

STRUCTURE, BONDING and PROPERTIES of SOLIDS

❑ LEARNING OBJECTIVES

- ❖ Structures of Solids
- ❖ Bonding in Solids: Ionic, Metals and semiconductors
- ❖ Crystal structures and Miller Indices & *Major Techniques of Structure Determination*
- ❖ Know the physical attributes that superconducting materials exhibit; Understand the classes of superconductor that exist; Have an elementary understanding of the mechanisms that give rise to the properties exhibited by superconducting materials; Be familiar with some of the applications of superconductors.
- ❖ How properties such as piezoelectricity arise from the crystal symmetry

Solids: Structure, Bonding and Properties

Introduction

Key points: The goal of this topic is to be familiar with the **structure and properties of solids**, especially some of the solid materials used in modern technology.

- ❑ We are familiar with the 3 (THREE) states of aggregation of a Matter: ***Solid, Liquid & Gas***
- ❑ **Liquids** form when we strengthen the intermolecular interactions enough to bring all the molecules together while still preserving some of the fluidity—the freedom of motion—that characterizes the gas phase. The molecular environment in a liquid is crowded and boisterous.
- ❑ **A solid** is what we get when we turn the intermolecular attractions up enough to *stifle* the freedom of motion.
 - Like the liquid, the solid is a condensed phase, but it is not fluid.
 - Both the *volume and shape of a solid substance are essentially independent of weak forces, such as gravity.*

Solids: Structure, Bonding and Properties

Introduction

- ❑ *Look around and see:* Most of the materials such as the cell phone, computer, wrist-watch, dress materials, etc. are solids.
- ❑ Solids are the materials used in many technologies: **alloys** for magnets and airplane turbines, **semiconductors** for solar cells and light-emitting diodes, and polymers for packaging and biomedical applications, and so on.
- ❑ Do you know that the *Integrated electronic circuit (intel®)* which is at the heart of many electronic devices is built from semiconductors like silicon, metals like copper, and insulators like hafnium oxide.

❑ **Classification of Solids** .. Classification of solids according to the ***types of bonding interactions*** that hold the atoms together. ***This classification helps us make general predictions*** about the **properties** of solids.

- **Ionic Solids:** *solids formed by the mutual attractions between cations and anions*
- **Metallic Solids & Metallic Bonding:** *close packing of atoms with mobile electrons*
- **Molecular Solids:** *molecules are held together by weak intermolecular forces*
- **Covalent-Network Solids:** *atoms are held together by extended networks of covalent bonds*
- **Polymers:** *covalently bonded chain-like molecules and various nonbonding interactions*
- **Nanomaterials:** *lower-dimensional forms of materials....sizes in the range of 1–100 nm*

BONDING and PROPERTIES in SOLIDS

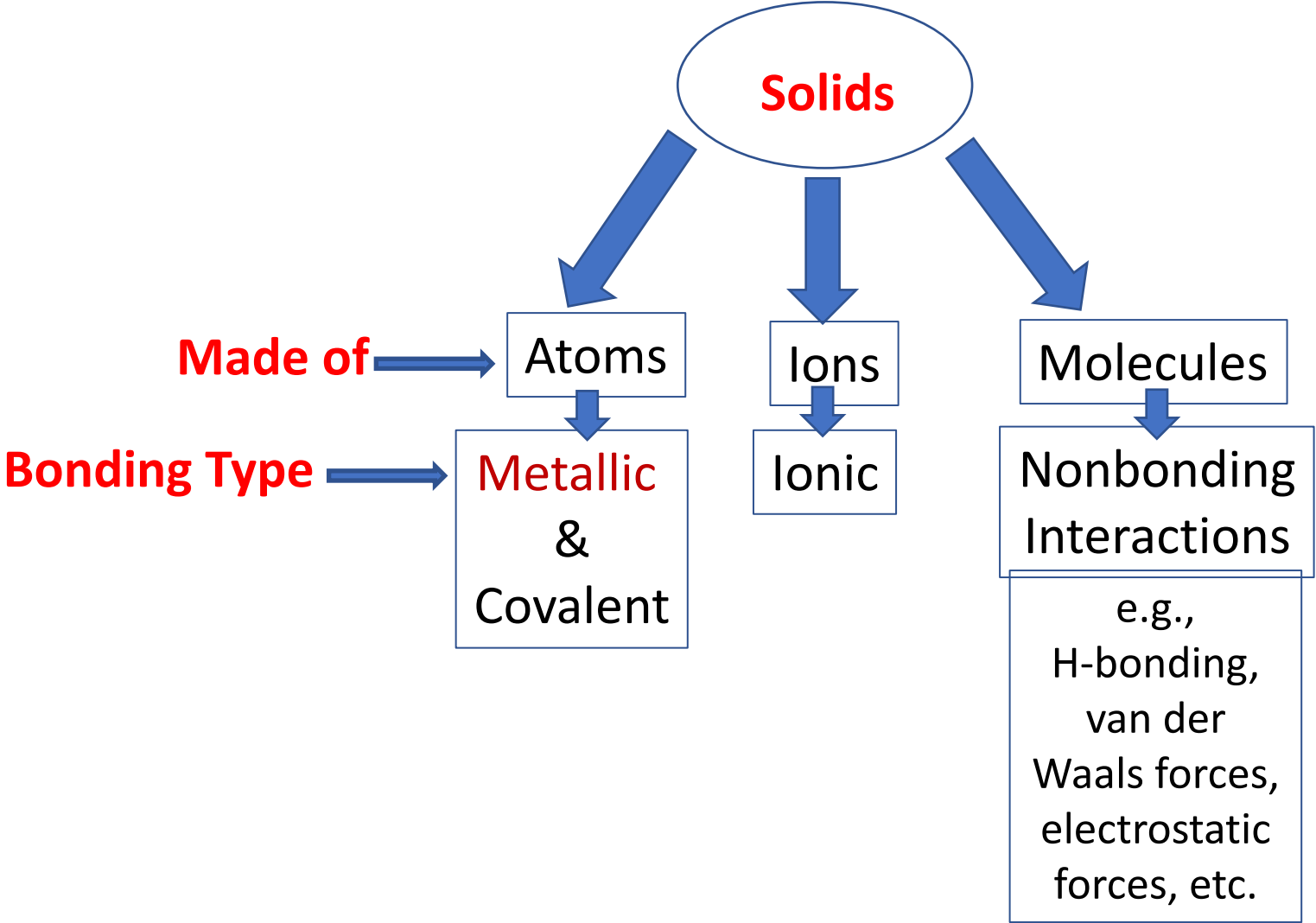


TABLE 10.9 Types of Crystalline ***Solids*** and Their Characteristics

Type of Solid	Intermolecular Forces	Properties	Examples
<i>Ionic</i>	Ion–ion forces	Brittle, hard, high-melting	NaCl, KBr, MgCl ₂
<i>Metallic</i>	Metallic bonds	Variable hardness and melting point, conducting	Na, Zn, Cu, Fe
<i>Molecular</i>	Dispersion forces, dipole–dipole forces, hydrogen bonds	Soft, low-melting, nonconducting	H ₂ O, Br ₂ , CO ₂ , CH ₄
<i>Covalent network</i>	Covalent bonds	Hard, high-melting	SiO ₂ , C (diamond)

Amorphous Solids, Polymers, and Crystals

- The *molecular structures* of solids range between *two extremes*: ***nearly random*** like the **liquid**, and **highly ordered**.
- We begin our exploration of *solids by dividing them into these two classes*, and **also** briefly describing *a class that tends to lie between these two extremes*.

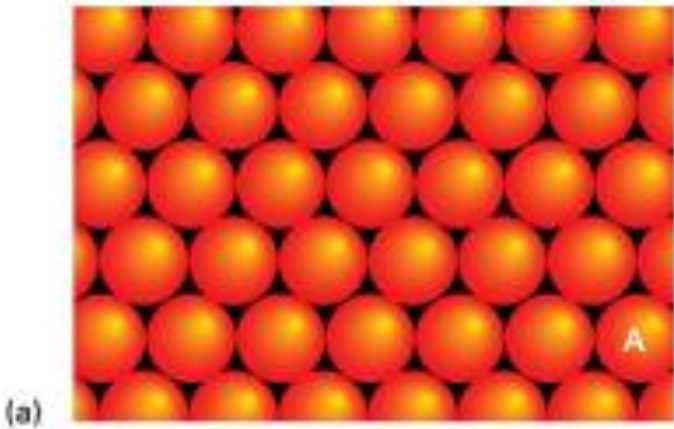
❑ Amorphous Solids

- Amorphous solids are solids that do not have long-range order.
- They include all forms of glass, which is the solid formed when a liquid cools to rigidity without adopting any ordered arrangement.
- *The amorphous liquid structure is preserved in a glass, but too little kinetic energy remains for the molecules to flow freely, even over long periods.*
- The short-range order of an amorphous solid may be characterized by determining the pair correlation function $G(R)$ (the probability of finding the center of a particle a given distance from the center of another particle). At values of R equal to two or three molecular diameters, $G(R)$ will converge rapidly to one, just as it does for the liquid. The only difference between a glass and a liquid is that the liquid will keep shifting in time.

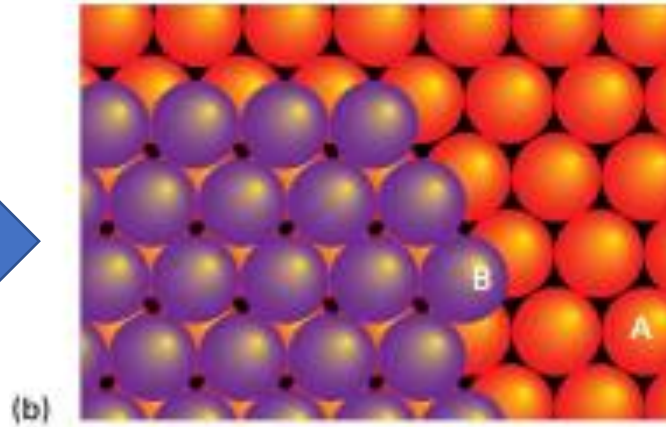
- Not all amorphous solids are glasses.
- For example, liquid silicon dioxide is structurally identical to window glass: the bonding mechanisms, short-range order, electrical properties, density, and so forth, are the same.
- ***Pure elemental silicon, on the other hand, has a liquid state that is very different from the amorphous solid state. The liquid is a metal, and correspondingly dense,*** whereas the amorphous solid has a much less dense, tetrahedrally bound structure akin to that of diamond and is not metallic.
- ✓ If silicon could be made to form a glass, it would be a dense metal, like the liquid.

Metallic solids

- Most metallic elements crystallize in one of three simple forms, *two of which* can be explained *in terms of stacking rigid spheres as close together as possible*.
- In such close-packed structures the spheres representing the atoms are packed together with least waste of space and each sphere has the greatest possible number of nearest neighbors.
- A single close-packed layer, one with maximum utilization of space, of identical spheres can be formed as shown in Fig. given below.
- A second close-packed layer can then be formed by placing spheres in the depressions of the first layer (note there are two types of depressions: *downward triangles* and *upward triangles*).
- The third layer may be added in either of two ways, both of which result in the same degree of close packing.
- In one, the spheres are placed so that they reproduce the first layer, to give an **ABAB** pattern of layers.
- Alternatively, the spheres may be placed over the gaps in the first layer (where the 2nd layer spheres were not placed), so giving an **ABC ABC** pattern.

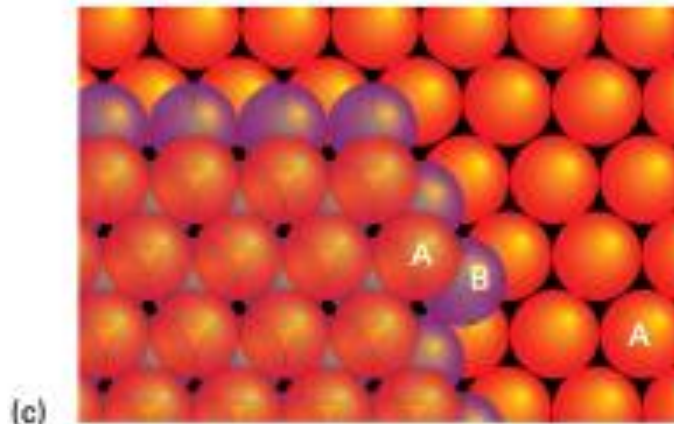


2nd Layer

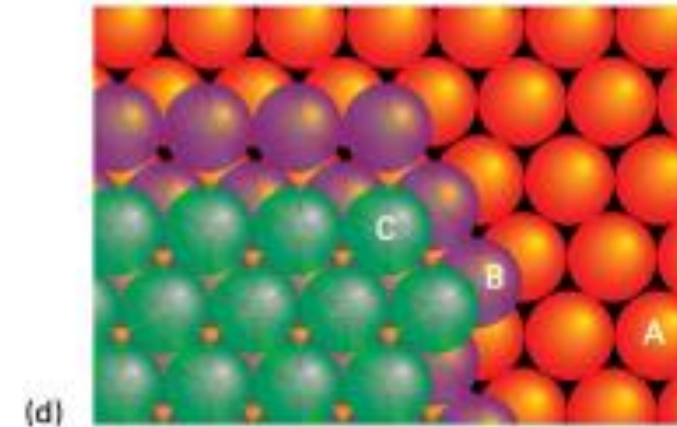


3rd Layer

The spheres are placed so that they reproduce the first layer.
AB AB AB



Hexagonal close packing (hcp)

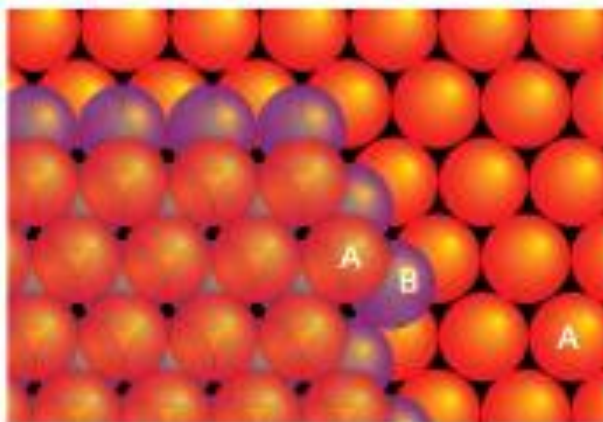


Cubic close packing (ccp)

The spheres are placed over the gaps in the first layer.
ABC ABC ABC

The spheres are placed so that they reproduce the first layer.
AB AB AB

(c)



Hexagonal close packing (hcp)

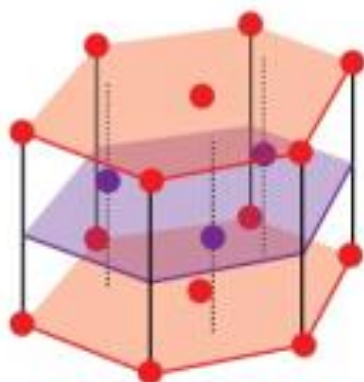
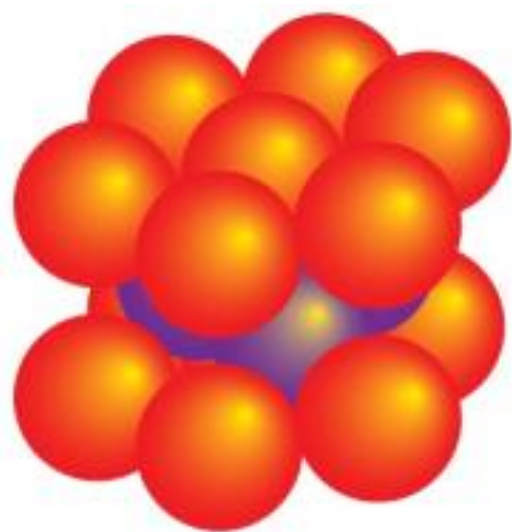
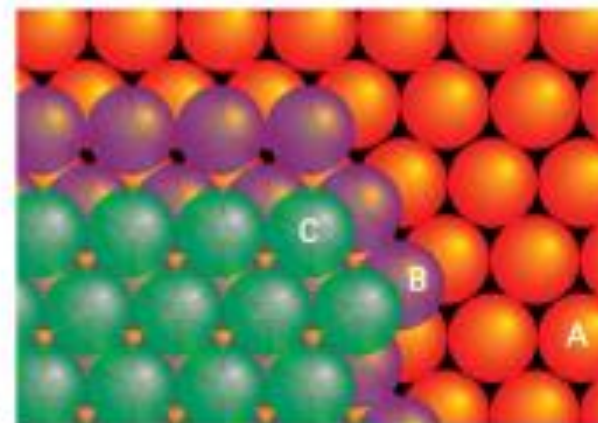


Fig. 2 A hexagonal close-packed structure.

(d)



The spheres are placed over the gaps in the first layer.
ABC ABC ABC

Cubic close packing (ccp)

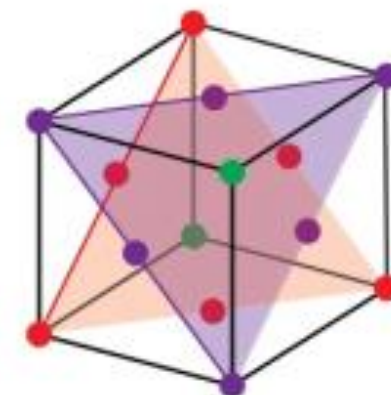
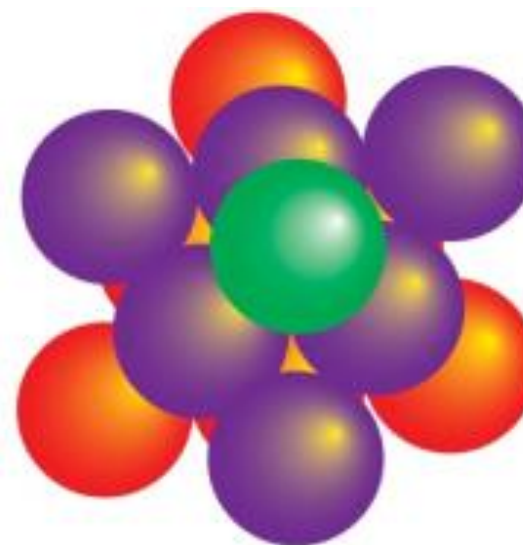
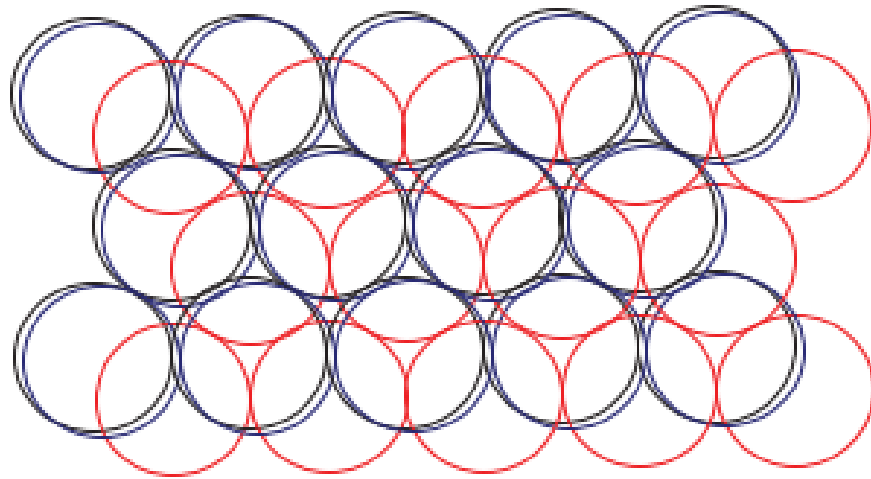
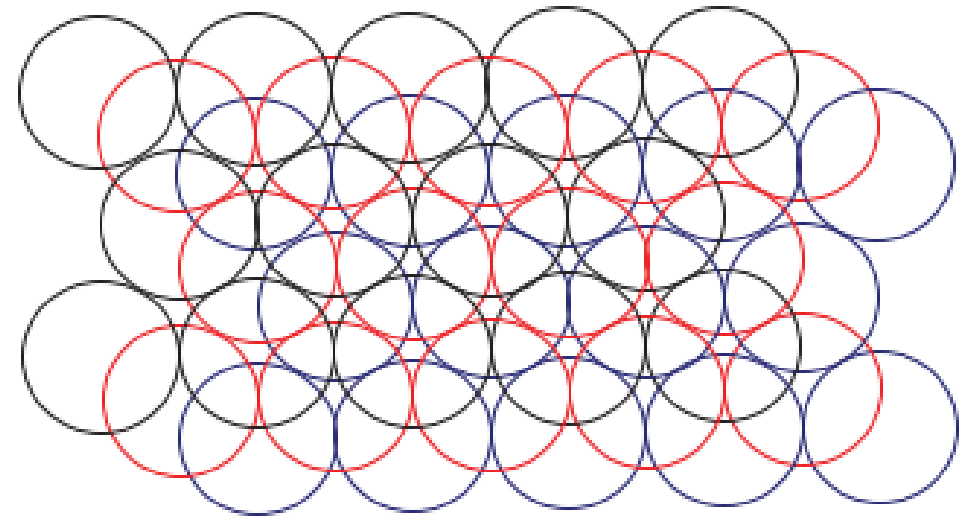


Fig. 3 A cubic close-packed structure.



(a)



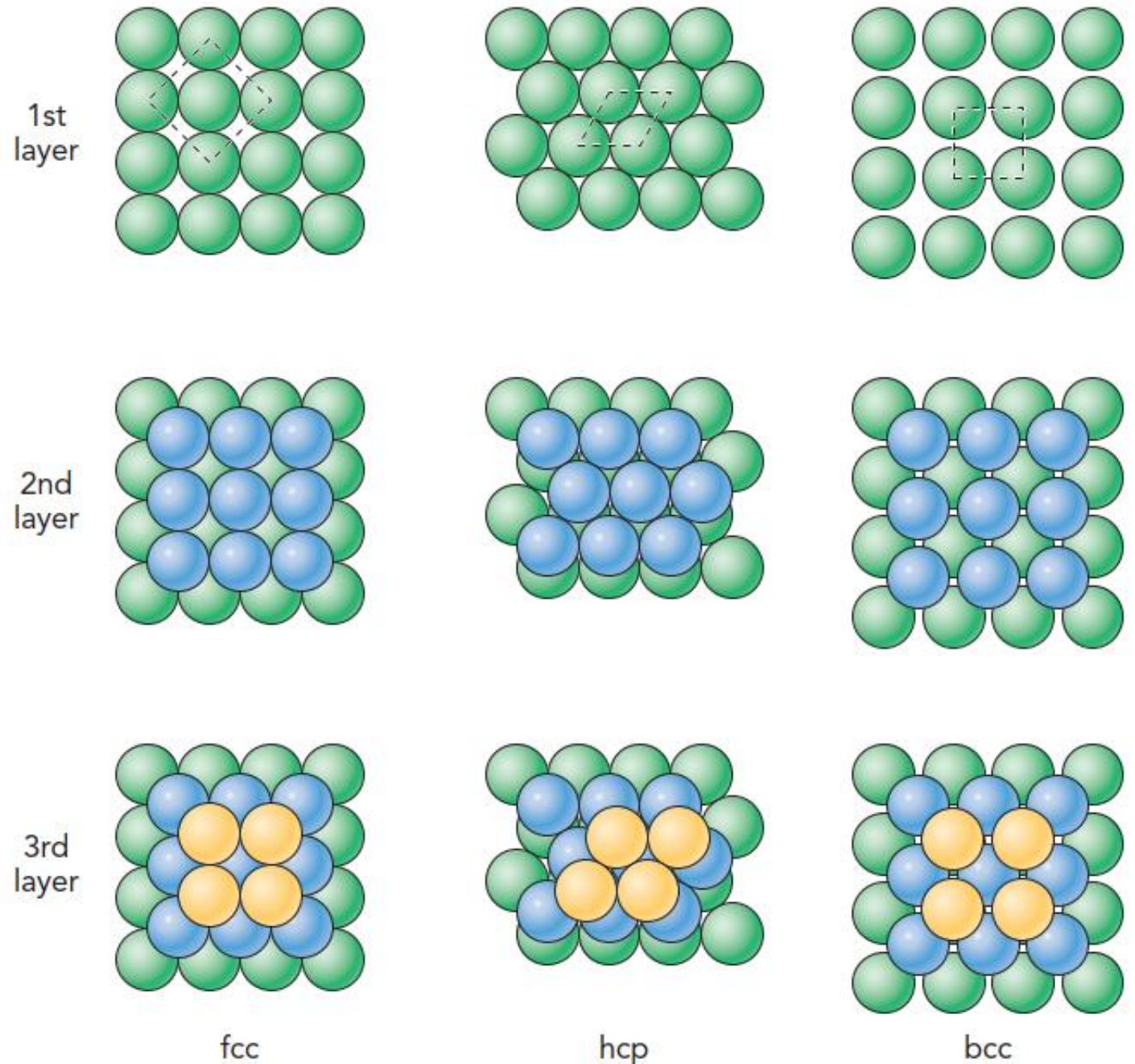
(b)

Addition of a third layer to the closest-packing of spheres in the first two layers. (a) If the third (blue) layer occupies the downward-pointing indentations of the second (red) layer, then the first (black) and third layers will become coincident, forming an ABABAB repeat pattern. (b) If the third layer occupies the upward-facing indentations, then an ABCABC repeating lattice will result.

- The spheres are hexagonally close-packed (hcp) if the ABA pattern is repeated to give the sequence of layers ABABAB... .
- The name reflects the symmetry of the unit cell (Fig.2).
- *Metals with hcp structures include beryllium, cadmium, cobalt, manganese, titanium, and zinc.* Solid helium (which forms only under pressure) also adopts this arrangement of atoms.
- Alternatively, the spheres are cubic close-packed (ccp) if the ABC pattern is repeated to give the sequence of layers ABCABC
- Here too, the name reflects the symmetry of the unit cell (Fig. 3).
- *Metals with this structure include aluminium, silver, gold, calcium, copper, nickel, lead, and platinum.* The noble gases other than helium also adopt a ccp structure in the solid state.
- The **compactness** of the ccp and hcp structures is indicated by their **coordination number**, the number of atoms immediately surrounding any selected atom, which is **12** in both cases. Another ***measure of their compactness is the packing fraction***, the fraction of space occupied by the spheres, which is 0.740, as you have learnt earlier.
- That is, in a close-packed solid of identical hard spheres, 74.0 per cent of the available space is occupied and only 26.0 per cent of the total volume is empty space.

- *Not all metals can take advantage of these arrangements, however, **because a high density of metal cations needs to be stabilized by a high density of valence electrons.***
- *Metals such as the **alkali metals**, having a low number of valence electrons, often tend instead to adopt the **body-centered cubic** (bcc) lattice shown in Fig. 13.8c.*
- *In this pattern, the first plane of atoms consists of identical rows of atoms with a spacing of $2/\sqrt{3}$ diameters between the centers of the nearest neighbor atoms. **The second plane is identical to the first but placed with the centers of its atoms over the gaps in the first plane.** The third plane is identical to the first, and each subsequent plane is identical to the plane two levels below it. **The coordination number is 8, and the packing efficiency is 68%.***

Figure 13.8 The structure of the face-centered cubic, hexagonal closest packing, and body-centered cubic lattices. To form each lattice, start with the first layer (green atoms), add the second layer as shown (blue atoms), and then the third layer (yellow atoms). The cycle repeats, with every other layer being identical in each lattice. One face of one unit cell is outlined on the first layer of each lattice. ***This representation illustrates the (100) surface of each lattice.***



❑ A ccp metal is more malleable than hcp metal

- The fact that many metals are close-packed accounts for one of their common characteristics, their high density. However, ***there is a difference between ccp and hcp metals.***
- In cubic close packing, the faces of the cubes extend throughout the solid, and give rise to a **slip plane**. Careful analysis of the ccp structure shows that there are *eight slip planes* in various orientations whereas an *hcp structure has only one set of slip planes* (parallel to the planes of atoms). ***When the metal is under stress, the layers of atoms may slip past one another along a slip plane.***
- Because a ccp metal has more slip planes than an hcp metal, ***a ccp metal is more malleable*** than an hcp metal. Thus, copper, which is ccp, is highly malleable, but zinc, which is hcp, is more brittle.
- *It must be born in mind*, however, that metals in real use are not single crystals: they are polycrystalline, with numerous grain-like regions and defects that permeate the structure. Much of metallurgy is associated with the control of the density of grains and grain boundaries.

- Ultimately, many factors determine ***whether a particular metal adopts*** the fcc, hcp, bcc lattice, or some other configuration.
- One of the conclusions is that ***the bcc lattice is better suited to metals with few valence electrons.***
- A more subtle argument allows us to distinguish between the hcp and fcc lattices. The crystallographic point group for the ***fcc lattice is O_h , significantly higher in symmetry than*** the D_{3h} point group of the hcp lattice.
- ***The greater symmetry results in a higher degeneracy of electronic energy levels in the fcc lattice*** than in the hcp.
- This means that ***metals with a high density of electrons are more likely to adopt the fcc*** than the hcp lattice because **highly degenerate levels can support more electrons without having to occupy high-energy states**. This tendency is shown schematically in Fig. 13.9.

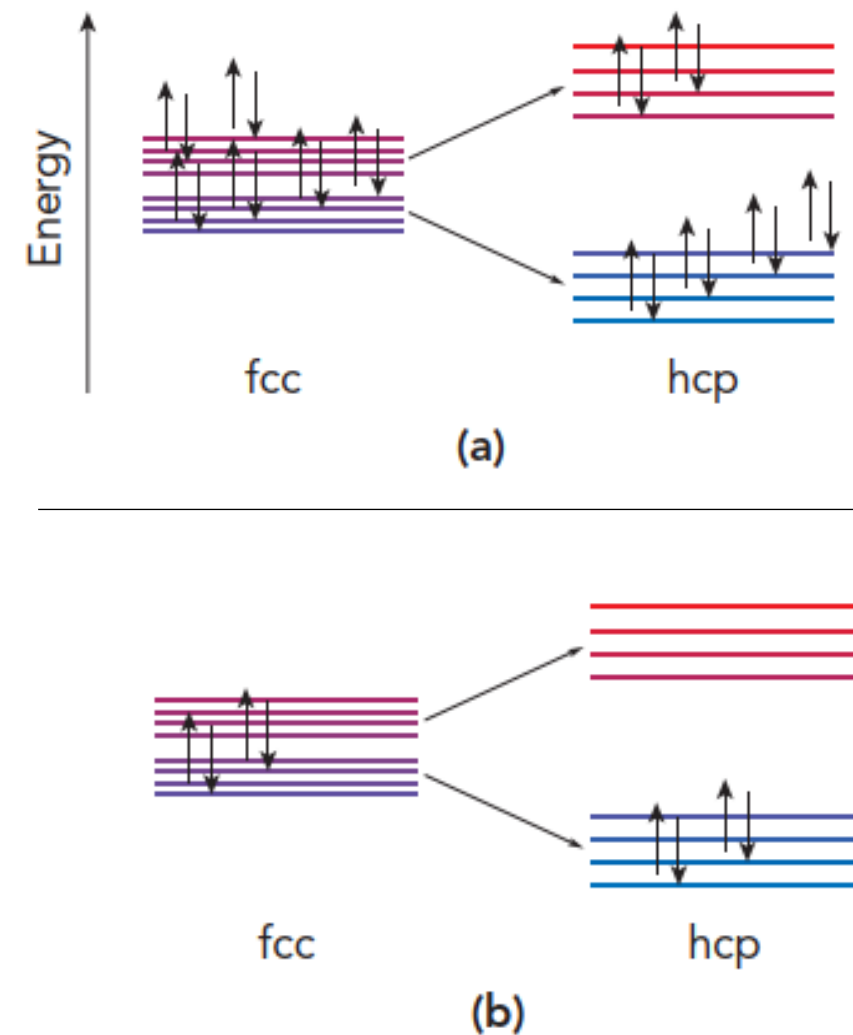


Figure 13.9 Schematic energy level diagrams of electronic states in the fcc and hcp lattices. The diagrams illustrate how **the higher degeneracy of the fcc lattice better accommodates electron-rich metals** (a), whereas electron-poor metals will tend to prefer the lower symmetry hcp lattice (b).

- As a general rule, therefore, we expect that **metals in the lower group numbers of the periodic table should tend to adopt either bcc or hcp lattices**, and the fcc lattice will be more stable for metals with high group numbers.
- But **there are several exceptions**, including lattice structures we haven't even discussed.
- The *exceptions* arise from less obvious contributions of the electronic wavefunctions to the stability of the solid, as well as other effects.
- ✓ For example, as we heat or cool a particular metal, we often observe that the most stable crystal structure changes. *Iron, heated above 912 K, changes from its bcc structure (called α -Fe) to fcc (γ -Fe).*
- ✓ *Tin, when cooled below 286 K, is more stable in a lattice with the structure of diamond, rather than the tetragonal crystal.*
- These **different crystal structures of the same material** are called **allotropes**.
- **One rule applies fairly well to both pure and alloyed metal crystals: the bond energy tends to increase with the number of unpaired electrons available for bonding.** *This accounts for the peak in melting points of the transition metals in Group 6 of the periodic table, because these atoms may have as many as six unpaired electrons.*

Lithium, Iron and thallium present all three types.

❑ High period packings

- Some structures are formed of dense and periodical planes of type AB/AB/... or ABC/ABC/..., but more complex structures of type ABAC/... for La, Pr, Nd and Am or of type ABACACBCB/... for Sm can sometimes be observed, and they all have the same packing density as they are close packings of planes that are in their turn close-packed. This is referred to as ***polytypism*** characterized by a sequence of high period packings.
- Random packings of close-packed planes are also observed but they correspond to amorphous materials and not to crystalline materials.

BONDING in SOLIDS: Metallic Bonding

Background: Consider the elements of the third period of the periodic table (Na–Ar) and their bondings (see Fig.).

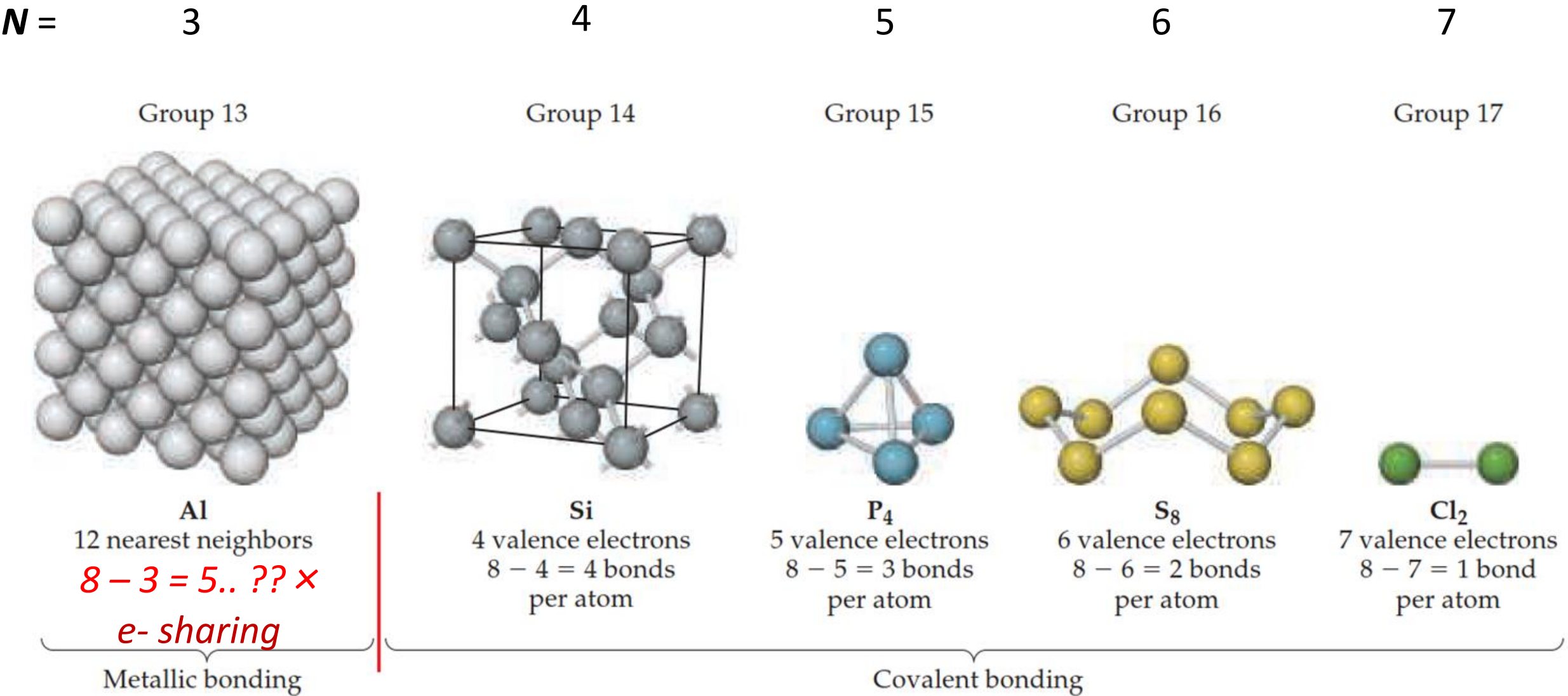
Each of these elements forms $(8 - N)$ bonds, where N is the number of valence electrons. This behavior can easily be understood through the application of the octet rule.

- Argon with eight valence electrons has a complete octet; as a result it does not form any bonds.
- Chlorine ($N=7$): each Cl atom forms one bond as in Cl_2 molecule, $(8 - 7 = 1)$;
- Sulfur ($N=6$): each S atom forms 2 bonds as in S_8 molecule $(8 - 6 = 2)$;
- Phosphorus ($N=5$): each P atom forms 3 bonds as in P_4 molecule $(8 - 5 = 3)$;
- Silicon ($N=4$): each Si atom forms 4 bonds which favors an extended network solid in which each atom is bonded to four equidistant neighbors.

If the $8 - N$ trend continued, we would expect **aluminum** (three valence electrons) to **form five bonds**. However, aluminum adopts a close-packed structure with 12 nearest neighbors. Magnesium and sodium also adopt metallic structures. **What is responsible for this abrupt change in the preferred bonding mechanism?** The answer is that **metals do not have enough valence-shell electrons to satisfy their bonding requirements by forming localized electron-pair bonds.** **WAY OUT??** In response to this deficiency, *the valence electrons are collectively shared*. A structure in which the atoms are close-packed facilitates this delocalized sharing of electrons.

Octet rule: *Elements form (8 – N) bonds (via electron sharing), where N is the number of valence electrons.*

Figure: Bonding in period 3 elements.



BONDING in SOLIDS: Metallic Bonding

- The majority of solids comprises ordered arrays of atoms, ions, or molecules.
- Some of the simplest solids are the metals, the structures of which can be described in terms of regular, space-filling arrangements of the metal atoms.
- These metal centers interact through metallic bonding, a type of bonding that can be described in two ways.

-**One view** is that bonding occurs in metals when each atom loses one or more electrons to a **common 'sea'** ("electron-sea model"). The strength of the bonding results from the combined attractions between all these freely moving electrons and the resulting cations.

-**An alternative view** is that metals are effectively enormous molecules with a multitude of atomic orbitals that overlap to produce **molecular orbitals** extending throughout the sample.

- *Metallic bonding is characteristic of **elements with low ionization energies**, such as those on the left of the periodic table, through the d block, and into part of the p block close to the d block.*
- ***Metallic bonding** also occurs in many other solids, especially **compounds of the d-metals** such as their **oxides and sulfides**. Compounds such as the lustrous-red rhenium oxide ReO_3 and 'fool's gold' (iron pyrites, FeS_2), illustrate the occurrence of metallic bonding in compounds.*

BONDING in SOLIDS: Metallic Bonding

- The familiar properties of a metal stem from the characteristics of its bonding and in particular *the delocalization of electrons throughout the solid*.
- Thus, metals are *malleable* (easily deformed by the application of pressure) and *ductile* (able to be drawn into a wire) because the ***electrons can adjust rapidly to relocation of the metal atom nuclei*** and there is *no directionality* in the bonding.
- They are lustrous because the electrons can respond almost freely to an incident wave of electromagnetic radiation and *reflect* it.
- The above properties can be explained by the "*electron-sea model*" of metallic bonding. Why do we need a different model for metallic bonding than the electron-sea model?
- ✓ Although it explains some general properties of metals, like malleability and conductivity, it *doesn't explain* the relative properties of metals, like their *hardness* and *melting points*.
- ✓ These properties depend on how strong the bonding in the metals is.
- ✓ By the electron-sea model, we might think that more electrons make the bonds stronger, so hardness and melting point would increase across the periodic table.

❑ The electronic structure of Metallic and Ionic Solids: MO Theory

- *Metallic and ionic solids* can both be treated by molecular orbital theory.
- The advantage of this approach is that both types of solid can be regarded as two extremes of a single kind.
- In each case, the electrons responsible for the bonding are delocalized throughout the solid (like in a benzene molecule, but on a much bigger scale).
- *In an elemental metal, the electrons can be found on all the atoms with equal probability*, which matches the primitive picture of metal as consisting of cations embedded in a nearly uniform electron 'sea'.
- In an ionic solid, the wavefunctions occupied by the delocalized electrons are almost entirely concentrated on the anions, so the Cl atoms in NaCl, for instance, are present as Cl^- ions, and the Na atoms, which have *low valence electron density*, are present as Na^+ ions.

- **To set up the molecular orbital theory of solids** consider initially a single, infinitely long line of identical atoms, each one having an s orbital available for forming molecular orbitals (as in sodium). In a homogeneous metallic solid, the valence AOs can combine with one another to form MOs.
- One atom of the solid contributes an s orbital with a certain energy (Fig. 10). When ***a second atom is brought up it forms a bonding and antibonding orbital***. For a homonuclear diatomic, such as Li_2 , there are two MOs: one bonding and one antibonding, as shown in Figures 10 & 12.12. For a metallic solid containing only three metal atoms, three MOs will result: one bonding MO (*with no nodes*), one nonbonding MO (*having one node*), and one antibonding MO (*having two nodes*).
- For n metal atoms, n MOs will form, each pair of which has a slightly different energy from its neighboring pair on the MO diagram. ***The relative energies of each MO can be determined on the basis of the number of nodal planes that exist.*** The ***lowest energy MO will have zero nodes*** and ***the highest will have $(n-1)$ nodes***.
- For an infinite number of metal atoms, the MOs become so closely spaced that they blur together into a “band” of MOs, as shown at the right in Figure 10.

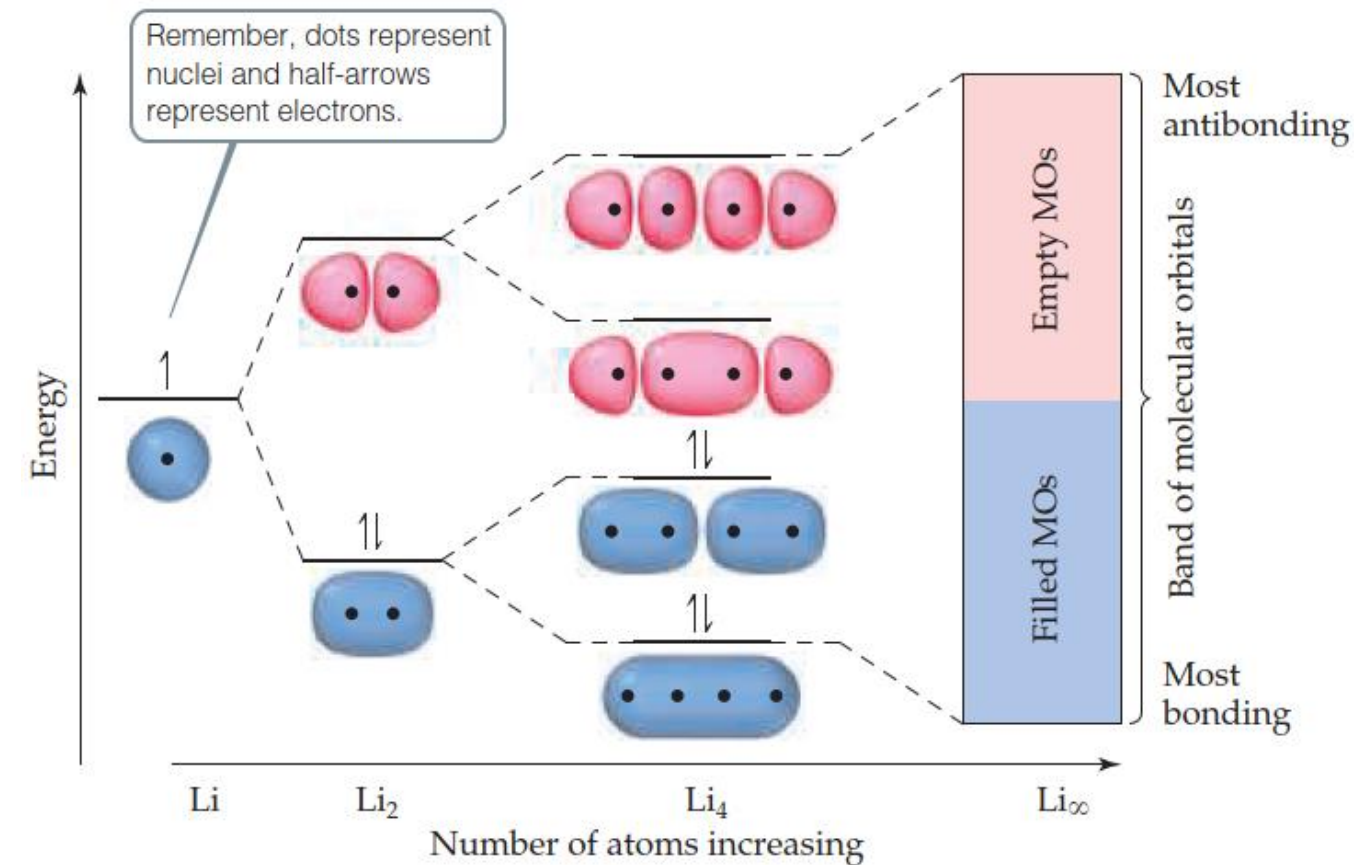


Figure 12.22 Discrete energy levels in individual molecules become continuous energy bands in a solid. Occupied orbitals are shaded blue, and empty orbitals pink.

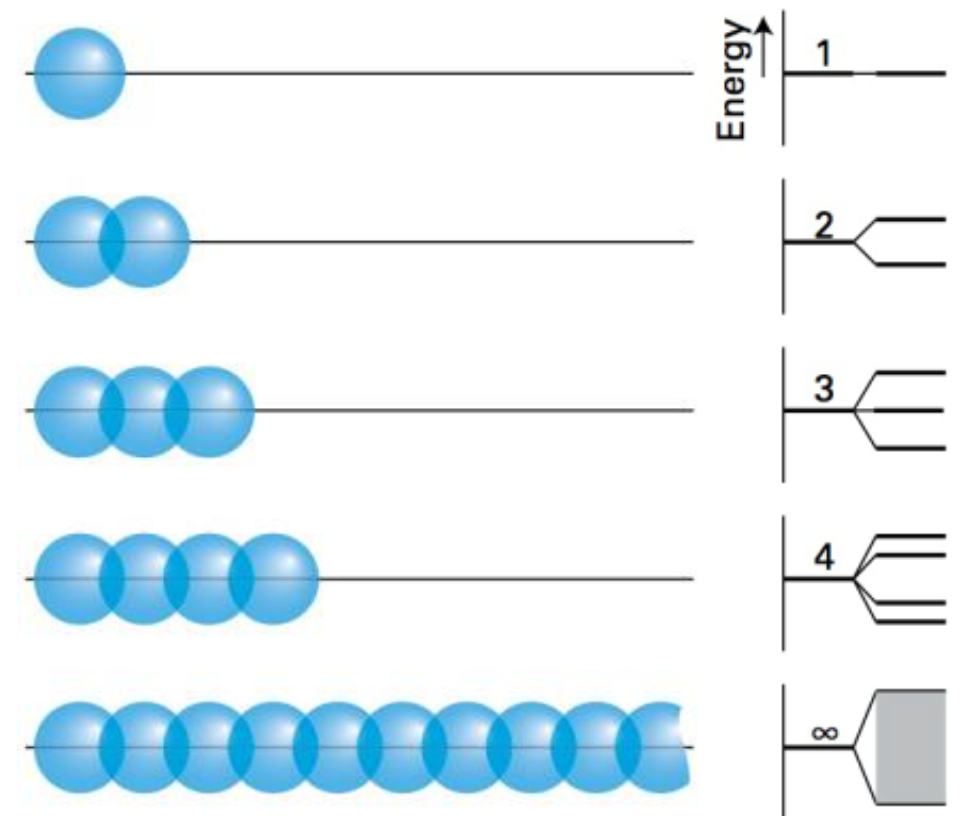


Fig. 10 The formation of a band of N molecular orbitals by successive addition of N atoms to a line. Note that the band remains of finite width, and although it looks continuous when N is large, it consists of N different orbitals.

- When we have a really big number of MOs, some interesting things happen.
- One mole of Fe is about 7 mL or 7 cc (a pretty small amount).
- In each atom of Fe, we have **one** 4s orbital, **five** 3d orbitals, and **three** 4p orbitals that can be *involved in bonding*.
- In a mole of Fe, we have **9** times Avogadro's number of AOs that can be involved in bonding. **That's about 10^{24} AOs**, which means the same number of MOs.
- ***There just isn't space to have much difference in energy between all those MOs.***
- The MOs have to have energies not too different from the AOs (they are definitely higher and lower, but not by too much), so they are limited to a relatively narrow range of energies. This means that the energies form **bands** *rather than separate energy levels*.

- When N atoms have been added to the line, there are N molecular orbitals covering a band of finite width. The lowest-energy orbital of this band is fully bonding and the highest-energy orbital is fully antibonding between adjacent atoms (Fig. 11).
- A band formed from overlap of s orbitals is called an ***s band***. If the atoms have p orbitals available, then the same procedure leads to a ***p band***.
- If the atomic p orbitals lie higher in energy than the s orbitals, then the p band lies higher than the s band, and there *may be* a ***band gap***, a range of energies for which no molecular orbitals exist. If the separation of the atomic orbitals is not large, the two types of bands might overlap.

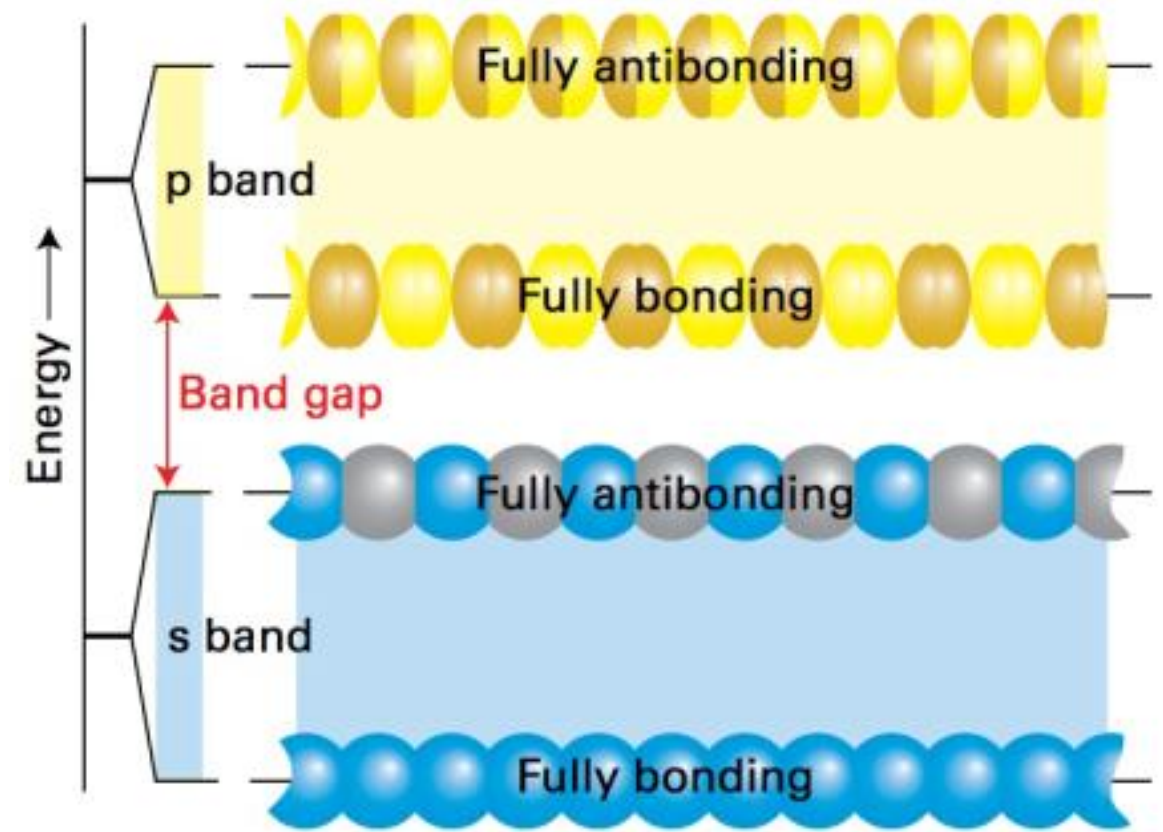


Fig. 11 The overlap of s orbitals gives rise to an s band, and the overlap of p orbitals gives rise to a p band. In this case *the s and p orbitals of the atoms are so widely spaced that there is a **band gap**. In many cases the separation is less, and the bands overlap.*

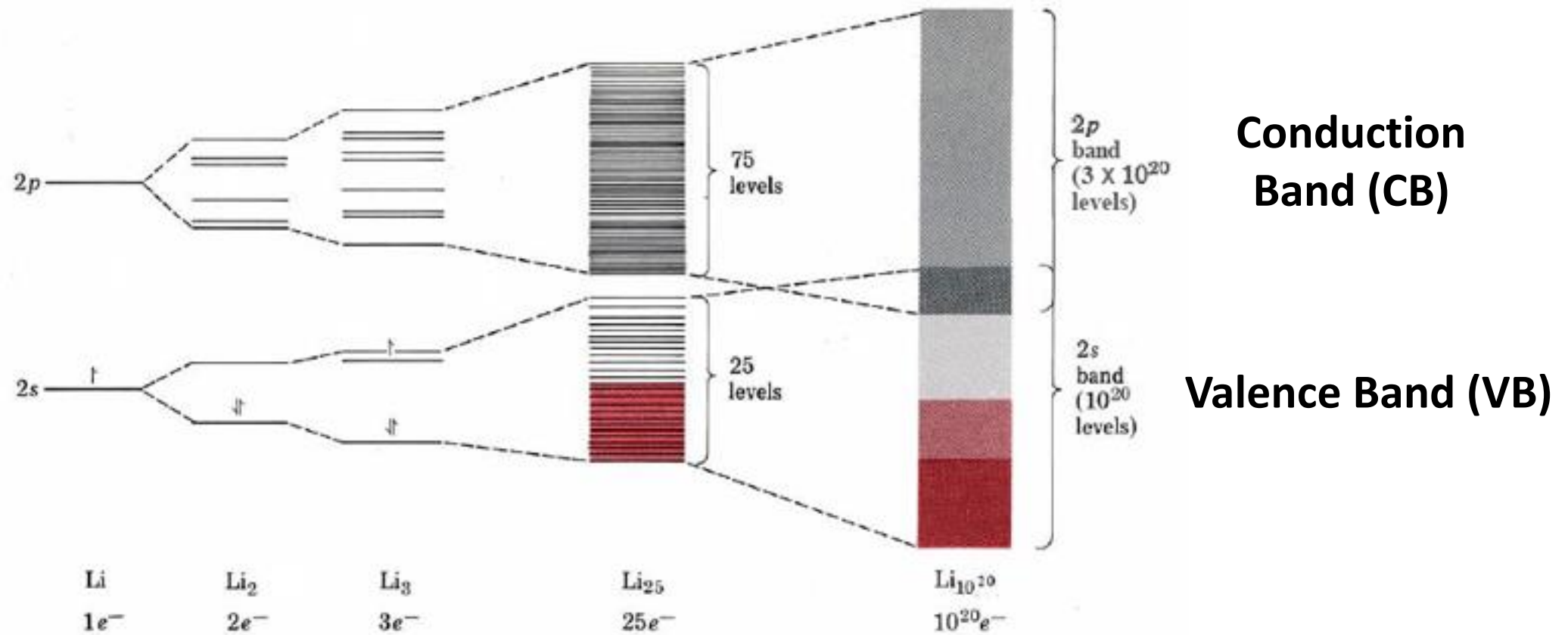


Figure 22.2.1: Molecular-orbital energies corresponding to delocalization of valence electrons over increasing numbers of Li atoms. A 1-mg sample of Li would contain nearly 10^{20} atoms. The corresponding orbital energies are so closely spaced that they constitute essentially continuous bands.

- To describe **an ionic solid**, consider a line of atoms with different electronegativities, such as a one-dimensional array of sodium and chlorine atoms rather than the identical atoms treated so far.
- Each sodium atom contributes an s orbital and one electron. Each chlorine atom contributes an electron from a p orbital.
- The s and p orbitals are used to build molecular orbitals that spread throughout the solid. Now, ***though, there is a crucial difference.***
- The ***orbitals on the two types of atom have markedly different energies***, so (just as in the construction of molecular orbitals for hetero-diatomic molecules) they ***can be considered separately.***

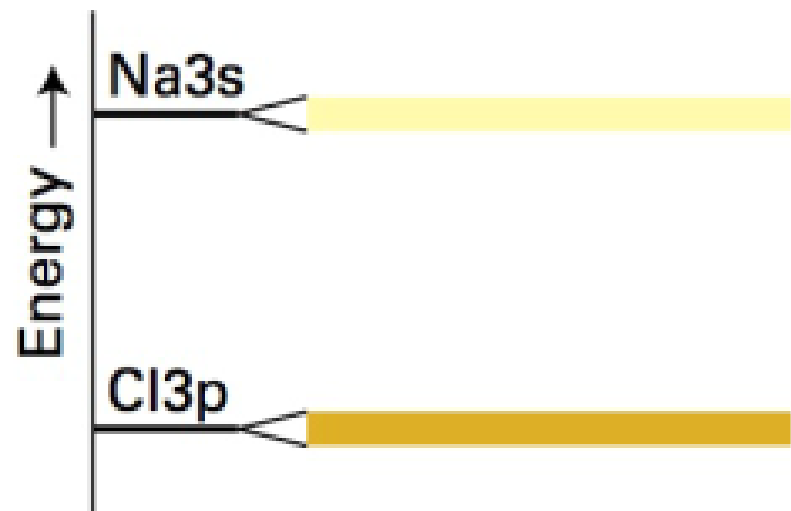


Fig. 13 The bands formed from two elements of *widely different electronegativity* (such as sodium and chlorine): they are widely separated. The bands are narrow because the *sodium atoms (and similarly Cl atoms) have very little overlap with one another (sodium atoms are separated by a chlorine atoms).*

- The Cl3p orbitals interact to form one band and the higher energy Na3s orbitals interact to form another band. However, because the *sodium atoms have very little overlap with one another (they are separated by a chlorine atom)*, the Na3s band is very narrow; so is the Cl3p band, for a similar reason.
- As a result, there is a **big gap between the two narrow bands** (Fig. 13).
- If there are N sodium atoms and N chlorine atoms, there will be 2N electrons to accommodate (one from each Na atom and one from each Cl atom).
- ***These electrons occupy and fill the lower Cl3p band.***
- As a result, *the electron density is almost entirely on the chlorine atoms*. In other words, *the solid can be thought of as composed of Na⁺ cations and Cl⁻ anions*, just as in an elementary picture of ionic bonding.

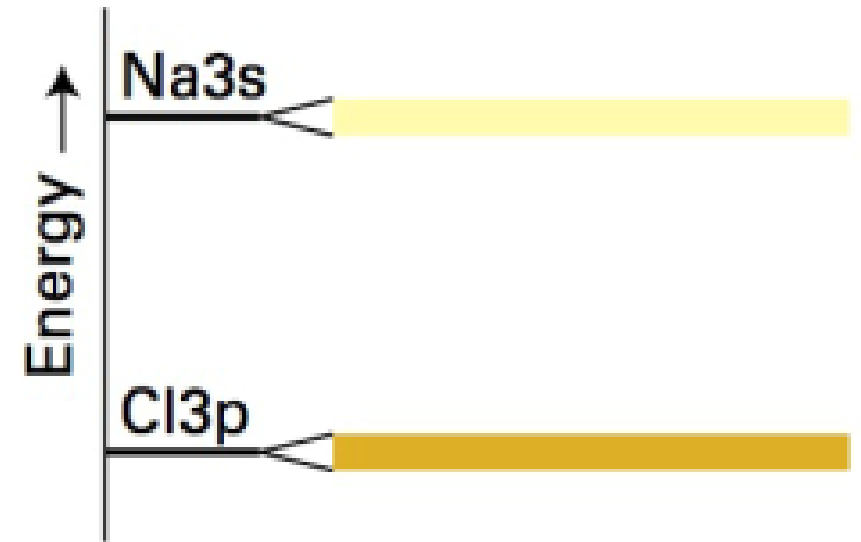


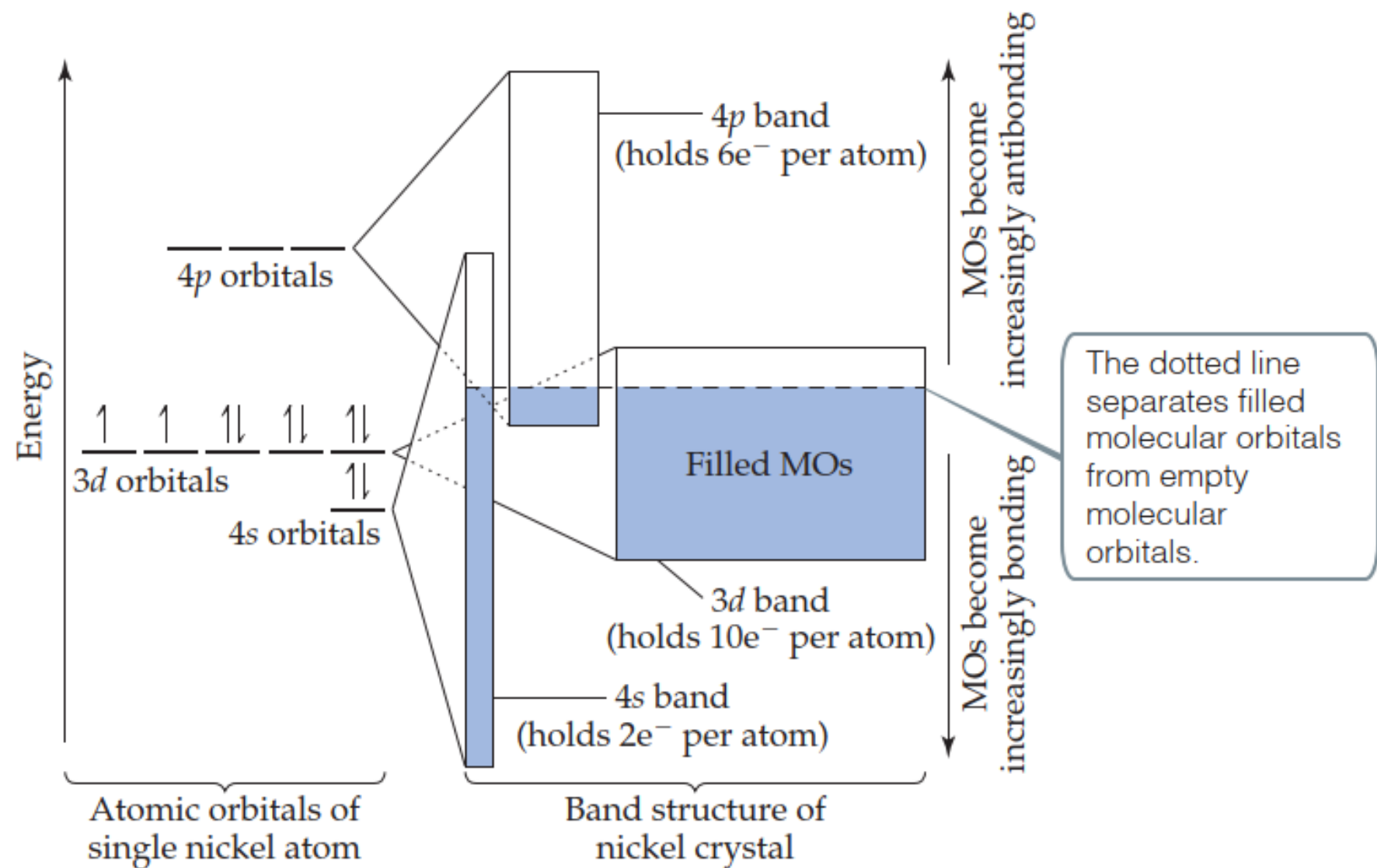
Fig. 13 The bands formed from two elements Na and Cl: they are widely separated and narrow. *If each atom provides one electron, the lower band is full and the substance is an insulator.*

➤ **Band theory** is a quantum-mechanical treatment of the bonding in metals.

- When the number of atoms N in a crystal is very large, the spacing between the energy levels in the band is infinitesimally small so that promotion to the next highest energy level within the band can occur quite readily.
- Whenever a band is fully occupied with valence electrons, it is known as the VB.
- If a band is unoccupied or empty, it is known as the CB.
- In a metal such as Li, as shown in Figure 22.2.1, the band constructed from a linear combination of the valence 2s AOs is exactly half-filled, so that the VB and the CB derive from the same set of orbitals and are only distinguished from each other by the presence or absence of electrons.
- The energy of the highest filled MO at 0K is known as the **Fermi level**. Because the Fermi level lies inside a band in Li, *this metal is a conductor*.
- For a metal such as Mg, the band formed by the 2s AO basis set (in other words, the VB) is completely filled. *The only reason that Mg is a conductor is because 2s band overlaps with the empty band formed by the 2p basis set* (or the CB), as shown in Figure 22.2.1.

- *In the ground electronic state of the solid, the occupied molecular orbitals make up the **valence band of the solid**. The **unoccupied orbitals**, if they extend over large distances in the solid, comprise **the conduction band**.*
- *If the valence band ends just where the conduction band begins, **the slightest electronic energy pushes the electrons into orbitals where they have more mobility**.*
- *It is the energies and shapes of these bands that will determine the physical and chemical properties of metals. This improvement over the **Drude–Sommerfield model of metallic bonding** is known as **band theory**.*
- *In practice, this approach is directly analogous to the way we made molecular orbitals in covalently bonded compounds by taking linear combinations of atomic orbitals having similar energies and the appropriate symmetry to yield a net nonzero overlap. Thus, if there are N atomic orbitals in the lattice, there will be N molecular orbitals (known as the **Bloch orbitals**) in the crystalline solid.*
- *The electronic structures of most metals are more complicated than those shown in Figure 12.22 because we have to consider more than one type of atomic orbital on each atom. Because each type of orbital can give rise to its own band, the electronic structure of a solid usually consists of **a series of bands**. The electronic structure of a bulk solid is referred to as a **band structure**.*

Figure 12.23 The electronic band structure of nickel.



- The band structure of a typical metal is shown schematically in Figure 12.23.
- The electron filling depicted corresponds to nickel metal, but the basic features of other metals are similar. The electron configuration of a nickel atom is $[\text{Ar}]4s^23d^8$, as shown on the left side of the figure.
- The energy bands that form from each of these orbitals are shown on the right side.
- The 4s, 4p, and 3d orbitals are treated independently, each giving rise to a band of molecular orbitals. In practice, *these overlapping bands are not completely independent of each other*, but for our purposes this simplification is reasonable.
- The 4s, 4p, and 3d ***bands differ from one another in the energy range they span*** (represented ***by the heights of the rectangles*** on the right side of Figure 12.23) and in *the number of electrons they can hold (represented by the area of the rectangles)*.
- The 4s, 4p, and 3d bands can hold 2, 6, and 10 electrons per atom, respectively, corresponding to two per orbital, as dictated by the Pauli exclusion principle.
- The ***energy range spanned by the 3d band is smaller than the range spanned by the 4s and 4p bands because the 3d orbitals are smaller and, therefore, overlap with orbitals on neighboring atoms less effectively.***

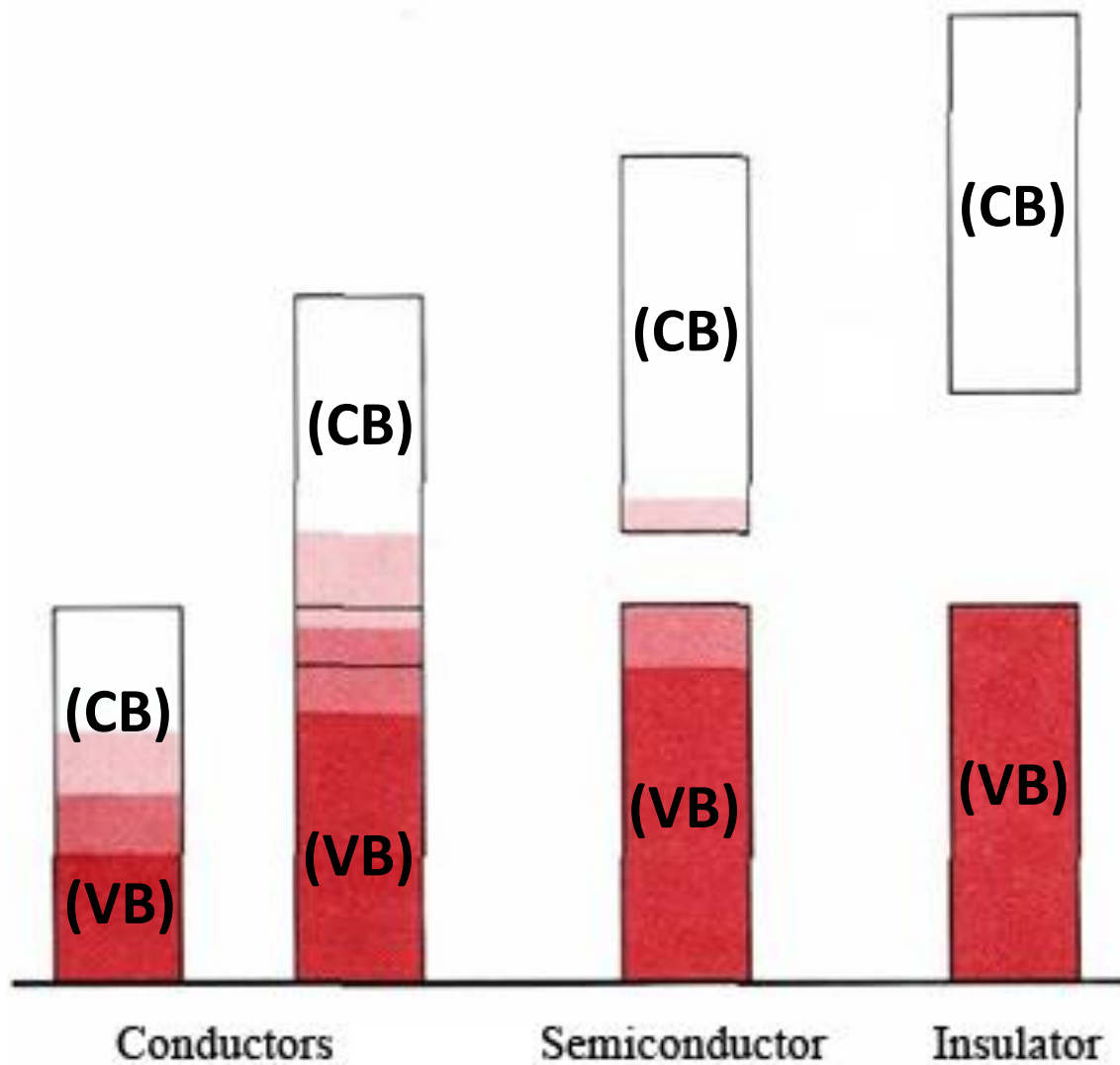


Figure 22.2.2: Band structures of conductors, semiconductors, and insulators.

Note that conductors may have a *partially filled band* or a *filled band which overlaps an empty one*.

In semiconductors and insulators, band separation becomes progressively larger containing electrons are color-coded.)

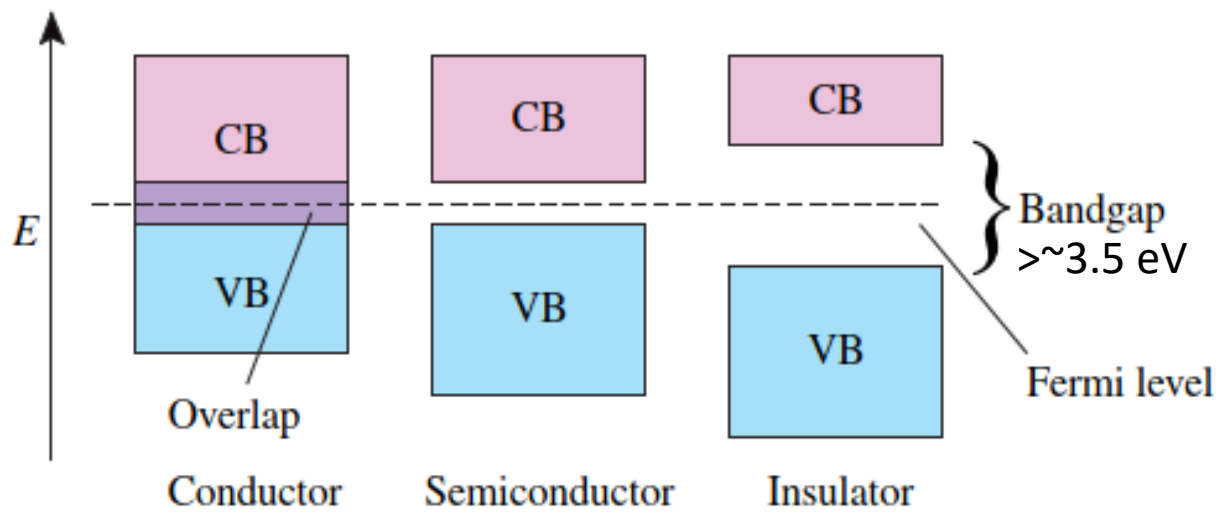
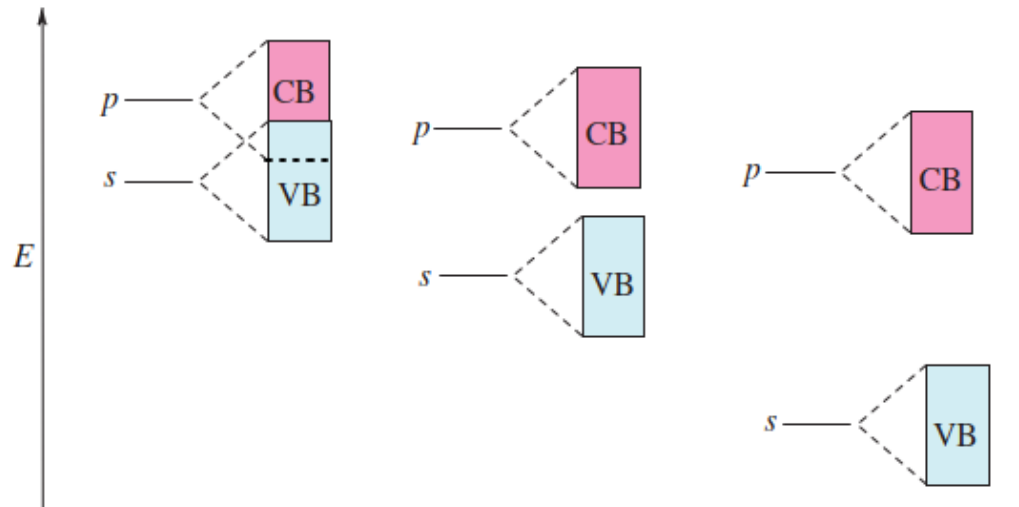


FIGURE 11.47 Simplified band diagram showing the differences between a conductor, a semiconductor, and an insulator. The main difference has to do with the band gap energy, or separation between the top of the valence band (VB) and the bottom of the conduction band (CB). The Fermi level is indicated by a dashed line on the diagram.



Metals

Metalloids

Non-metals

Left side of
Periodic Table

Middle of
Periodic Table

Right side of
Periodic Table

Zero band gap

Small band gap

Large band gap

Conductors

Semi-conductors

Insulators

FIGURE 11.48 A simplistic rationalization for the electrical conductivity of the elements in the periodic table based on their band structures.

- In the ground electronic state of the solid, the **occupied molecular orbitals** make up the **valence band of the solid**. The **unoccupied orbitals**, if they extend over large distances in the solid, comprise **the conduction band**.
- If the valence band ends just where the conduction band begins, the slightest electronic energy pushes the electrons into orbitals where they have more mobility.

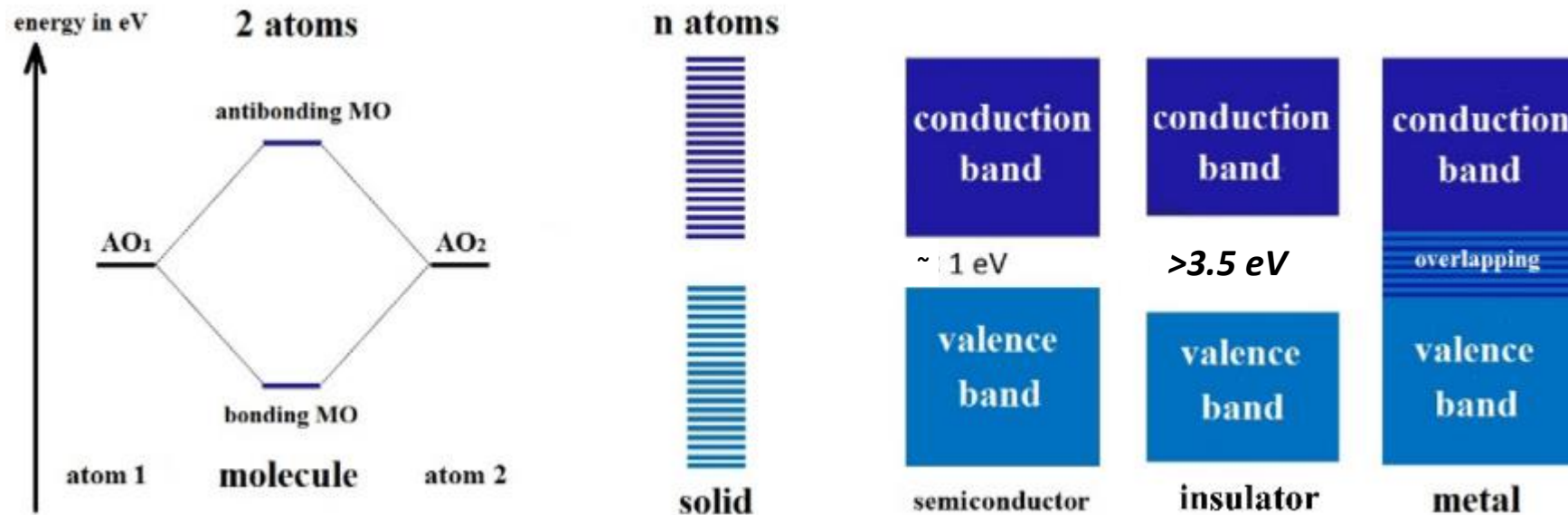


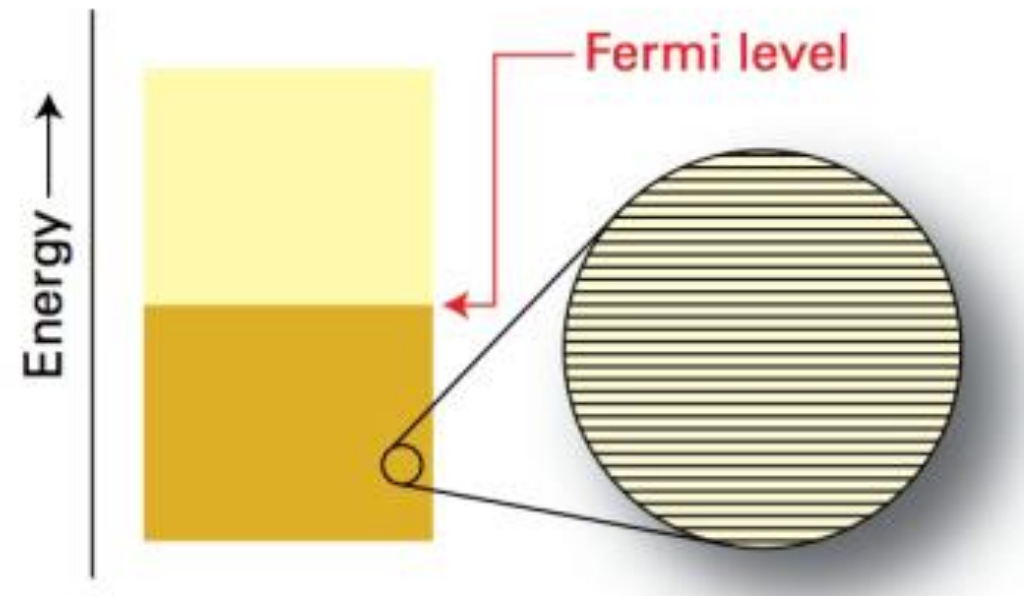
Figure 2.1. Simplified diagram of the energy-band model.

CONDUCTIVITY IN SOLIDS

- According to the ***band theory***, it is this partial filling which accounts for the high **electrical and thermal conductance of metals**.
- If an **electric field** is applied to a metallic conductor, some electrons can be forced into one end, occupying slightly higher energy levels than those already there. As a consequence of delocalization this increased electronic energy is available throughout the metal. It therefore can result in an almost instantaneous flow of electrons from the other end of the conductor.
- A similar argument applies to the **transfer of thermal energy**. Heating a small region in a solid amounts to increasing the energy of motion of atomic nuclei and electrons in that region. Since the nuclei occupy specific lattice positions, conduction of heat requires that energy be transferred among nearest neighbors. Thus when the edge of a solid is heated, atoms in that region vibrate more extensively about their average lattice positions. They also induce their neighbors to vibrate, eventually transferring heat to the interior of the sample. This process can be speeded up enormously if some of the added energy raises electrons to higher energy MO's within an incompletely filled band. Electron delocalization permits rapid transfer of this energy to other atomic nuclei, some of which may be quite far from the original source.

- Consider the electronic structure of a solid formed from atoms each of which is able to contribute one valence orbital and one electron (for example, the alkali metals).
- There are N atomic orbitals and therefore N molecular orbitals squashed into a band of finite width. There are N electrons to accommodate; they form pairs that occupy the lowest $\frac{1}{2}N$ molecular orbitals (Fig. 12). *The highest occupied molecular orbital is called the **Fermi level**.*
- However, unlike in the discrete molecules, there are empty orbitals just above and very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons.
- Some of the electrons are therefore very mobile and give rise to electrical conductivity.

Fig. 12 When N electrons occupy a band of N orbitals, it is **only half full** and the electrons near the Fermi level (the top of the filled levels) are mobile.



- *Without the overlap of energy bands, the periodic properties of metals could not be explained.*
- In the absence of overlapping p- and d-bands, we would expect the s-band to be half-filled for the alkali metals (group 1) and *completely filled for the alkaline-earth metals* (group 2). *If that were true, metals like magnesium, calcium, and strontium would not be good electrical and thermal conductors*, in disagreement with experimental observations.
- We can also **explain melting point, hardness, and other properties using MO theory.**
- While the conductivity of metals can be qualitatively understood using either the *electron-sea model* or the *molecular orbital model*, many physical properties of transition metals, such as the melting points plotted in Figure 22.2.1, can be explained only with the latter model.
- In this case, we imagine combining many atomic orbitals (1 or more for each atom) to make an equal number of MOs that extend over the whole solid.
- Some MOs will have fewer nodes and be lower energy, while others will have more nodes and be higher energy.
- Each MO can hold **no** more than 2 electrons.

- *The molecular orbital model predicts that bonding first becomes stronger as the number of valence electrons increases, and the bonding orbitals are increasingly populated.*
- *Filling the lower energy MOs (bonding MOs) makes the bonds stronger.*
- *Upon moving past the middle elements of the transition metal series, the bonds grow weaker as electrons populate antibonding orbitals.*
- **Strong bonds between atoms lead to metals with higher melting and boiling points, higher heat of fusion, higher hardness, and so forth.**
- **Alkali metals have low melting points and are soft for not many bonding MOs filled.**
- **Filling the higher energy MOs (**antibonding** MOs) makes the bonds weaker, which is why Cu, Ag, Au and Zn are soft and melt at low temperatures (Hg is a liquid at RT!).**

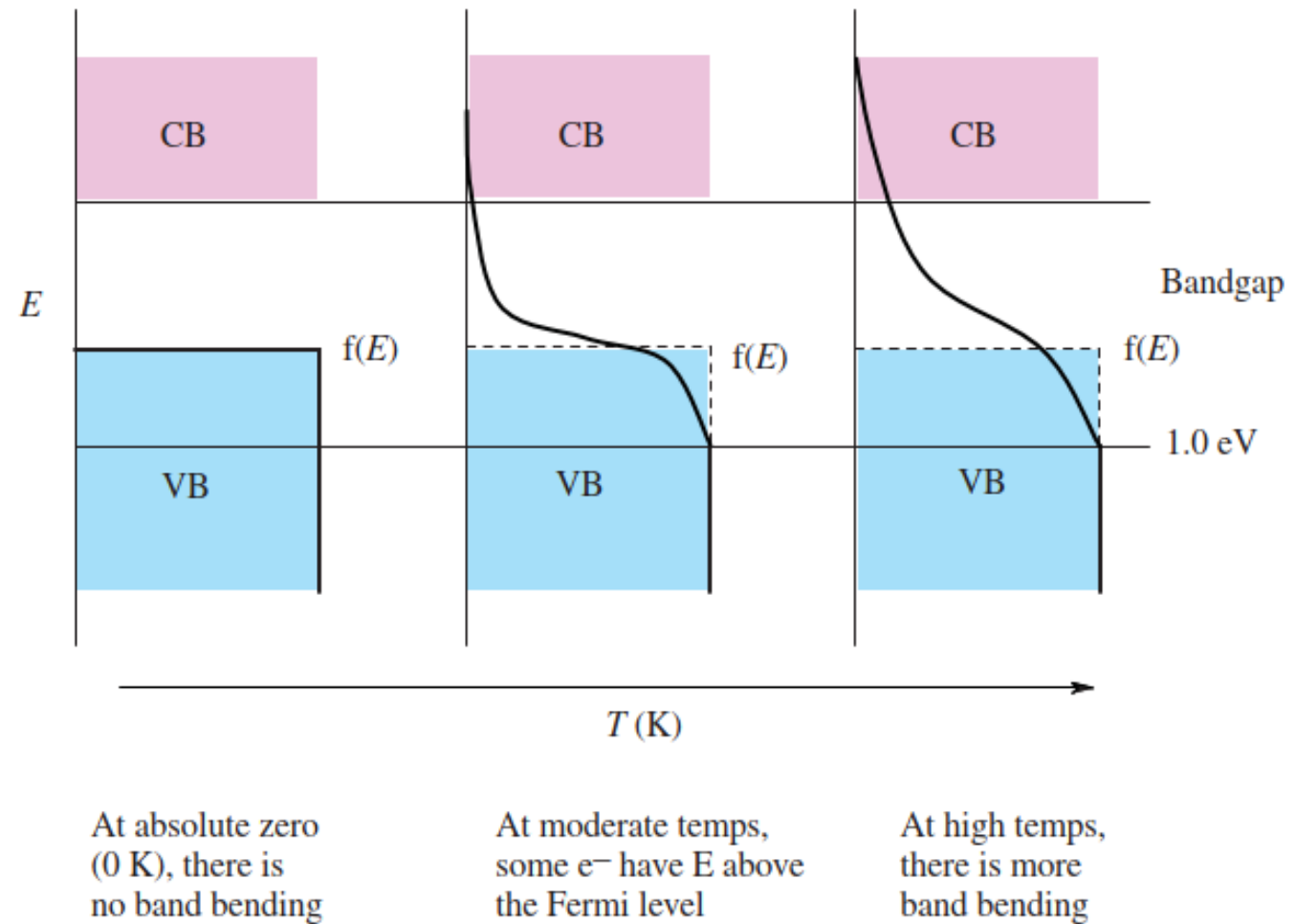
- A simplified version of band theory can therefore be used to make a rather sweeping generalization about the electrical properties of the elements, as shown in Figure 11.48.
- ***One primary difference between the metals and nonmetals is related to the energies of their valence s and p AOs. This energy difference increases across a row of the periodic table because of increased shielding of the p -electrons by the more penetrating s -electrons.***
- *The metals, which lie to the left in the periodic table, are excellent electrical conductors because their valence and CBs overlap and there is essentially no energy gap at all between the bands.*
- On the other end of the spectrum, the nonmetals, which lie to the right in the periodic table, are typically electrical insulators because of the sizable band gap that exists between their VBs and CBs.
- In the *middle of the periodic table*, there is a gray area that is intermediate in its electrical properties between those of a metal and those of a nonmetal. These are the ***metalloids***, which are usually delineated by a bold diagonal “staircase” on the periodic table. The metalloids tend to be semiconductors because they have only a small band gap.

- Often **metal** is defined as a material that has an electrical conductivity *greater than 10^2 S/m* (where S is the SI unit Siemens, which has the value $1\text{S}=1\Omega^{-1}$).
- The *conductivities of metals typically decrease with increasing temperature* because there are *more disruptive lattice vibrations* at higher temperatures.
- An **insulator** is defined as a material that has an electrical conductivity of less than 10^{-5} S/m .
- Lastly, **semiconductors are defined as having conductivities between 10^{-5} and 10^2 S/m** .
- The **band gap** (E_g , the energy gap between the VB and CB) in a semiconductor is fairly small (typically less than 2 eV); but unlike the metals, the bands do not overlap with one another.
- At low temperatures, a semiconductor will act as an insulator; but as the temperature is raised and an external potential is applied, a portion of the electrons in the VB can “jump” across the band gap into the CB.
- This is because of the temperature dependence of the Fermi–Dirac distribution, which spreads out at higher temperatures over a greater range of energy levels, as shown in Figure 11.50.
- *Unlike the metals*, whose conductivities generally decrease with increasing temperature, ***the conductivity of a semiconductor increases as the temperature*** is raised because a greater fraction of the electrons possess enough thermal energy to jump across the barrier. The electrons can also cross the band gap in a semiconductor by the absorption of visible light.

FIGURE 11.50

The Fermi–Dirac distribution as a function of temperature in a semiconductor.

The Fermi–Dirac distribution is really nothing more than a modified Boltzmann distribution that takes into account the fact that each energy level can hold no more than two electrons. The shape of the Fermi–Dirac distribution *decays exponentially* according to Equation(11.26), where μ is the field potential.

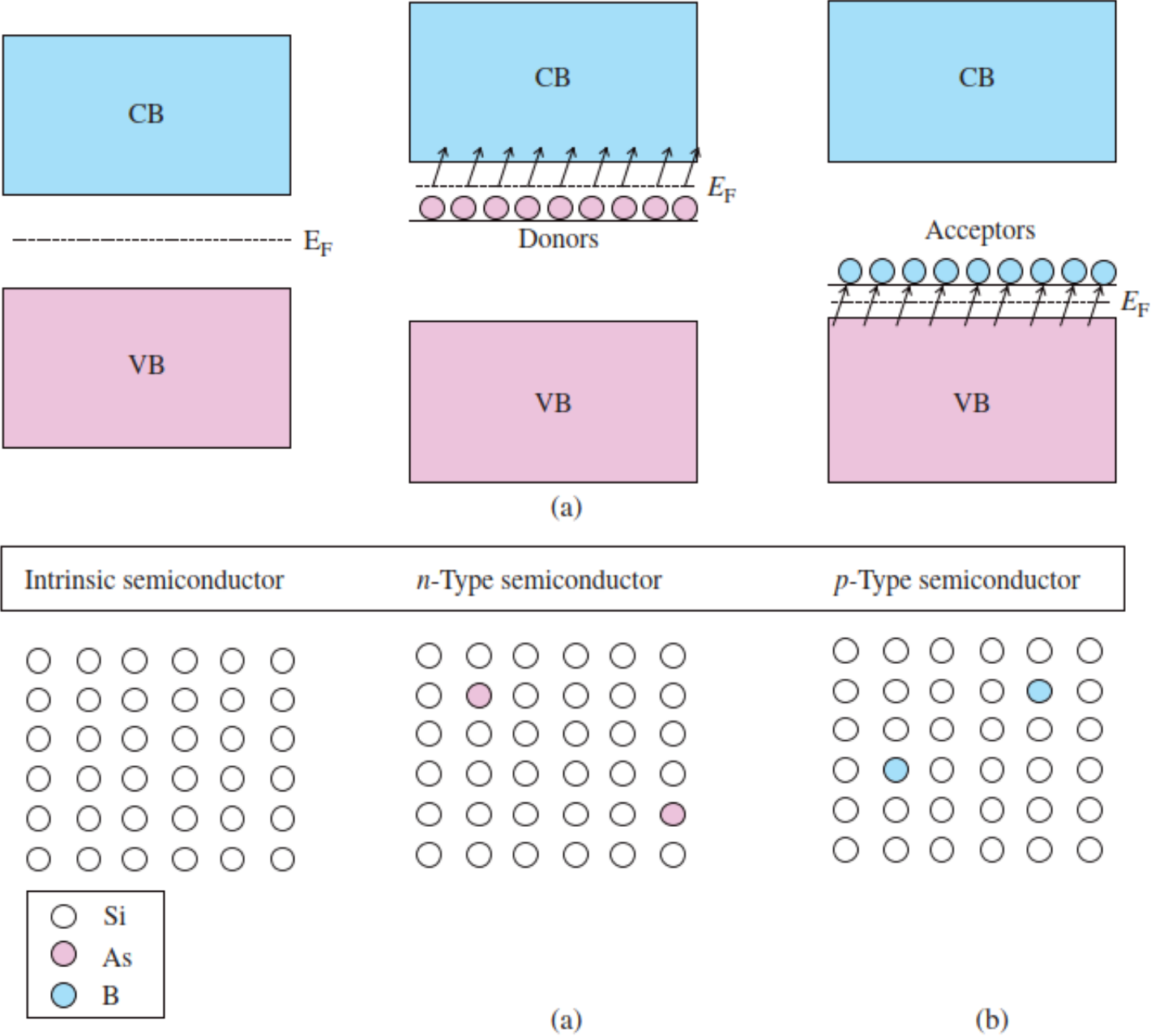


$$f(E) = \frac{1}{e^{(E-\mu)/kT} + 1}$$

- Some of the metalloids, such as Si (band gap= 1.1 eV) and Ge (band gap= 0.74 eV), are ***intrinsic semiconductors***, which means that the pure substance can exhibit semiconducting properties.
- ✓ This is one of the reasons that the entire modern electronics era is based on Si microchips.
- ***Band gaps greater than ~3.5 eV*** are so large that the material is not a semiconductor; it is ***an insulator*** and does not conduct electricity.
- The **conductivity of Si can be enhanced**, however, with the addition of small amounts of ***dopants*** that increase the number of charge carriers. For every so many Si atoms, for example, if we were to replace one of these Si atoms with an As atom, the conductivity would increase because the lattice acquires an extra electron (As has five valence electrons, while Si only has four).
- There is no room for the extra electrons from the As atoms to occupy MOs in the VB of Si, so they occupy a very narrow set of orbitals of their own (narrow because they are few and far between so that their valence orbitals have very little overlap).
- The As ***orbital energies are intermediate between those of the VB and CB*** of Si, as shown in Figure 11.51(a).

- Whenever the dopant adds electrons to the lattice, the material is called an ***n-type semiconductor*** because the dopant adds negative charge carriers. The conductivity of an n-type semiconductor is enhanced because the electrons in the As orbitals lie higher in energy than those in the VB of Si.
- The energy difference (band gap) between the highest occupied MOs and the lowest unoccupied MOs is now significantly smaller. This makes it easier for electrons to jump across the barrier into the CB.
- An ***alternative way to improve the conductive properties of a semiconductor*** (or to convert an insulator into an extrinsic semiconductor) is to *dope* it with an element that contains less electrons.
- ✓ One example is to dope a Si wafer such that dopant atoms occupy some of the lattice sites of the material. Because ***dopant atom*** has only ***three valence electrons***, the dopant provides a set of ***low-lying empty MOs***, as shown in Figure 11.51(b).
- ✓ The band gap between the top of the VB for Si and these empty MOs is very small, so that some of the electrons in the VB can be thermally excited into the empty dopant MOs.
- ✓ When this occurs, the electron deficiency creates holes in the VB, which act as ***positive charge carriers***. Because the dopant increases the number of positive charge carriers, the material is called a ***p-type semiconductor***.
- Almost every modern electronic device (from laptops to cell phones to mp3 players) contains a p–n junction as part of its integrated circuitry.

FIGURE 11.51
 (a, b) The difference between an
 intrinsic semiconductor, an
 n-type semiconductor, and a
 p-type semiconductor.



❑ Superconductors

- As mentioned previously, *the conductivity of a semiconductor will increase* (resistance decreases) *as the temperature is raised* because there are more charge carriers at the higher temperature.
- *By contrast, the conductivity of a metal decreases as the temperature is raised* because there will be a greater number of lattice distortions, causing an electronic instability.
- ✓ The **resistance** to flow of electrical current of a normal metallic conductor **decreases** smoothly with **decreasing temperature** *but never vanishes*.
- However, a **superconductor** conducts electricity without resistance once the temperature is below the critical temperature, T_c .
- In **a superconductor**, there is *zero resistance* to the flow of electricity at temperatures lower than a certain critical temperature, T_c , which is characteristic of the material.
- *Even in the absence of an applied potential, a small current can still flow* with zero resistance through the superconductor.
- In 1911, Heike Kamerlingh Onnes discovered that Hg becomes superconducting at temperatures lower than 4.2K, the normal boiling point of liquid helium.
- Metals, such as tungsten, mercury, and lead, have T_c values below about 10 K.

- If cooled to near absolute zero, all metals become superconducting. Several metals and alloys superconduct even at marginally higher temperatures of 10–15 K. To maintain a superconductor at these extremely low temperatures requires liquid helium (bp, 4 K) as a coolant.
- In the mid-1980s, materials made of lanthanum, strontium, copper, and oxygen were found to become superconducting at 30 K. This was a much higher temperature for superconductivity than had been previously achieved. More surprising, the new materials were not metals but *ceramics*!
- In 1986, Bednorz and Müller discovered that if La_2CuO_4 is doped with Ba and partially oxidized, it will become superconducting at $T_c = 35\text{K}$. By changing the cations to Y, the familiar 1–2–3 superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ was discovered to have $T_c > 90\text{K}$, a temperature higher than the boiling point of liquid nitrogen (77K), and the modern field of **high-temperature superconductors (HTSCs)** was born. In short order, other types of ceramic superconductors were discovered.
- One of these new types was particularly easy to make. When a stoichiometric mixture of yttrium oxide (Y_2O_3), barium carbonate (BaCO_3) and copper(II) oxide (CuO) is heated in a stream of $\text{O}_2(\text{g})$, a ceramic is produced with the approximate formula $\text{YBa}_2\text{Cu}_3\text{O}_x$ (where x is slightly less than 7), which is an oxygen-deficient version of the ceramic shown in

Figure 23-17).

- This so-called YBCO ceramic becomes superconducting at the remarkably high temperature of 92 K. Although a temperature of 92 K is still quite low, it is far above the boiling point of helium. In fact, it is above the boiling point of nitrogen (77 K). Thus, inexpensive liquid nitrogen can be used as the coolant.

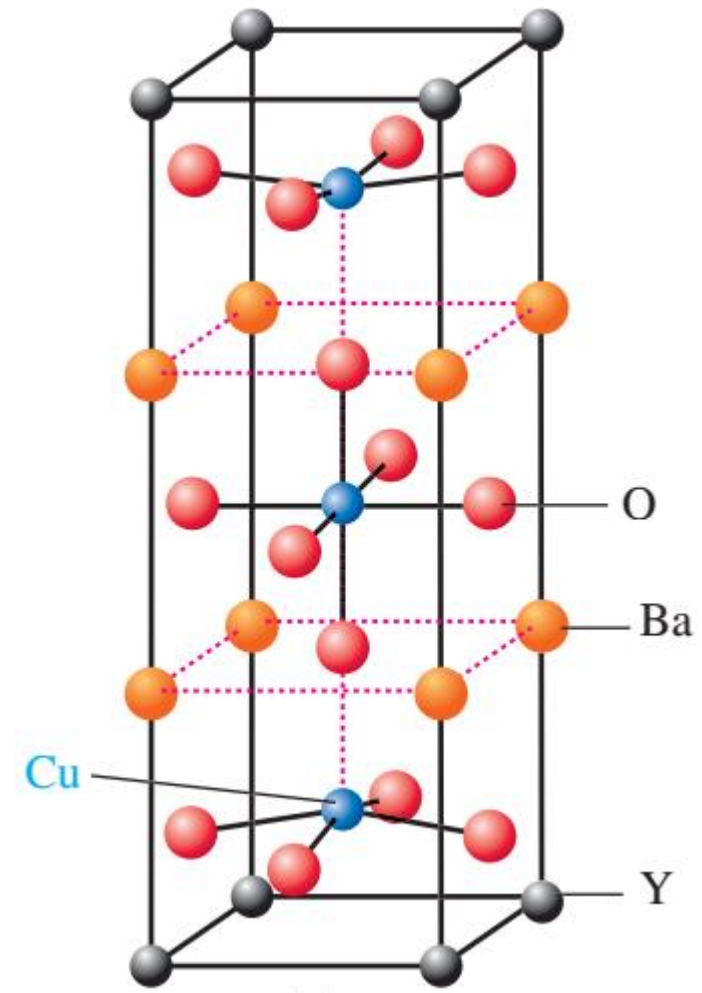


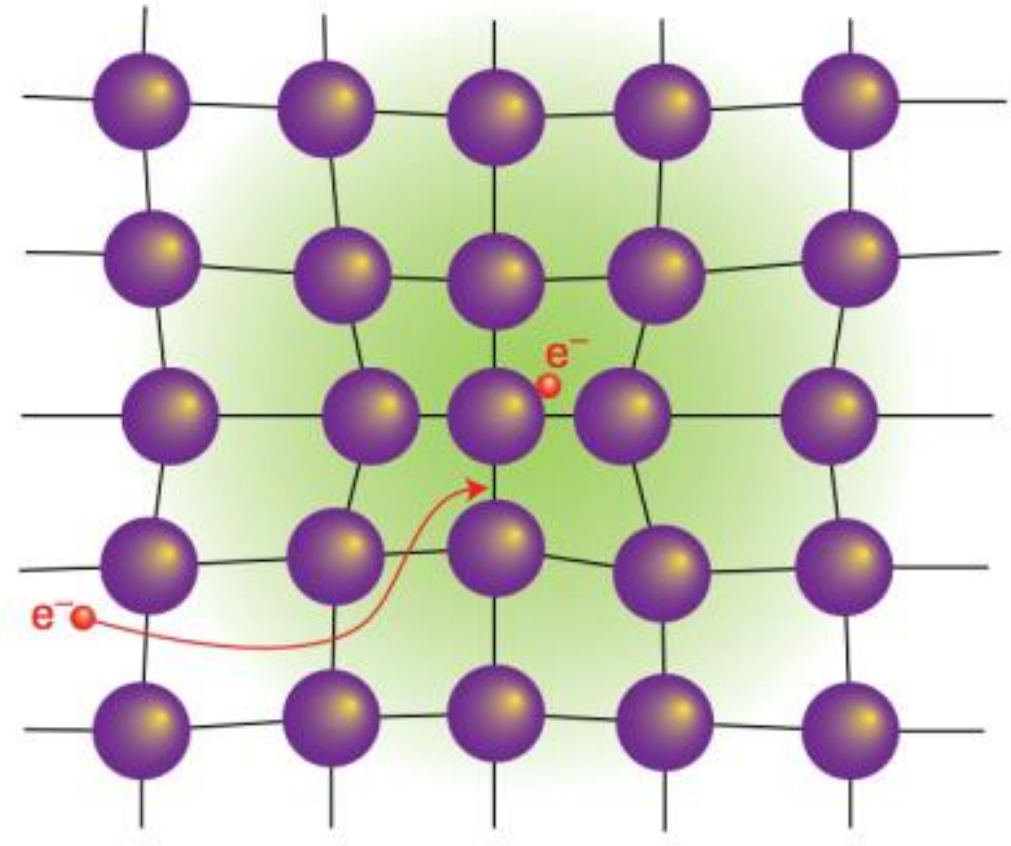
FIGURE 23-17. Structure of YBa₂Cu₃O₇ superconductor.

- Several *ceramics*, inorganic powders that have been fused and hardened by heating to a high temperature, containing oxocuprate motifs, Cu_mO_n , are now known with T_c values well above 77 K, the boiling point of the inexpensive refrigerant liquid nitrogen. For example, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ has $T_c = 153$ K.
- Many variations of the basic YBCO formula are possible. Almost any lanthanide element can be substituted for yttrium, and combinations of group 2 elements can be substituted for barium. All these variations yield materials that are superconducting at relatively high temperatures, but of the group, the yttrium compound is superconducting at the highest temperature.
- The record high temperature for superconductivity set by the YBCO ceramics was soon eclipsed by another group of ceramics containing bismuth and copper, such as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. One of these is superconducting at 110 K, but this record was also short-lived. A ceramic containing thallium and copper, with the approximate formula $\text{TlBa}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ (where y is slightly larger than 10), was found to become superconducting at 125 K. Now, the search continues for materials that might become superconducting at room temperature (about 293 K).

- The **mechanism of superconduction** is well-understood for *low-temperature materials*. The principal *model of superconductivity* is the **BCS theory**, which was proposed by Bardeen, Cooper, and Schrieffer in 1957, for which they won the 1972 Nobel Prize.
- According to the BCS theory, **the conducting electrons in a superconducting solid *cause* a *transitory deformation* in the lattice**, which ***creates a region of positive charge density***.
- Thus, if one electron is in a particular region of a solid, the nuclei there move towards it to give a distorted local structure (Fig. 15E.9).

Figure 15E.9 The formation of a **Cooper pair**. One electron distorts the crystal lattice and the second electron has a lower energy if it goes to that region. These electron–lattice interactions effectively bind the two electrons into a pair.

In one analogy, the Cooper pair moves through the lattice similar to *fans in a stadium doing the wave*.



- Because that ***local distortion is rich in positive charge***, it is *favorable for a second electron to join the first*. Hence, a second electron having ***opposite spin*** is then attracted to the positive charge and they move together as a pair (known as a ***Cooper pair***) as there is a virtual attraction or a certain binding energy between the two electrons.
- A ***Cooper pair*** is a pair of electrons that exists on account of the ***indirect*** electron–electron interactions mediated by the nuclei of the atoms in the lattice.
- The ***local distortion is disrupted by thermal motion*** of the ions in the solid, so ***the virtual attraction occurs only at very low temperatures***.
- *The local distortion is disrupted by thermal motion of the ions in the solid, so the virtual attraction occurs only at very low temperatures.*
- ***As long as the binding energy of the Cooper pair is greater than the energy of the lattice vibrations that tend to disrupt the pair***, the ***two electrons will travel together throughout the lattice having zero resistance***.
- This will be *true at lower temperatures*, where the disrupting forces from the oscillating atoms in the lattice have *insufficient energy to overcome the binding energy of the Cooper pair*.

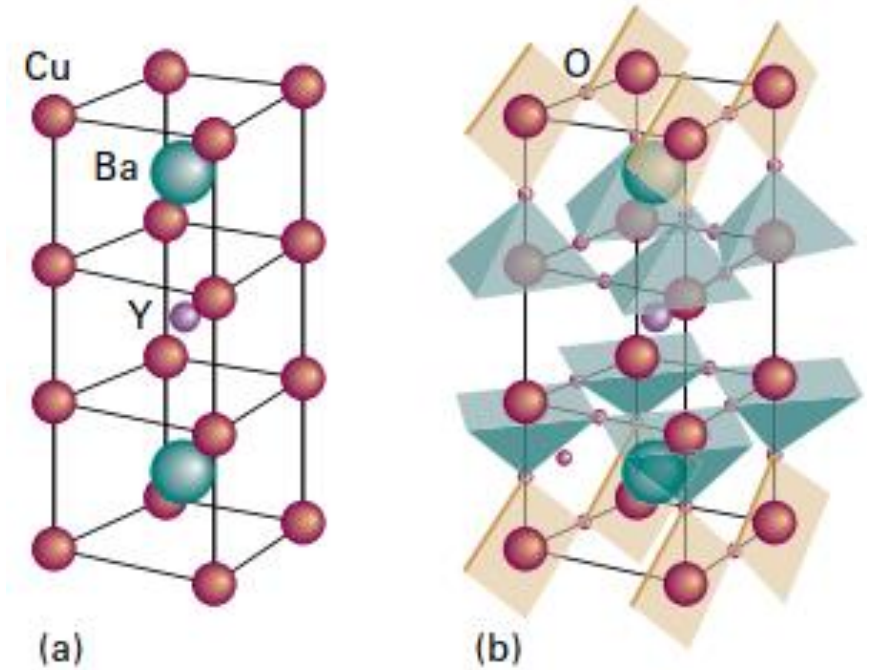
- ***A Cooper pair undergoes less scattering than an individual electron*** as it travels through the solid because ***the distortion caused by one electron can attract back the other electron should it be scattered out of its path in a collision.***
- ***Because the Cooper pair is stable against scattering, it can carry charge freely through the solid, and hence give rise to superconductivity.***
- The Cooper pairs responsible for low-temperature superconductivity are likely to be important in HTSCs, but *the mechanism for pairing is hotly debated.*
- The superconducting properties of the high-temperature copper oxides, such as $\text{YBa}_2\text{Cu}_3\text{O}_7$, are *believed to result from systematic vacancies in the oxide layers of the tetragonal perovskite-type structure.*
- One of the most widely studied oxocuprate superconductors $\text{YBa}_2\text{Cu}_3\text{O}_7$ (informally known as '123' on account of the proportions of the metal atoms in the compound) has the structure shown in Fig. 15E.8.
- The square-pyramidal CuO_5 units arranged as two-dimensional layers and the square planar CuO_4 units arranged in sheets are common structural features of oxocuprate HTSCs.
- There is evidence implicating the arrangement of CuO_5 layers and CuO_4 sheets in the mechanism.

➤ It is believed that *movement of electrons along the linked CuO_4 units accounts for superconductivity*, whereas the linked CuO_5 units act as 'charge reservoirs' that maintain an appropriate number of electrons in the superconducting layers.

Figure 15E.8 Structure of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor.

(a) Metal atom positions.

(b) The polyhedra show the positions of oxygen atoms and indicate that the Cu ions are either in square-planar or square-pyramidal coordination environments.



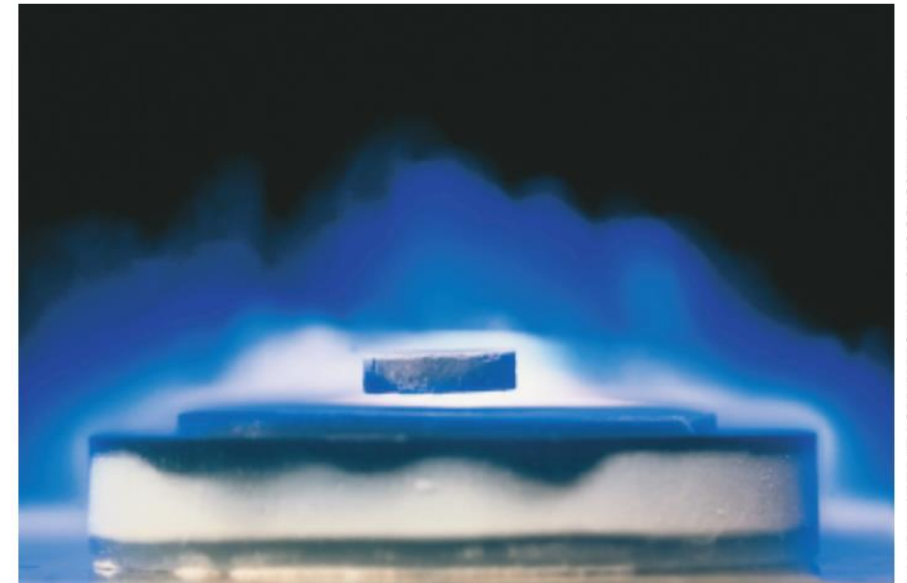
- The current theory of superconductivity, developed in the 1950s, explains the superconducting behavior of metals at very low temperatures but not the higher-temperature superconductivity of ceramics. It seems that the electrons in all known superconductors move through the material in pairs—a sort of buddy system that allows the electrons to move without resistance.
- The mechanism by which electron pairs form in high-temperature superconductors, however, is clearly different from that in low-temperature superconductors.
- Lack of a suitable theory complicates the search for higher-temperature superconductors. When the mechanism for high-temperature superconductors is better understood, new breakthroughs might be easier to accomplish. Perhaps a room-temperature superconducting material will be possible.
- Despite this less-than-complete understanding of high-temperature superconductors, engineers are already building devices that use the new materials. Wires have been made that are superconducting at liquid nitrogen temperatures, and new devices for precise magnetic field measurements using ceramic superconductors are now being produced. Ultimately, ceramic superconductors may find application in low-cost, energy-efficient electric power transmission.

- Superconductors offer no resistance to an electric current, so electricity is conducted with no loss of energy.
- In 1933, Meissner Ochsenfeld noticed that ***superconductors exclude an internal magnetic field***, a phenomenon now known as the ***Meissner effect***. Thus, ***a superconducting solid cooled below its T_c will appear to float above a bar magnet***.
- As a result of the *Meissner effect*, superconducting materials have found practical application in the magnets of nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI), and particle accelerators.
- Magnetically levitated trains, magnetic resonance imaging (MRI) for medical diagnoses, and particle accelerators used in high-energy physics all require high magnetic fields generated by superconducting electromagnets.
- Because **HTSC** materials can be cooled relatively inexpensively using liquid nitrogen, high-temperature superconductors have been envisioned in a variety of practical applications, including high-performance transformers, electric motors, and **magnetically levitated high-speed trains**.
- They are already commercially employed in superconducting quantum interference devices (SQUIDs), which are the most sensitive magnetometers on the market.

- Superconductors have unique **magnetic properties**.
- Some superconductors, classed as **Type I superconductors**, show ***abrupt loss of superconductivity when an applied magnetic field exceeds*** a critical value H_c characteristic of the material.
- Type I superconductors are also completely diamagnetic – the lines of force are completely excluded – below H_c . This exclusion of a magnetic field in a material is known as the **Meissner effect**, which can be demonstrated by the **levitation of a superconductor above a magnet**.
- It is also the basis for a number of potential applications of superconductors that include magnetic levitation, as in **‘maglev’ trains**.
- **Type II superconductors**, which include the HTSCs, ***show a gradual loss of superconductivity and diamagnetism with increasing magnetic field***.

FIGURE 23-16. Magnet levitation using a superconductor

The small magnet induces an electric current in the superconductor below it. Associated with this current is another magnetic field that opposes the field of the small magnet, causing it to be repelled. The magnet remains suspended above the superconductor as long as the superconducting current is present, and the current persists as long as the temperature of the superconductor is maintained at 10–15 K.



❑ OPTICAL PROPERTIES OF SOLIDS

- The electrical properties of semiconductors can be put to good use in optical devices. As shown in Fig. 7 there is a frequency $\nu_{min} = E/h$ below which light absorption cannot occur. Above this frequency threshold, a wide range of frequencies can be absorbed by the material.

Brief illustration: The optical properties of a semiconductor

The energy of the band gap in the semiconductor cadmium sulfide (CdS) is 2.4 eV (equivalent to 0.38 aJ). It follows that the minimum electronic absorption frequency is

$$\nu_{min} = \frac{3.8 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 5.8 \times 10^{14} \text{ s}^{-1}$$

This frequency, of 580 THz, corresponds to a wavelength of 520 nm (green light). Lower frequencies, corresponding to **yellow, orange, and red, are not absorbed and consequently CdS appears yellow-orange.**

Self-test:

Show that the colors of the following materials, given their band-gap energies (in parentheses): GaAs (1.43 eV), HgS (2.1 eV), and ZnS (3.6 eV) are **black**, **red**, and **colorless**, respectively.

➤ $E \text{ (eV)} = 1239.8 / \lambda \text{ (nm)}$

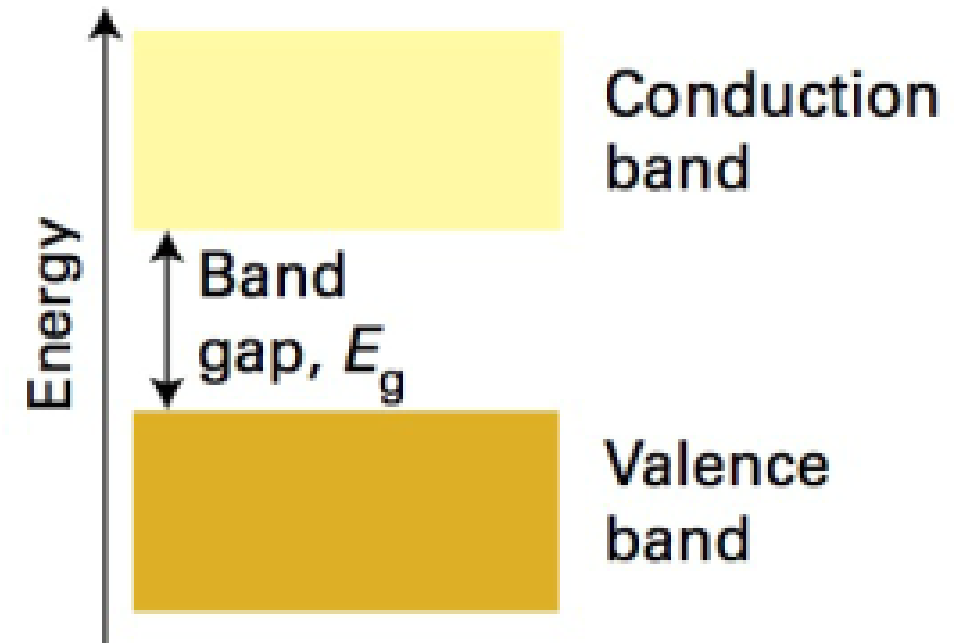
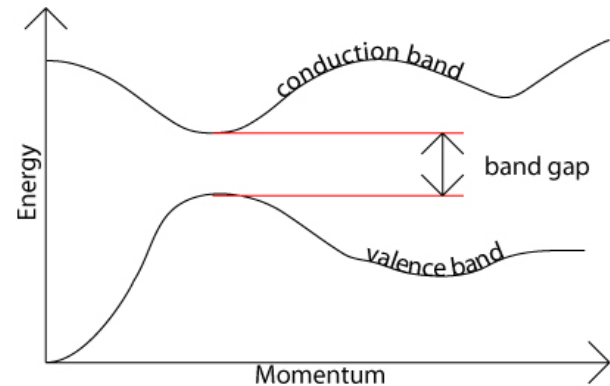


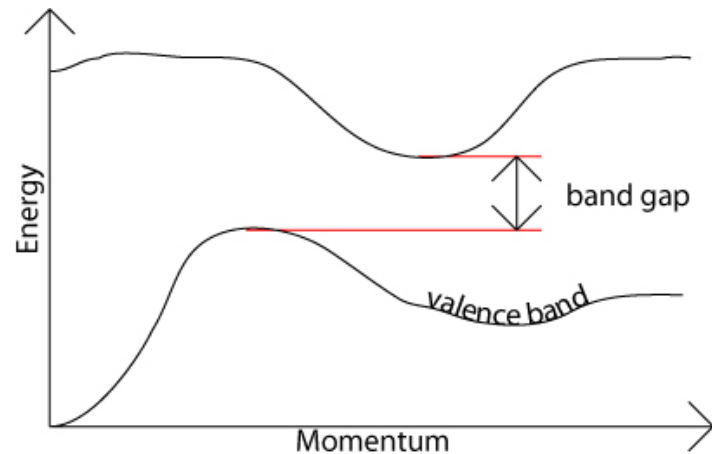
Fig . 7 In some materials, the band gap E , is very large and electron promotion can occur only by excitation with electromagnetic radiation.

Direct and Indirect Band Gap Semiconductors

➤ The band gap represents the minimum energy difference between the top of the valence band and the bottom of the conduction band, However, the top of the valence band and the bottom of the conduction band are not generally at the same value of the electron momentum. In a **direct band gap semiconductor**, the top of the valence band and the bottom of the conduction band occur at the same value of momentum, as in the schematic below.



➤ In an **indirect band gap semiconductor**, the maximum energy of the valence band occurs at a different value of momentum to the minimum in the conduction band energy:



➤ List of some semiconducting elements and compounds together with their bandgaps at 300 K.

	Material	Direct / Indirect Bandgap	Band Gap Energy at 300 K (eV)
Elements	C (diamond)	Indirect	5.47
	Ge	Indirect	0.66
	Si	Indirect	1.12
	Sn (grey)	Direct	0.08
Groups III-V compounds	GaAs	Direct	1.42
	InAs	Direct	0.36
	InSb	Direct	0.17
	GaP	Indirect	2.26
	GaN	Direct	3.36
	InN	Direct	0.70
Groups IV-IV compounds	α-SiC	Indirect	2.99
Groups II-VI compounds	ZnO	Direct	3.35
	CdSe	Direct	1.70
	ZnS	Direct	3.68

Data from R.E. Hummel, Electronic Properties of Materials, 3rd edition, Appendix 4, p. 413.

- The difference between the two is most important in optical devices. As has been mentioned in the section charge carriers in semiconductors, a photon can provide the energy to produce an electron-hole pair.
- Each photon of energy E has momentum $p = E / c$, where c is the velocity of light. An optical photon has an energy of the order of 10^{-19} J, and, since $c = 3 \times 10^8$ ms⁻¹, a typical photon has a very small amount of momentum.
- A photon of energy E_g , where E_g is the band gap energy, can produce an electron-hole pair in a direct band gap semiconductor quite easily, because the electron does not need to be given very much momentum. However, ***an electron must also undergo a significant change in its momentum for a photon of energy E_g to produce an electron-hole pair in an indirect band gap*** semiconductor. This is possible, but it requires such an electron to interact not only with the photon to gain energy, but also with a lattice vibration called a phonon in order to either gain or lose momentum.
- The ***indirect process proceeds at a much slower rate***, as it requires three entities to intersect in order to proceed: an electron, a photon and a phonon. This is analogous to chemical reactions, where, in a particular reaction step, a reaction between two molecules will proceed at a much greater rate than a process which involves three molecules.
- The same principle applies to recombination of electrons and holes to produce photons. The recombination process is much more efficient for a direct band gap semiconductor than for an indirect band gap semiconductor, where the process must be mediated by a phonon.
- As a result of such considerations, gallium arsenide and other direct band gap semiconductors are used to make optical devices such as LEDs and semiconductor lasers, whereas silicon, which is an indirect band gap semiconductor, is not. The table in the next section lists a number of different semiconducting compounds and their band gaps, and it also specifies whether their band gaps are direct or indirect.

❑ p-n Junction and Light-emitting diodes (LEDs)

- We know that major savings in energy is realized if incandescent lights are replaced by **light-emitting diodes (LEDs)**.
- A *light-emitting diode (LED)* is a *p-n junction semiconductor diode that emits light when current is passed*.
- Let us take a closer look at the operation of an LED.
- The heart of an LED is a p-n diode, which is formed by bringing an n-type semiconductor into contact with a p-type semiconductor. A p-n junction can be constructed from two pieces of silicon, one of which is n-type and the other p-type.
- The Fermi levels in the differently doped materials are different but when they are placed in contact *electrons will flow from the n-type (high potential) to the p-type (low potential) region across the junction so as to reach an equilibrium distribution in which the Fermi levels are equal*.

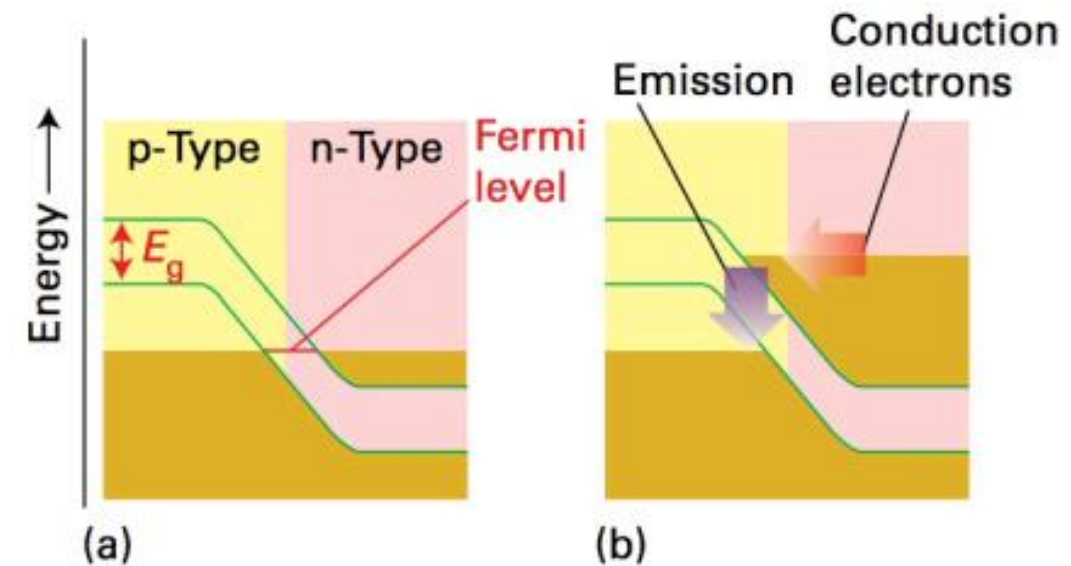


Figure. The band structure of a p-n junction (a) without bias, (b) with bias (that is, with a potential difference applied).

- The surplus of electrons in the n-type semiconductor is attracted to the surplus of holes in the p-type semiconductor. When the electrons and holes meet in the center, they annihilate each other in a process known as **recombination** and a nonconductive **depletion zone** (or barrier) is formed.
- In the absence of an applied potential, there is no net flow of charge carriers in the p–n junction.
- When the p–n junction is connected to an external power source, such as a battery, with the positive electrode attached to the p-type semiconductor and the negative electrode attached to the n-type semiconductor, the material operates under a *forward bias* (Figure 11.53(a)).
- The holes in the p-type semiconductor are repelled away from the positive terminal and toward the depletion zone, while the electrons in the n-type semiconductor are repelled away from the negative terminal toward the depletion zone. As a result of this bias, the **barrier at the p–n junction gets thinner** and, ultimately, **electrons are able to tunnel across the barrier** so that current flows through the material from right to left in the diagram.

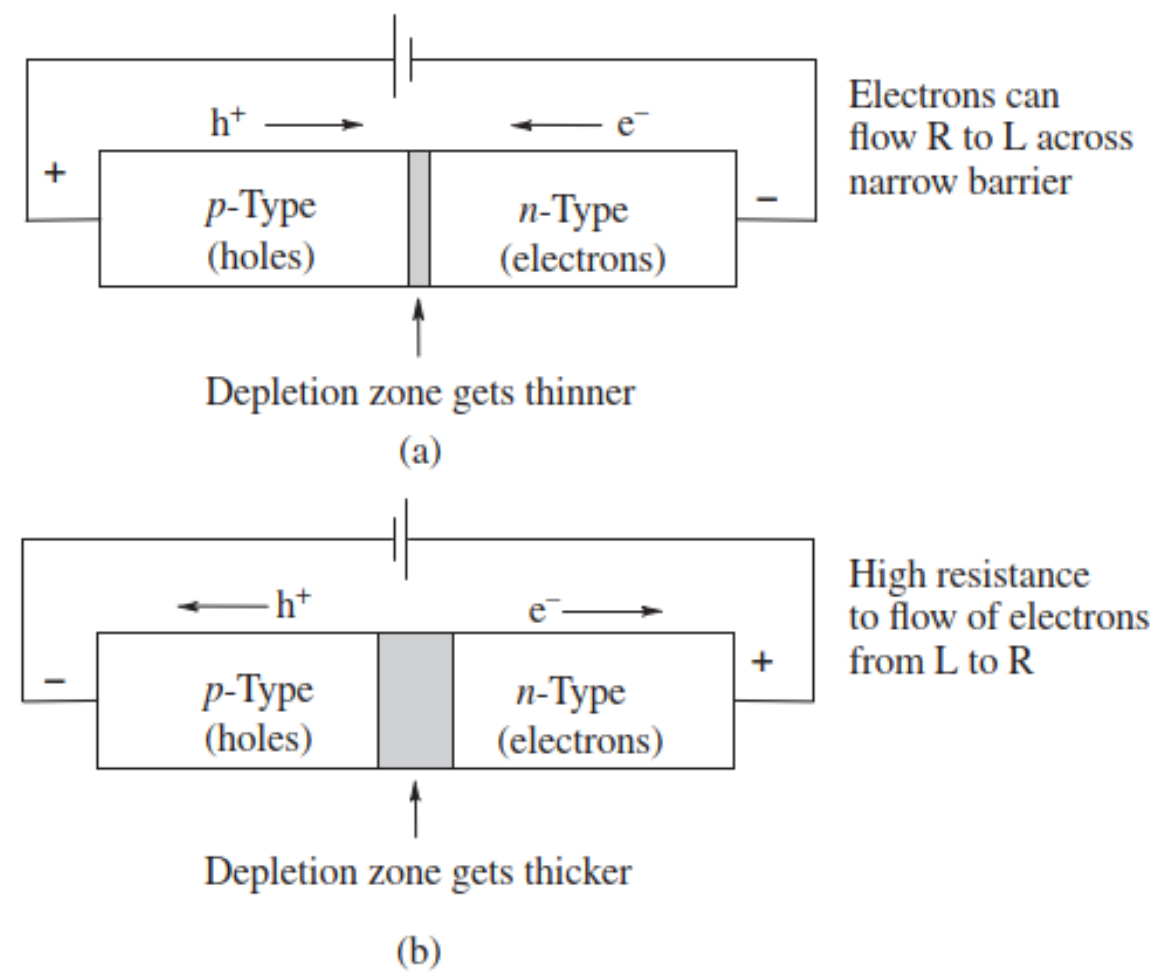


FIGURE 11.53 A p–n junction under: (a) forward bias allows the flow of electrons from right to left and (b) reverse bias prevents the flow of electrons from left to right.

- On the other hand, if the p-type semiconductor is connected to the negative terminal of a power source and the n-type semiconductor connected to the positive terminal, the material acts under a *reverse bias*, as shown in Figure 11.53(b). The holes in the p-type semiconductor are attracted to the negative terminal and the electrons in the n-type semiconductor are attracted to the positive terminal. The net result is that the ***depletion zone at the p–n junction gets larger*** and there is a *high resistance to electron flow across the circuit*. Thus, **the p–n junction acts as a diode**, an electrical switch that allows current to flow in only one direction (from right to left in Figure 11.53) and not in the opposite direction.
- Diodes lie at the heart of all sorts of electronic devices, from photovoltaic cells (where light energy is used to produce the charge carriers) to transistors (which consist of two p–n junctions in series, such as the common n–p–n bipolar junction transistor, or BJT).
- The unique electrical properties of p–n junctions between semiconductors can be put to good use in ***optical devices, light-emitting diodes (LEDs)***.
- ✓ In some materials, the ***energy from electron–hole recombination is released not as heat but is carried away by photons*** as electrons move across the junction driven ***by the appropriate potential difference***.
- ✓ Practical ***light-emitting diodes*** of this kind are widely used in electronic displays.

- *When an appropriate voltage is applied, electrons are driven from the conduction band of the n-doped side into the junction, where they meet holes that have been driven from the valence band of the p-doped side. The electrons fall into the empty holes, and their energy is converted into light whose photons have energy equal to the band gap (Figure 12.32).*
- ***As the electrons fall from the upper band into the lower, they release energy.** This way electrical energy is converted into **thermal** or **optical** energy.*

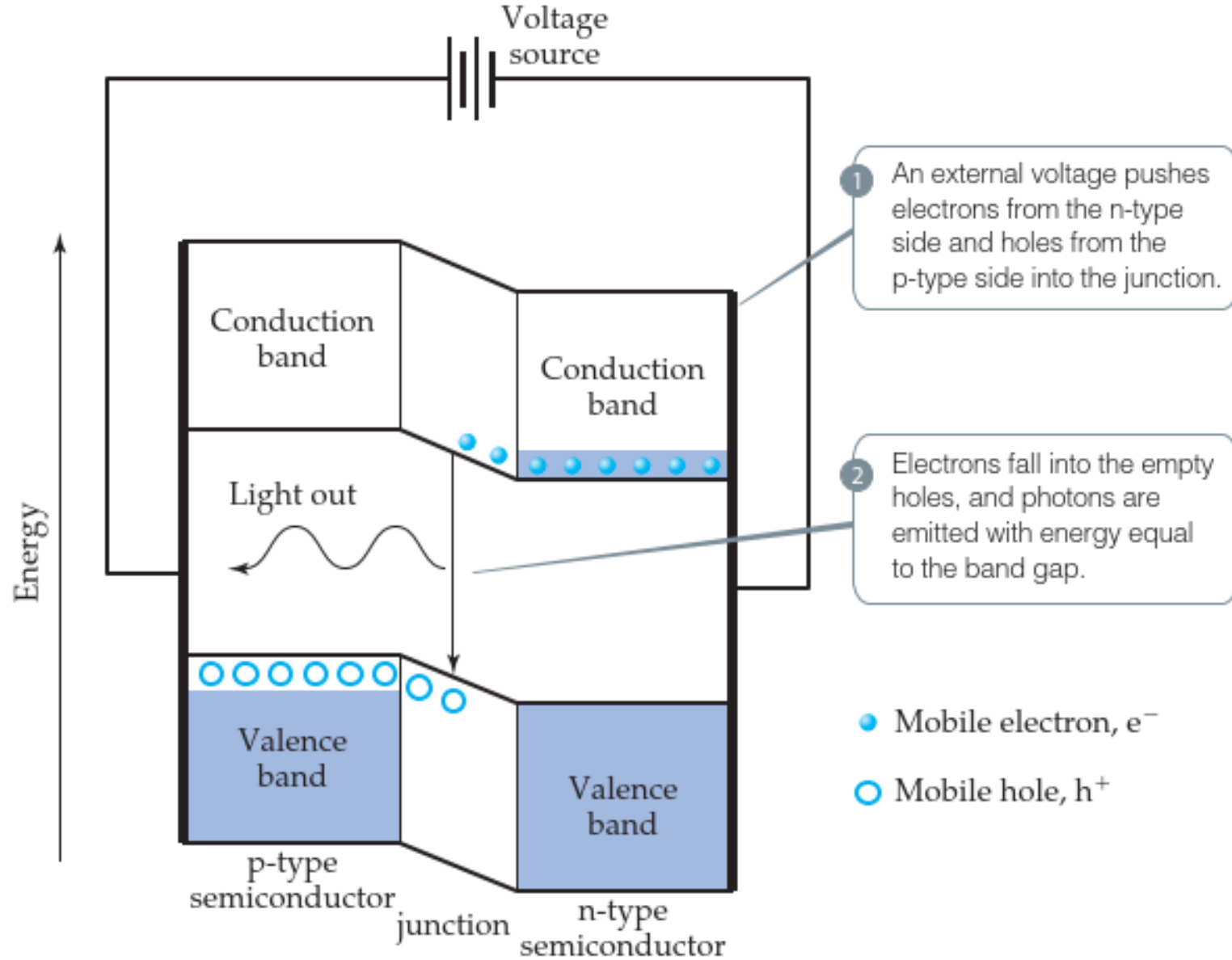


Figure 12.32 Light-emitting diodes. An applied voltage drives electrons and holes together at the light-emitting diode is a p-n junction where they combine and give off light.

- In some solids the wavelengths of the wavefunctions in the upper and lower states are different, which means that *the **linear momenta** (through the de Broglie relation, $p = h/\lambda$) of the electron in the initial and final states are **different**. As a result, the transition can occur only if the electron transfers linear momentum to the lattice: the device becomes **warm*** as the atoms are stimulated to vibrate.
- ✓ This is the case for silicon semiconductors and is one reason why computers need efficient cooling systems.
- **In some materials**, most notably gallium arsenide, GaAs, *the wavefunctions of the initial and final states of the electron have the same wavelengths and therefore correspond to **the same linear momentum***. As a result, transitions can occur without the lattice needing to participate by mopping up the difference in linear momenta. ***The energy difference is therefore emitted as light.***
- Practical light-emitting diodes of this kind are widely used in electronic displays.

- *Because the wavelength of light that is emitted depends on the band gap of the semiconductor, the color of light produced by the LED can be controlled by appropriate choice of semiconductor.*
- Most red LEDs are made of a mixture of GaP and GaAs. The band gap of GaP is 2.26 eV (3.62×10^{-19} J), which corresponds to a green photon with a wavelength of 549 nm, while GaAs has a band gap of 1.43 eV (2.29×10^{-19} J), which corresponds to an infrared photon with a wavelength of 867 nm.
- Gallium arsenide (GaAs) itself emits infrared light, but the width of the **band gap is increased by incorporating phosphorus**. By forming solid solutions of these two compounds, with stoichiometries of $\text{GaP}_{1-x}\text{As}_x$, *the band gap can be adjusted to any intermediate value*. Thus, **$\text{GaP}_{1-x}\text{As}_x$ is the solid solution of choice for red, orange, and yellow LEDs**. Green LEDs are made from mixtures of GaP and AlP ($E_g = 2.43$ eV, $\lambda = 510$ nm).
- ✓ For example, a material of composition approximately $\text{GaAs}_{0.6}\text{P}_{0.4}$ emits red light, and diodes emitting orange and amber light can also be made with different proportions of Ga, As, and P.
- The spectral region ranging from yellow to blue can be covered by using gallium phosphide (yellow or green light) and gallium nitride (green or blue light).
- White LEDs are commonly formed from yellow and blue LEDs mixed in various proportions.

- Red LEDs have been in the market for decades, but to make white light, an efficient blue LED was needed. The first prototype bright blue LED was demonstrated in a Japanese laboratory in 1993. In 2010, less than 20 years later, over \$10 billion worth of blue LEDs were sold worldwide.
- The blue LEDs are based on combinations of GaN ($E_g = 3.4$ eV, $\lambda = 365$ nm) and InN ($E_g = 2.4$ eV, $\lambda = 517$ nm).
- Many colors of LEDs are now available and are used in everything from barcode scanners to traffic lights.

LED colours

LED colour	Chip material	
	Low brightness	High brightness
Red	GaAsP/GaP	AlInGaP
Orange	GaAsP/GaP	AlInGaP
Amber	GaAsP/GaP	AlInGaP
Yellow	GaP	—
Green	GaP	GaN
Turquoise	—	GaN
Blue	—	GaN

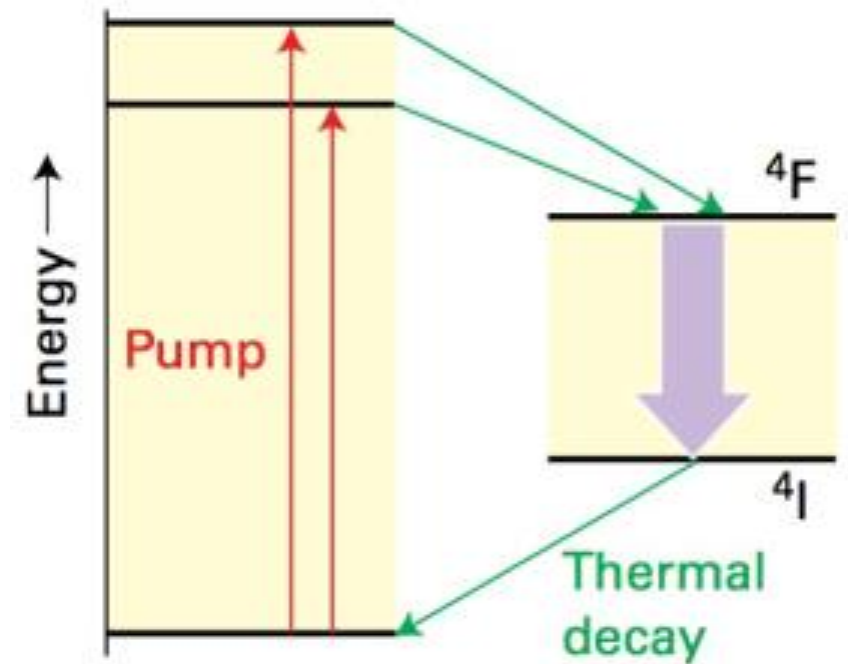
- LEDs are *highly monochromatic*, emitting a pure color in a narrow frequency range. ***The color is controlled by the band gap***, with small band gaps producing radiation in the infrared and red regions of the electromagnetic spectrum and larger band gaps resulting in emission in the blue and ultraviolet regions (see table).
- It is possible to produce white light with a single LED by using a phosphor layer (Ce:YAG, cerium-doped yttrium aluminium garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) on the surface of a blue, gallium nitride, LED. These white light LEDs are highly efficient at converting electricity into light, much more so than incandescent lamps and even 'low-energy' fluorescent lights. Because the light emission results from *semiconductor structures that can be made extremely small and because they emit little heat*, **LEDs are replacing standard incandescent and fluorescence light bulbs in many applications.**

❑ Diode lasers

- Another advantage of being able to produce blue LEDs is that they can be used as lasers in high-capacity optoelectronic storage devices.
- In **diode lasers** are used in **CD players** and *bar-code readers*.
- *A light-emitting diode is not a laser because stimulated emission is not involved.*
- In diode lasers, light emission due to electron–hole recombination is employed as the basis of laser action, and ***the population inversion can be sustained by sweeping away the electrons that fall into the holes of the p-type semiconductor.*** This process is arranged to occur in a cavity formed by making use of the abrupt difference in refractive index between the different components of the junction, and the radiation trapped in the cavity enhances the production of more radiation.
- One widely used material is GaAs doped with aluminium ($\text{Ga}_{1-x}\text{Al}_x\text{As}$), which produces 780 nm red laser radiation and is widely used in CD players.
- The newer generation of DVD players that use blue rather than red laser radiation, so allowing a greater density of information on the surface of the disc, use GaN as the active material.

High-power diode lasers are also used to pump other lasers. One example is the pumping of Nd:YAG lasers by $\text{Ga}_{0.91}\text{Al}_{0.09}\text{As}/\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ diode lasers.

Fig. 10 The transitions involved in a neodymium laser. The neodymium laser is an example of a four-level solid-state laser. In one form it consists of Nd^{3+} ions at low concentration in yttrium aluminium garnet (YAG, specifically $\text{Y}_3\text{Al}_5\text{O}_{12}$) and is then known as a Nd:YAG laser. A neodymium laser operates at a number of wavelengths in the infrared. The most common wavelength of operation is 1064 nm, which corresponds to the electronic transition from the ^4F to the ^4I state of the Nd^{3+} ion.



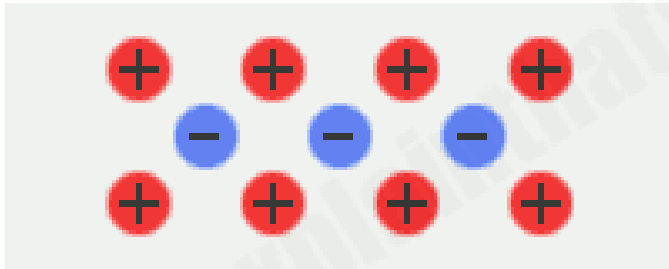
❑ Other Electrical and Optical Properties of Crystals

❖ Electrical Properties of Crystals: Piezoelectricity

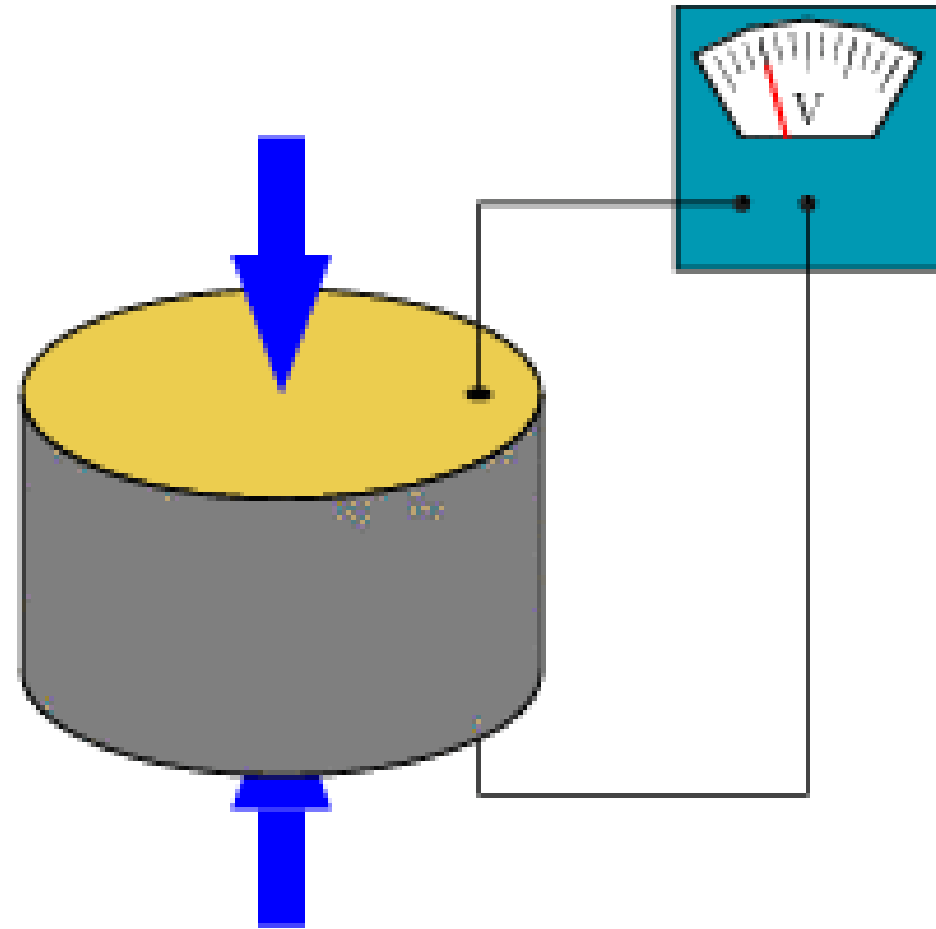
- The symmetry elements of a molecule tell us much about its properties, and the symmetry elements of a unit cell tell us much about the properties of the crystal.
- For example, the unit cell of a crystal has no dipole moment if it meets either or both of these criteria:
 - 1. All the bond dipoles lie perpendicular to either a C_n proper rotation axis or to a σ mirror plane.
 - 2. The molecule has a S_{2n} symmetry element (including inversion, because $I = S_2$).
- As a result, only certain crystallographic point groups yield polar unit cells.
- ***If the unit cell is polar, the charge density at one end of the unit cell is greater than at the other end, and this pattern is repeated throughout the crystal.***
- *Polar crystals, whatever the bonding mechanism, may exhibit some useful electrical characteristics that arise from the high degree of order not found in amorphous solids.*
- A ferroelectric crystal has a ***net charge separation from one end to the other*** due to a large number of co-aligned dipole moments. ***Such a crystal, if left to move freely, will align itself under the influence of an electric field.***

- The *aligned dipole moments in the ferroelectric crystal correspond to a net charge separation throughout the crystal* and therefore correspond to an electrostatic potential energy—what we call *voltage*—from one end of the crystal to the other.
- This voltage is sensitive to the *spacing between the molecular dipoles*, so when the crystal is compressed, the voltage changes.
- Looking at it from the other perspective, applying a voltage to such a crystal can compress it or expand it.
- Crystals that deform under the influence of applied voltages are called **piezoelectric crystals**.
- **Piezoelectricity** is possible in crystals belonging to any of the crystallographic point groups *except* O (orthogonal group) and those *with centers of inversion* (called centrosymmetric crystals).
- Of the 20 remaining crystallographic point groups, some are polar and will compress or expand along one axis when a voltage is applied. Some others are not normally polar (and therefore not ferroelectric) but may become polar when twisted.
- The piezoelectric crystal is a common component in *applications that require very fast and precise distance adjustments*. The crystal dimensions are usually changed by a factor of only 10^{-6} or less using the piezoelectric effect, but for *small distance measurements*, such as those in *atomic force microscopy*, this is ideal.

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- A related effect is **pyroelectricity**, which is the **generation of voltage** by the **heating** or **cooling of a crystal**.
- Because substances tend to expand when heated and contract when cooled, ***changes in temperature of polar crystals tend to change the overall dipole moment and voltage of the crystal.***
- Many polar crystals also have valuable **optical properties** resulting from the interaction of the electrons with the electric field of the radiation. For example, **the frequency of a beam of electromagnetic radiation may be doubled by sending the beam through a non-centrosymmetric crystal.**
- The incident radiation carries an oscillating electric field through the crystal, a field that deforms the electronic wavefunction, and therefore the electric field, of the crystal. ***The extent to which the electric field of the crystal is changed increases with the polarizability of the electrons and with the intensity of the radiation.***
- In any of the *non-centrosymmetric crystals*, the *electron distribution is more easily pushed in one direction than in the opposite direction by the radiation's electric field*. This is equivalent to multiplying a fraction of the incident radiation by a damping factor that varies at the frequency of the radiation's electric field.

❑ Other Electrical and Optical Properties of Crystals

❖ Nonlinear optical phenomena

- ***Nonlinear optical phenomena arise*** from changes in the optical properties of a material *in the presence of intense electromagnetic radiation*.
- In frequency doubling (or '***second harmonic generation***'), an intense laser beam is converted to radiation with twice (and in general a multiple) of its initial frequency as it passes through a suitable material.
- It follows that frequency doubling and tripling of an Nd:YAG laser, which emits radiation at 1064 nm, produce green light at 532 nm and ultraviolet radiation at 355 nm, respectively.
- Common materials that can be used for frequency doubling in laser systems include crystals of potassium dihydrogenphosphate (KH_2PO_4), lithium niobate (LiNbO_3), and β -barium borate ($\beta\text{-BaB}_2\text{O}_4$).

❖ Nonlinear optical phenomena

- Frequency doubling can be explained by examining how a substance responds nonlinearly to incident radiation of frequency $\omega = 2\pi\nu$.
- Radiation of a particular frequency arises from oscillations of an electric dipole at that frequency and the *incident **electric field** E of the radiation induces an electric dipole moment of magnitude μ* , in the substance.
- At low light intensity, most materials respond linearly, in the sense that $\mu = \alpha E$, where **α is the polarizability**.
- At high light intensity, the **hyperpolarizability β** of the material becomes important and the induced dipole becomes $\mu = \alpha E + \frac{1}{2}\beta E^2 + \dots$.
- The *nonlinear term βE^2* can be expanded as follows if it is supposed that *the incident electric field is $E_0 \cos \omega t$* :
$$\beta E^2 = \beta (E_0 \cos \omega t)^2 = \beta E_0^2 \cos^2 \omega t = \frac{1}{2} \beta E_0^2 (1 + \cos 2\omega t). \quad (\text{using } \cos^2 \theta = \frac{1}{2}(1 + \cos 2\theta))$$
- Hence, ***the nonlinear term contributes an induced electric dipole that includes a component that oscillates at the frequency 2ω and that can act as a source of radiation of that frequency.***