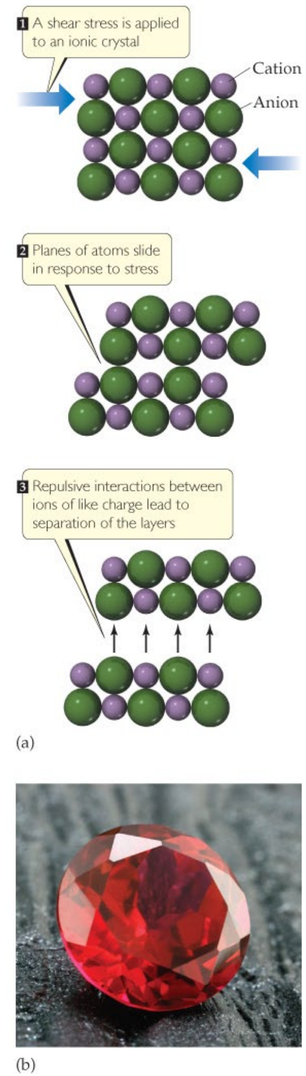
Ionic Solids

- In ionic solids, the lattice comprises alternately charged ions.
- Ionic solids have very high melting and boiling points and are quintessential crystals.



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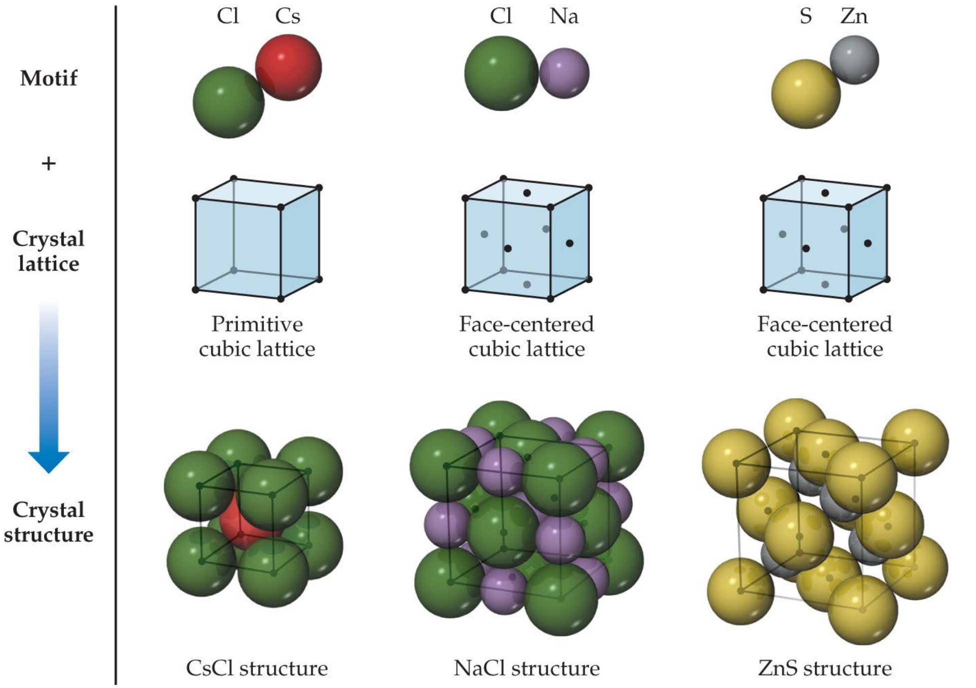
Ionic Solids

- 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



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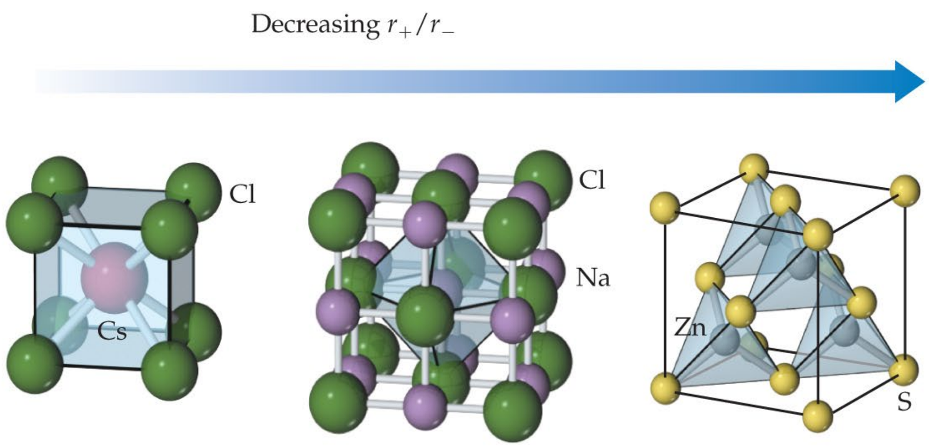
Effect of Ion Size on Structure

- 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
r_+/r_-	1.08	0.69	0.52
Cation coordination number	8	6	4
Anion coordination number	8	6	4

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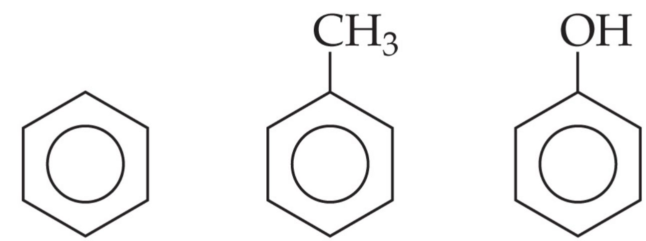
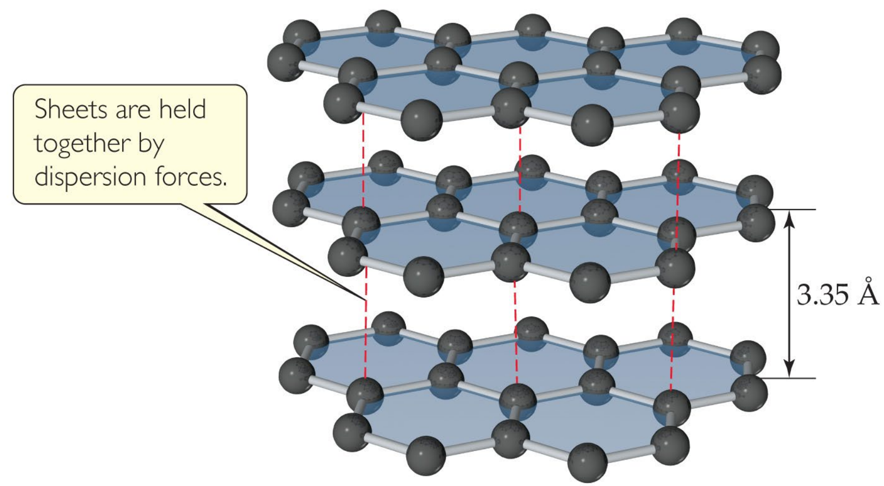
Molecular Solids

- 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



(b) Graphite

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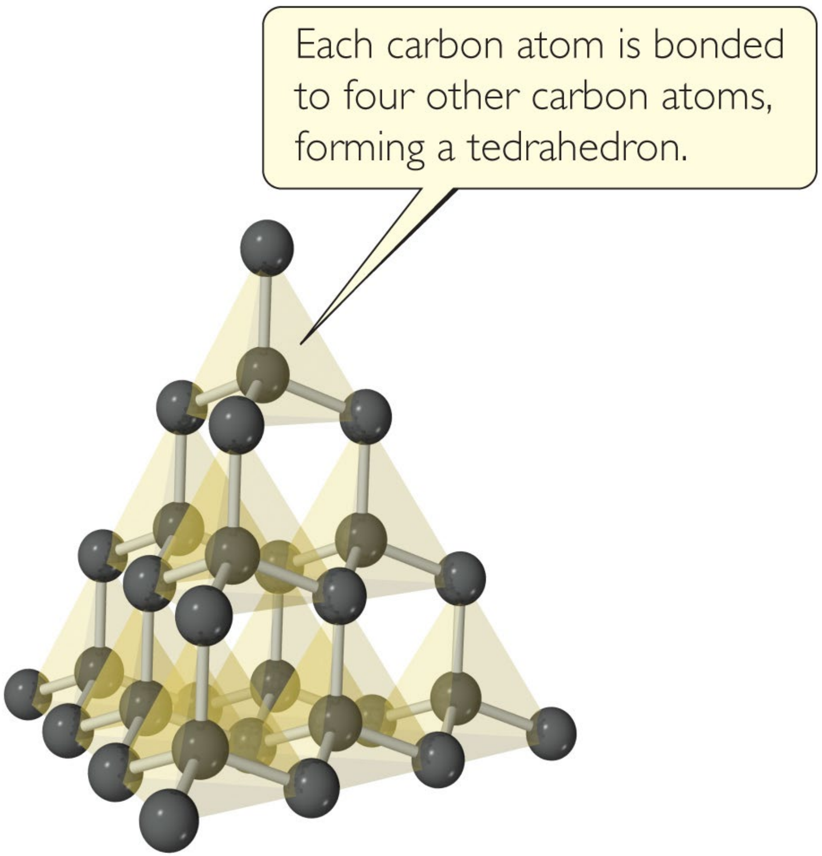
Covalent-Network Solids



(a) Diamond

- 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.

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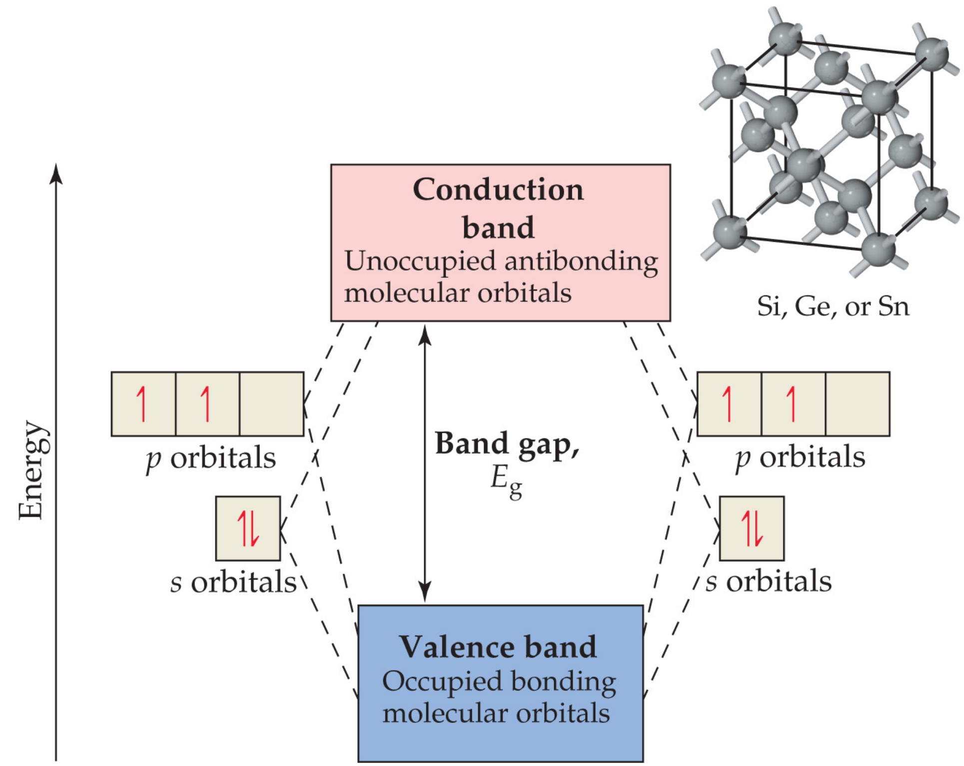
Semiconductors

- 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.

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Critical Role of Alkyl Chain Branching of Organic Semiconductors in Enabling Solution-Processed N-Channel Organic Thin-Film Transistors with Mobility of up to 3.50 $cm^2\ V^{-1}\ s^{-1}$

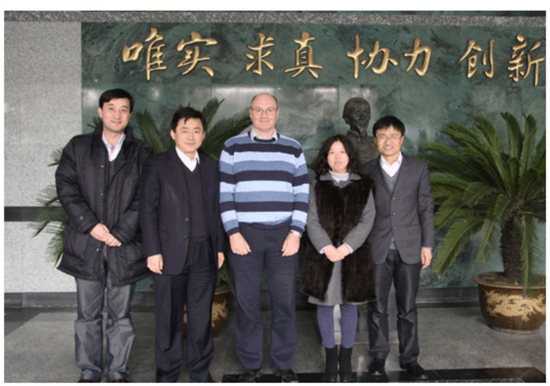
Fengjiao Zhang,[†,∇] Yunbin Hu,[‡,∇] Torben Schuettfort,[§] Chong-an Di,[*,†] Xike Gao,[*,‡] Christopher R. McNeill,[*,∥] Lars Thomsen,[⊥] Stefan C. B. Mannsfeld,[#] Wei Yuan,[‡] Henning Sirringhaus,[§] and Daoben Zhu[*,†]

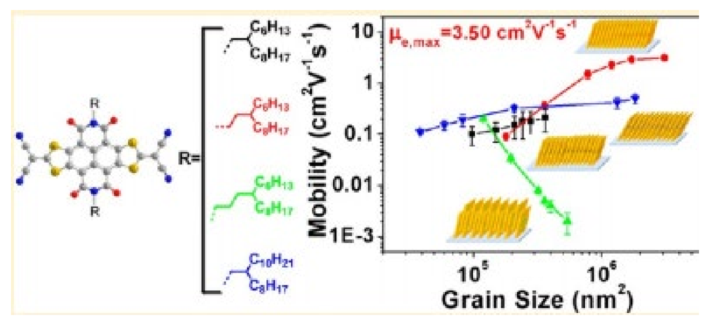
上海有机所与默克化工合作研发有机半导体材料

2012-02-16 科研处 | 【大 中 小】【打印】【关闭】

2012年2月8日，默克化工英国南安普敦奇尔沃思技术中心的研发高管Frank Meyer和默克中国的盛玉梅经理访问上海有机所，丁奎岭所长、高希珂副研究员和科研处的负责同志参加了会谈。上海有机所与默克化工将在有机半导体材料方面展开深入合作，双方签署了第一年的研发合作协议，共同致力于新型高性能n-型有机半导体材料的研发。

丁奎岭所长欢迎Frank一行的来访，并对合作寄予希望，他表示，默克化工是全球领先的化学化工公司，上海有机所在合成化学领域具有深厚的研究基础和优秀的人才团队，希望双方的合作能加速新型有机半导体材料的研发进程，争取实现从“材”到“器”的跨越。Frank对丁奎岭所长和上海有机所的合作支持表示感谢，希望能与上海有机所建立长期的合作关系，合作的材料体系将由n-型有机半导体扩展到双极性有机半导体及有机太阳能受体等，希望双方能在“好的科学”的基础上，共同推进“好的应用”。





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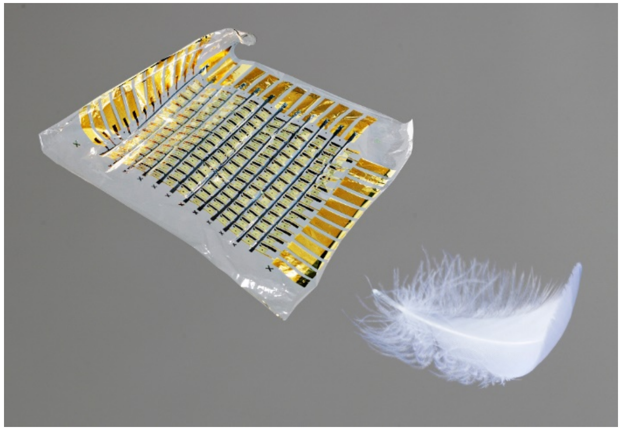

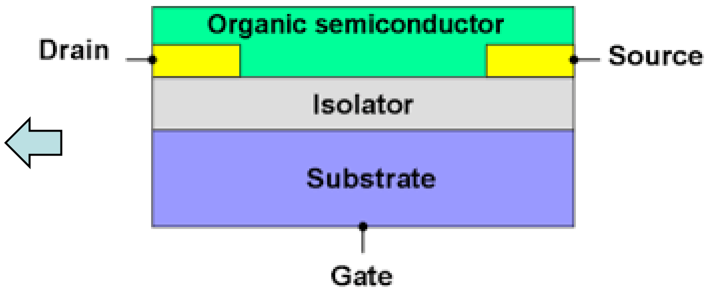

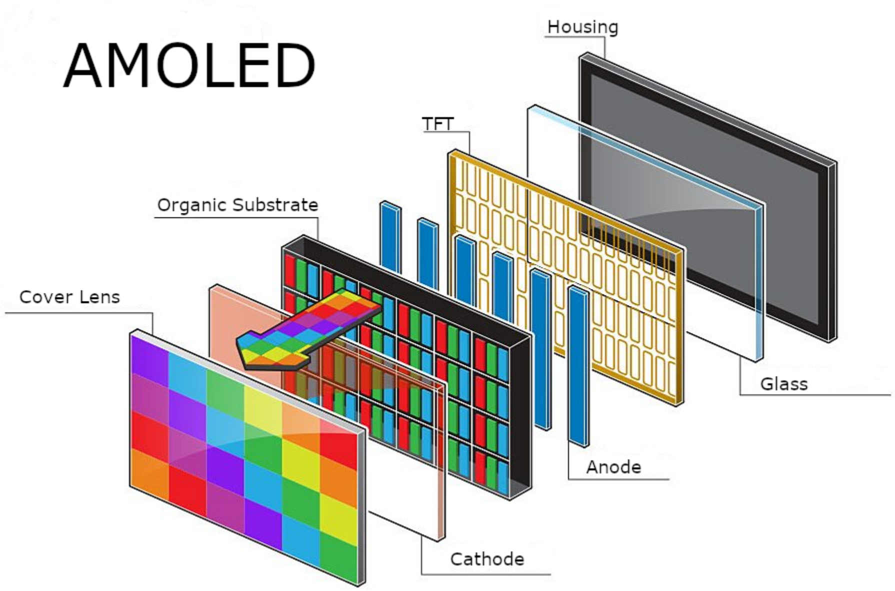

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What Forms a Semiconductor?

- Among elements, only Group IVA, all of which have 4 valence electrons, are semiconductors.
- Inorganic semiconductors (like GaAs) tend to have an average of 4 valence electrons (3 for Ga, 5 for As).

Table 12.4 Band Gaps of Select Elemental and Compound Semiconductors

Material	Structure Type	E_g, eV[†]
Si	Diamond	1.11
AlP	Zinc blende	2.43
Ge	Diamond	0.67
GaAs	Zinc blende	1.43
ZnSe	Zinc blende	2.58
CuBr	Zinc blende	3.05
Sn[‡]	Diamond	0.08
InSb	Zinc blende	0.18
CdTe	Zinc blende	1.50

[†] Band gap energies are room temperature values, 1 eV = 1.602×10^{-19} J.
[‡] These data are for gray tin, the semiconducting allotrope of tin. The other allotrope, white tin, is a metal.

	13 Al	14 Si	15 P	
30 Zn	31 Ga	32 Ge	33 As	34 Se
48 Cd	49 In	50 Sn	51 Sb	52 Te

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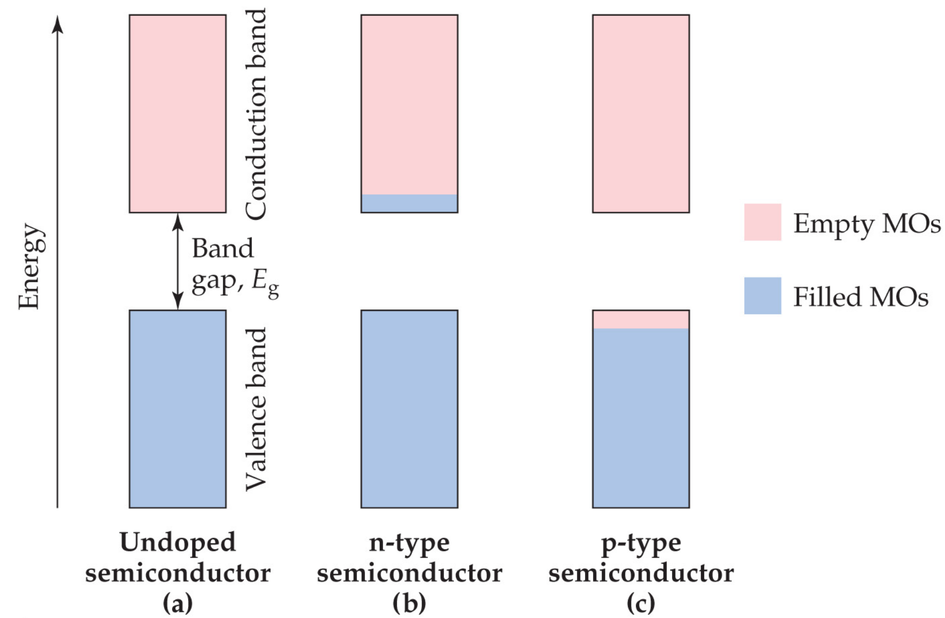
Doping

- changing the conductivity of semiconductors by adding an element with 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.



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Polymers

- **Polymers** are molecules of high molecular weight made by joining smaller molecules, called **monomers**.
- There are two primary types of polymers:
  - **Addition polymers** are formed when a bond breaks, and the electrons in that bond make two new bonds.
  - **Condensation polymers** are formed when a small molecule is removed between two large molecules.

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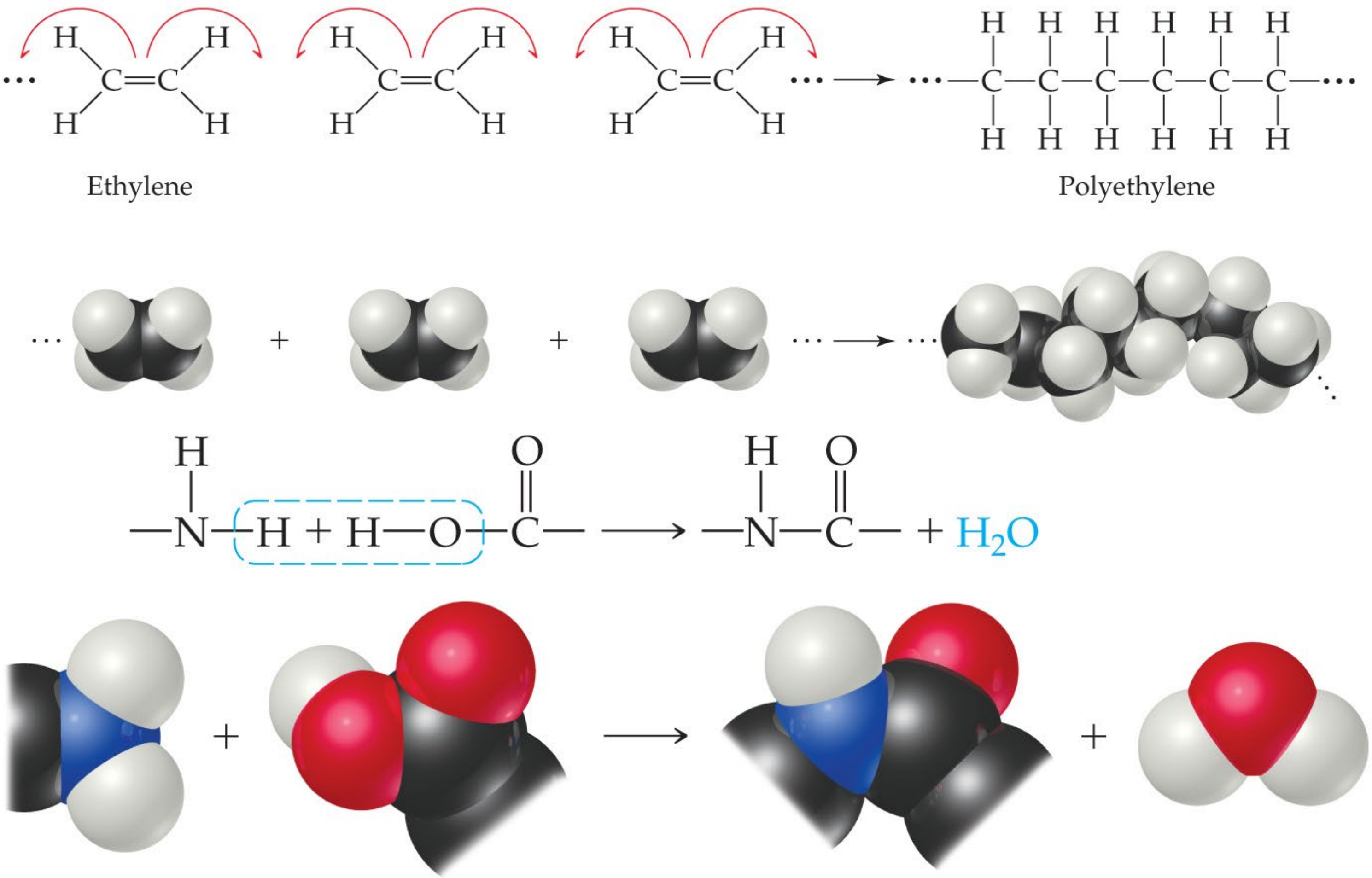
Addition vs. Condensation Polymerization



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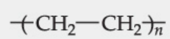
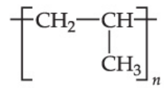
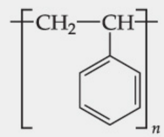
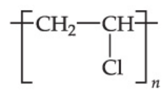
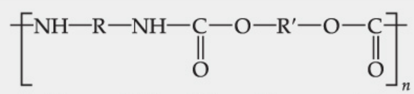
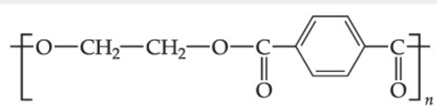
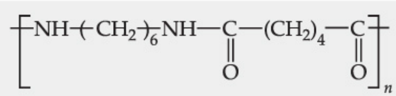
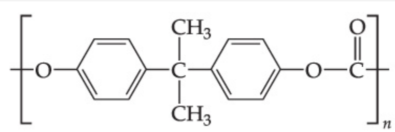
Some Common Polymers

Table 12.5 Polymers of Commercial Importance

Polymer	Structure	Uses
Addition Polymers		
Polyethylene		Films, packaging, bottles
Polypropylene		Kitchenware, fibers, appliances
Polystyrene		Packaging, disposable food containers, insulation
Polyvinyl chloride (PVC)		Pipe fittings, plumbing
Condensation Polymers		
Polyurethane	 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, soft-drink bottles
Nylon 6,6		Home furnishings, apparel, carpet, fishing line, toothbrush bristles
Polycarbonate		Shatterproof eyeglass lenses, CDs, DVDs, bulletproof windows, greenhouses

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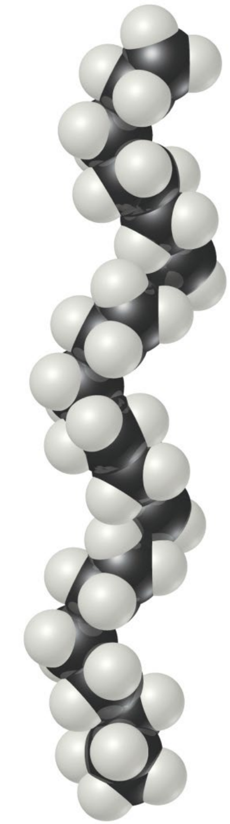
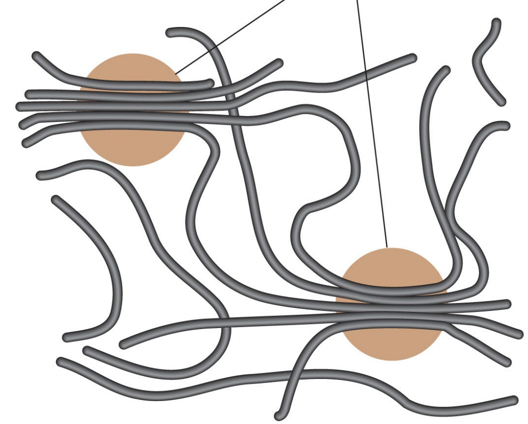
Bulk Properties of Polymers

- The molecules are *not* straight lines—the longer the chain, the more twisting happens.
- Chains can have a variety of lengths, and therefore a variety of molecular weights.
- The material can be very flexible (plastics).
- Short range order can lead to **crystallinity** in the solid.





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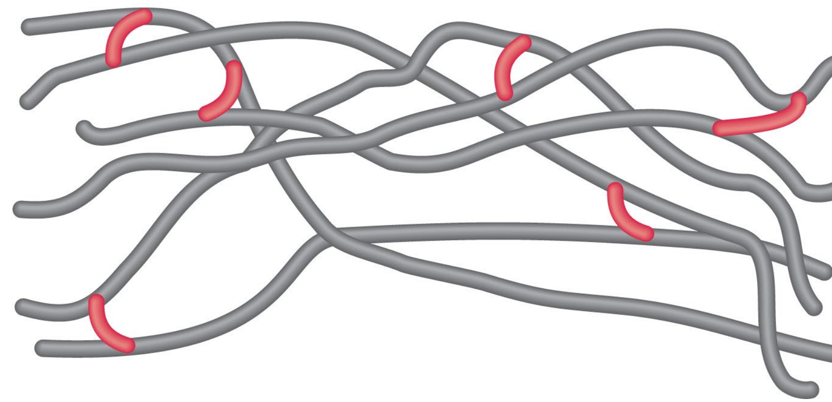
Changing the Polymer's Physical Properties

- Chemically bonding chains of polymers to each other can stiffen and strengthen the substance.
- In **vulcanization**, chains are cross-linked by short chains of sulfur atoms, making the rubber stronger.



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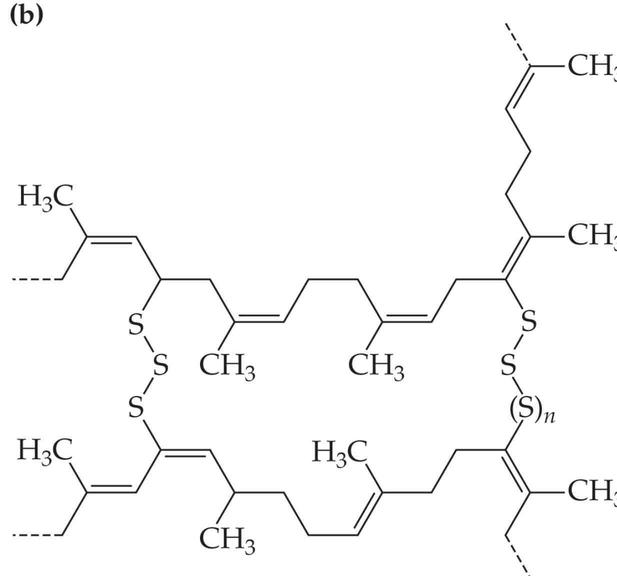

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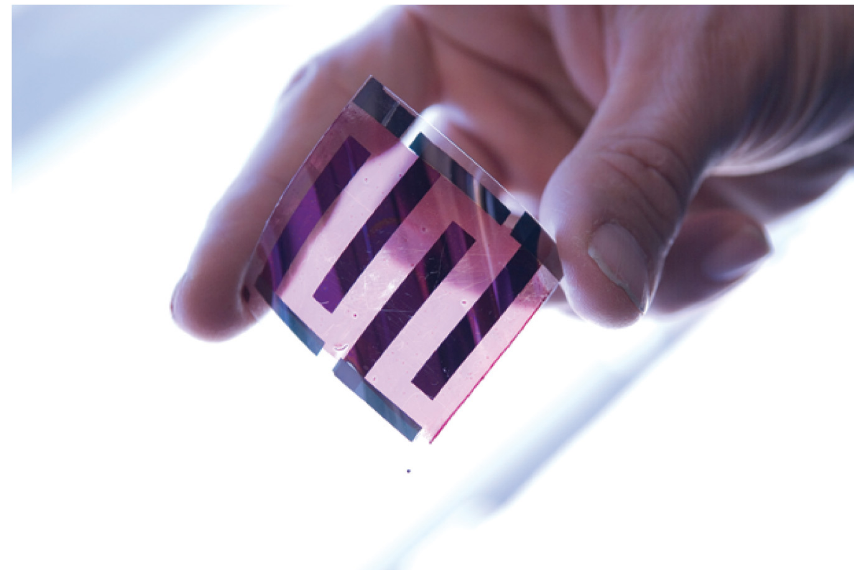
Nanomaterials

- Particles that have three dimensions on the 1–100 nm size
- Their properties are the study of many labs around the world.



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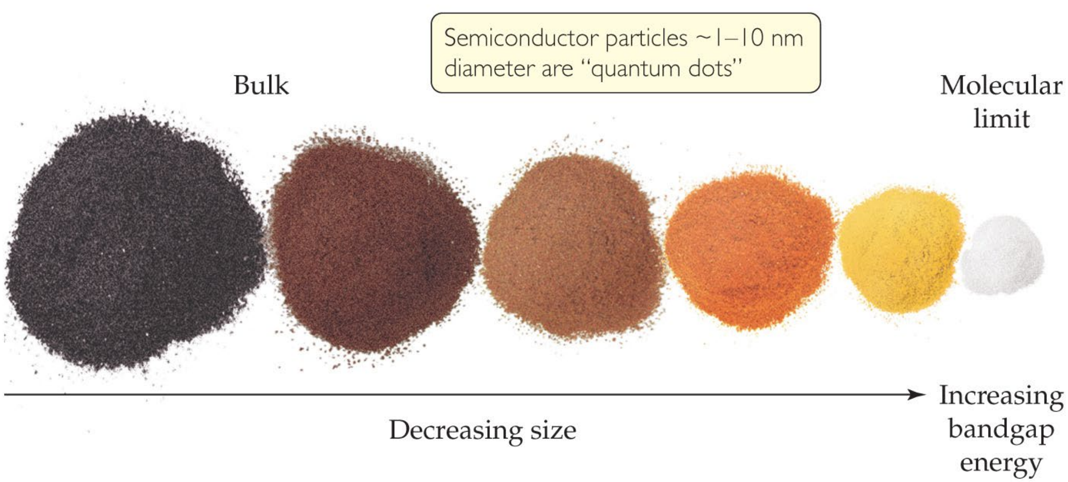
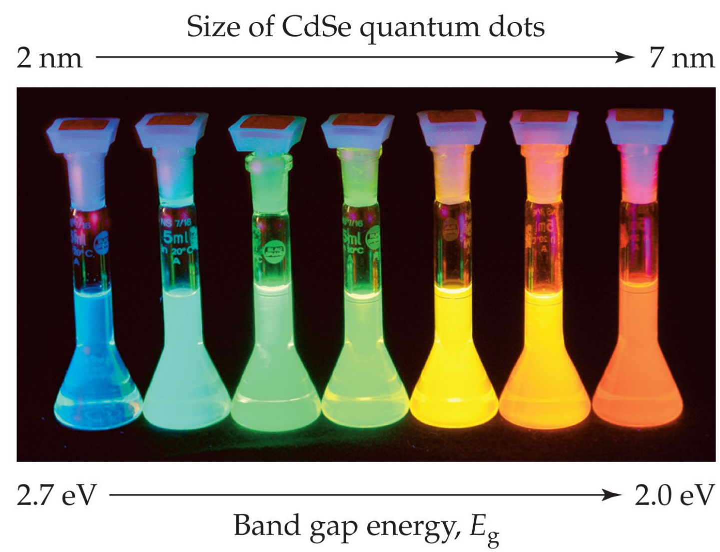
Semiconductors on the Nanoscale

- Small molecules have discrete orbitals; macroscale materials have bands. Where does it switch over?
- Theory tells us 1–10 nm (about 10–100 atoms).
- **Quantum dots** are semiconductors this size.





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Metals on the Nanoscale

- Finely divided metals can have quite different properties than larger samples of metals.
- Would you like “red gold” as in many old stained glass windows?

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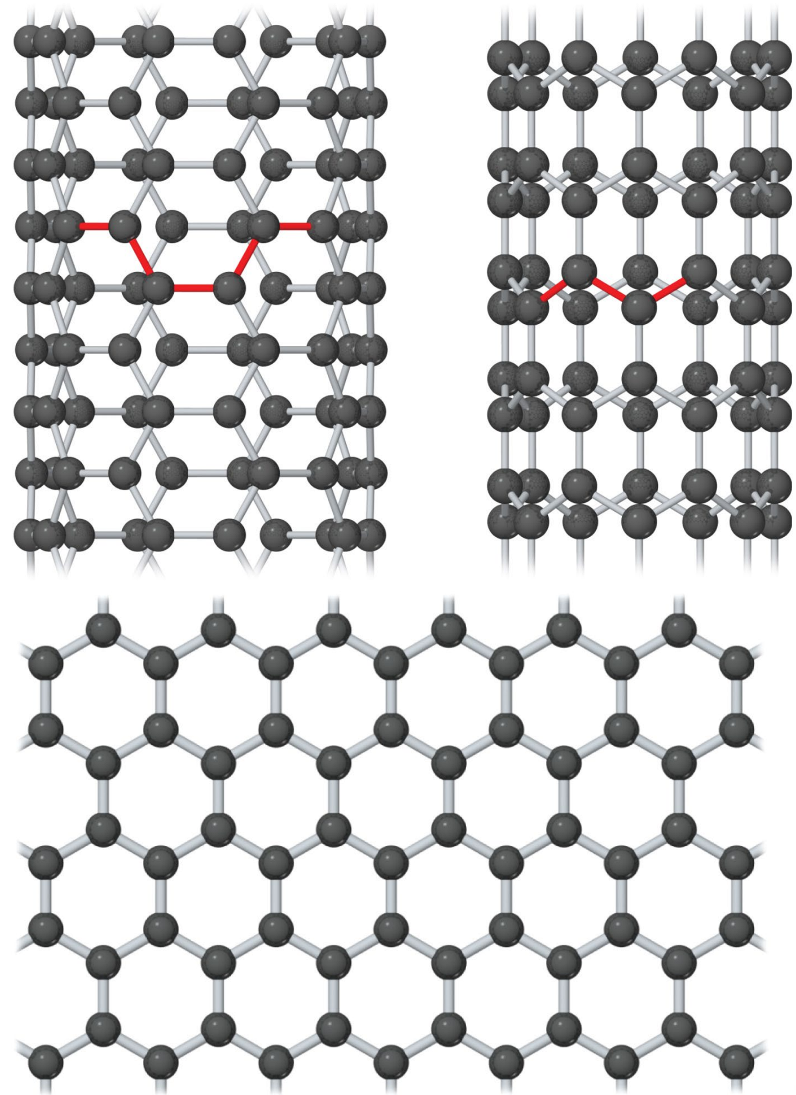
Carbon on the Nanoscale

- 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.



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