

# **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

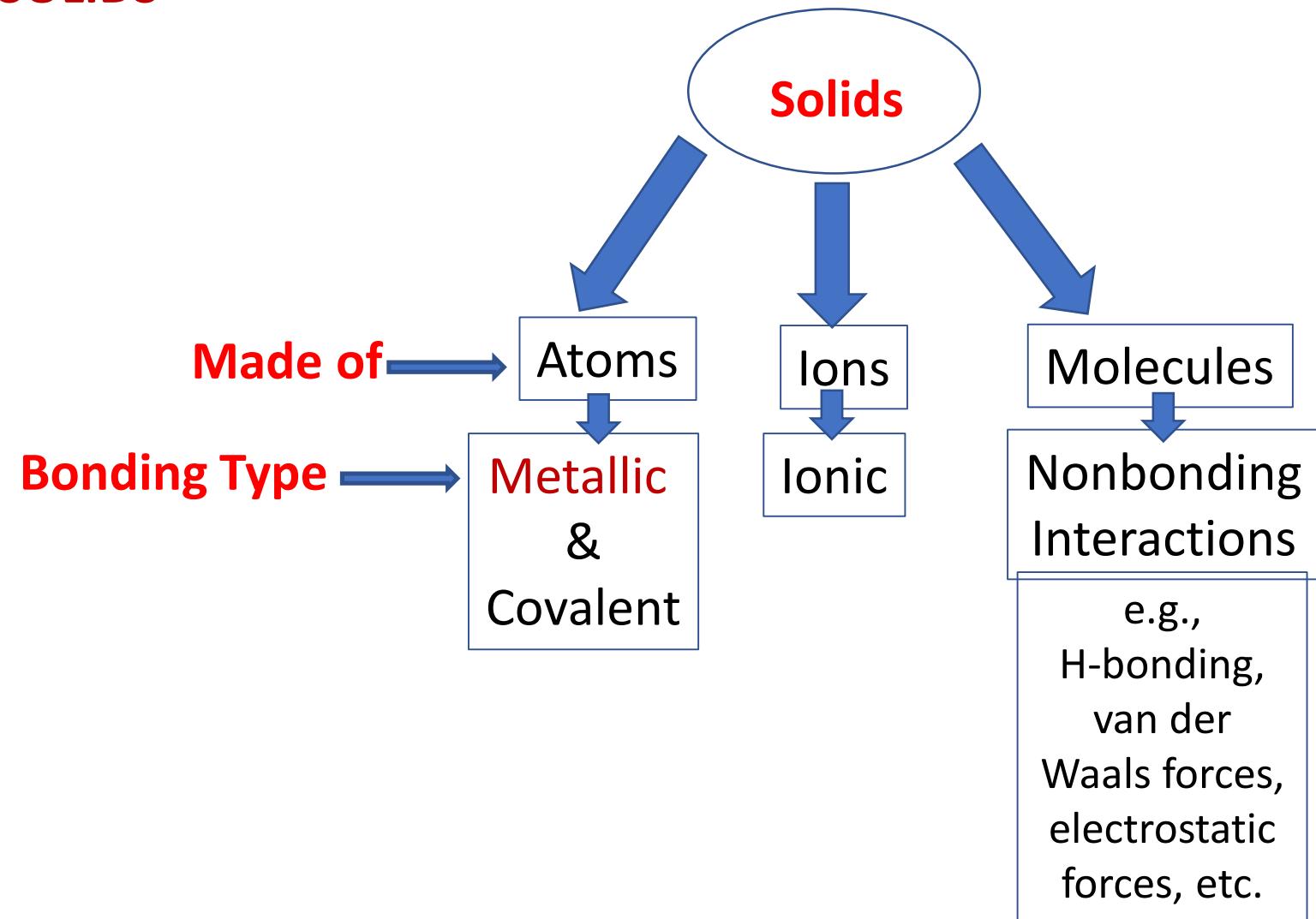
## Introduction

- *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 ( $\text{HfO}_2$ , also known as hafnium dioxide or hafnia. This colorless solid is an electrical insulator with a band gap of 5.3~5.7 eV. The advantage for transistors is its high dielectric constant: the dielectric constant of  $\text{HfO}_2$  is 4–6 times higher than that of  $\text{SiO}_2$ ).

□ 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 <sub>2</sub>
<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 <sub>2</sub> O, Br <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub>
<i>Covalent network</i>	Covalent bonds	Hard, high-melting	SiO <sub>2</sub> , 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*.

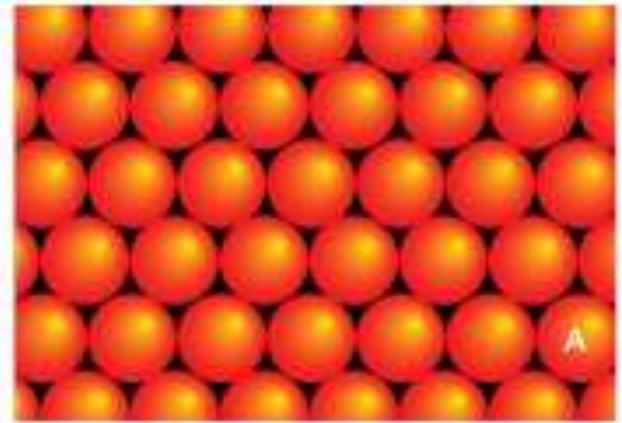
### □ Amorphous Solids

- 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.

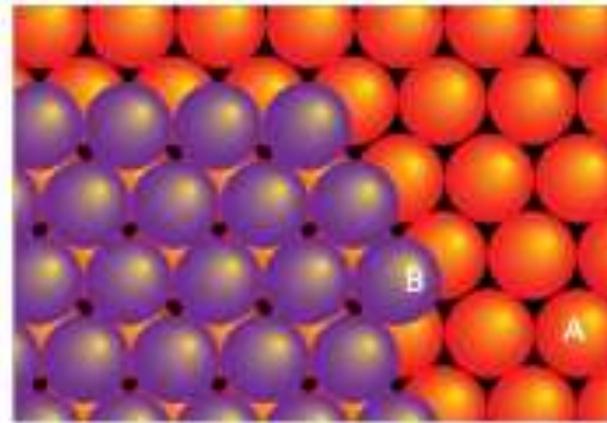
- Not all amorphous solids are glasses.
- For example, liquid silicon dioxide is structurally identical to window glass: the bonding mechanisms, short-range order, electrical properties, density, and so forth, are the same.
- ***Pure elemental silicon, on the other hand, has a liquid state that is very 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

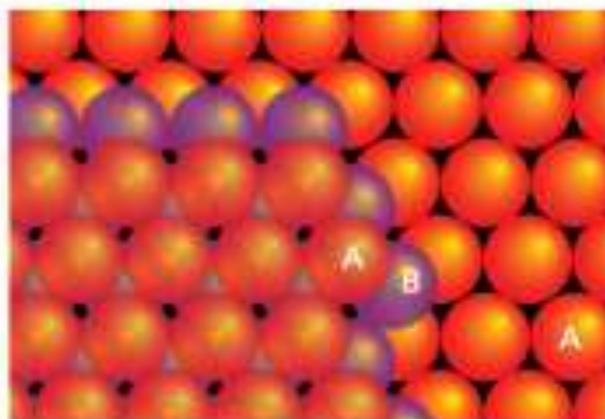
- Most metallic elements crystallize in one of three simple forms, *two of which* can be explained *in terms of stacking rigid spheres as close together as possible*.
- In such close-packed structures the spheres representing the atoms are packed together with least waste of space and each sphere has 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 2<sup>nd</sup> layer spheres were not placed), so giving an ***ABC ABC*** pattern.



2<sup>nd</sup> Layer

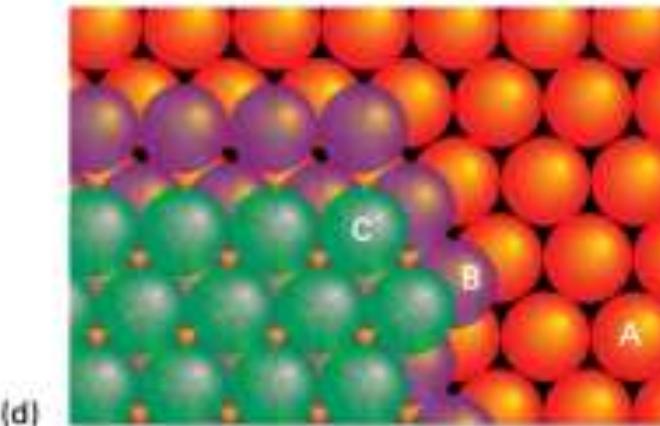


3<sup>rd</sup> Layer



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

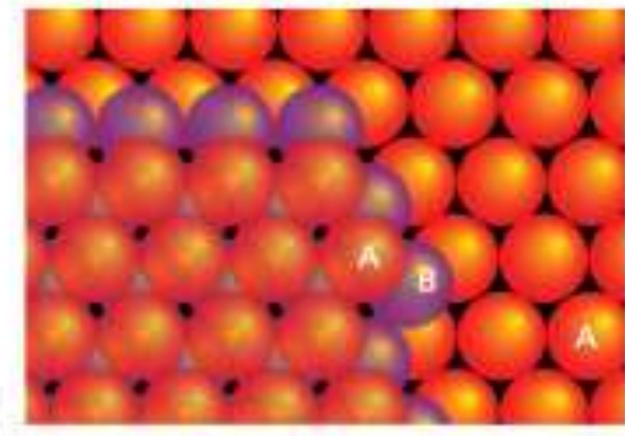
Hexagonal close packing (hcp)



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



Hexagonal close packing (hcp)

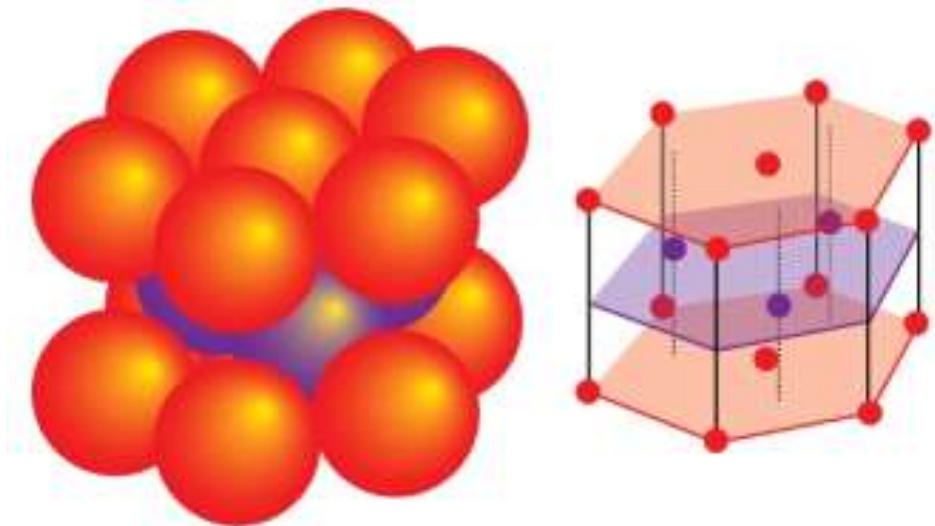
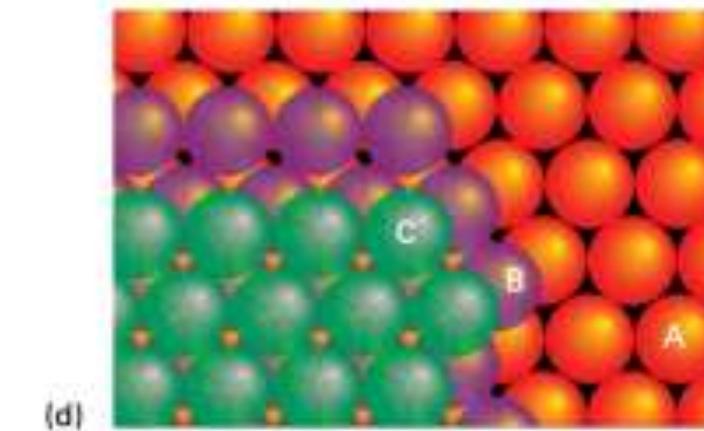


Fig. 2 A hexagonal close-packed structure.



Cubic close packing (ccp)

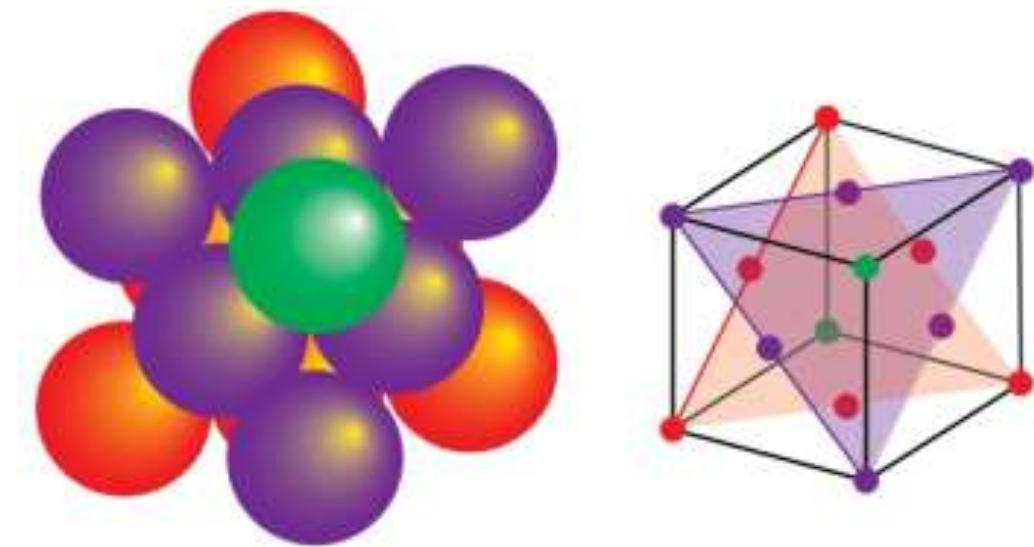
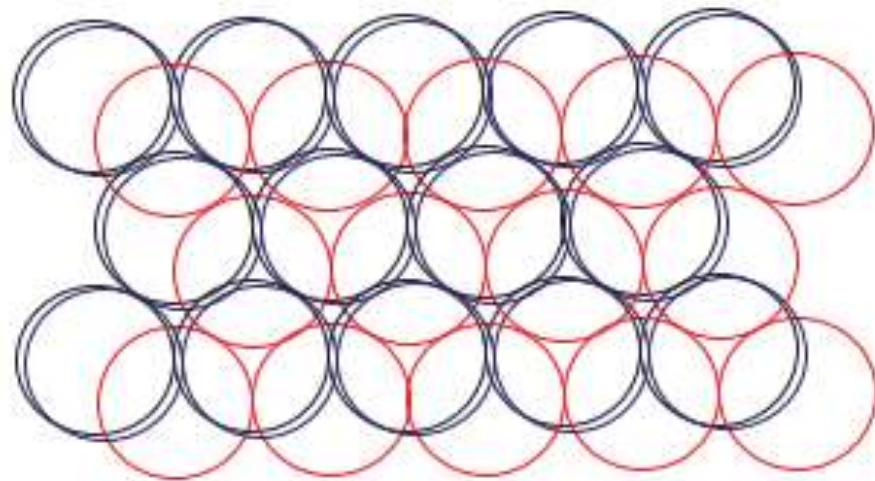
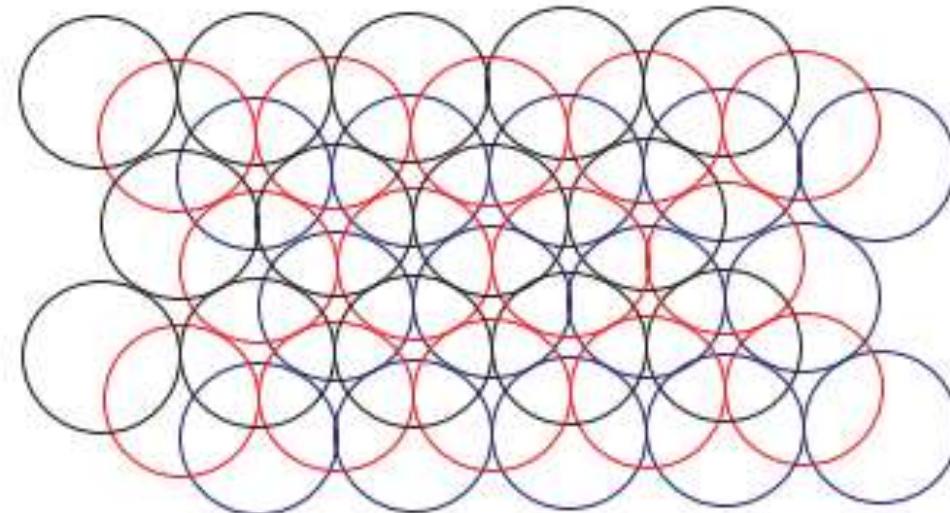


Fig. 3 A cubic close-packed structure.

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



(a)



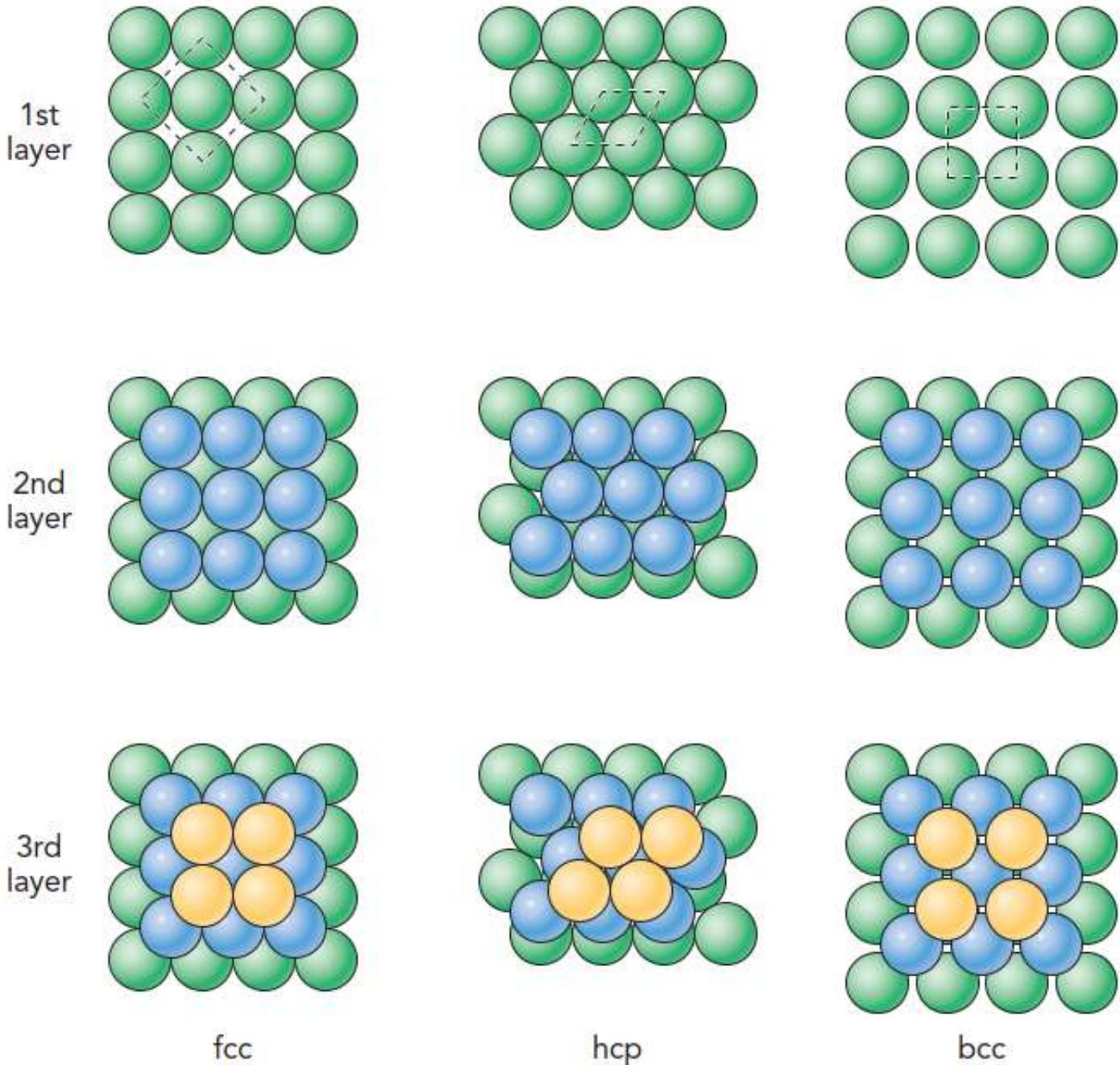
(b)

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.

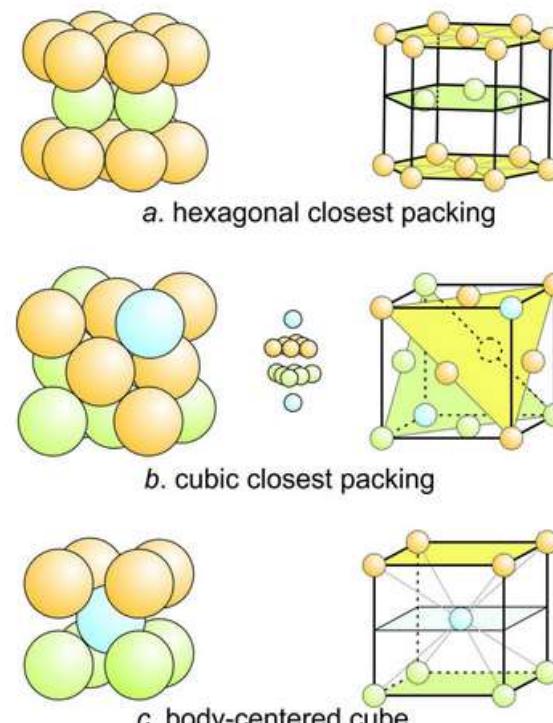
- Not all metals can take advantage of these arrangements, however, because a high density of metal cations **needs** to be **stabilized** by a high density of valence electrons.
- Metals such as the **alkali metals**, having a low number of valence electrons, often tend instead to adopt the **body-centered 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: Copper, which is ccp, is highly malleable, but zinc, which is hcp, is more brittle.

- 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.



❖ **Metals with a high density of electrons are more likely to adopt the fcc.**

- Many factors determine **whether a particular metal adopts** the fcc, hcp, bcc lattice, or some other configuration. 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.
- **One of the conclusions is that the bcc lattice is better suited to metals with few valence electrons.**

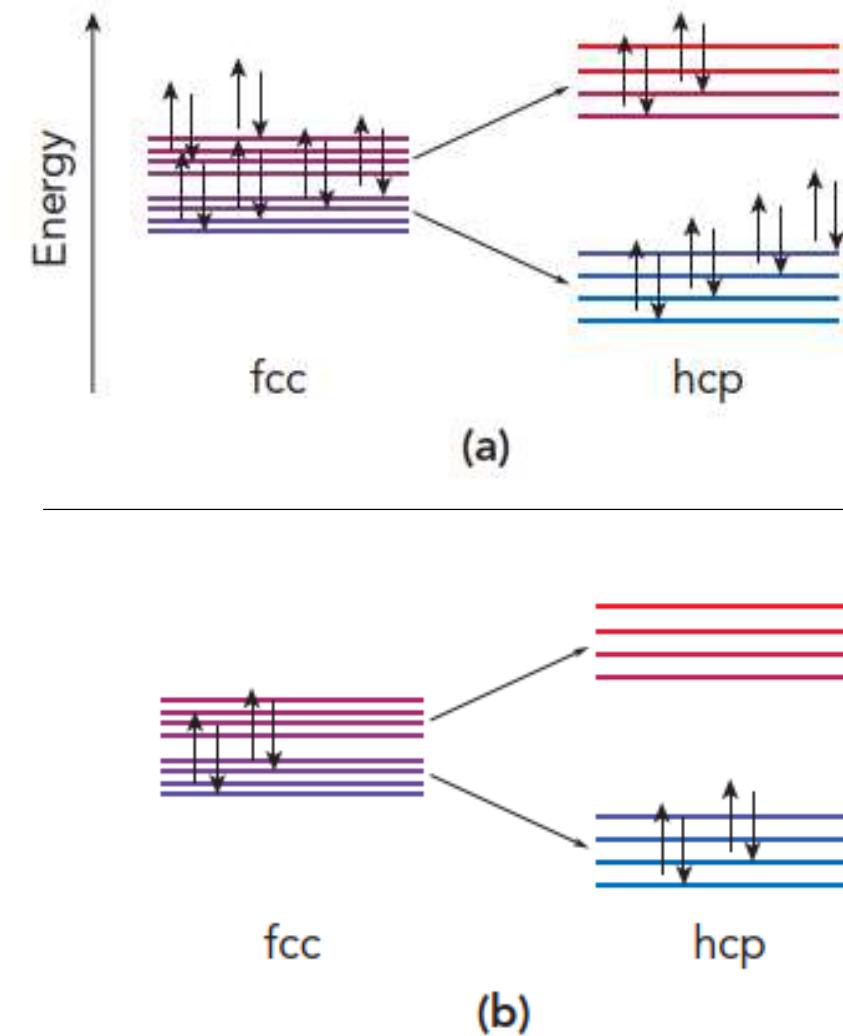
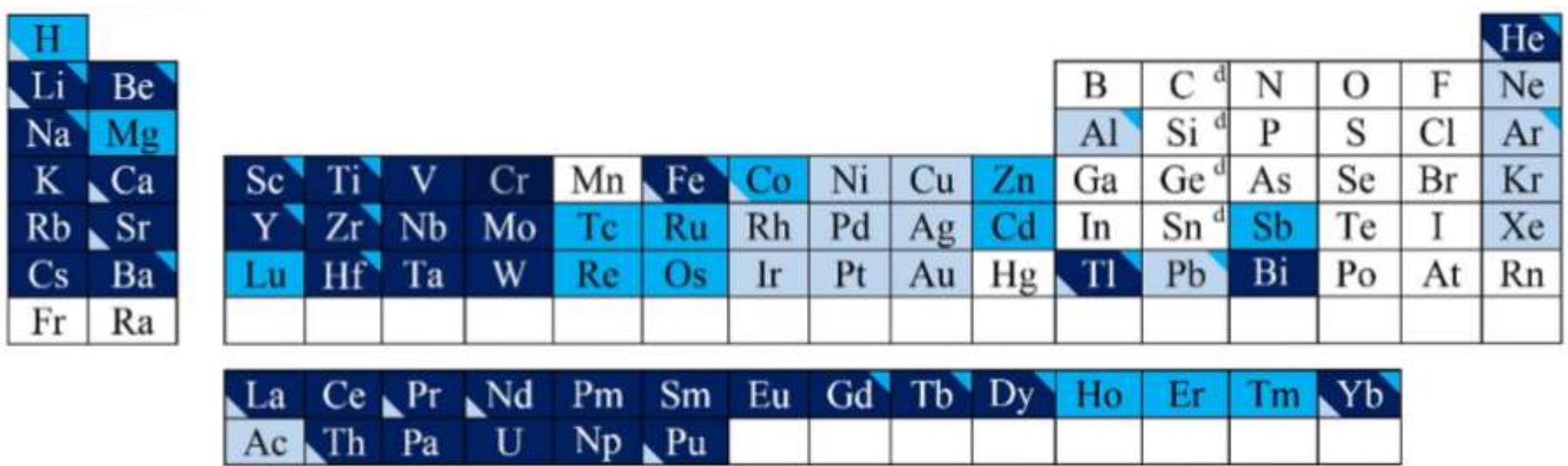


Figure 13.9 Schematic energy level diagrams of electronic states in the fcc and hcp lattices. The diagrams illustrate how **the higher degeneracy of the fcc lattice better accommodates electron-rich metals (a)**, whereas electron-poor metals will tend to prefer the lower symmetry hcp lattice (b).

- 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  $\alpha$ -Fe) to fcc ( $\gamma$ -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.*

Three types of packing present in the metals are represented in a classification: there are

- 40 of cubic I (**dark blue**),
  - 33 elements of hexagonal close-packed type (**medium blue**), and
  - 28 of cubic F (**light blue**) that refer to metals and rare gases (see Figure 2.14).
  - Non-metals (except for rare gases) yield diversified types that have not been mentioned here.
  - Only the diamond packing is evidenced for column 14 (except for lead).
  - Some metals may have various types of packing depending on temperature; for example, lithium, iron and thallium present all three types.



**Figure 2.14.** Main types of packing in metals.

## 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  $\text{Cl}_2$  molecule,  $(8 - 7 = 1)$ ;
- Sulfur ( $N=6$ ): each S atom forms 2 bonds as in  $\text{S}_8$  molecule  $(8 - 6 = 2)$ ;
- Phosphorus ( $N=5$ ): each P atom forms 3 bonds as in  $\text{P}_4$  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 (fcc) 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**.

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

**Figure: Bonding in period 3 elements.**

$$N =$$

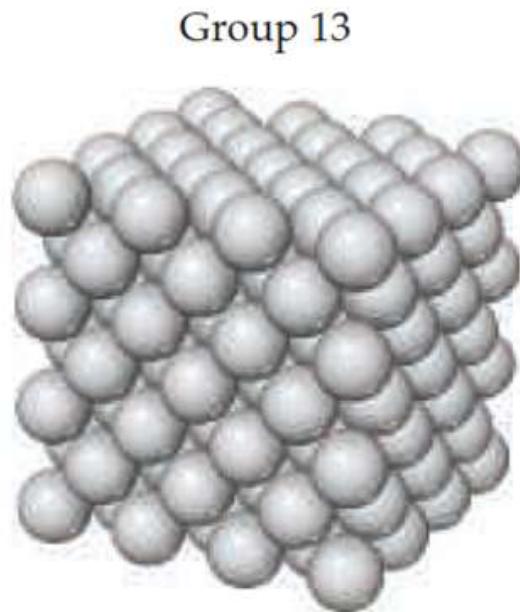
3

4

5

6

7

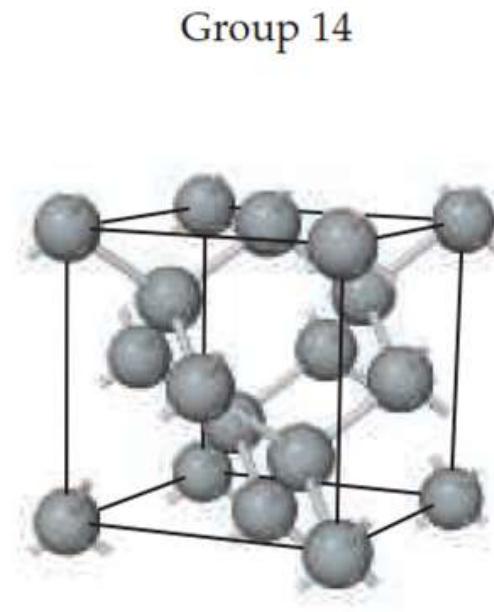


Al  
12 nearest neighbors

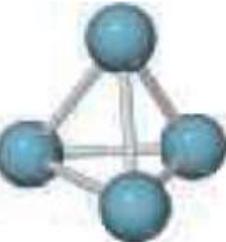
$$8 - 3 = 5 \dots ?? \times$$

*e- sharing*

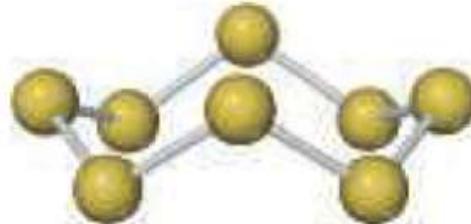
Metallic bonding



Si  
4 valence electrons  
 $8 - 4 = 4$  bonds per atom



5 valence electrons  
 $8 - 5 = 3$  bonds per atom



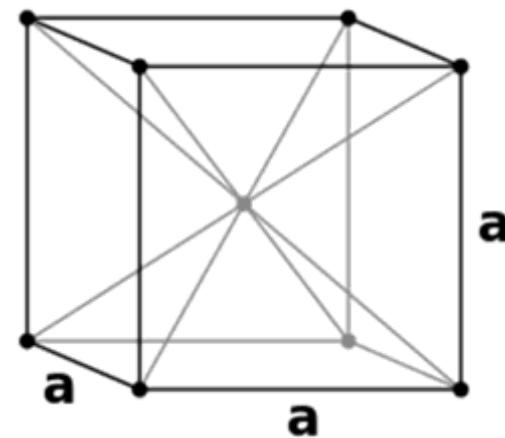
$S_8$   
6 valence electrons  
 $8 - 6 = 2$  bonds per atom



7 valence electrons  
 $8 - 7 = 1$  bond per atom

Covalent bonding

- The electron pair description of chemical bonds, which was the basis of the ***octet rule*** for p-block compounds, ***breaks down for metals***. This is illustrated well by Na metal, the structure of which is shown at the left. Na has too few valence electrons to make electron pair bonds between each pair of atoms. We could think of the Na unit cell as having eight no-bond resonance structures in which only one Na-Na bond per cell contains a pair of electrons.
- Sodium metal crystallizes in the ***body-centered cubic*** structure, in which each atom has eight nearest neighbors. Since the electronic configuration of Na is [Ar]3s<sup>1</sup>, there are ***only two valence electrons per unit cell*** that are shared among eight Na-Na bonds. This means that the ***Na-Na bond order is 1/8 in Na metal***.
- 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.



## 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  $\text{ReO}_3$  and ‘fool’s gold’ (iron pyrites,  $\text{FeS}_2$ ), illustrate the occurrence of metallic bonding in compounds.

## BONDING in SOLIDS: Metallic Bonding

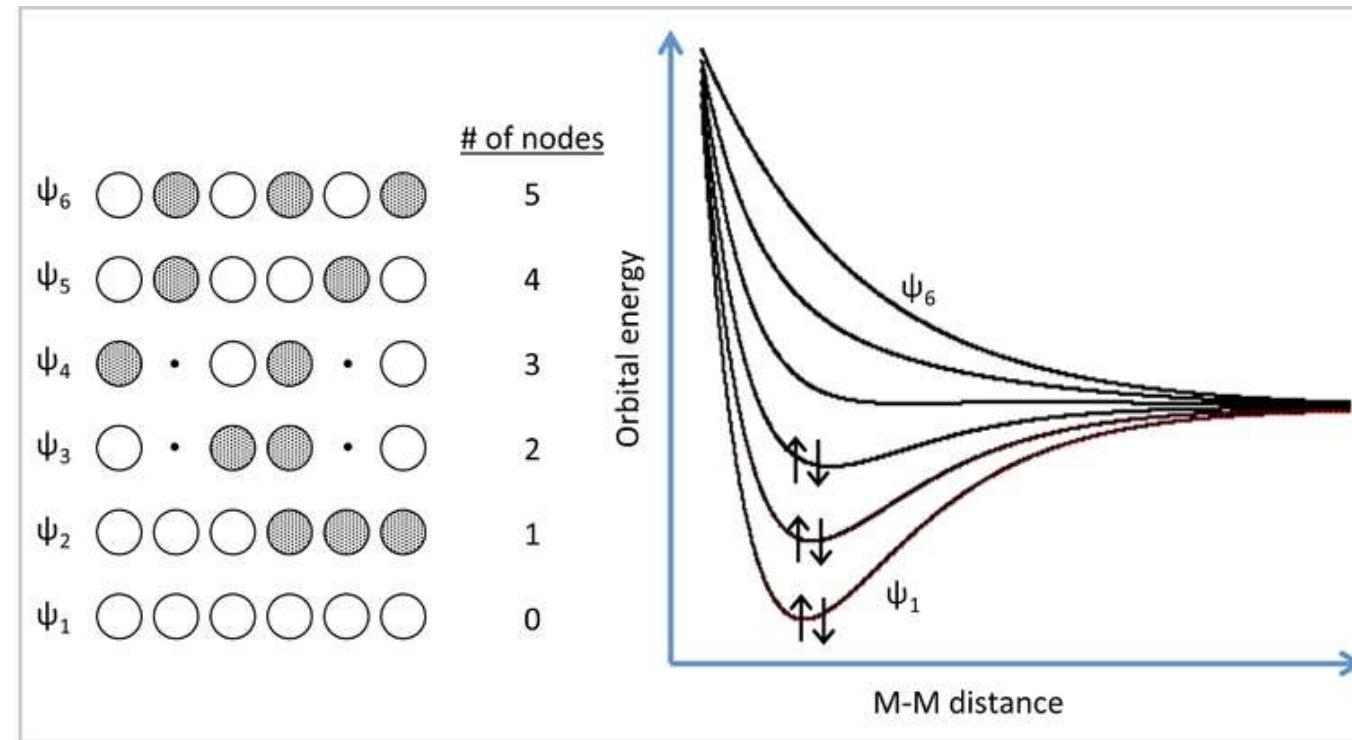
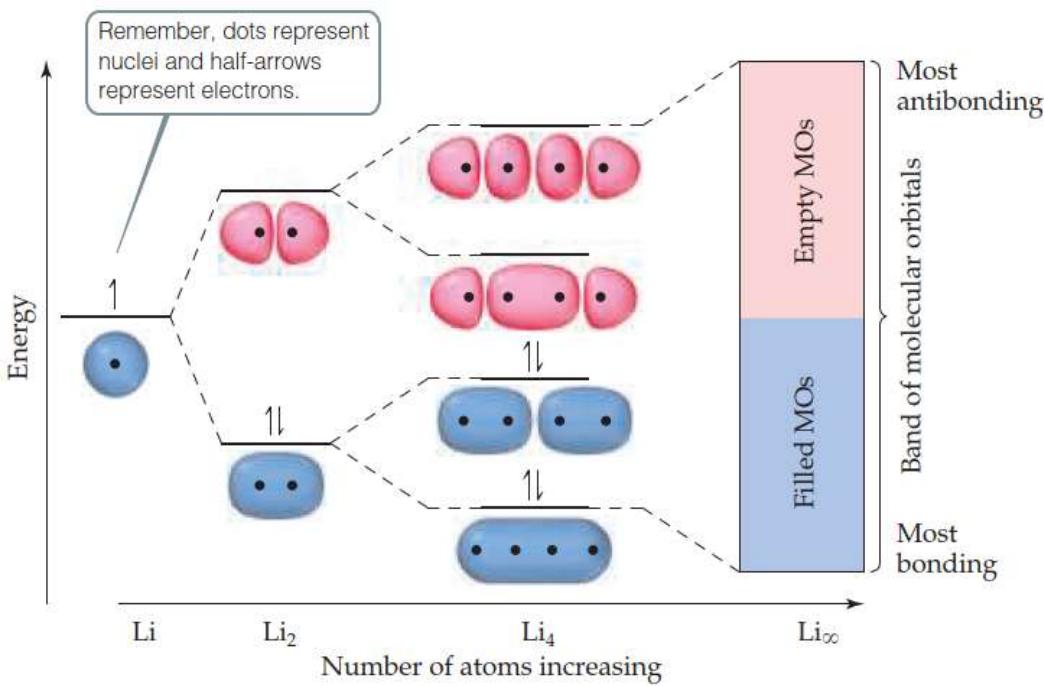
- The familiar properties of a metal stem from the characteristics of its bonding and in particular *the delocalization of electrons throughout the solid*.
- Thus, metals are *malleable (easily deformed by the application of pressure)* and *ductile (able to be drawn into a wire)* because the **electrons 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 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  $\text{Cl}^-$  ions, and the Na atoms, which have *low valence electron density*, are present as  $\text{Na}^+$  ions.
- A more realistic way to describe the bonding in solids is through **band theory**.

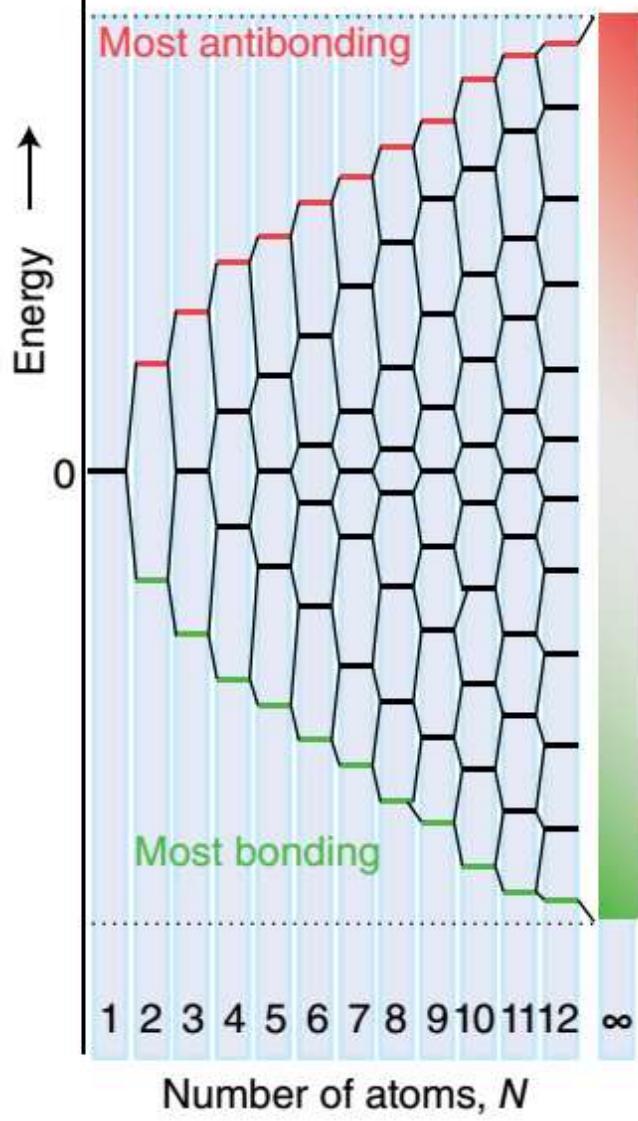
- To set up the molecular orbital theory of solids consider initially a single, infinitely long line of identical atoms, each one having an *s* orbital available for forming molecular orbitals (as in sodium). In a homogeneous metallic solid, the valence AOs can combine with one another to form MOs.
- One atom of the solid contributes an *s* orbital with a certain energy (Fig. 12.12). When *a second atom is brought up it forms a bonding and antibonding orbital*. For a homonuclear diatomic, such as  $\text{Li}_2$ , there are two MOs: one bonding and one antibonding, as shown in Figure 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*).
- In general, **n** atomic orbitals will generate **n** molecular orbitals with **n-1** possible nodes.
- We showed that the energy versus internuclear distance graph for a two-hydrogen atoms system has a low energy level and a high energy level corresponding to the bonding and antibonding molecular orbitals, respectively. These two energy levels were well separated from each other, and the two electrons in  $\text{H}_2$  energetically prefer the lower energy level.
- If more atoms are introduced to the system, there will be a number of additional levels between the lowest and highest energy levels.

➤ 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.***



**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.

MO picture for a linear chain of six Li atoms. Three of the six MOs can accommodate all six valence electrons. Adding more atoms to the chain makes more molecular orbitals of intermediate energy, which eventually merge into a continuous band of orbitals. For Li, the 2s band is always half-filled because each MO can accommodate two electrons.

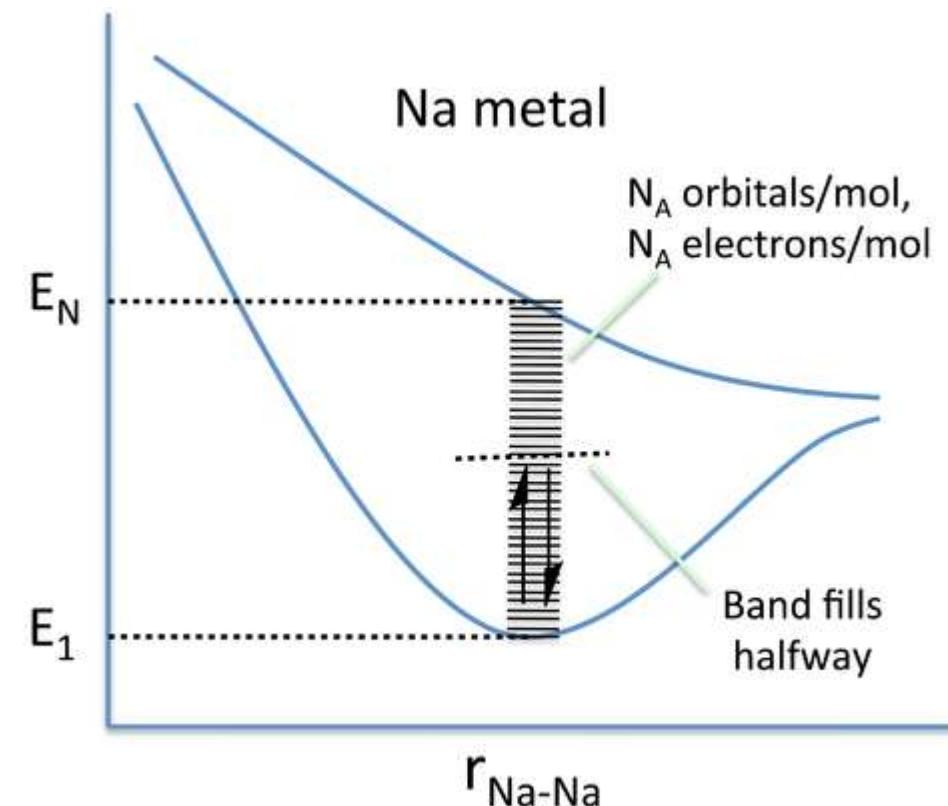


- The formation of a band of  $N$  molecular orbitals by successive addition of  $N$  atoms to a line. Note that **the band remains of finite width**, and although it looks continuous when  $N$  is large, it consists of  $N$  different orbitals.

**FIGURE 4.63** The energies of the orbitals that are formed when  $N$  atoms are brought up to form a one-dimensional array. This produces a density-of-states diagram similar to that shown in Fig. 4.68.

- When we have a **really big number** of MOs, some interesting things happen.
- Let us consider an example. 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.
- Note that **the band remains of finite width**. 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 *there just isn't space to have much difference in energy between all those MOs*. The MOs form **bands rather than separate energy levels**.
- In other words, for an infinite number of metal atoms, the MOs become so closely spaced that they blur together into a “**band**” of MOs.

- In band theory, the atom chain is extrapolated to a very large number - on the order of  $10^{22}$  atoms in a crystal - so that the different combinations of bonding and anti-bonding orbitals create "bands" of possible energy states for the metal. In the language of physics, this approach of building the bands from discrete atomic orbitals is called the "tight-binding" approximation. The number of atoms is so large that the energies can be thought of as a continuum rather than a series of distinct levels. A metal will only partially fill this band, as there are fewer valence electrons than there are energy states to fill. In the case of Na metal, this results in a half-filled 3s band.



- 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*. By the same logic, *p* orbitals lead 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** (as in the case of insulators and semi-conductors), 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 (e.g. metals).

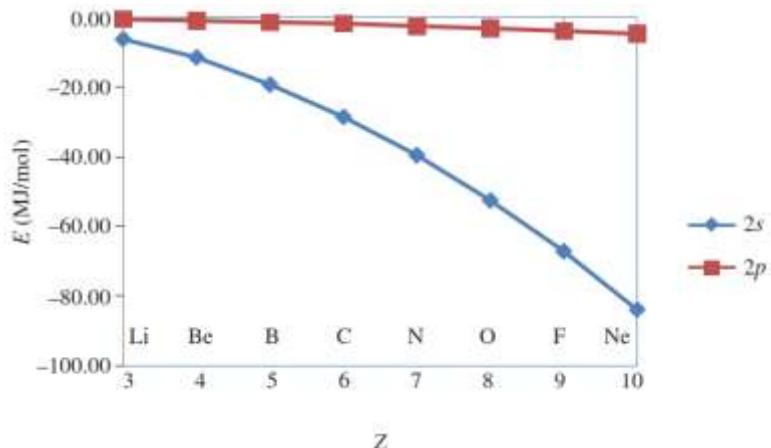
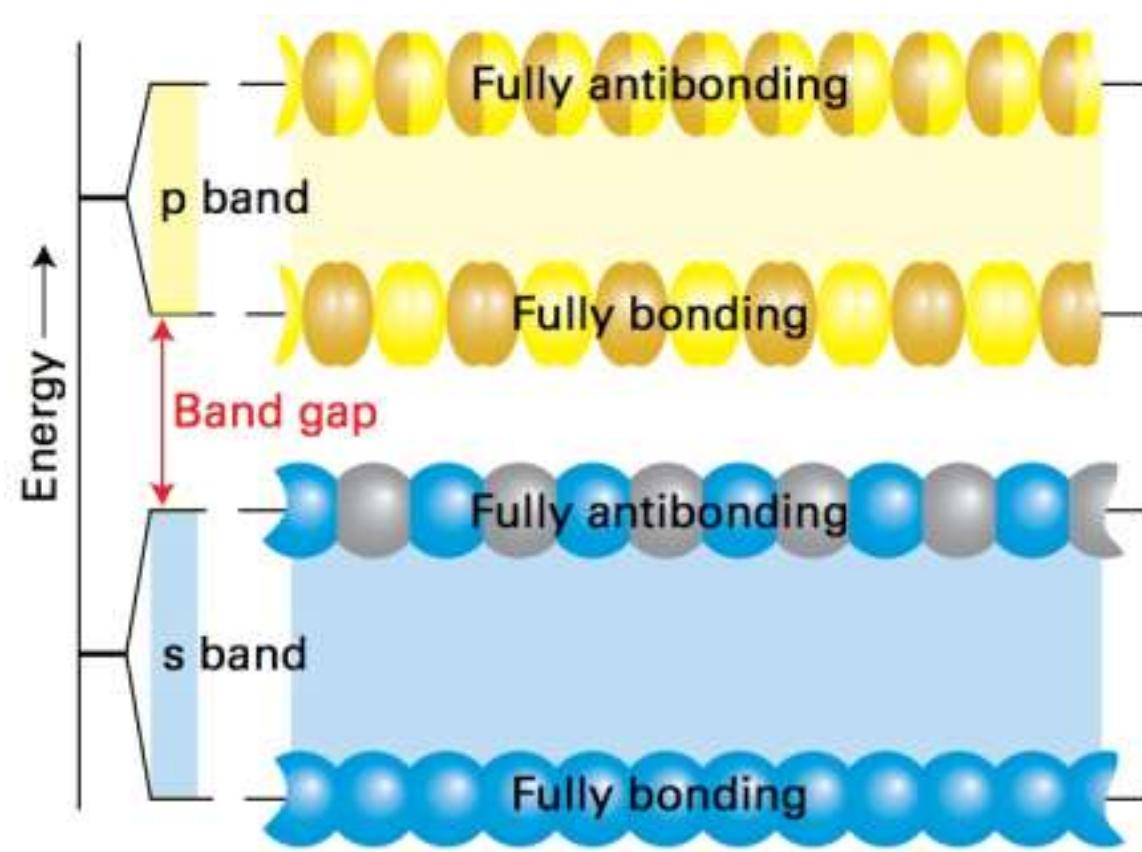


FIGURE 10.27. Relative energies of the valence orbitals for the Period 2 elements.



**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.*

## Overlapping bands

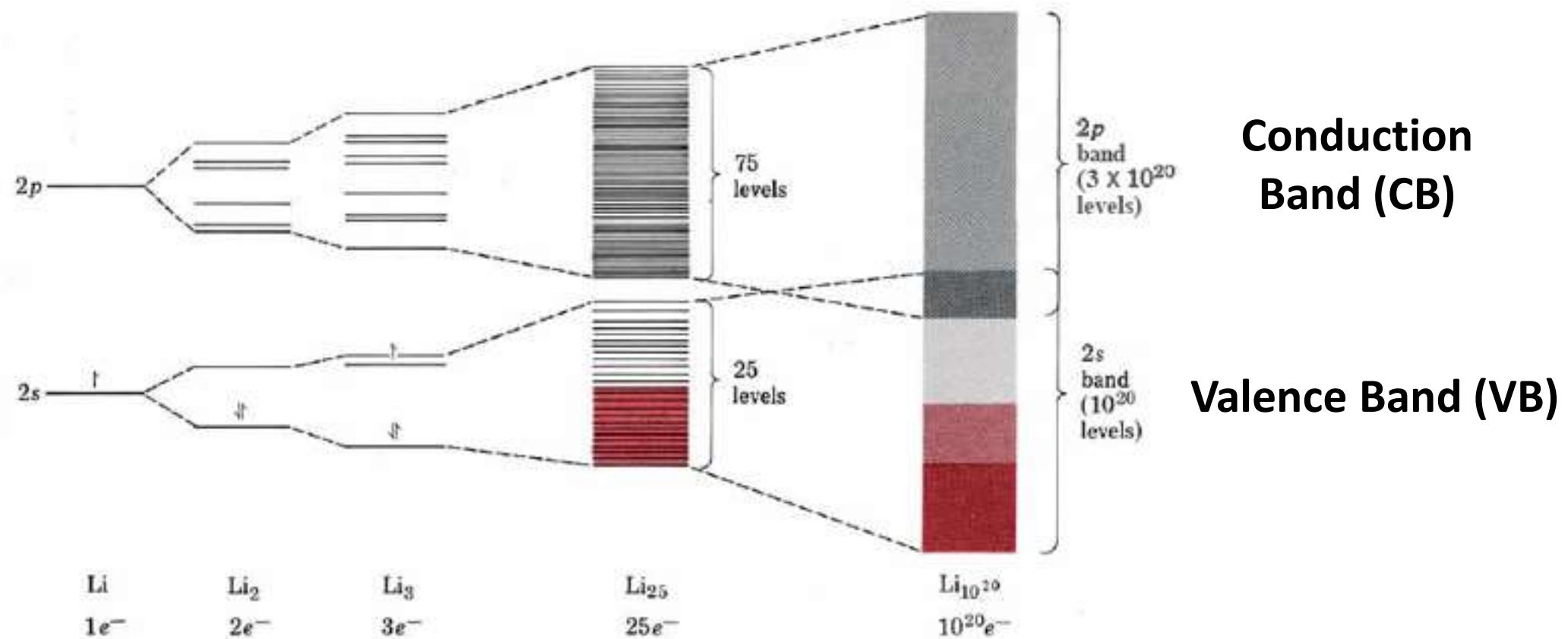
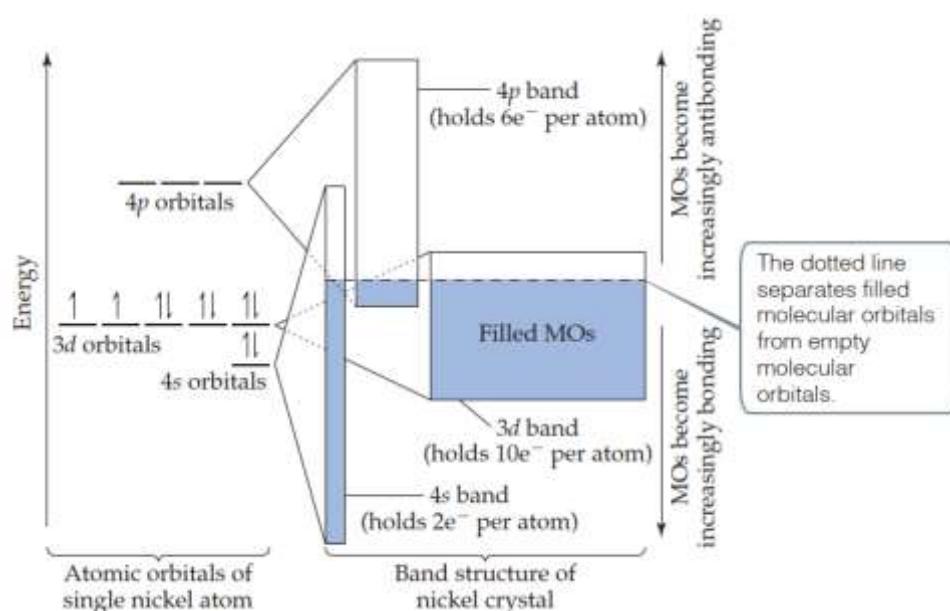


Figure 22.2.1: Molecular-orbital energies corresponding to delocalization of valence electrons over increasing numbers of Li atoms. A 1-mg sample of Li would contain nearly  $10^{20}$  atoms. The corresponding ***orbital energies are so closely spaced that they constitute essentially continuous bands.***

- 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  $[Ar]4s^23d^8$ , 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 12.23** The electronic band structure of nickel.

- In the ground electronic state of the solid, the occupied molecular orbitals make up the **valence band (VB)** of the solid. The **unoccupied orbitals** comprise **the conduction band (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 0 K* 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.
- **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*.
- 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.

- The ***formation of bands is not restricted to one type of atomic orbital*** and bands ***may be formed in compounds by combinations of different orbital types***; for example, the ***d orbitals of a metal atom may overlap the p orbitals of neighbouring O atoms*** (e.g.  $\text{ReO}_3$ ).
- In general, a band structure diagram can be produced for any solid and it is constructed using the frontier orbitals on all the atoms present. The energies of these bands, and whether they overlap, will depend on the energies of the contributing atomic orbitals, and ***bands may be empty, full, or partially filled depending on the total number of electrons in the system***.
- **Band theory** is a *quantum-mechanical treatment of the bonding in metals*. 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. 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.***
- 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***.

Rhenium trioxide ( $\text{ReO}_3$ ) structure: **Metallic but Oxide**

**KEY POINT:** *The rhenium trioxide structure can be constructed from  $\text{ReO}_6$  octahedra sharing all vertices in three dimensions.*

- The rhenium trioxide structure type is very simple, consisting of a primitive cubic unit cell with Re atoms at the corners and O atoms at the midpoint of each edge (Fig. 24.16). Alternatively, the structure can be considered to be derived from  $\text{ReO}_6$  octahedra sharing all vertices. The structure is also closely related to a perovskite structure (the general formula  $\text{ABX}_3$ , in which the 12-coordinate hole of  $\text{BX}_3$  (as in  $\text{ReO}_3$ ) is occupied by a large A ion) in which the A-type cation has been removed from the unit cell. Materials adopting the rhenium trioxide structure are relatively rare. This rarity is in part due to the requirement of the oxidation state M(VI) when M is in combination with oxygen. Rhenium(VI) oxide,  $\text{ReO}_3$ , itself and one form of  $\text{UO}_3$  ( $\delta\text{-UO}_3$ ) have this structure type as do some metal trifluorides such as  $\text{ScF}_3$ . At room temperature  $\text{WO}_3$  exists in a modified version of the  $\text{ReO}_3$  structure where the  $\text{WO}_6$  octahedra are slightly distorted and tilted relative to each other so that the W–O–W bond angle is not  $180^\circ$ .
- Rhenium trioxide itself is a bright-red, *lustrous solid*. Its **electrical conductivity at room temperature is similar to that of copper metal**.
- The band structure for this compound contains a band derived from the Re  $t_{2g}$  orbitals and the O2p orbitals (Fig. 24.17). This band can contain up to six electrons per Re atom but is only partially filled for the  $\text{Re}^{6+} \text{d}^1$  configuration, so **producing the observed metallic properties**.

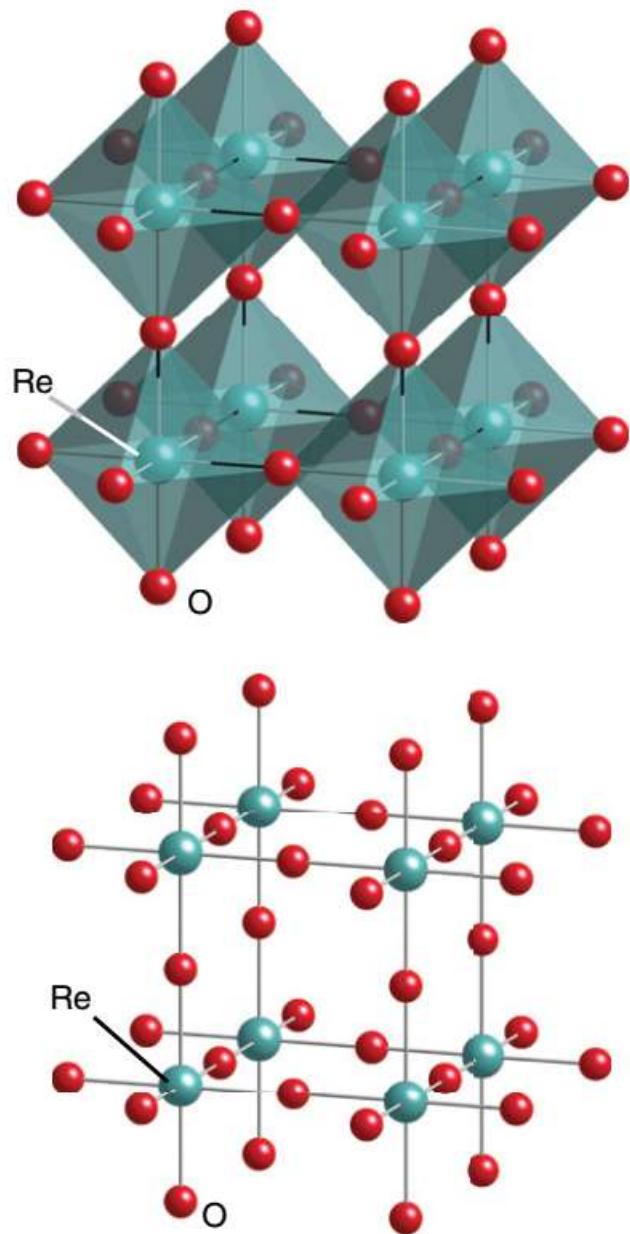


FIGURE 24.16 The  $\text{ReO}_3$  structure shown as the unit cell, and the  $\text{ReO}_6$  octahedra forming the unit cell.

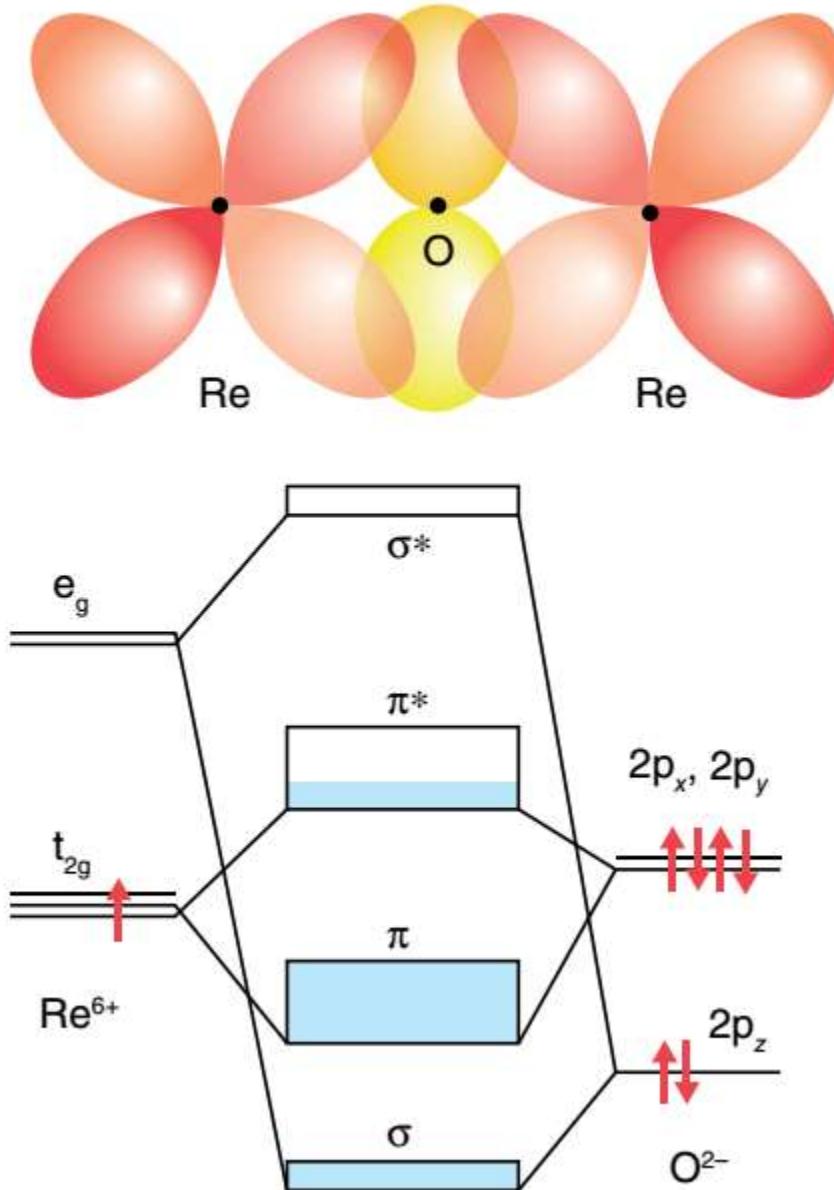


FIGURE 24.17 The band structure of  $\text{ReO}_3$ .

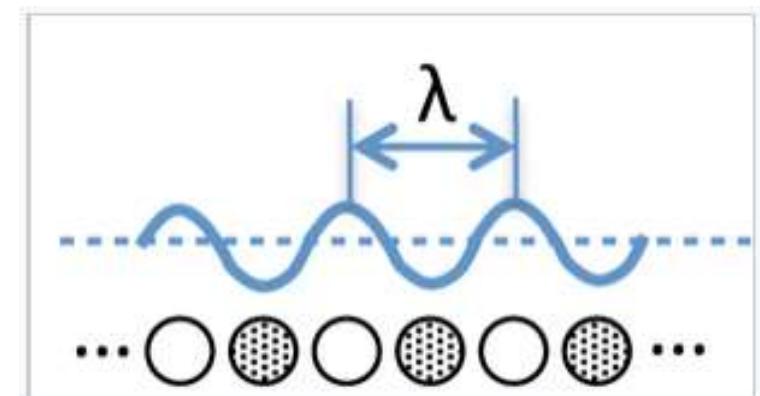
## Nearly free electron model

- In metals, the valence electrons are delocalized over many atoms.
- The total energy of each electron is given by the sum of its kinetic and potential energy:  $KE + V = (\mathbf{p}^2/2m) + V$ , where  $\mathbf{p}$  is the momentum of the electron (a vector quantity),  $m$  is its mass, and  $V$  is an average potential that the electron feels from the positive cores of the atoms. This potential holds the valence electrons in the crystal but, in the free electron model, is essentially uniform across the crystal.

### □ Electron wavelength and wavenumber

- What are the consequences of this model for band theory? For a hypothetical infinite chain (i.e., a 1D crystal) of Na atoms, the molecular orbitals at the bottom of the 3s band are fully bonding and the wavelength of electrons (2x the distance between nodes) in these orbitals is very long. At the top of the band, the highest orbital is fully antibonding and the wavelength is 2 times the distance between atoms ( $2a$ ), since there is one node per atom. Remember that the wavelength of an electron ( $\lambda$ ) is inversely proportional to its momentum  $p$ , according to the de Broglie relation  $\lambda = h/p$ .

- For a (nearly) free electron, the kinetic energy can be expressed in terms of its wavelength, using  $KE = p^2/2m$  and the de Broglie relation:
- $KE = p^2/2m = h^2/2m\lambda^2$ .
- At this point, it is convenient to define the wavenumber of the electron as  $k$ , which has units of ***inverse length and is inversely proportional to  $\lambda$*** .  $k$  is also directly proportional to the momentum  $p$ . Like  $p$ ,  $k$  is a **vector quantity**. In a 1D crystal,  $k$  can be either positive or negative, corresponding to an electron moving to the left or right along the chain.
- $k = 2\pi/\lambda = 2\pi p/h$  where  $h$  is Planck's constant . (6.5.2)
- The ***most important property of  $k$  is that it is directly proportional to the number of nodes  $n$  in a molecular orbital within the band.***



We can think of the wavelength of an electron in a molecular orbital as twice the distance between nodes. If there are  $N$  atoms in a linear chain, the wavelength of the  $n$ th orbital is given by  $\lambda = 2Na/n$ , where  $a$  is the distance between atoms.

- For a 1D crystal of sodium atoms that contains N unit cells, each separated by a distance  $a$ , a molecular orbital with  $n$  nodes has a wavelength  $\lambda = 2Na/n$  and the wavenumber  $k = \pi n/Na$ . We can see from this definition that  $k = 0$  at the bottom of the band (where  $\lambda$  is infinite) and  $k = \pi/a$  at the top of the band where the MO contains N nodes and  $\lambda = 2a$ .

## □ Energies of orbitals in a metallic crystal

- ***Electrons with long wavelengths do not "feel" the individual atoms in the lattice and so they behave as if they are nearly free*** (but confined to the crystal). Near the bottom of the band, the electron energy increases parabolically with the number of nodes ( $KE \propto n^2$ ), since the momentum  $p$  is directly proportional to  $n$ . Because  $p$  is also directly proportional to  $k$ , we can write:

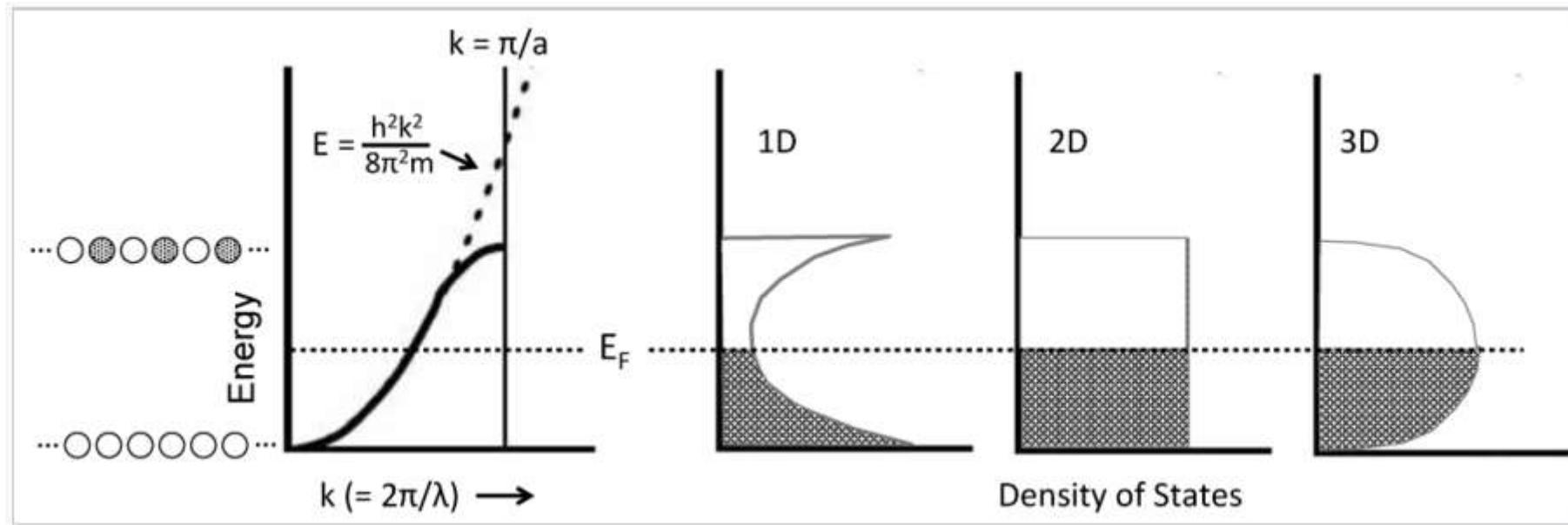
$$KE = p^2/2m = h^2k^2/8\pi^2m \quad (6.5.3)$$

- This parabolic relationship is followed as long as the electron wavelength is long compared to the distance between atoms. Near the top of the band, the wavelength becomes shorter and the electrons start to feel the positively charged atomic cores. In particular, the electrons prefer to have the maxima in their wavefunctions line up with the atomic cores, which is the

- most electrostatically favorable situation. The electron-atom attraction lowers the energy and causes the E vs. k curve to deviate from the parabolic behavior of a "free" electron as shown in the figure below.

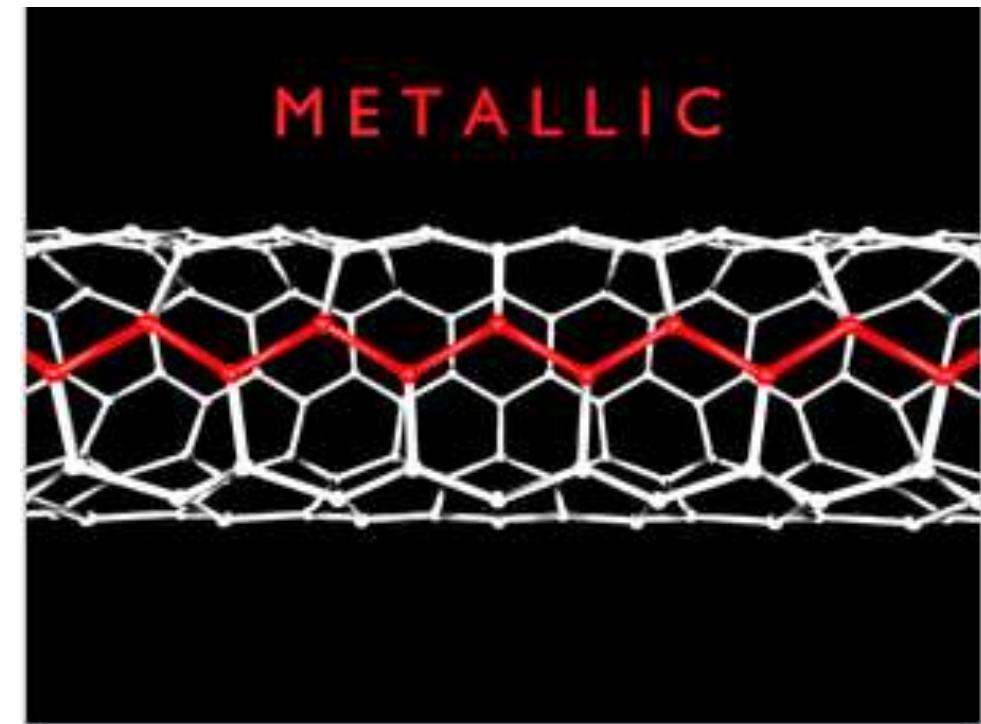
## □ Density of States (DOS)

- The ***density of states*** is defined ***as the number of orbitals per unit of energy within a band***. Because of the parabolic relation between E and k, the density of states for a 1D metallic crystal is highest near the bottom and top of the energy band where the slope of the E vs. k curve is closest to zero. The shape of the DOS curve is different in crystals of higher dimensionality as shown in the figure in the left, because statistically there are more ways to make an orbital with  $N/2$  nodes than there are with zero or  $N$  nodes. The situation is analogous to the numbers you can make by rolling dice. With one die, the numbers 1-6 have equal probability. However, with two dice there is only one way to make a two (snake eyes) or a twelve (boxcars), but many ways to make a seven (a winner!).



Electrons in metals follow a parabolic dispersion curve, where the energy increases with the square of the wavenumber,  $k$ . Near the top of the band, the dispersion curve deviates from the parabolic dotted line. Because there is one MO for each value of  $k$ , the number of orbitals per unit energy (the density of states, DOS) is highest at the bottom and top of the band for a 1D chain of atoms. The density of states is constant with energy for a 2D crystal, and has a maximum in the middle of the band for a 3D crystal. At low temperature, all the MOs below the Fermi level  $E_F$  are occupied, and all the MOs above it are empty.

- While most of the time we will talk about ***3D crystals that have their maximum DOS near the middle of the energy band***, there are examples of **quasi-1D** systems, such as carbon nanotubes (CNTs). **Metallic** carbon nanotubes have strong optical absorption bands that correspond to transitions between the two regions of high DOS (the van Hove singularities) near the bottom and top of the bands.



- Single-walled carbon nanotubes with "**armchair**" chirality are metallic and have characteristic sharp absorption bands in the infrared.

## Metals, semiconductors, and insulators: Densities of states and width of bands

**KEY POINT:** *The density of states is not uniform across a band: in most cases, the states are densest close to the center of the band.*

- The number of energy levels in an energy range divided by the width of the range is called the density of states,  $\rho$  (Fig. 4.68a). The *density of states is not uniform across a band because the energy levels are packed together more closely at some energies than at others*.
- In three dimensions, the variation of density of states is like that shown in Fig. 4.69, with the **greatest density of states near the center** of the band and the **lowest density at the edges**. The reason for this behavior can be traced to the number of ways of producing a particular linear combination of atomic orbitals. There is only one way of forming a fully bonding molecular orbital (the lower edge of the band) and only one way of forming a fully antibonding orbital (the upper edge). However, there are many ways (in a three-dimensional array of atoms) of forming a molecular orbital with an energy corresponding to the interior of a band.
- The number of orbitals contributing to a band determines the total number of states within it—that is, the area enclosed by the density of states curve. Large numbers of contributing atomic orbitals which have strong overlap produce broad (in energy terms) bands with a high density of states. If only a relatively few atoms contribute to a band and these are well separated in the solid, as is the case for a dopant species, then the band associated with this dopant atom type is narrow and contains only a few states (Figure 4.68b).

## Densities of states and width of bands

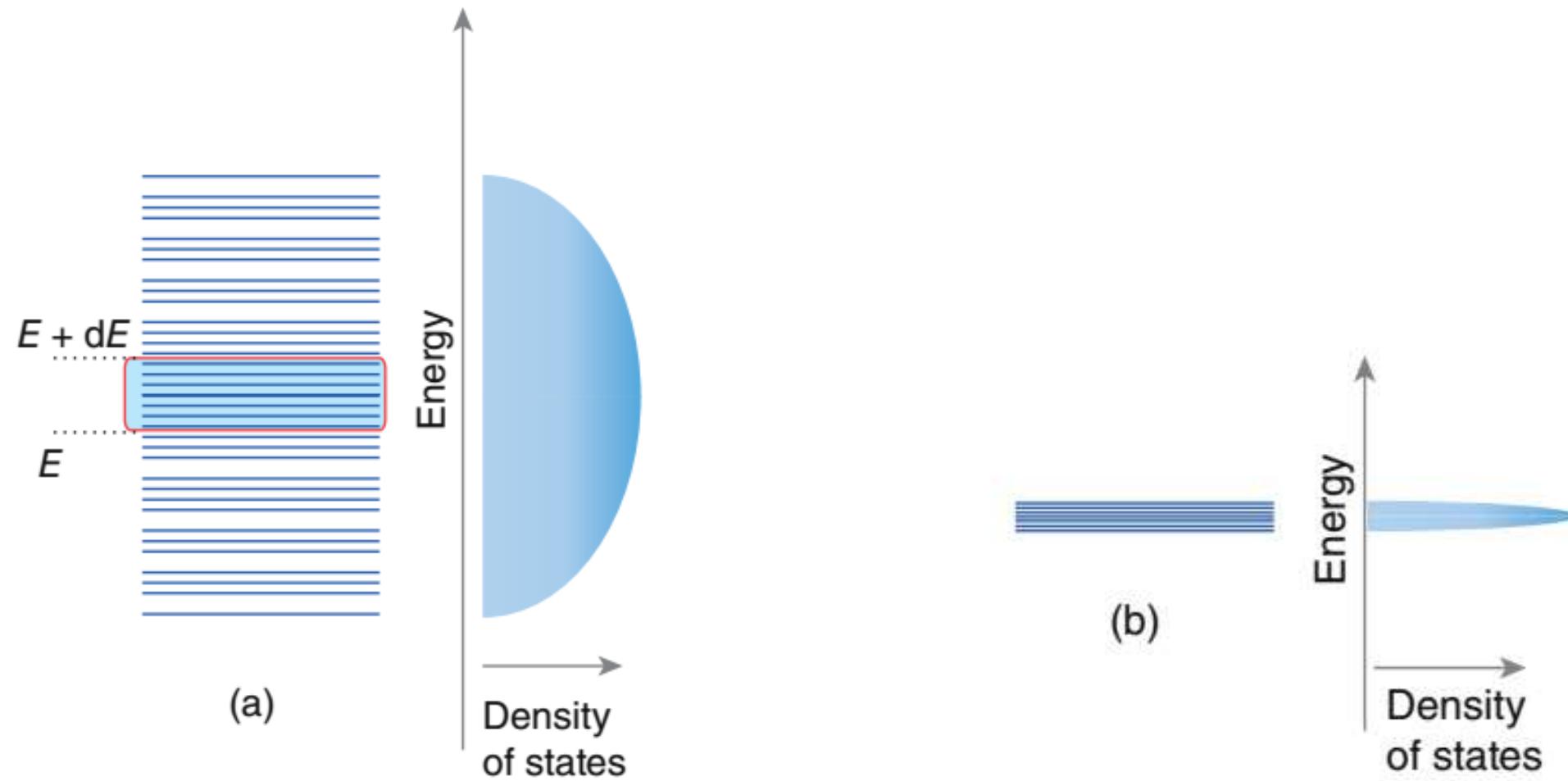


FIGURE 4.68 (a) The density of states in a metal is the number of energy levels in an infinitesimal range of energies between  $E$  and  $E+dE$ . (b) The density of states associated with a low concentration of dopant.

- The degree to which bands fill determines whether a crystalline solid is a metal, semiconductor, or insulator.
- If the highest occupied molecular orbitals lie within a band - i.e., if the *Fermi level  $E_F$  cuts through a band of orbitals* - then *the electrons are free to change their speed and direction* in an electric field and the solid is metallic.
- However, *if the solid contains just enough electrons to completely fill a band*, and *the next highest set of molecular orbitals is empty*, then it is a **semiconductor** or **insulator**.
- In this case, there is an *energy gap* between the *filled* and *empty bands*, which are called the **valence** and **conduction bands**, respectively. Although the distinction is somewhat arbitrary, *materials with a large gap (> 3 eV) are called insulators*, and those with smaller gaps are called semiconductors.

## Densities of states and width of bands

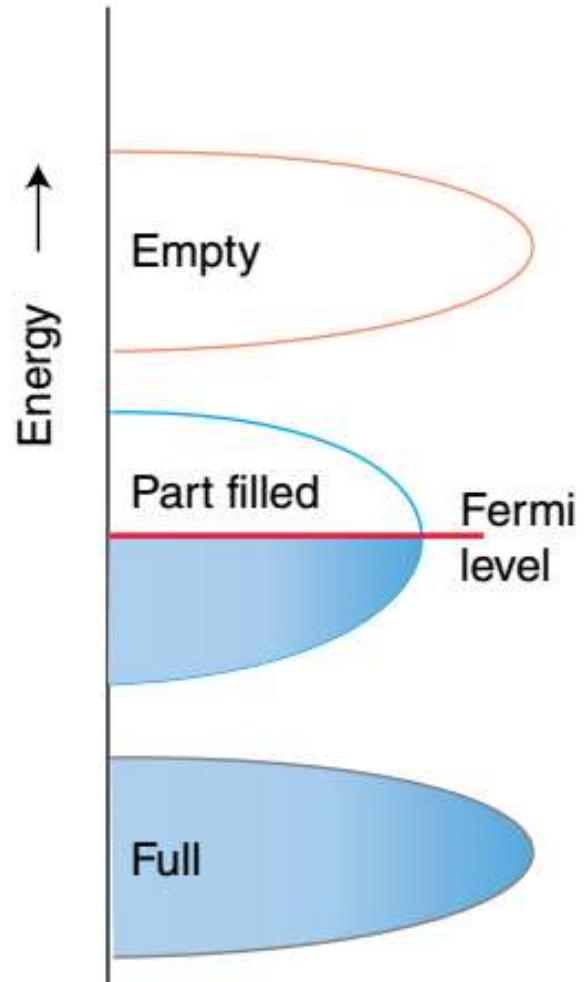


FIGURE 4.69 Typical density of states diagram for a three-dimensional **metal**.

- The ***density of states is zero in the band gap itself—there is no energy level in the gap***. In certain special cases, however, ***a full band and an empty band might coincide in energy but with a zero density of states at their conjunction*** (Fig. 4.70). Solids with this band structure are called **semimetals**. One important example is **graphite**, which ***is a semimetal in directions parallel to the sheets of carbon atoms***.

#### A NOTE ON GOOD PRACTICE

- This use of the term ‘semimetal’ should be distinguished from its other use as a synonym for metalloid. In this text we avoid the latter usage.

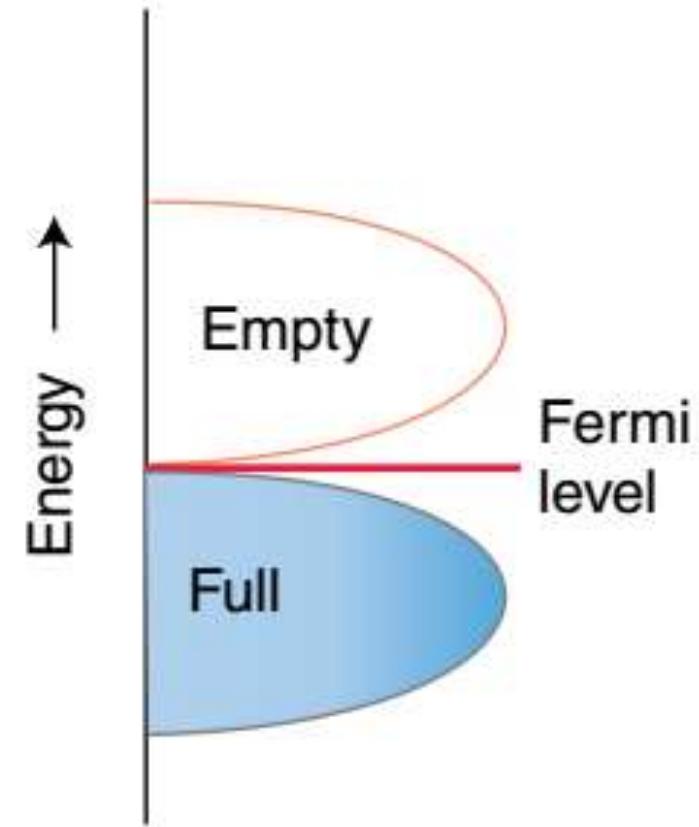


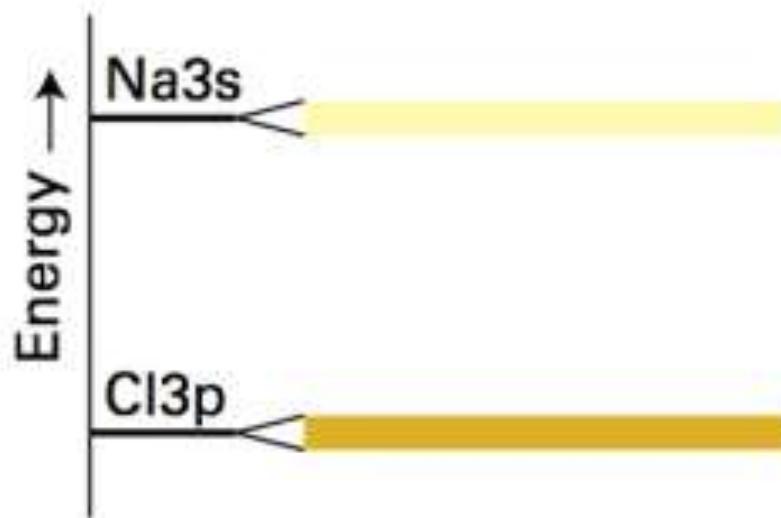
FIGURE 4.70 The density of states in a semimetal.

## Insulators

**KEY POINT:** An insulator is a solid with a large band gap.

- A solid is an insulator if enough electrons are present to fill a band completely and there is a considerable energy gap before an empty orbital and its associated band become available (Fig. 4.71). In a sodium chloride crystal, for instance, the  $N \text{Cl}^-$  ions are nearly in contact and their 3s and three 3p valence orbitals overlap to form a narrow band consisting of  $4N$  levels. The  $\text{Na}^+$  ions are also nearly in contact and also form a band. The electronegativity of chlorine is so much greater than that of sodium that the chlorine band lies well below the sodium band, and the band gap is about 7eV. A total of  $8N$  electrons are to be accommodated (seven from each Cl atom, one from each Na atom). These  $8N$  electrons enter the lower chlorine band, fill it, and leave the sodium band empty. Because the energy of thermal motion available at room temperature is  $kT \approx 0.03\text{eV}$  ( $k$  is Boltzmann's constant), very few electrons have enough energy to occupy the orbitals of the sodium band.
- In an insulator the band of highest energy that contains electrons (at  $T=0$ ) is normally termed the valence band. The next-higher band (which is empty at  $T=0$ ) is called the conduction band.
- In NaCl the ***band derived from the Cl orbitals is the valence band*** and the ***band derived from the Na orbitals is the conduction band***.
- We normally think of an ionic or molecular solid as consisting of discrete ions or molecules. According to the picture just described, however, they can be regarded as having a band structure. The two pictures can be reconciled because it is possible to show that a full band is equivalent to a sum of localized electron densities. In sodium chloride, for example, a full band built from Cl orbitals is equivalent to a collection of discrete  $\text{Cl}^-$  ions, and an empty band built from Na orbitals is equivalent to the array of  $\text{Na}^+$  ions.

- 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-diatom 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 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.*

- The Cl<sub>3</sub>p orbitals interact to form one band and the higher energy Na<sub>3</sub>s 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 Na<sub>3</sub>s band is very narrow; so is the Cl<sub>3</sub>p 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 Cl<sub>3</sub>p 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<sup>+</sup> cations and Cl<sup>-</sup> anions*, just as in an elementary picture of ionic bonding.

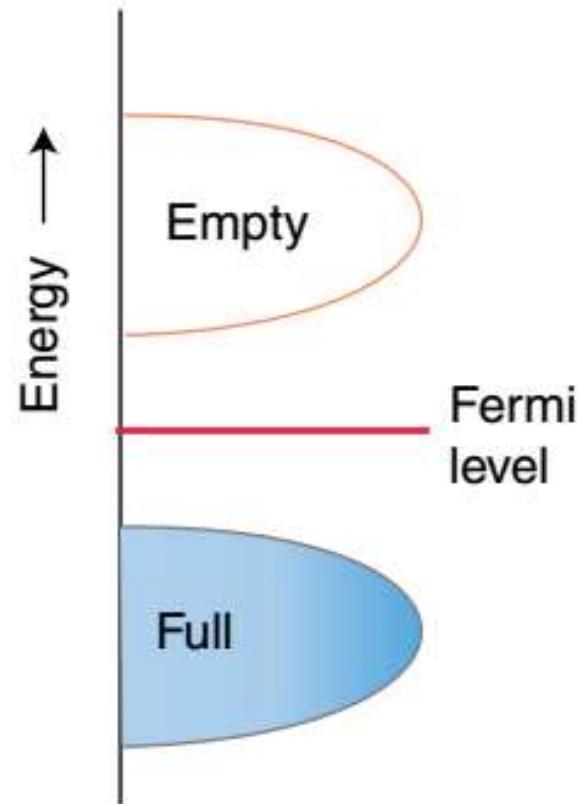


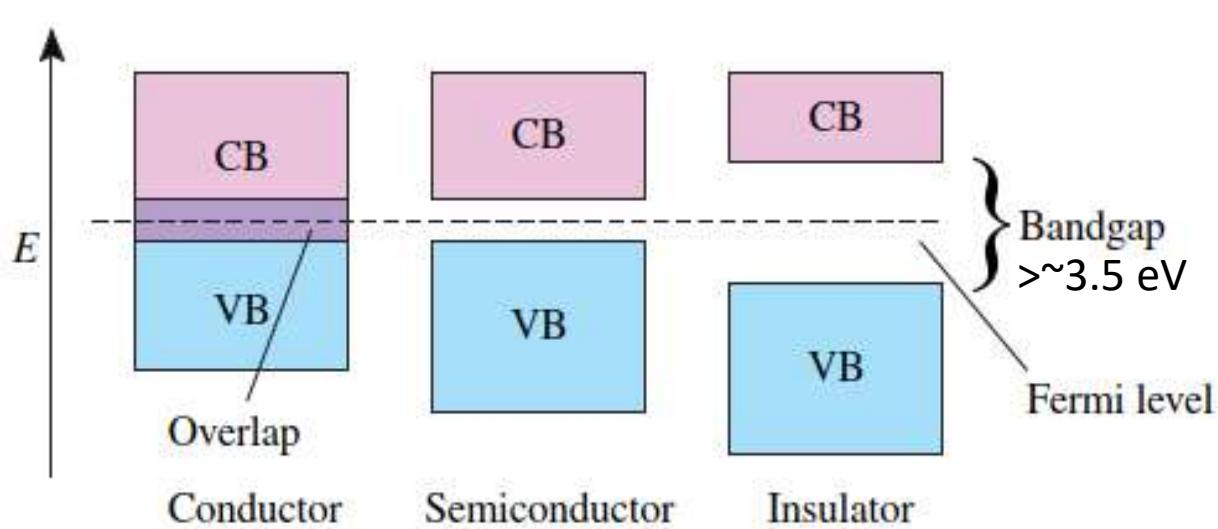
FIGURE 4.71 The structure of a typical insulator: there is a significant gap between the filled and empty bands.

## Semiconductors

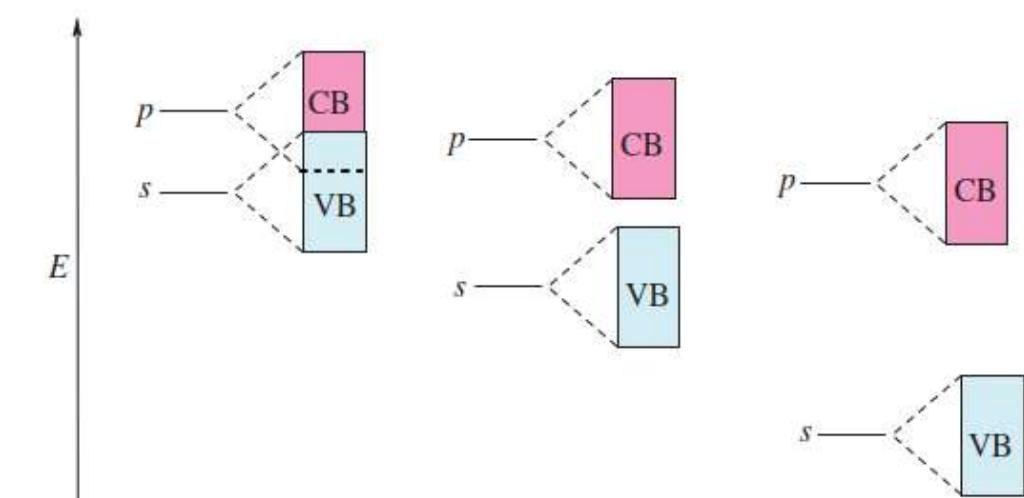
- Semiconductor materials are essential components of all modern electronic circuits and some devices.
- The ***characteristic physical property of a semiconductor is that its electrical conductivity increases with increasing temperature***. At room temperature, the conductivities of semiconductors are typically intermediate between those of metals and insulators.
- The ***dividing line between insulators and semiconductors is a matter of the size of the band gap*** (Table 4.13); the conductivity itself is an unreliable criterion because, as the temperature is increased, a given substance may have in succession a low, intermediate, and high conductivity. The values of the band gap and conductivity that are taken as indicating semiconduction rather than insulation depend on the application being considered.

TABLE 4.13 Some typical band gaps at 298K

Material	$E_g$ /eV
Carbon (diamond)	5.47
Silicon carbide	3.00
Silicon	1.11
Germanium	0.66
Gallium arsenide	1.35
Indium arsenide	0.36



**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.



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

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

## (a) Intrinsic semiconductors

**KEY POINT:** The band gap in a semiconductor controls the temperature dependence of the conductivity through an Arrhenius-like expression.

- In an **intrinsic semiconductor**, the band gap is so small that the thermal energy results in some electrons from the valence band populating the empty upper band (Fig. 4.72). **This occupation of the conduction band introduces positive holes, equivalent to an absence of electrons, into the lower band, and as a result the solid is conducting because both the holes and the promoted electrons can move.**
- A semiconductor at room temperature generally has a much lower conductivity than a metallic conductor because only very few electrons and holes can act as charge carriers. The strong, increasing with temperature, dependence of the conductivity follows from the exponential Boltzmann-like temperature dependence of the electron population in the upper band.
- It follows from the exponential form of the population of the conduction band that the conductivity of a semiconductor should show an Arrhenius-like temperature dependence of the form

$$\sigma = \sigma_0 e^{-E_g/2kT} \quad (4.8)$$

where  $E_g$  is the width of the band gap. That is, the conductivity of a semiconductor can be expected to be Arrhenius-like with an **activation energy** equal to **half the band gap**,  $E_a \approx E_g/2$ . This is found to be the case in practice.

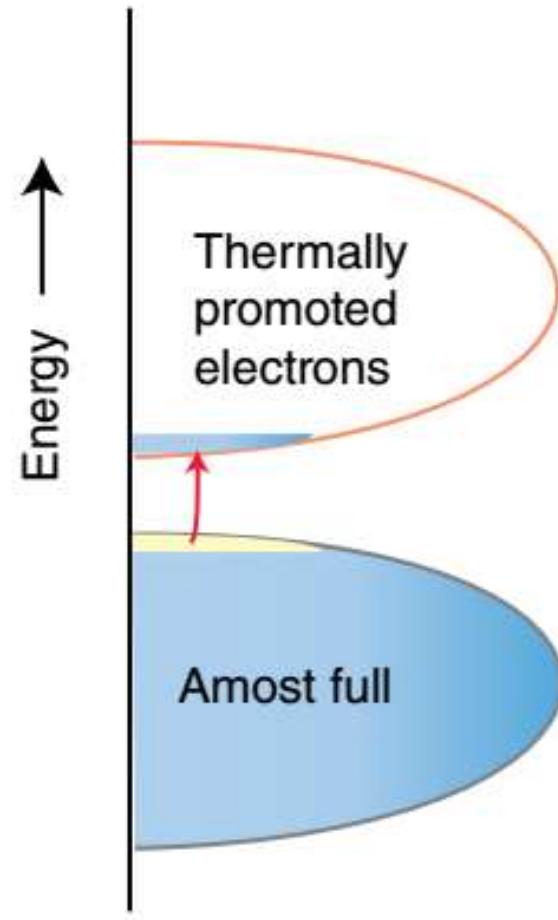


FIGURE 4.72 In an **intrinsic semiconductor**, the band gap is so small that the Fermi distribution results in the population of some orbitals in the upper band.

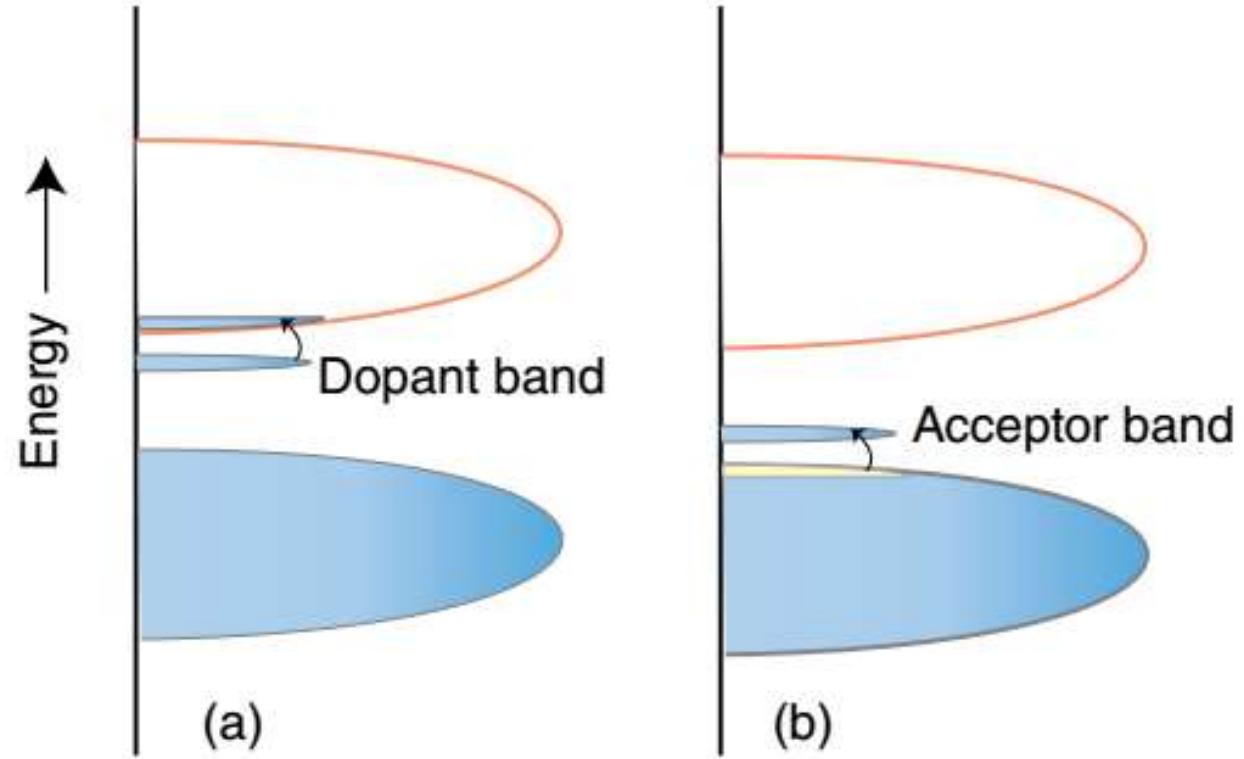


FIGURE 4.73 The band structure in (a) an **n-type semiconductor** and (b) a **p-type semiconductor**.

## (b) Extrinsic semiconductors

**KEY POINTS:** *p-Type semiconductors are solids doped with atoms that remove electrons from the valence band; n-type semiconductors are solids doped with atoms that supply electrons to the conduction band.*

- An **extrinsic semiconductor is a substance that is a semiconductor on account of the presence of intentionally added impurities (called dopants)**. The number of electron carriers can be increased if atoms with more electrons than the parent element can be introduced by doping. Remarkably low levels of dopant concentration are needed—only about one atom per  $10^9$  of the host material—so it is essential to achieve very high purity of the parent element initially.
- If arsenic atoms ( $[Ar]4s^24p^3$ ) are introduced into a silicon crystal ( $[Ne]3s^23p^2$ ), one additional electron will be available for each dopant atom that is substituted. Note that the **doping is substitutional in the sense that the dopant atom takes the place of an Si atom in the silicon structure**.
- If the donor atoms, the As atoms, are far apart from each other, their electrons will be localized and the donor band will be very narrow (Fig. 4.73a). Moreover, the foreign atom levels will lie at higher energy than the valence electrons of the host structure and the filled dopant band is commonly near the empty conduction band. For  $T > 0$ , some of its electrons will be thermally promoted into the empty conduction band. In other words, thermal excitation will lead to the transfer of an electron from an As atom into the empty orbitals on a neighbouring Si atom. From there it will be able to migrate through the structure in the band formed by Si–Si overlap. This process gives rise to **n-type semconductivity**, the ‘n’ indicating that the charge carriers are negatively charged (i.e. electrons).

- An alternative substitutional procedure is to dope the silicon with atoms of an element with fewer valence electrons on each atom, such as gallium ( $[Ar]4s^24p^1$ ). A dopant atom of this kind effectively introduces holes into the solid. More formally, the dopant atoms form a very narrow, empty acceptor band that lies above the full Si band (Fig. 4.73b). At  $T=0$  the acceptor band is empty but at higher temperatures it can accept thermally excited electrons from the Si valence band. By doing so, it introduces holes into the latter and hence allows the remaining electrons in the band to be mobile. Because the *charge carriers are now effectively positive holes in the lower band*, this type of conductivity is called ***p-type semiconductivity***.

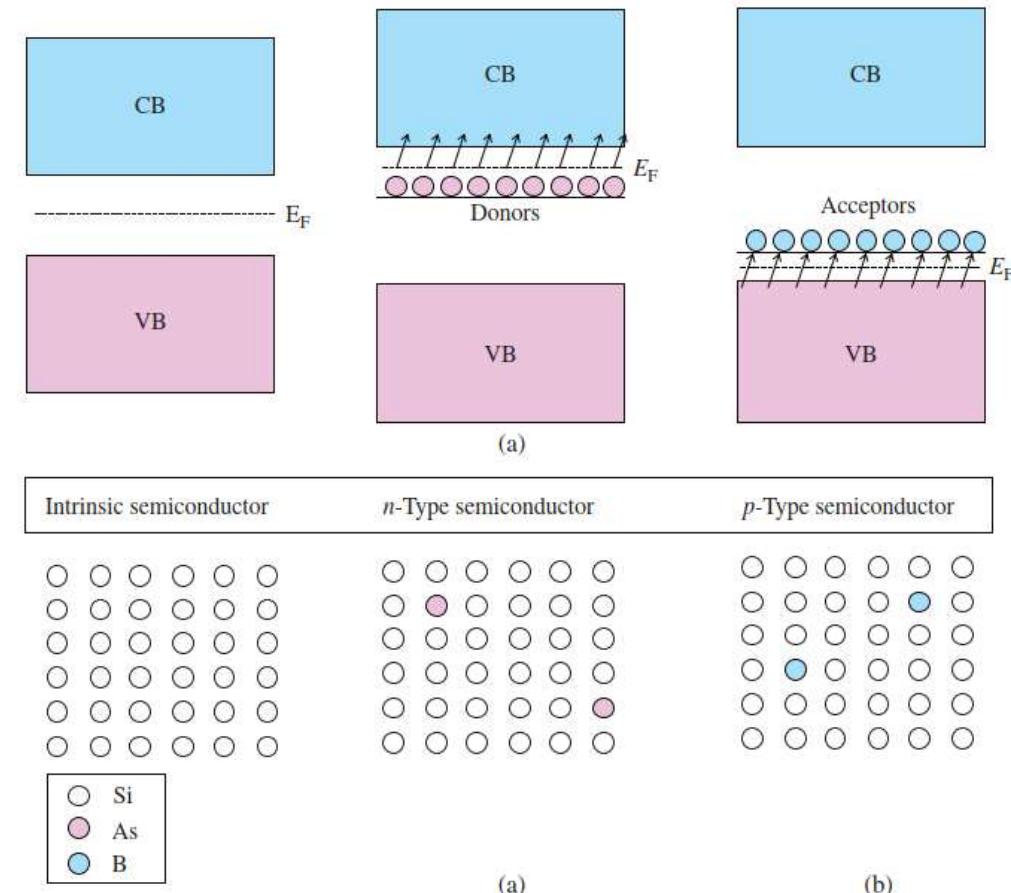


FIGURE 11.51. (a, b) The difference between an intrinsic semiconductor, an *n*-type semiconductor, and a *p*-type semiconductor.

- Several ***d*-metal oxides**, including ZnO and Fe<sub>2</sub>O<sub>3</sub>, are ***n*-type semiconductors**. In their case, the property is due to small variations in stoichiometry and ***a small deficit of O atoms***. ***The electrons that should be in localized O atomic orbitals (giving a very narrow oxide band, essentially localized individual O<sup>2-</sup> ions) occupy a previously empty conduction band formed by the metal orbitals*** (Fig. 4.74).
- ✓ The ***electrical conductivity decreases after the solids have been heated in oxygen*** and cooled slowly back to room temperature because the deficit of O atoms is partly replaced and, as the atoms are added, electrons are withdrawn from the conduction band to form oxide ions. However, ***when measured at high temperatures the conductivity of ZnO increases as further oxygen is lost from the structure***, so increasing the number of electrons in the conduction band.
- ***p-Type semiconduction is observed for some low oxidation number d-metal chalcogenides and halides***, including Cu<sub>2</sub>O, FeO, FeS, and Cul. In these compounds, ***the loss of electrons can occur through a process equivalent to the oxidation of some of the metal atoms, with the result that holes appear in the predominantly metal band***.
- ✓ The ***conductivity increases when these compounds are heated in oxygen*** (or sulfur and halogen sources for FeS and Cul, respectively) because ***more holes are formed in the metal band as oxidation progresses***.

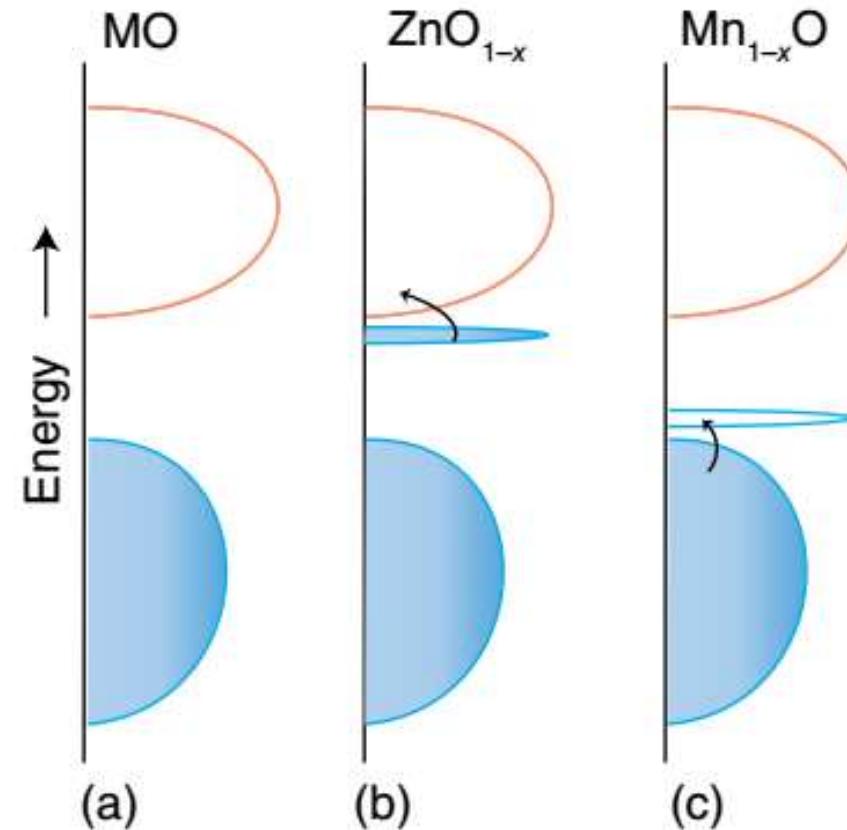


FIGURE 4.74 The band structure in  
 (a) a ***stoichiometric*** oxide,  
 (b) an ***anion-deficient*** oxide, and  
 (c) an ***anion-excess*** oxide.

- **n-Type semiconductivity**, however, *tends to occur for oxides of metals in higher oxidation states*, as the metal can be reduced to a lower oxidation state by occupation of a conduction band formed from the metal orbitals. Thus, typical n-type semiconductors include  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{CuO}$ .
- By contrast, p-type semiconductivity occurs when the metal is in a low oxidation state, such as  $\text{MnO}$  and  $\text{Cr}_2\text{O}_3$ .

## EXAMPLE 4.22 Predicting extrinsic semiconducting properties

- ❖ **Which of the oxides  $\text{WO}_3$ ,  $\text{MgO}$ , and  $\text{CdO}$  are likely to show p- or n-type extrinsic conductivity?**

Answer The type of conductivity depends on the defect levels that are likely to be introduced, which is, in turn, **determined by whether the metal present can easily be oxidized or reduced.**

- **If the metal can easily be oxidized** (which may be the case if it has a low oxidation number), then **p-type** conductivity is expected.
- On the other hand, if the metal can **easily be reduced** (which may be the case if it has **a high oxidation number**), then **n-type** conductivity is expected.
- Thus,  $\text{WO}_3$ , with tungsten present in the high oxidation state W(VI), is **readily reduced** and accepts electrons from the  $\text{O}^{2-}$  ions, which escape as elemental oxygen. The excess electrons enter a band formed from the W d orbitals, resulting in n-type conductivity. Similarly,  $\text{CdO}$ , like  $\text{ZnO}$ , readily loses oxygen and is predicted to be an n-type semiconductor.
- In contrast,  $\text{Mg}^{2+}$  ions are **neither** easily oxidized nor reduced, so  $\text{MgO}$  does not lose or gain even small quantities of oxygen and is an **insulator**.

- ❖ **Self-test 4.22 Predict p- or n-type extrinsic conductivity for  $\text{V}_2\text{O}_5$  and  $\text{CoO}$ .**

Ans.... Vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) is n-type conductivity. ...  $\text{CoO}$  is p-type semiconductor. materials and CoP

...Common n-type MOX:  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$ , etc.

...Common p-type MOX:  $\text{CuO}$ ,  $\text{NiO}$ ,  $\text{Cr}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ , CoP, etc.

- ❖ **Q. Classify the following as to whether they are likely to show n- or p-type conductivity:  $\text{Ag}_2\text{S}$ ,  $\text{VO}_2$ ,  $\text{CuBr}$ .**

- ❖ **Q. Describe the difference between a semiconductor and a semimetal.**

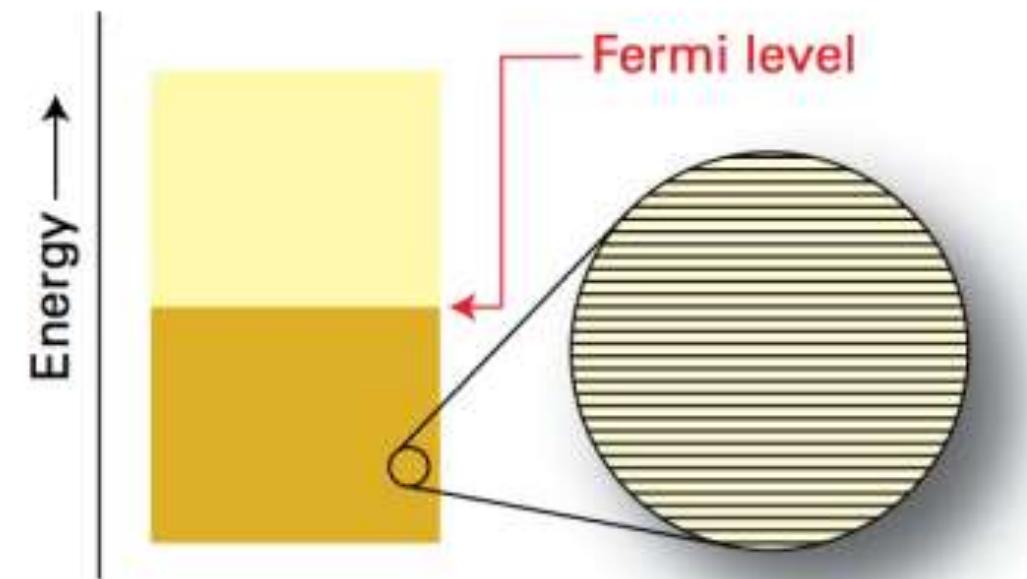
❖ Q4.51 Graphite is a semimetal with a band structure of the type shown in Fig. 4.70. Reaction of graphite with potassium produces  $C_8K$  while reaction with bromine yields  $C_8Br$ . Assuming the graphite sheets remain intact and potassium and bromine enter the graphite structure as  $K^+$  and  $Br^-$  ions, respectively, discuss whether you would expect the compounds  $C_8K$  and  $C_8Br$  to exhibit metallic, semimetallic, semiconducting, or insulating properties.

## 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**.*

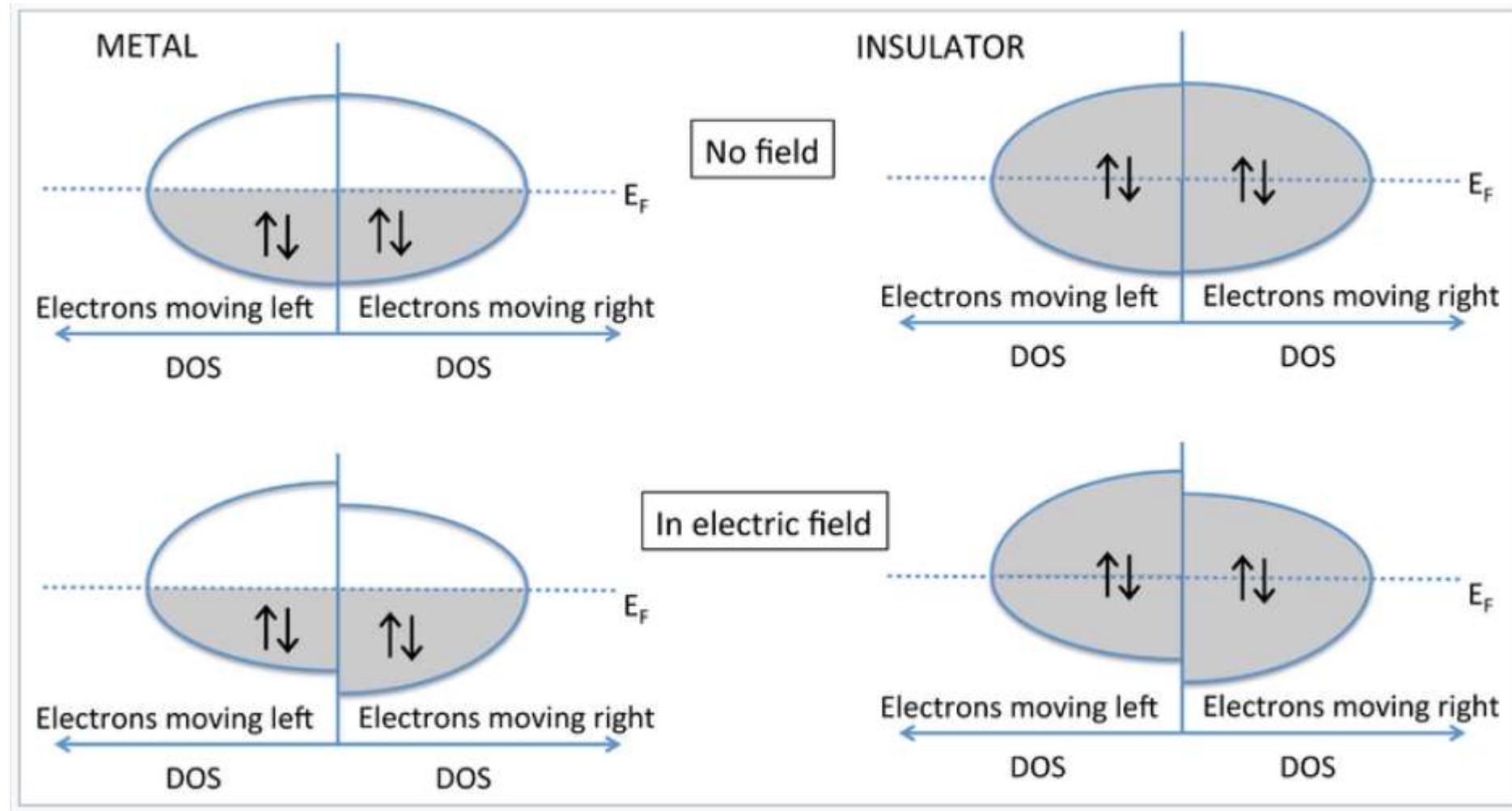
- However, unlike in the discrete molecules, there are empty orbitals just above and very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons.
- Some of the electrons are therefore very mobile and give rise to electrical conductivity.
- *Without the 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.

**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.



## Why don't insulators conduct electricity?

- The energy vs. DOS diagram below shows what happens when an electric field is applied to a metal or an insulator.
- In this case we have changed the diagram to show explicitly the energies of electrons moving left and right. These energies are the same in the absence of an electric field. Once we apply a field (e.g., by putting a voltage across a metal wire), ***the electrons moving in the direction of the field have lower energy*** than those moving in the opposite direction.
- ***In the case of the metal***, the populations of electrons ***moving with*** and ***against*** the electric field are different, and ***there is a net flow of current***. Note ***that this can happen only when the Fermi level cuts through a partially filled band***.
- With a semiconductor or insulator, the valence band is filled and the conduction band is empty. Applying an electric field changes the energies of electrons traveling with and against the field, but because the band is filled, the same number are going in both directions and there is ***no net current flow***.
- Note that in this picture, all the molecular orbitals extend over the entire crystal. The valence electrons are ***delocalized***, even in the case of a semiconductor or insulator. However, there can be no net movement of electrons unless the band is partially filled.



E vs. DOS diagrams comparing the behavior of metals and insulators in an applied electric field.

- 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 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. The orbital of lowest energy has no nodes between neighboring atoms and the orbital of highest energy has a node between every pair of neighbors. The remaining orbitals have successively 1, 2, . . . internuclear nodes and a corresponding range of energies between the two extremes.
- 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 AO<sub>s</sub>. 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  $10^2 \text{ S/m}$***  (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** has an electrical conductivity of less than  $10^{-5} \text{ S/m}$ .
- Lastly, **semiconductors are having conductivities between  $10^{-5}$  and  $10^2 \text{ S/m}$ .**
- 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.

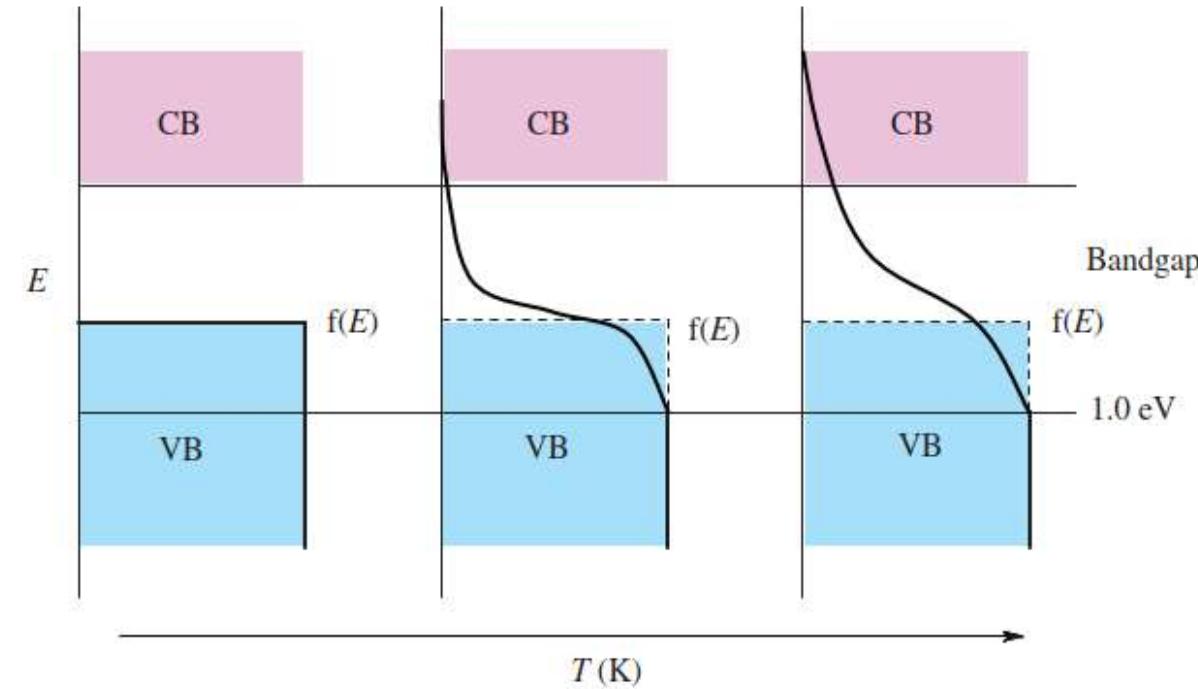
- At low temperatures, a semiconductor will act as an insulator; but as the temperature is raised and an external potential is applied, a portion of the electrons in the VB can “jump” across the band gap into the CB.
- This is because of the temperature dependence of the Fermi–Dirac distribution, which 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.

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

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 the above Equation, where  $\mu$  is the field potential.



At absolute zero  
(0 K), there is  
no band bending

At moderate temps,  
some  $e^-$  have  $E$  above  
the Fermi level

At high temps,  
there is more  
band bending

- 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.
- **Almost every modern electronic device (from laptops to cell phones to mp3 players) contains a p–n junction as part of its integrated circuitry.**
- Other III–V combinations have different band gaps and are useful in particular applications. Indium antimonide (InSb), for example, has a small enough band gap that absorption of infrared radiation causes electrons to be excited from the valence to the conduction band, and an electric current then flows when a small potential difference is applied. This compound is therefore used as a detector of infrared radiation.
- Still other compounds formed between the zinc group (zinc, cadmium, and mercury) and Group VI elements such as sulfur also have the same average number of valence electrons per atom as silicon and make useful semiconductors.

## Semiconductor chemistry

- The basic inorganic chemistry of semiconducting materials, particularly their electronic band structures, was covered above. The aim of this section is to discuss the inorganic semiconducting compounds themselves in more detail and to describe some of the applications that result from using chemistry to control their electronic properties.
- **Semiconductors** are classified on the basis of their composition. To produce materials with band gaps typical of a semiconductor (a few electronvolts, corresponding to 100–200 kJ mol<sup>-1</sup>), compounds usually contain the p-block metals and Group 13/14 metalloids, often in combination with heavier chalcogenides and pnictides. For these combinations, the atomic orbitals form into bands with energies such that **the valence and conduction band separation is in the desired range of 0.2–4 eV**.
- *Materials based on more electropositive and electronegative elements* (for example, alkaline earth metal oxides) are much more ionic in character with much wider separations of the valence and conduction bands and **are insulators**.
- A further factor that influences the **band gap in semiconductors is particle size: the smaller the particle size, the wider the band gap**.

## Group 14 semiconductors

- ***Key point: Crystalline and amorphous silicon are cheap semiconducting materials and are widely used in electronic devices.***
- The most important semiconducting material is Si, which in its pure crystalline form (with a diamond structure) has a band gap of 1.1 eV. As would be expected from considerations of atomic radii, orbital energies, and the extent of orbital overlap, Ge has a smaller band gap, 0.66 eV, and **C as diamond** has a band gap of 5.47 eV.
- The conductivity of pure Si, an intrinsic semiconductor, is around  $10^{-2}$  S cm<sup>-1</sup> at room temperature but increases by several orders of magnitude on **doping** with either a Group 13 element (to give a **p-type semiconductor**) or a Group 15 element (to give an **n-type semiconductor**) and thus the properties of doped Si can be tuned for a particular semiconductor application.
- When doped with a Group 13 or 15 element, Si—and indeed C and Ge—are extrinsic semiconductors.
- **Doping** silicon **brings donor levels close enough to the conduction band or acceptor levels close enough to the valence band** that **thermal excitation can cause electrons to move into a conducting state**. Thus, doping of insulators or wide band-gap semiconductors can bring donor or acceptor states into positions where **visible light can be absorbed or emitted**. This changes the colors and optical properties of the materials.
- **Nitrogen doped in diamond gives a donor impurity level** in the band gap. Transitions to this level can **absorb some blue light**, giving the **diamond an undesirable yellowish color**. In contrast, **boron doped** into diamond gives an acceptor level that **absorbs red light** most strongly and gives the highly prized and rare “**blue diamond**”.

➤ Amorphous Si can be obtained by chemical vapour deposition or by heavy-ion bombardment of crystalline Si. The deposited material, which is often obtained by thermal decomposition of  $\text{SiH}_4$ , contains a small proportion of H that is present in Si-H groups in a three-dimensional glass-like structure with many Si-Si links. The lack of regular structure in this material and the presence of Si H groups alters the semiconducting properties of the material considerably. One of the main applications of amorphous Si is in silicon solar cells. Thin films of p- and n-type amorphous Si forming a p–n junction generate current when illuminated. The electron and hole pairs produced from the energy supplied by the incident photon separate rather than recombine because of the normal p–n junction bias, with the tendency for the electrons to travel towards the p-type Si and holes towards the n-type. If a load is connected across the junction then a current can flow and electrical energy is generated from the electromagnetic illumination. The efficiency of such devices depends on a number of factors. For example, amorphous Si absorbs solar radiation 40 times more efficiently than does single-crystal Si, so a film only about 1  $\mu\text{m}$  thick can absorb 90 per cent of the usable solar energy. Also, the lifetimes and mobility of the electrons and holes are longer in amorphous Si, which results in high photoelectric efficiencies (the proportion of radiant energy converted into electrical energy) of the order of 10 per cent. Other economic advantages are that amorphous Si can be produced at a lower temperature and can be deposited on low-cost substrates. Amorphous Si solar cells are widely used in pocket calculators but, as production costs diminish, are likely to find much wider applications as renewable energy devices.

## Semiconductor systems isoelectronic with silicon

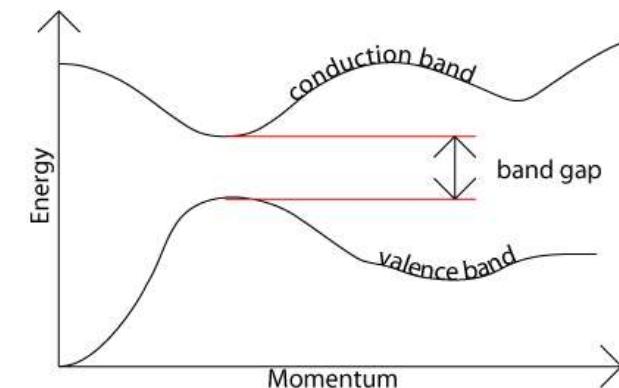
**Key points:** Semiconductors formed from equal amounts of Group 13/15 or Group 12/16 elements are isoelectronic with silicon and can have enhanced properties based on changes in the electronic structure and electron motion.

- Gallium arsenide, GaAs, is one of a number of so-called Group 13/15 (or, still more commonly, III/V semiconductors), which also include GaP, InP, AlAs, and GaN, formed by combination of equal amounts of a Group 13 and a Group 15 element. Ternary and quaternary Group 13/15 compounds, such as  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ,  $\text{InAs}_{1-y}\text{P}_y$ , and  $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y$ , can also be formed and many of them also have valuable semiconducting properties. Note that these compositions are isoelectronic with pure Group 14 elements, but the changes in the element electronegativity and thus bonding type (for instance, pure Si can be considered as having purely covalent bonding whereas GaAs has a small degree of ionic character due to the difference in the electronegativities of Ga and As) leads to changes in the band structures and fundamental properties associated with electron motion through the structures. One of the advantageous properties of GaAs is that semiconductor devices based on it respond more rapidly to electrical signals than those based on silicon. This responsiveness makes GaAs better than silicon for a number of tasks, such as amplifying the high-frequency (1–10 GHz) signals of satellite TV. Gallium arsenide can be used with signal frequencies up to about 100 GHz. At even higher frequencies materials such as indium phosphide (InP) may be used. At present, frequencies above about 50 GHz are rarely used commercially, so most of the electronics in the world tend to be based on silicon, with some GaAs, and only a few InP devices. Gallium arsenide is also far more expensive than Si, both in terms of the cost of raw materials and the chemical processes required to produce the pure material.

- In some Group 13/15 semiconductors, such as GaN, the cubic, diamond-like, sphalerite structure is only metastable, the stable polymorph being the hexagonal, wurzite structure. Both structures can be grown by altering the synthetic routes and conditions. Because of their large and direct energy band gaps, these semiconductors allow the fabrication of luminescent devices that produce blue light at high intensity, and their stabilities to high temperatures and good thermal conductivities also make them valuable for the fabrication of high-power transistors.
- The Group 12/16 (II/VI) semiconductors comprise the compounds containing Zn, Cd, and Hg as cations and O, S, Se, and Te as anions. These semiconductor materials can crystallize in either the cubic sphalerite phase or the hexagonal wurzite phase and the form synthesized has characteristic semiconducting properties. For example, the band gap is 3.64 eV in cubic ZnS but 3.74 eV in hexagonal ZnS. These Group 12/16 compounds are more ionic in nature than the Group 13/15 semiconductors and Group 14 elements, particularly for the lighter elements, and the band gap is around 3–4 eV for ZnO and ZnS but 1.475 eV for CdTe. Although amorphous Si is the leading thin-film photovoltaic (PV) material, cadmium telluride (CdTe) is also being studied for similar applications.
- The current world record thin-film solar cell efficiency of 17.7 per cent is held by a device based on copper indium diselenide ( $\text{CuInSe}_2$ ; CIS), which has a similar structure to cubic ZnS but with an ordered distribution of Cu and In atoms in the tetrahedral holes.

## Direct and Indirect Band Gap Semiconductors

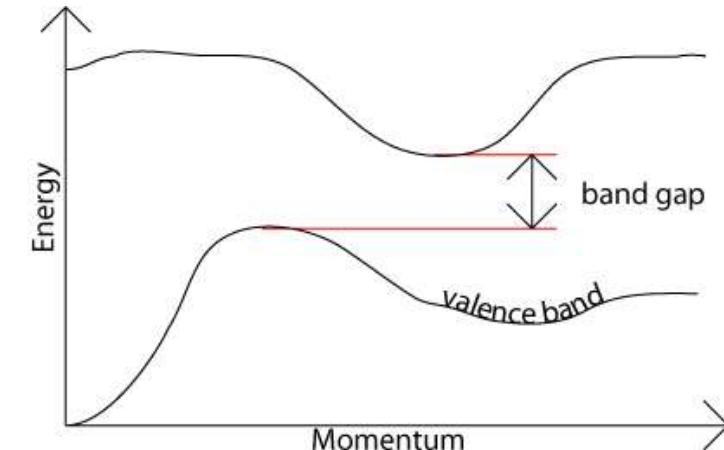
- The **band gap** represents the minimum energy difference between the top of the valence band and the bottom of the conduction band. However, the **top** of the valence band and the **bottom** of the conduction band *are not generally* at the same value of the electron momentum. In a **direct band 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:

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		
$\alpha$ -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***.
- 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 above lists a number of different semiconducting compounds and their band gaps, and it also specifies whether their band gaps are direct or indirect.

## 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.

- The criterion for distinguishing between a metallic conductor and a semiconductor is the temperature dependence of the electric conductivity (Fig. 4.60):
  - A metallic conductor is a substance with an electric conductivity that decreases with increasing temperature.
  - A semiconductor is a substance with an electric conductivity that increases with increasing temperature.
- It is also generally the case (but not the criterion for distinguishing them) that the conductivities of metals at room temperature are higher than those of semiconductors.
- Typical values are given in Fig. 4.60. A solid insulator is a substance with a very low electrical conductivity. However, when that conductivity can be measured, it is found to increase with temperature, like that of a semiconductor. For some purposes, therefore, it is possible to disregard the classification ‘insulator’ and to treat all solids as either metals or semiconductors. Superconductors are a special class of materials that have zero electrical resistance below a critical temperature.

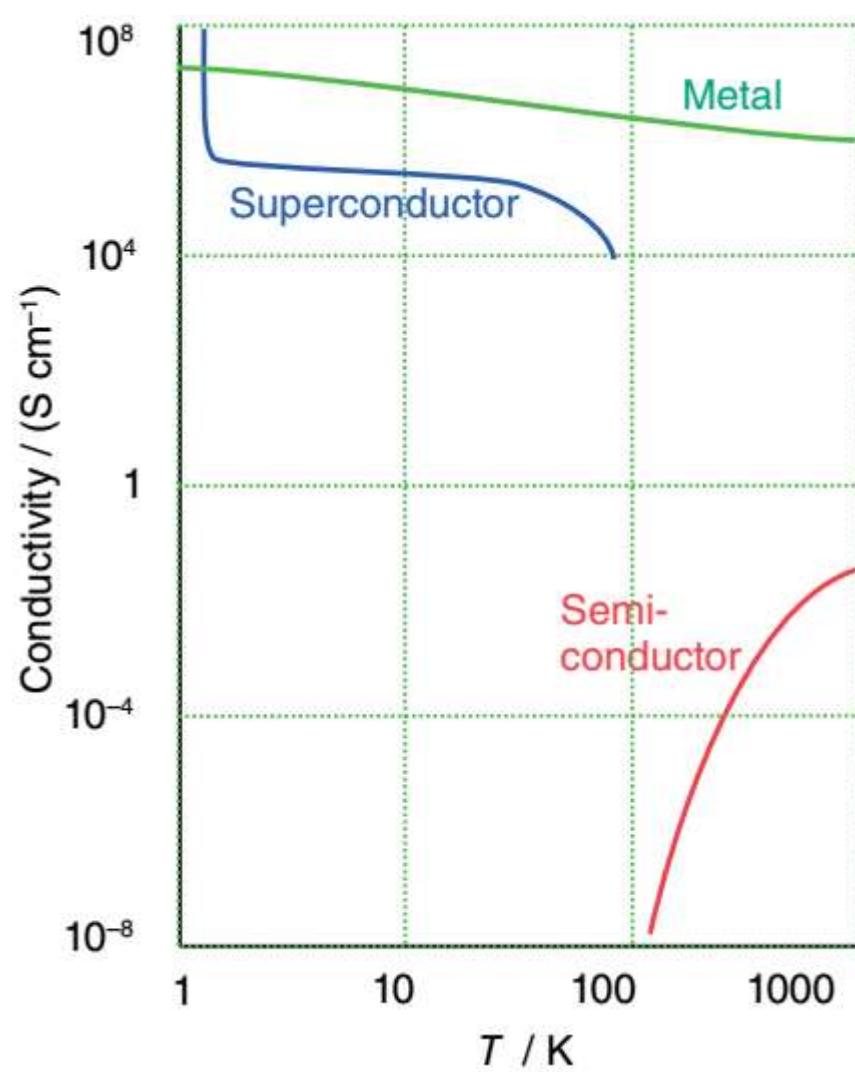


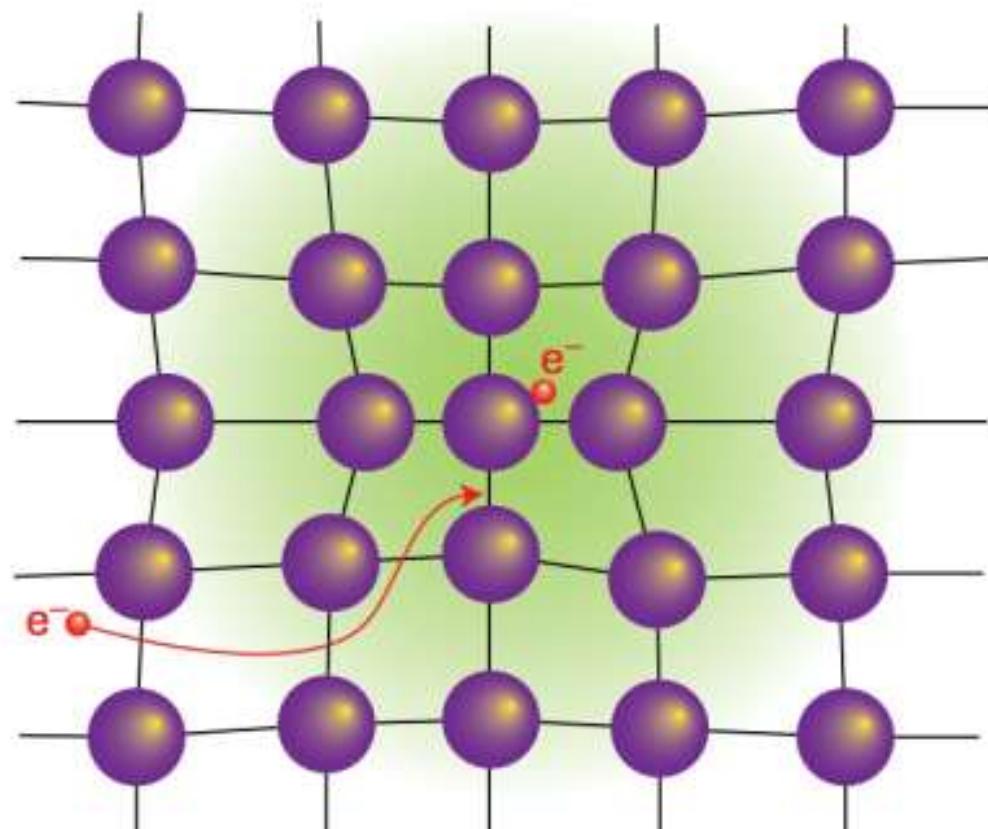
FIGURE 4.60 The variation of the electrical conductivity of a substance with temperature is the basis of the classification of the substance as a metallic conductor, a semiconductor, or a superconductor.

- The **mechanism of superconductivity** 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***.
- ***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***.
- 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.

- Figure 24.23 shows that there is a degree of periodicity in the elements that exhibit superconductivity. Note in particular that the ferromagnetic metals Fe, Co, and Ni do not display superconductivity, nor do the alkali metals or the coinage metals Cu, Ag, and Au.

Most of these superconducting materials were metal alloys, although superconductivity had been found in many oxides and sulfides; magnesium diboride is superconducting below 39K.

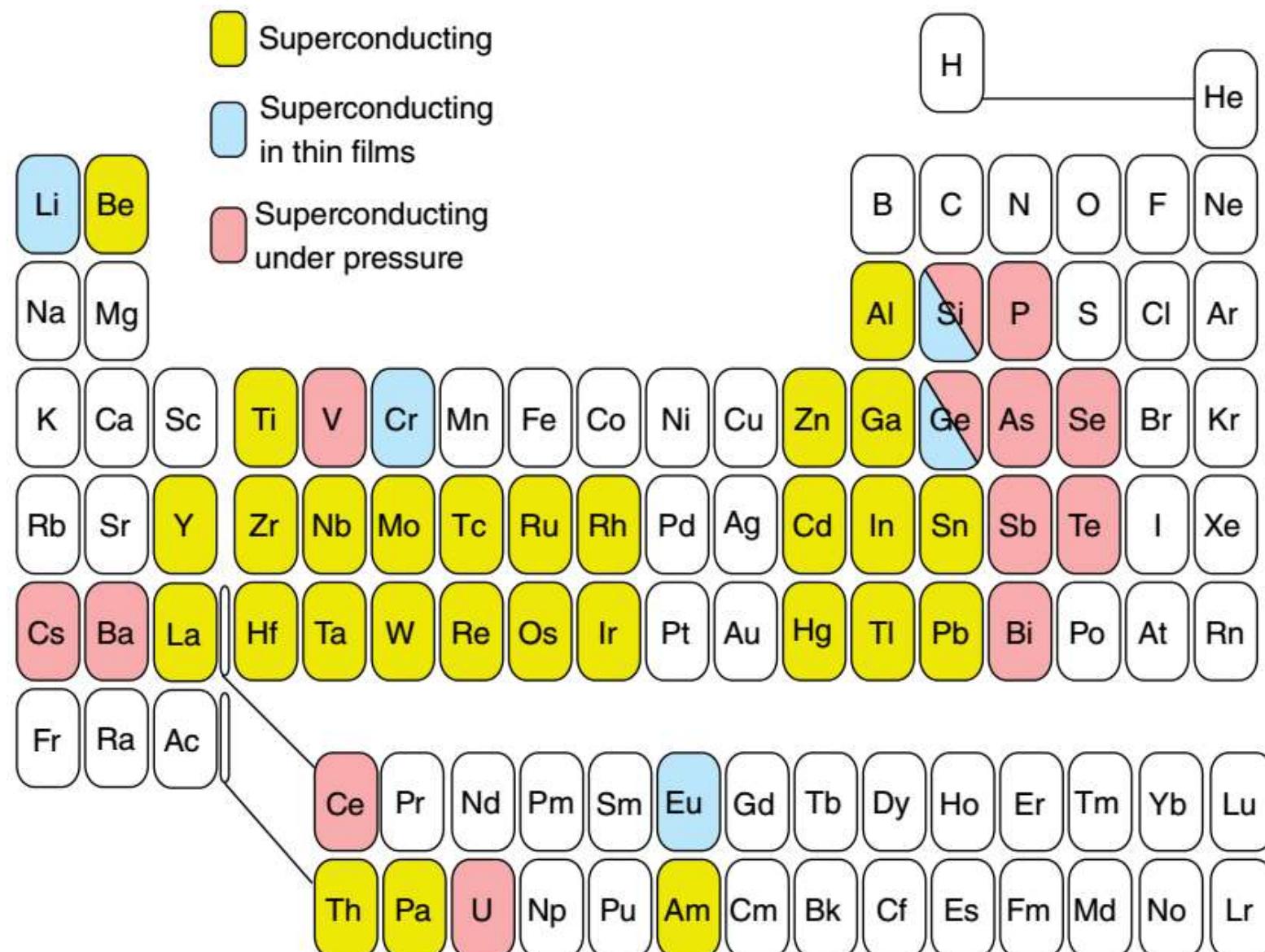


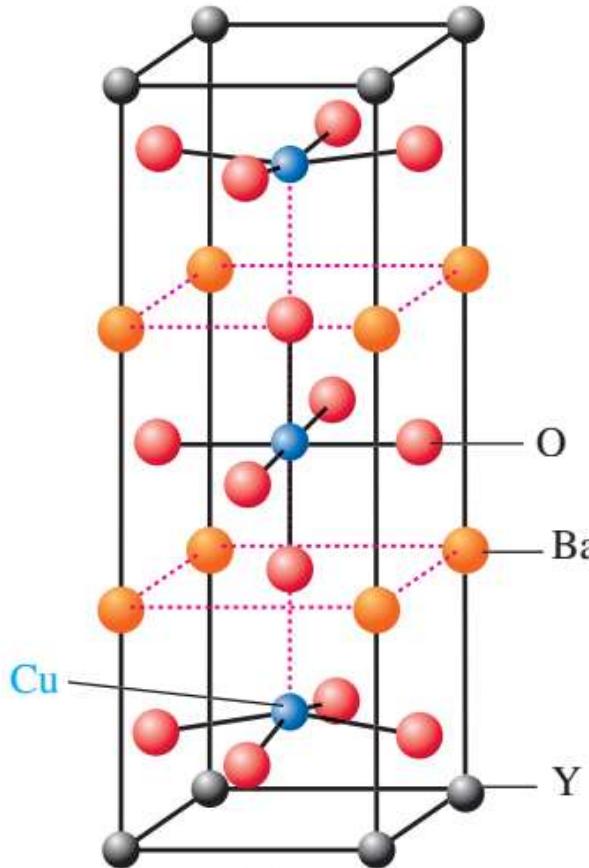
FIGURE 24.23 Elements that show superconductivity under the specified conditions.

- Following the discovery in 1911 that mercury is a superconductor below 4.2K, physicists and chemists made slow but steady progress in the discovery of superconductors with higher values of  $T_c$ . 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  $\text{La}_2\text{CuO}_4$  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 ( $\text{Y}_2\text{O}_3$ ), barium carbonate ( $\text{BaCO}_3$ ) and copper(II) oxide ( $\text{CuO}$ ) 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***.
- 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.

- Several *ceramics*, inorganic powders that have been fused and hardened by heating to a high temperature, containing oxocuprate motifs,  $\text{Cu}_m\text{O}_n$ , 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.
- 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 superconductors of a critical temperature *below that of liquid helium* are referred to as **low-temperature superconductors**.
- Substances which have a  $T_c$  between *higher than nitrogen's boiling temperature* of 77 K are referred to as **high-temperature superconductors (HTSs)**.

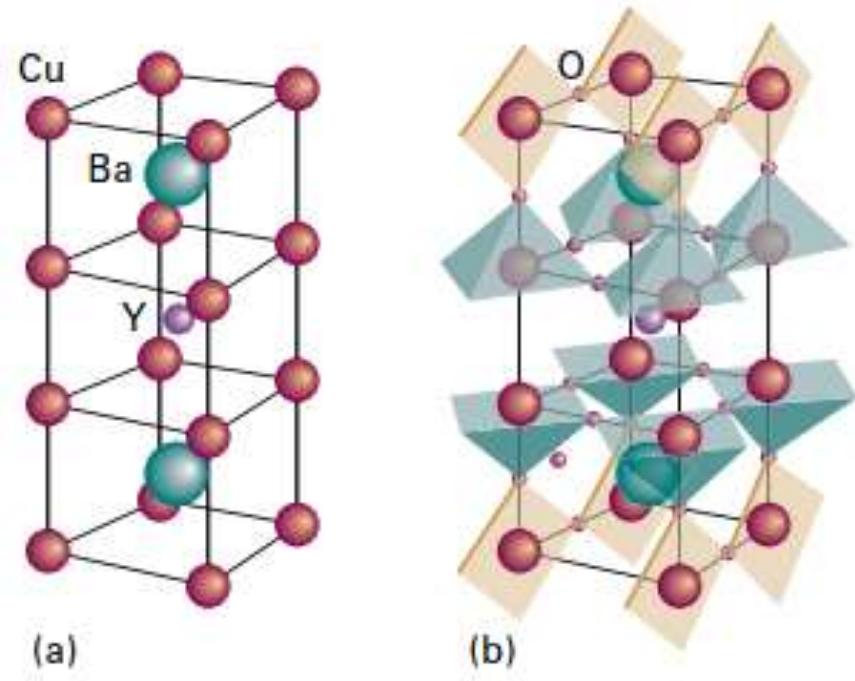
FIGURE 23-17. Structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  superconductor.



- 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.
- The mechanism by which electron pairs form in high-temperature superconductors, however, is clearly different from that in low-temperature superconductors.
- 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  $\text{CuO}_5$  units arranged as two-dimensional layers and the square planar  $\text{CuO}_4$  units arranged in sheets are common structural features of oxocuprate HTSCs.
- There is evidence implicating the arrangement of  $\text{CuO}_5$  layers and  $\text{CuO}_4$  sheets in the mechanism.
- It is believed that *movement of electrons along the linked  $\text{CuO}_4$  units accounts for superconductivity*, whereas the linked  $\text{CuO}_5$  units act as 'charge reservoirs' that maintain an appropriate number of electrons in the superconducting layers.
- There is, as yet, no settled explanation of high-temperature superconductivity. It is believed that the movement of pairs of electrons, 'Cooper pairs' and responsible for conventional superconductivity, is also important in the high-temperature superconductor materials, but the mechanism for pairing is hotly debated.

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.

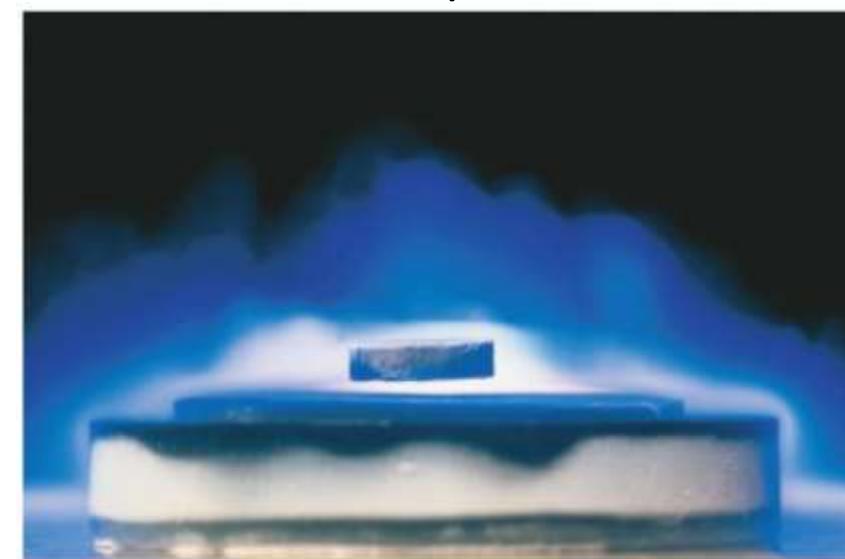


- **Lack of a suitable theory complicates the search for higher-temperature superconductors.** When the mechanism for high-temperature superconductors is better understood, new breakthroughs might be easier to accomplish. Perhaps a room-temperature superconducting material will be possible.
- Despite 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.
- Superconductors have unique **magnetic properties**.
- Two types of superconductors are known:
  - **Type I superconductors** show *abrupt loss of superconductivity* when *an applied magnetic field exceeds a value* characteristic of the material.
  - **Type II superconductors**, which include high-temperature materials (HTSCs), show *a gradual loss of superconductivity* and diamagnetism with increasing magnetic field above a critical field, denoted  $H_c$ .
- In 1933, Meissner Ochsenfeld noticed that *superconductors exclude an internal magnetic field*, a phenomenon now known as the **Meissner effect**.
- Type I superconductors are **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**. Thus, **a superconducting solid cooled below its  $T_c$  will appear to float above a magnet**, which can be demonstrated by the **levitation of a superconductor above a magnet**. It is also the basis for a number of that include magnetic levitation, as in '**maglev**' trains.

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.



- 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 explored in a variety of practical applications, including high-performance transformers, electric motors, most sensitive magnetometers like superconducting quantum interference devices (SQUIDs), and **magnetically levitated high-speed 'maglev' trains**.

FIGURE 6.31 Superconductors have the ability to levitate vehicles with embedded magnets. This picture shows an experimental zero-friction train in Japan, built to use helium-cooled metal superconductors.



## Is hydrogen sulfide useful?

- Superconducting materials conduct electricity without resistance below a superconducting transition temperature,  $T_c$ . The search for high temperature superconductors still fascinates researchers and success will have an immediate and lasting impact on technology and industry. Recently, ***H<sub>2</sub>S under very high pressures has been found to be superconducting with a T<sub>c</sub> of 190K at pressures in excess of 95GPa.***
- Hydrogen sulfide ***begins to behave as a semiconductor at pressures in excess of 50GPa*** when the conductance is temperature dependent.
- ***As the pressure is increased to above 90GPa metallic conductance is exhibited and we can describe the hydrogen sulfide as being metallic.***
- However, ***traces of sulfur are observed in the system*** which indicates that some decomposition is taking place. In fact the H<sub>2</sub>S decomposes to H<sub>3</sub>S and S at these pressures:  $3\text{H}_2\text{S} \rightarrow 2\text{H}_3\text{S} + \text{S}$
- The ***species responsible for the superconductivity are the H<sub>3</sub>S molecules arranged in a bcc-like structure*** (Fig. B16.3).
- The superconductivity in H<sub>3</sub>S is due to the ***proximity in energy of the H1s orbitals and the sulfur 3s and 3p orbitals at high pressures, leading to metallic conduction and then superconductivity.*** The same reason is given for the superconductivity of MgB<sub>2</sub>.

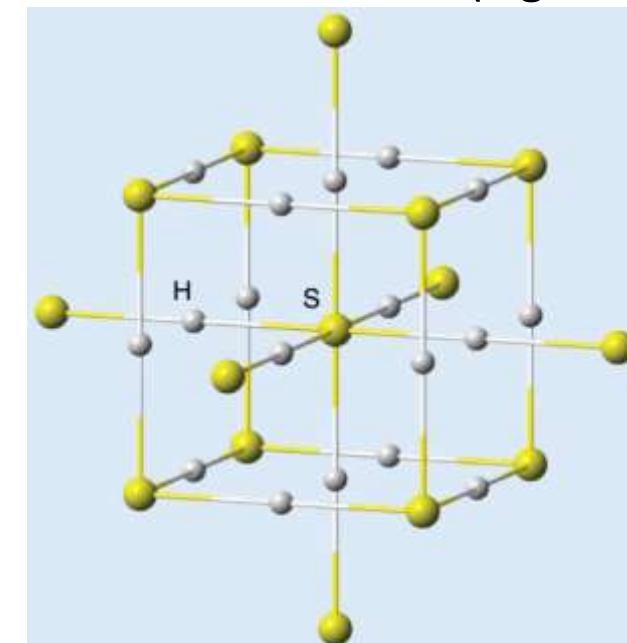


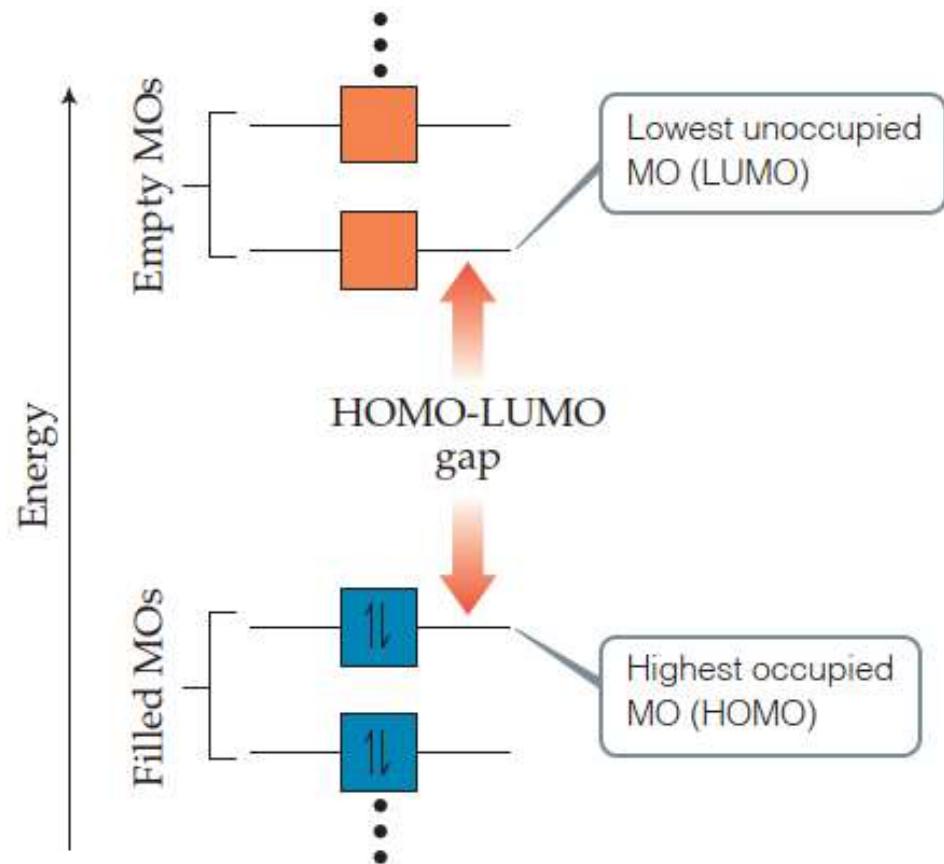
FIGURE B16.3 The structure of superconducting H<sub>3</sub>S.

## OPTICAL PROPERTIES OF SOLIDS

- Many inorganic solids are intensely coloured and are used as pigments in colouring inks, plastics, glasses, and glazes. Whereas many insoluble organic compounds (for example the C.I. Pigment Red 48, which is calcium 4-((5-chloro-4-methyl-2-sulfophenyl)azo)-3-hydroxy-2-naphthalenecarboxylic acid) are also used as pigments, ***inorganic materials often have advantages in terms of applications associated with their chemical, light, and thermal stability.***
- Pigments were originally developed from naturally occurring compounds such as hydrated iron oxides, manganese oxides, lead carbonate, vermillion ( $\text{HgS}$ ), orpiment ( $\text{As}_2\text{S}_3$ ), and copper carbonates. These compounds were even used in prehistoric cave paintings.
- Synthetic pigments, which are often analogues of naturally occurring compounds, were developed by some of the earliest chemists and alchemists, and the first synthetic chemists were probably those involved in making pigments. Thus, the pigment Egyptian blue ( $\text{CaCuSi}_4\text{O}_{10}$ ) was made from sand, calcium carbonate, and copper ores as long as 3000 years ago. This compound and a structural analogue, Chinese blue ( $\text{BaCuSi}_4\text{O}_{10}$ ), which was first made about 2500 years ago, have a structure containing square-planar copper(II) ions surrounded by  $\text{Si}_4\text{O}_{10}$  groups.
- Inorganic pigments continue to be important commercial materials, and this section summarizes some of the recent advances in this field.
- As well as producing the colours of ***inorganic pigments as a result of the absorption and reflection of visible light, some solids are able to absorb energy of other wavelengths*** (or types, for example ***electron beams***) and emit light in the visible region. This ***luminescence*** is responsible for the properties of ***inorganic phosphors***.

## ➤ OPTICAL PROPERTIES OF SOLIDS

- In discussing light absorption by molecules, we can focus on the two **frontier MOs** shown in Figure 9.47. The highest occupied molecular orbital (**HOMO**) is the MO of the highest energy that has electrons in it. The lowest unoccupied molecular orbital (**LUMO**) is the MO of the lowest energy that does not have electrons in it.
- The energy difference between the HOMO and the LUMO—known as the **HOMO–LUMO gap**—is related to the **minimum energy needed to excite an electron in the molecule**.
- The frequency of *light absorption* is given by:  $\nu = E/h$ .
- The minimum energy needed to excite an electron from the HOMO to the LUMO in  $N_2$  corresponds to light with a wavelength of less than 200 nm, which is far into the ultraviolet part of the spectrum. As a result,  $N_2$  **cannot absorb visible light and is therefore appears colorless**.
- In solids, the HOMOs and the LUMOs form **valence** and **conduction bands** respectively (Fig. 7). The energy difference between the valence and conduction bands is called band gap ( $E_g$ ).



▲ Figure 9.47 Definitions of the highest occupied and lowest unoccupied molecular orbitals. The energy difference between these is the HOMO-LUMO gap.

## □ OPTICAL PROPERTIES OF SOLIDS

- 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.
- 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**.

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

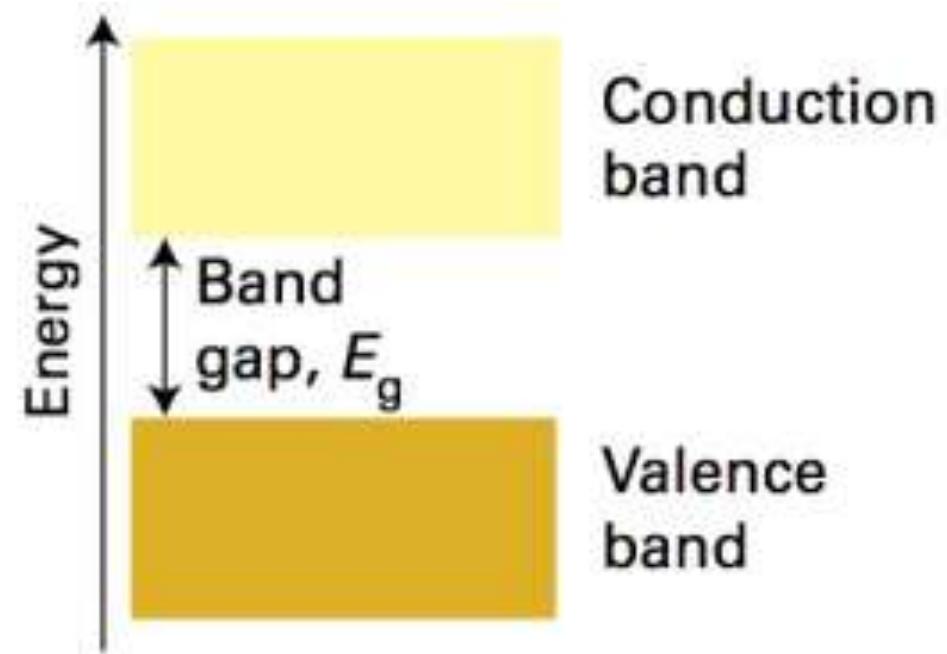
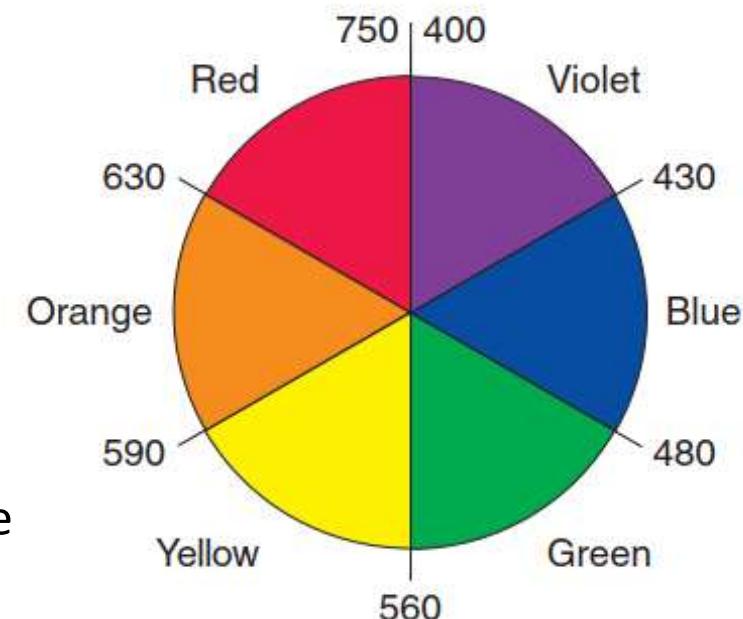


Fig . 7 In some materials, the band gap  $E_g$ , is very large and electron promotion can occur only by excitation with electromagnetic radiation.

- The brilliant colors around you have a **particular color** for one of two reasons:
  - It **reflects** (or **transmits**) light of that color. Thus, if an object absorbs all wavelengths except green, the reflected (or transmitted) light is seen as green.
  - It **absorbs** light of the *complementary color*. Thus, if the object absorbs only red, the complement of green, the remaining mixture of reflected (or transmitted) wavelengths is also seen as green.
- **No Absorption:** Colorless or white substances usually have such a large HOMO–LUMO gap that visible light is not energetic enough to excite an electron to a higher level.
- **Complete Absorption:** Solids with **band gaps of less than  $2.8 \times 10^{-19} \text{ J}$**  absorb all wavelengths of visible light and appear black. These include silicon, germanium, and gallium arsenide.

❖ **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.



**Figure 22.15** An artist's wheel. Colors, with approximate wavelength ranges (in nm), are shown as wedges.

## Coloured solids

**Key point:** *Intense colour in inorganic solids can arise through d-d transitions, charge transfer (and the analogous interband electron transfer), or intervalence charge transfer.*

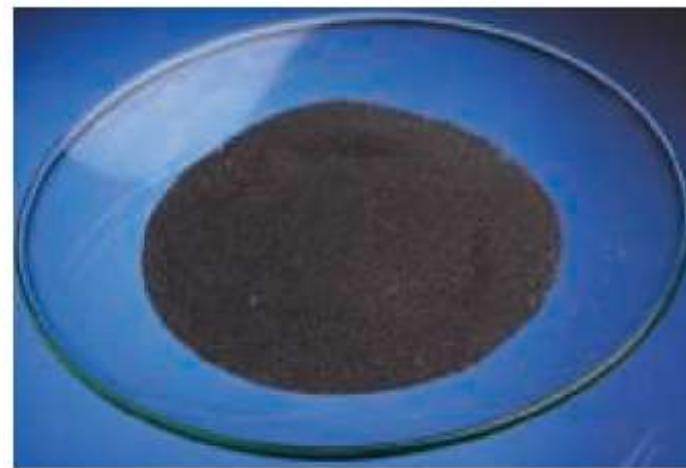
- ❖ The blue colour of  $\text{CoAl}_2\text{O}_4$  and  $\text{CaCuSi}_4\text{O}_{10}$  stems from the presence of **d-d transitions (absorption)** in the visible region of the electromagnetic spectrum. The characteristic intense colour of cobalt aluminate is a result of having a noncentrosymmetric tetrahedral site for the metal ion, which removes the constraint of the **Laporte selection rule** of octahedral environments. The chemical and thermal stabilities are due to the location of the  $\text{Co}^{2+}$  ion in the close-packed oxide arrangement. Other inorganic pigments with colours based on d-d transitions include Ni-doped  $\text{TiO}_2$  (yellow) and  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  (green).
- ❖ Colour also arises in many inorganic compounds from **charge transfer** or what is often electronically an equivalent process in solids, *the promotion of an electron from a valence band (derived mainly from anion orbitals) into a conduction band (derived mainly from metal orbitals)*. Charge-transfer pigments include compounds such as lead chromate ( $\text{PbCrO}_4$ ), containing the yellow-orange chromate(VI) anion, and  $\text{BiVO}_4$  with the yellow vanadate(V) anion. The compounds  $\text{CdS}$  (yellow) and  $\text{CdSe}$  (red) both adopt the wurtzite structure and their **colour arises from transitions from the filled valence band (which is mainly derived from chalcogenide p orbitals) to orbitals based mainly on Cd**.
- ✓ For a material with a band gap of 2.4 eV (as for  $\text{CdS}$  at 300 K) these transitions occur as a **broad absorption corresponding to wavelengths shorter than 515 nm, thus CdS is bright yellow as the blue part of the visible spectrum is fully absorbed**. For  $\text{CdSe}$  the band gap is smaller on account of the higher energies of the Se4p orbitals and the absorption edge shifts to lower energies. As a result, only red light is not absorbed by the material.

## ❖ Charge-Transfer Color

The CF model is concerned solely with the energies of the d-electron states but the intense colors of many transition-metal complexes, e.g., the purple color of  $[\text{MnO}_4]^-$  and the blood red of  $[\text{Fe}(\text{CNS})_6]^{3-}$ , arise **not from** d  $\rightarrow$  d transitions, which as we have seen above are normally very weak, but from **charge-transfer transitions in which electrons are transferred from the ligands to the metal (LMCT)**.

$[\text{Fe}(2,2'\text{-bipyridine})_3]^{2+}$  shows a strong absorption at 522 nm due to the reverse process, a **metal-to-ligand charge transfer (MLCT)**.

Transitions of this type are further evidence of covalency and require a molecular orbital treatment for their quantitative understanding.



$\text{KMnO}_4$



$\text{K}_2\text{CrO}_4$

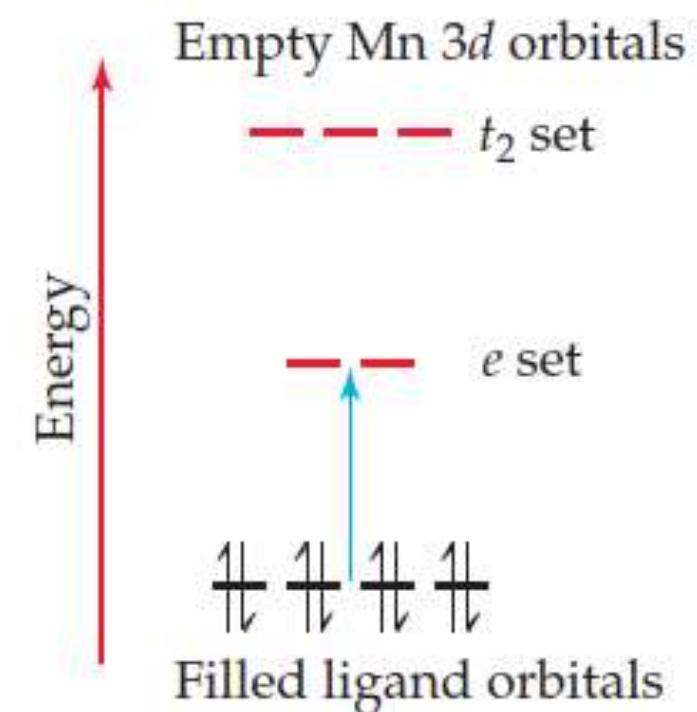


$\text{KClO}_4$

**Figure 23.35** The colors of compounds can arise from charge-transfer transitions.  $\text{KMnO}_4$  and  $\text{K}_2\text{CrO}_4$  are colored due to ligand-to-metal charge-transfer transitions in their anions. Higher energy ultraviolet photons are needed to excite the charge-transfer transition in the perchlorate ion, therefore  $\text{KClO}_4$  is white.

- You have probably seen many colorful transition-metal compounds, including those shown in Figure 23.35. Many of these compounds are colored because of d-d transitions.
  - Some colored complexes, however, including the violet permanganate ion,  $\text{MnO}_4^-$ , and the yellow chromate ion,  $\text{CrO}_4^{2-}$ , derive their color from a different type of excitation involving the d orbitals.
  - A complex may absorb radiation as a result of the *transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa*. This mode of chromophore activity is shown by the permanganate ion,  $\text{MnO}_4^-$ , and accounts for its intense violet color. In this oxoanion, the electron migrates from an orbital that is largely confined to the O atom ligands to an orbital that is largely confined to the Mn atom. It is therefore an example of a **ligand-to-metal charge-transfer** transition (**LMCT**).
  - The reverse migration, a **metal-to-ligand charge-transfer** transition (**MLCT**), can also occur. An example is the transfer of a d electron into the antibonding  $\pi$  orbitals of an aromatic ligand. The resulting excited state may have a very long lifetime if the electron is extensively delocalized over several aromatic rings, and such species can participate in photochemically induced redox reactions.
  - The permanganate ion strongly absorbs visible light (which arises from strong absorption within the range of 420–700 nm), with maximum absorption at 565 nm. Because violet is complementary to yellow, this strong absorption in the yellow portion of the visible spectrum is responsible for the violet color of salts and solutions of the ion.
- ✓ What is happening during this absorption of light?

- ✓ The  $\text{MnO}_4^-$  ion is a complex of Mn(VII). Because **Mn(VII)** has a  $[\text{Ar}]3\text{d}^0$  electron configuration, ***the absorption cannot be due to a d-d transition because there are no d electrons to excite!***
- ✓ That does not mean, however, that the d orbitals are not involved in the transition. The excitation in the  $\text{MnO}_4^-$  ion is due to a **charge-transfer transition**, ***in which an electron on one oxygen ligand is excited into a vacant d orbital on the Mn ion*** (Figure 23.36).
- ✓ In essence, an electron is transferred from a ligand to the metal, so this transition is called a **ligand-to-metal charge-transfer (LMCT) transition**.
- ✓ An LMCT transition is also responsible for the color of the  $\text{CrO}_4^{2-}$ , which contains the Cr(VI) ion with an  $[\text{Ar}]3\text{d}^0$  electron configuration.



**Figure 23.36** Ligand-to-metal charge-transfer transition in  $\text{MnO}_4^-$ . As shown by the blue arrow, an electron is excited from a nonbonding orbital on O into one of the empty d orbitals on Mn.

- A salt of the perchlorate ion ( $\text{ClO}_4^-$ ) appears colorless (as shown in Figure 23.35). Like  $\text{MnO}_4^-$ ,  $\text{ClO}_4^-$  is tetrahedral and has its central atom in the +7 oxidation state. However, because the Cl atom **does not have low-lying d orbitals**, exciting an electron from O to Cl **requires a more energetic photon** than does it does in  $\text{MnO}_4^-$ . The first absorption for  $\text{ClO}_4^-$  is in the ultraviolet portion of the spectrum, so no visible light is absorbed and the salt appears white.
- Other complexes exhibit charge-transfer excitations in which an electron from the metal atom is excited to an empty orbital on a ligand. Such an excitation is called a **metal-to-ligand charge-transfer (MLCT)** transition.
- Lastly, **metal-to-metal charge-transfer (MMCT)** bands occur between metal-centered orbitals on two different metals within the same complex, such as those in Prussian blue. In the case of mixed-valence compounds, **one of the metals must be in a low oxidation state so that it can act as an electron donor, while the other metal exists in a high oxidation state and acts as the electron acceptor.**
- ❖ In some **mixed-valence compounds**, electron transfer between differently charged metal centres can also occur in the visible region, and as these transfers are often fully allowed they give rise to intense colour. Prussian blue,  $[\text{Fe(III)}]_4[\text{Fe(II)}(\text{CN})_6]_3$  (Fig. 24.64), is one such compound containing both iron(II) and iron(III) linked together by cyanide ligands ( $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ) and its dark blue colour has resulted in its widespread use in inks.
- ❖ Intensely coloured Ru compounds, such as the tris(carboxyl)-terpyridine complex  $[\text{Ru}(2,2,2-(\text{COOH})_3\text{-terpy})(\text{NCS})_3]$ , absorb efficiently right across the visible and near IR regions of the spectrum and are used as photosensitizers in Gräztel-type solar cells.
- ❖ Many metal-containing pigments used for oil painting, such as cadmium yellow ( $\text{CdS}$ ), chrome yellow ( $\text{PbCrO}_4$ ), and red ochre ( $\text{Fe}_2\text{O}_3$ ), have intense colors because of **charge-transfer transitions**.

- ***Charge-transfer transitions are generally more intense than d-d transitions.***
- ❖ Inorganic radicals often have fairly low-energy electronic transitions that can occur in the visible region. Two examples are  $\text{NO}_2$  (brown) and  $\text{ClO}_2$  (yellow). One inorganic pigment is based on an inorganic radical, but because of the high reactivity normally associated with main-group compounds containing unpaired electrons, this species is trapped inside a zeolite cage. Thus the royal-blue pigment ultramarine, a synthetic analogue of the naturally occurring semi-precious stone lapis lazuli, has the idealized formula  $\text{Na}_8[\text{SiAlO}_4]_6 \cdot (\text{S}_3)_2$  and contains the  $\text{S}_3^-$  polysulfide radical anion occupying a sodalite cage formed by the aluminosilicate framework (Fig. 24.65).

## **Pigments and Phosphors: Optical Displays**

- The band gap of an insulator or semiconductor has a significant effect on its color. Pure diamond has a large band gap, so even blue light does not have enough energy to excite electrons from the valence band to the conduction band. As a result, light in the visible region of the electromagnetic spectrum passes through diamonds without being absorbed and the diamonds are colorless.
- Cadmium sulfide (CdS; Fig. 22.28) has a band gap of  $3.8 \times 10^{-19}$  J, which corresponds to a wavelength of 510 nm in the visible region of the spectrum. The absorption cross section of CdS increases as the incident photon wavelength is decreased to 450 nm. **Cadmium sulfide thus primarily absorbs violet and blue light but strongly transmits yellow, giving it a deep yellow color.** Cadmium sulfide is the **pigment** called **cadmium yellow**.
- Cinnabar (HgS) has a smaller band gap of  $3.2 \times 10^{-19}$  J and **absorbs all light except red**. It has a **deep red color** and is the **pigment vermilion**.
- Semiconductors with **band gaps of less than  $2.8 \times 10^{-19}$  J absorb all wavelengths** of visible light and **appear black**. These include silicon, germanium, and gallium arsenide.

FIGURE 22.28 Mixed crystals of two semiconductors with different band gaps, CdS (yellow) and CdSe (black), show a range of colors, illustrating a decrease in the band gap energy as the composition of the mixture becomes richer in Se.



## White and black pigments

- Some of the most important compounds used to modify the visual characteristics of polymers and paints have visible-region absorption spectra that result in them appearing either ***white (ideally no absorption in the visible region)*** or **black (complete absorption between 380 and 800 nm)**.

### (a) White pigments

**Key point:** Titanium dioxide is used almost universally as a white pigment.

- White inorganic materials can also be classified as pigments and vast quantities of these compounds are synthesized for applications such as the production of white plastics and paints. Important commercial compounds of this class that have been used extensively historically are  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{ZnS}$ , lead(II) carbonate, and lithopone (a mixture of  $\text{ZnO}$  and  $\text{BaSO}_4$ ); note that ***none of the metals in these materials has an incomplete d-electron shell that might otherwise induce colour through d-d transitions***. The desirable qualities of  $\text{TiO}_2$  as a white pigment derive from its excellent light scattering power, which in turn is a result of its high refractive index ( $n_r = 2.70$ ), the ability to produce very pure materials of a desired particle size, and its good light-fastness and weather resistance. Uses of titanium dioxide, which nowadays dominates the white-pigment market, include paints, coatings, and printing ink (where it is often used in combination with coloured pigments to increase their brightness and hiding power), plastics, fibres, paper, white cements, and even foodstuffs (where it can be added to icing sugar, sweets, and flour to improve their brightness).

## (b) Black, absorbing, and specialist pigments

**Key points:** Special colour, light absorbing, and interference effects can be induced in inorganic materials used as pigments.

- The most important black pigment is **carbon black**, which is a better defined, industrially manufactured form of soot. Carbon black is obtained by partial combustion or pyrolysis (heating in the absence of air) of hydrocarbons. The material **has excellent absorption properties right across the visible region of the spectrum** and applications include printing inks, paints, plastics, and rubber.
- Copper(II) chromite,  $\text{CuCr}_2\text{O}_4$ , with the spinel structure is used less frequently as a black pigment.
- These **black pigments also absorb light outside the visible region, including the infrared**, which means that they **heat up** readily on exposure to sunlight. Because this heating can have drawbacks in a number of applications, there is interest in **the development of new materials that absorb in the visible region but reflect infrared wavelengths**;  $\text{Bi}_2\text{Mn}_4\text{O}_{10}$  is one compound that exhibits these properties.
- Examples of more specialist inorganic pigments are magnetic pigments based on coloured ferromagnetic compounds such as  $\text{Fe}_3\text{O}_4$  and  $\text{CrO}_2$ , and anticorrosive pigments such as zinc phosphates. The deposition of inorganic pigments as thin layers on to surfaces can produce additional optical effects beyond light absorption. Thus deposition of  $\text{TiO}_2$  or  $\text{Fe}_3\text{O}_4$ , as thin layers a few hundred nanometres thick, on flakes of mica produces lustrous or pearlescent pigments where interference effects between light scattered from the various surfaces and layers produces shimmering and iridescent colours.

- **Phosphors** are *wide band-gap materials with dopants selected to create new levels such that particular colors of light are emitted*. Electrons in these materials are excited by light of other wavelengths or by electrons hitting their surfaces, and *light is then emitted as they return to lower energy states*. A **fluorescent lamp**, for example, is a **mercury-vapor lamp** in which the inside of the tube has been coated with phosphors. The phosphors absorb the violet and ultraviolet light emitted by mercury vapor and emit at lower energies and longer wavelengths, giving a nearly white light that is more desirable than the bluish light that comes from a mercury-vapor lamp without the phosphors.
- **Phosphors are also used in television screens**. The picture is formed by scanning a beam of electrons (from an electron gun) over the screen. The electrons strike the phosphors coating the screen, exciting their electrons and causing them to emit light. In a **black-and-white television tube**, the phosphors are a mixture of silver doped into ZnS, which gives blue light, and silver doped into  $Zn_xCd_{1-x}S$ , which gives yellow light. The combination of the two provides a reasonable approximation of white. A **color television** uses three different electron guns, with three corresponding types of phosphor on the screen. **Silver doped in ZnS gives blue**, **manganese doped in  $Zn_2SiO_4$  is used for green**, and **europium doped in  $YVO_4$  gives red light**. Masks are used to ensure that each electron beam encounters only the phosphors corresponding to the desired color.

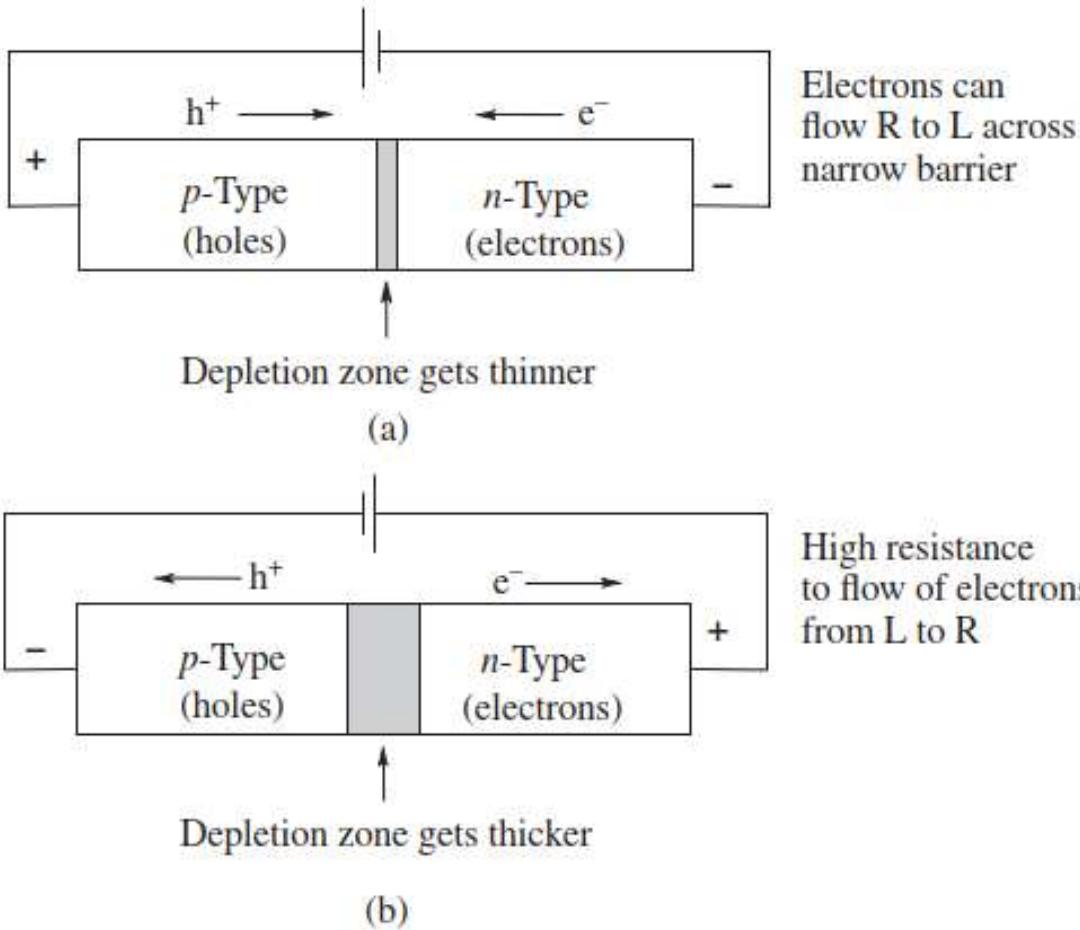
## ❖ Solar Energy

- Asked to identify the **major technological challenge for the twenty-first century, you might say “energy,”** reasoning that development of sustainable energy sources is crucial to meet the needs of future generations of people on our planet. *One of the most remarkable sources of clean energy is the Sun, which sends enough energy to power the world for millions of years.* Our challenge is to capture enough of this energy in a form that allows us to use it as needed. ***Photovoltaic solar cells convert the light from the Sun into usable electricity,*** and the development of more efficient solar cells is one way to address Earth’s future energy needs.
- ***How does solar energy conversion work?*** Fundamentally, we need to be able to use photons from the Sun, especially from the visible portion of the spectrum, to excite electrons in molecules and materials to different energy levels. The magnitude of the ***energy gap between filled and empty electronic states*** is critical for ***solar energy conversion.*** Ideally, we want a substance that absorbs as many solar photons as possible and then converts the energy of those photons into a useful form of energy. Titanium dioxide is a readily available material that can be reasonably efficient at converting light directly into electricity. However, ***TiO<sub>2</sub> is white and absorbs only a small amount of the Sun’s radiant energy.*** Scientists are working to make solar cells in which TiO<sub>2</sub> is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light to absorb more of the solar spectrum. If the HOMO of these molecules is higher in energy than the HOMO of TiO<sub>2</sub>, the excited electrons will flow from the molecules into the TiO<sub>2</sub>, thereby generating electricity when the device is illuminated with light and connected to an external circuit.
- Efficient solar energy conversion promises to be one of the most interesting and important areas of both scientific and technological development in our future. Many of you may ultimately end up working in fields that have an impact on the world’s energy portfolio.

## 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.
- 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 n-type to p-type (from right to left in Figure 11.53) and not in the opposite direction. The ***p–n junction thus forms the basis of a rectifier, allowing current to pass in only one 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.

➤ Light-emitting diodes (LEDs) contain p–n junctions. The circuit in an LED is arranged so that electrons from the power source **flow into the conduction band of the n-type side**. As electrons continue to flow, they are **pushed to the conduction band of the p-type side**, which can hold more electrons. These electrons **enter the conduction band of the p-type side**, because they already occupy the higher-energy band in the n-type side. However, **once the electrons are in the higher-energy band of the p-type side, they fall into the lower-energy band unless it is full (where electrons meet holes that have been driven from the valence band of the p-doped side)**. As these electrons make transitions to the lower-energy band (electrons fall into the empty holes), **energy is released in the form of light** whose photons have energy equal to the band gap (Figure 12.32). This way electrical energy is converted into **optical or thermal energy**.

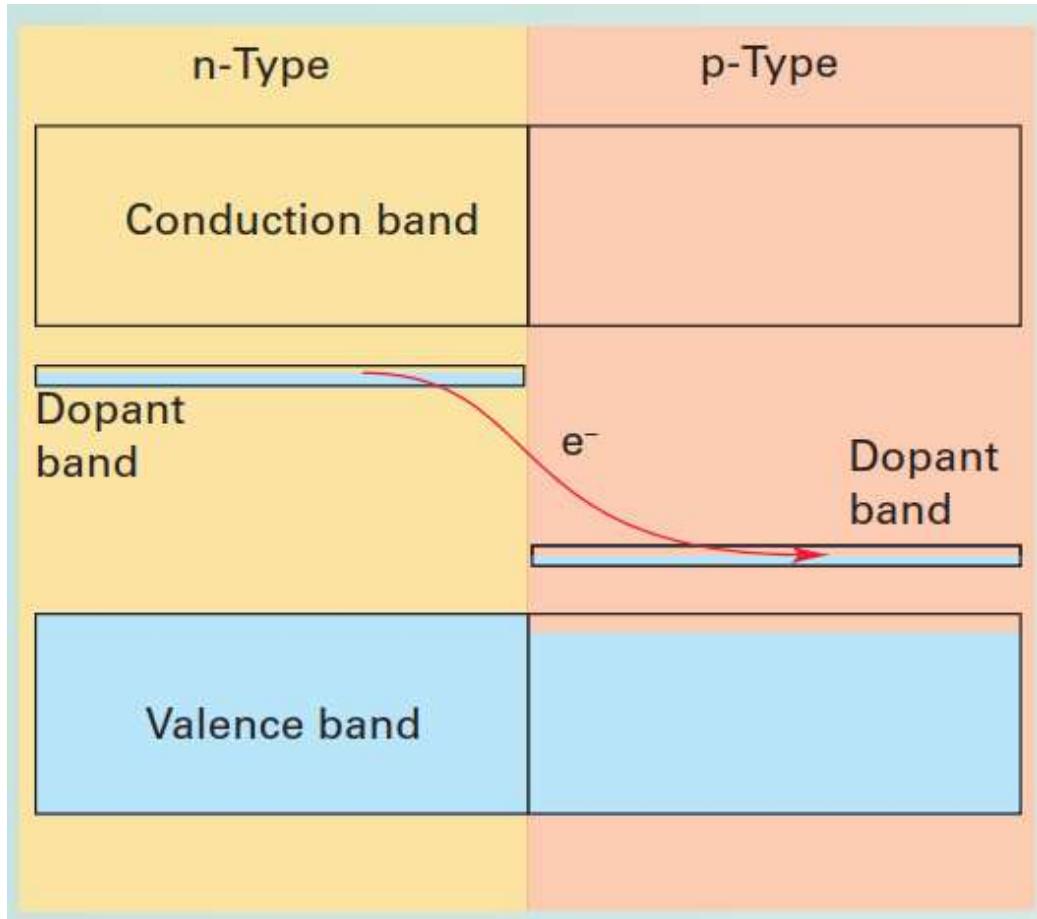
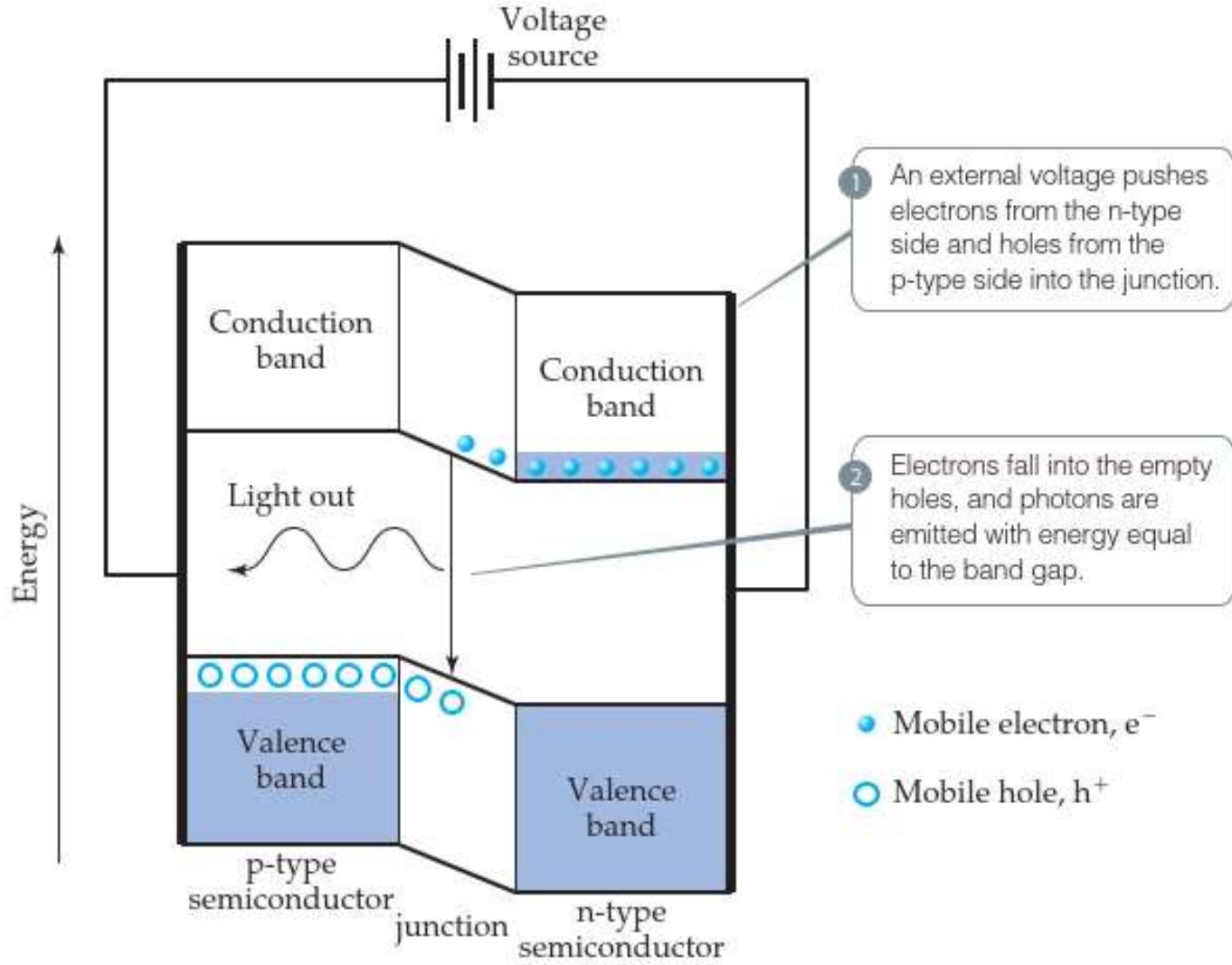


Figure B24.2 The structure of a p–n junction.



**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 LEDs 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  $2.26 \text{ eV}$  ( $3.62 \times 10^{-19} \text{ J}$ ), which corresponds to a **green photon** with a wavelength of  $549 \text{ nm}$ , while **GaAs** has a band gap of  $1.43 \text{ eV}$  ( $2.29 \times 10^{-19} \text{ J}$ ), which corresponds to an **infrared photon** with a wavelength of  $867 \text{ nm}$ .
- 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** ( $E_g = 2.43 \text{ eV}$ ,  $\lambda = 510 \text{ nm}$ ).

- ✓ 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)**.
- 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 ( $E_g = 3.4 \text{ eV}$ ,  $\lambda = 365 \text{ nm}$ ) and InN ( $E_g = 2.4 \text{ eV}$ ,  $\lambda = 517 \text{ nm}$ )**. An advantage of being able to produce blue LEDs is that they can be used as lasers in high-capacity optoelectronic storage devices. The wavelength of blue light produced by these LEDs (405 nm) is shorter than that used in DVD format devices (red light, 650 nm), which allows data to be written in smaller bits on an optical disc.
- **White LEDs are commonly formed from yellow and blue LEDs mixed in various proportions.** 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**.

- Many colors of LEDs are now available and are used in everything from barcode scanners to traffic lights. 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).

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

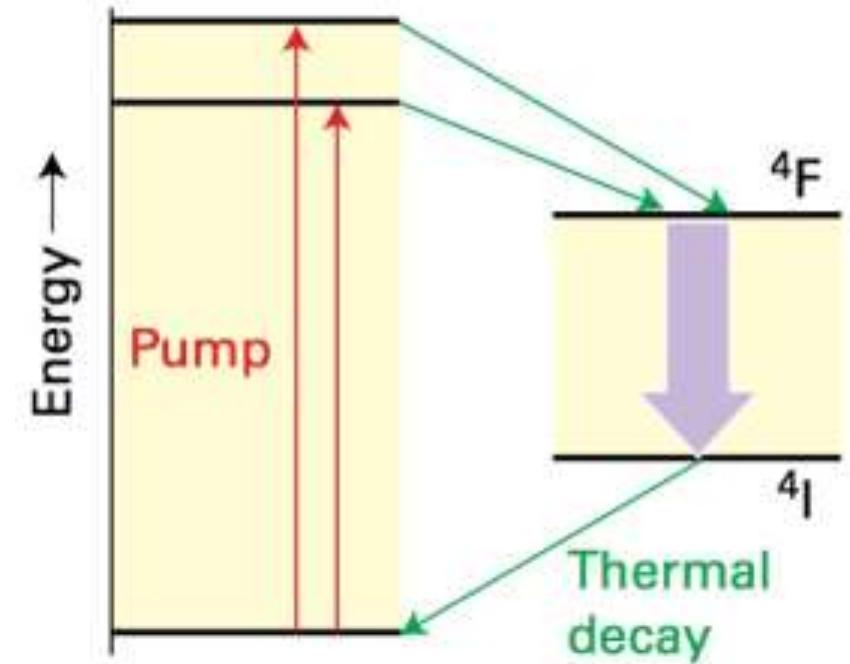
## Diode lasers

- 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  $\text{Nd}^{3+}$  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  $^4\text{F}$  to the  $^4\text{I}$  state of the  $\text{Nd}^{3+}$  ion.



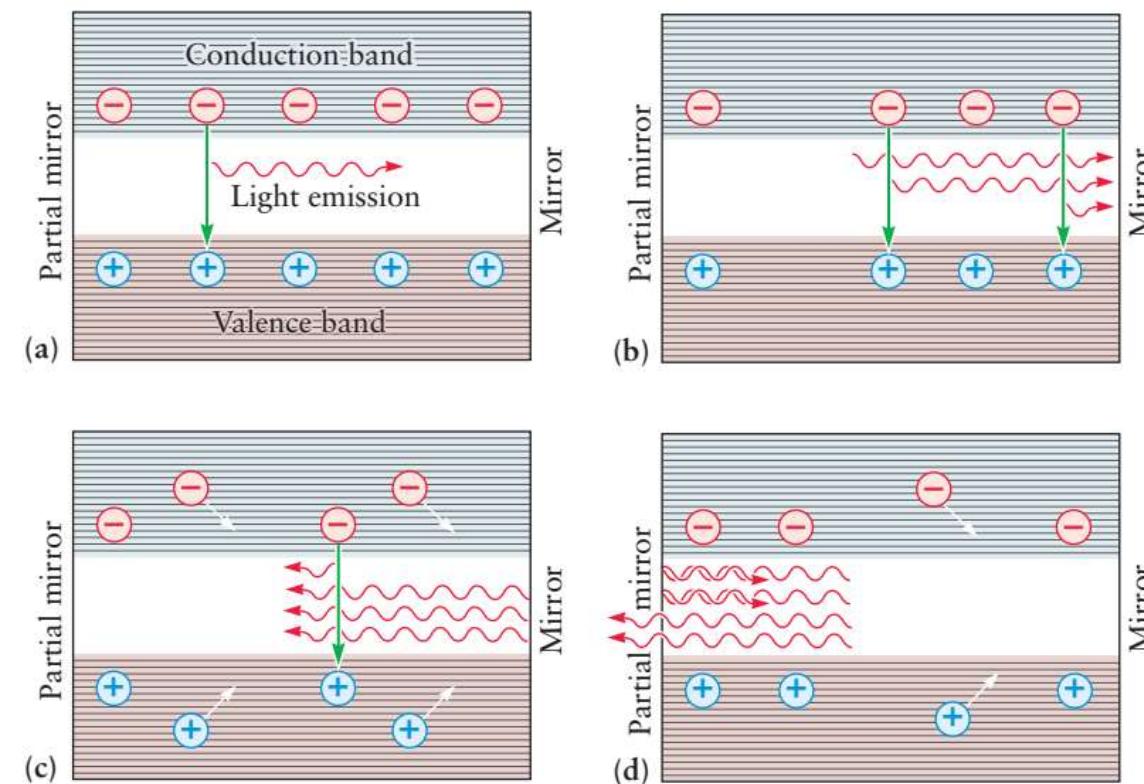
➤ Gallium arsenide and other semiconductors also provide materials for making **solid-state lasers**, which have applications ranging from reading compact discs to performing delicate eye surgery. When an electric current is passed through a material containing n–p junctions, electrons from the n regions and holes from the p regions flow toward the junctions, where they recombine and emit light. The light moves through the material, stimulating additional recombinations at other junctions and the emission of additional photons (Fig. 22.25). Critical to the operation of a laser is that these photons are coherent (in phase with one another), so the corresponding electric fields add constructively to create a plane wave. The light is reflected by a mirror at one end of the material and sets up a standing wave inside the semiconductor. At the other end, a partially reflecting mirror allows an intense beam of coherent light with a fixed wavelength to leave.

FIGURE 22.25 (a) In **this solid-state laser**, photons are emitted as electrons and holes recombine.

(b) An emitted photon can stimulate the emission of additional photons.

(c) Then reflection by a mirror on the right side sends coherent waves back through the laser medium and further amplification occurs by stimulated emission.

(d) Some of the waves pass through a partially reflecting mirror on the left side.



- Semiconductors perform a wide range of electronic functions that formerly required the use of vacuum tubes. Vacuum tubes occupy much more space, generate large amounts of heat, and require considerably more energy to operate than a transistor does, their semiconductor counterparts. More importantly, semiconductors can be built into integrated circuits and made to store information and process it at great speeds.
- Solar cells based on silicon or gallium arsenide provide a way to convert the radiant energy of the sun directly into electrical work by a technology that is virtually nonpolluting.

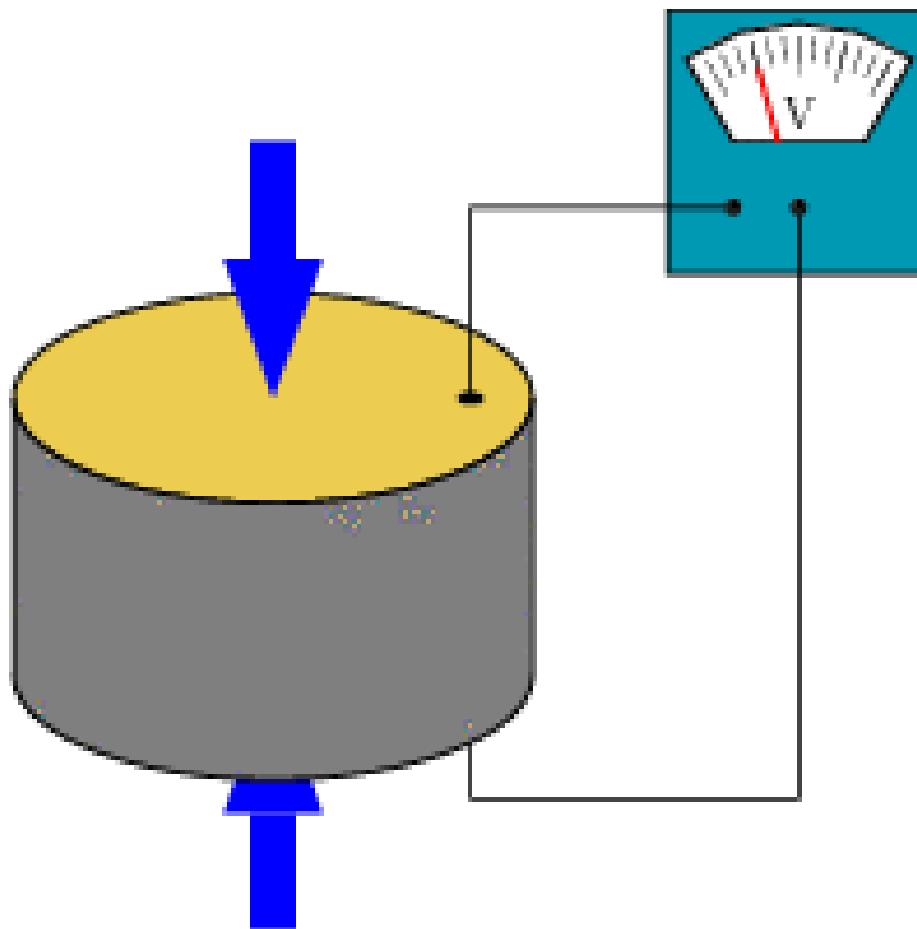
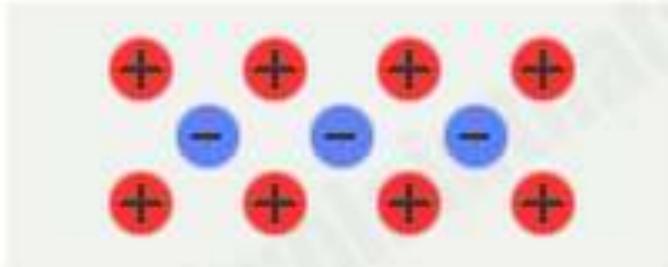
## Other Electrical and Optical Properties of Crystals

### ❖ 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  $\sigma$  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.

1



- 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 ( $\text{KH}_2\text{PO}_4$ ), lithium niobate ( $\text{LiNbO}_3$ ), and  $\beta$ -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  $\mu$* , in the substance.
- At **low light intensity**, most materials respond linearly, in the sense that  $\mu = \alpha E$ , where  **$\alpha$  is the polarizability**.
- At **high light intensity**, the **hyperpolarizability  $\beta$**  of the material becomes important and the induced dipole becomes  $\mu = \alpha E + \frac{1}{2} \beta E^2 + \dots$ .
- The *nonlinear term  $\beta E^2$*  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  $2\omega$  and that can act as a source of radiation of that frequency*.