# Bonding and Properties of Solid II

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- Bonding in solids –free-electron and band theory of solids.
- Optical properties of solids.
- Magnetic properties of solids
- Electrical properties of solids

# Free Electron Model for Solids

- According to this theory, a metal consists of electrons which are free to move about in the crystal like molecules of a gas in a container.
- Mutual repulsion between electrons is ignored and hence potential energy is taken as zero. Therefore, the total energy of the electron is equal to its kinetic energy.
- This model provided a satisfactory explanation for certain properties (e.g., electrical conductivity, electronic emission and electronic emission).
- Failed to explain that why some solids are good conductor some are semiconductor and other are insulators.
- It also fails to explain the specific heat of metals and magnetic susceptibility of paramagnetic metals.
- This theory was developed by Drude and Lorentz and hence is also known as Drude-Lorentz theory

# Postulates of free electron model

1. The outermost electrons of the constituent atom of the metal are weakly bound with the atoms. Hence these electrons get separated from their atoms and move freely inside the substance and are called free electrons.
2. There are large number of free electrons inside the metals and they behave like molecules of a gas enclosed in a container. Hence it is called free electron gas. These free electrons are responsible for the thermal and electrical conduction inside the metal. Hence they are also called conduction electrons.
3. The free electrons in thermal equilibrium obey Maxwell-Boltzmann statistics. Which states that the free energy per electron at an absolute temperature T is 1/2 kT, where k is Boltzmann's constant.
4. Inside the metal, free electrons move randomly with high velocity and it depends on temperature of the metal. During the motion, their velocity and direction changes in such a way that the rate of flow of electron in a particular direction is zero.
5. When the metal is kept in external electric field, the free electrons get attracted in the direction opposite to the direction to the external electric field. They start moving with a constant average velocity called drift velocity.

# Band Theory of Solids

- Band theory of solids describes the quantum state that an electron takes inside a metal solid. Every molecule comprises various discrete energy levels. The way electrons behave inside a molecule is well explained through band theory.
- Band Theory was developed from the knowledge gained during the quantum revolution in science.
- In 1928, Felix Bloch applied quantum theory to solids.
- In atoms, electrons are filled in respective energy orbits following Pauli's exclusion principle. Two atomic orbitals combine to form a molecular orbit with two distinct energy levels.
- In solids, $10^{23}$ stacked up lines confined in a tiny space would look like a band. Thereby forming an energy continuum called energy bands.
- Band theory helps to visualize the difference between conductor, semiconductor, and an insulator by plotting available energies for an electron in a material.

# Energy Bands in Solids

- In band theory of solids, there exists three important energy bands: Valence Band, Conduction Band and Forbidden Band

**Valence band**

- The energy band that consists of valence electrons energy levels, is known as the valence band.
- The valence band is present below the conduction band and the electrons of this band are loosely bound to the nucleus of the atom.

**Conduction band**

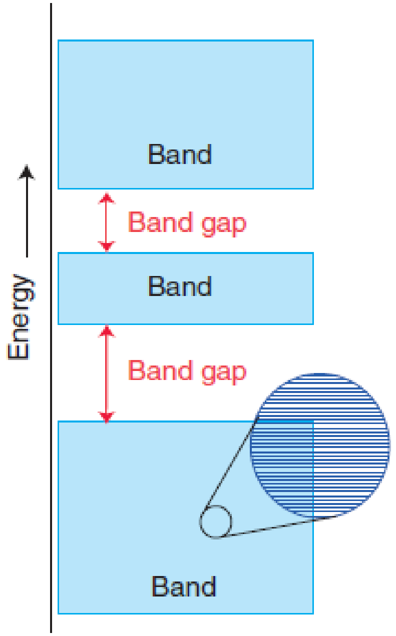
- The energy band that consists of free electrons energy levels, is known as the conduction band.
- For electrons to be free, external energy must be applied such that the valence electrons get pushed to the conduction band and become free.

**Forbidden band**

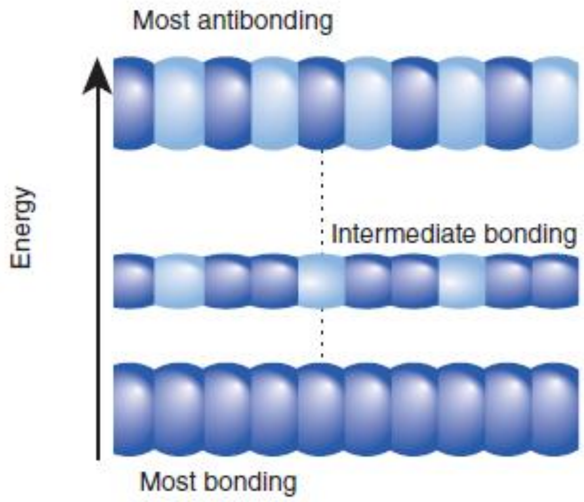
- The energy gap between the valence band and the conduction band is known as the forbidden band which is also known as the forbidden gap.
- The electrical conductivity of a solid is determined from the forbidden gap and also the classification of the materials as conductors, semiconductors, and insulators.

# Bonding in solids - Band theory

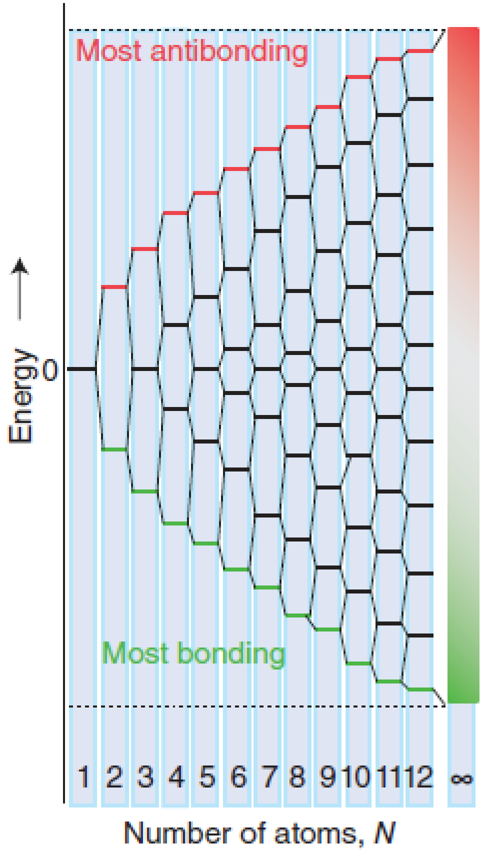
- The overlap of a large number of AOs in a solid leads to a large number of MOs that are closely spaced in energy, and forms an almost continuous **band** of energy levels.
- Bands are separated by **band gaps**, which are values of the energy for which there is no MO.
- The formation of bands can be understood by considering a line of atoms, and assuming each atom has an s-orbital that overlaps with the s-orbitals on its immediate neighbors.
- When the line consists of only two atoms, there is a bonding and an antibonding MO. When a third atom joins them, there are three MOs viz. bonding, non bonding (central orbital) and antibonding).
- As more atoms are added, each one contributes an AO, and hence one more MO is formed.
- When there are *N* atoms in the line, there are *N* molecular orbitals.
- 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 & a corresponding range of energies between the two extremes.
- The total width of the band, which remains finite even as *N* approaches infinity, depends on the strength of the interaction between neighboring atoms.
- The greater the strength of interaction (large overlap), greater is the energy separation of the non-node orbital & the all-node orbital.
- Whatever be the number of AOs used to form the MOs, there is only a finite spread of orbital energies.
- The separation in energy between neighboring orbitals must approach zero as *N* approaches infinity (for finite orbital energies) i.e., a band consists of a countable number but near-continuum of energy levels.

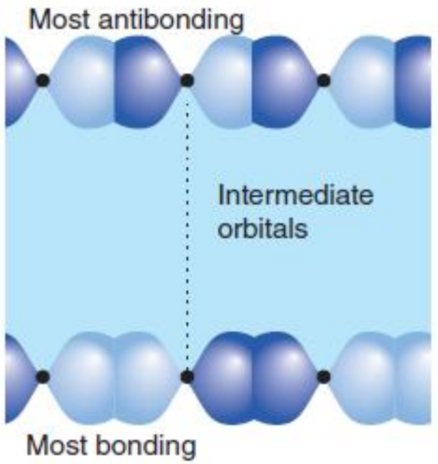


A band can be thought of as formed by bringing up atoms successively to form a line of atoms. *N* atomic orbitals give rise to *N* molecular orbitals.

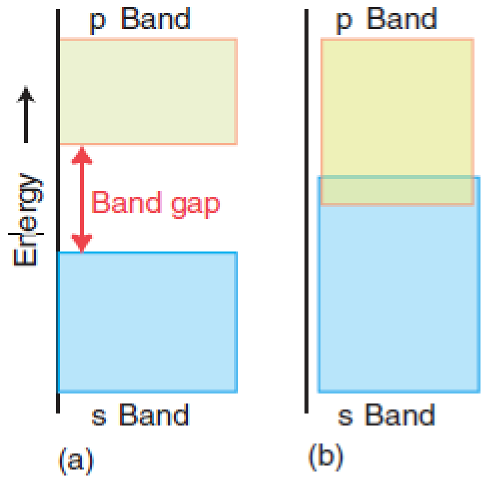


The energies of the orbitals that are formed when *N* atoms are brought up to form a one-dimensional array

- The band just described is built from s-orbitals and is called an **s band**.
- If there are p-orbitals available, a **p band** can be constructed from their overlap.
- Because p-orbitals lie higher in energy than s-orbitals of the same valence shell, there is often an energy gap between the s band and the p band.
- However, if the bands span a wide range of energy and the atomic s and p energies are similar, then the two bands overlap.
- The **d band** is similarly constructed from the overlap of d-orbitals.
- 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
- Band structure diagram can constructed using the FMOs of all the atoms.
- Energies of these bands depends on the energies of the contributing AOs, & depending on the number of electrons it can be empty, full, or partially filled



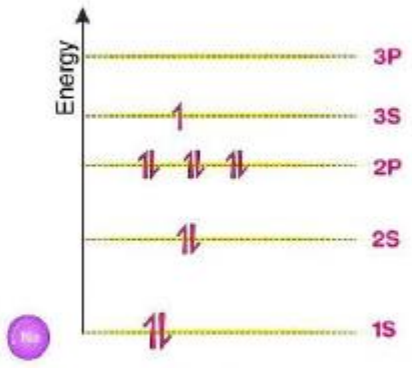
p band in a one-dimensional solid



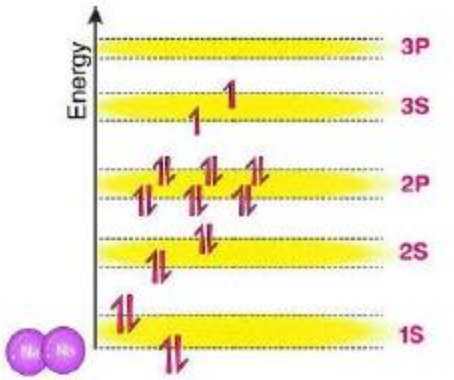
(a) The s and p bands of a solid and the gap between them. Whether or not there is in fact a gap depends on the separation of the s and p orbitals of the atoms and the strength of the interaction between them in the solid. (b) If the interaction is strong, the bands are wide and may overlap.

# **Illustration:** Sodium atom

- Na has 11 electrons and energy levels are filled up following Pauli’s exclusion principle.
- **Energy levels inside a molecule made up of two atoms:** When two Na-atoms come very close to each other, respective energy bands will overlap with each other and transform into MO.
- The 1s orbit of individual Na atoms combines to form 1s MO. As two AOs are overlapping, the MO ends up having two discrete energy levels. The Lower energy level is called a bonding orbital, and the Higher energy level is called an anti-bonding orbital. This will repeat for all orbits.

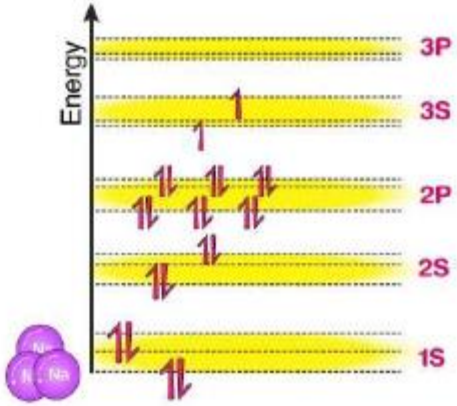


Energy levels in Na atom

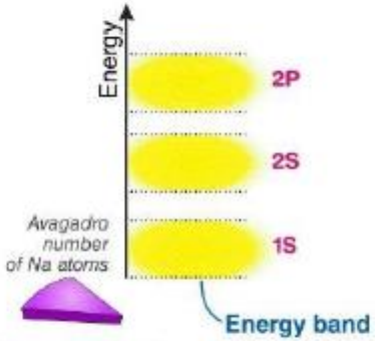


Energy levels inside a molecule made up of two Na atoms

- **Energy levels inside a molecule made up of three atoms: When** a third sodium atom is to the mix, three AOs will be overlapping, forming a single MO with three discrete energy levels.
- **Energy levels inside a solid made up of Avogadro number of atoms:** If we have an entire solid made of Na with $10^{23}$ atoms packed together, each MO of this solid will have $10^{23}$ discrete energy levels.
- These energy levels are stacked together in such a way that band gap is very small, no longer remain as individual energy levels. As a result, it is convenient to think of it as continuous energy or energy continuum and can be referred to as energy band instead of a molecular orbit.

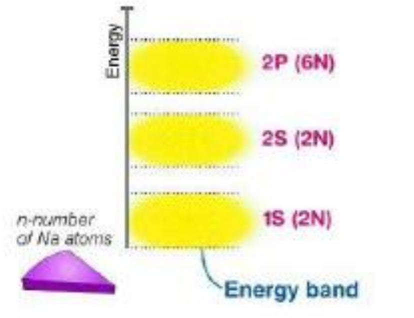


Energy levels inside a molecule made up of three Na atoms



Energy levels inside a molecule made up of Avagadro number of Na atoms

- **Energy levels inside a solid made up of n-number of atoms:** If there are n-number of atoms, there will be n discrete energy levels in each energy band. In such a system of n number of atoms, the MOs are called energy bands.
- Single 1s orbital and 2s orbital can fit 2 electrons each. Thus, the total number of electrons a 1s and 2s energy band can fit is 2n. A single 2p level can fit 6 electrons so that a 2p energy band can fit 6n electrons so on and so forth.
- **Energy levels inside material of different states of matter:** In case of a single atom or gas (atoms are far apart; assumed them as single atom), every atom has a discrete energy level. If an electron wants to go from one level to another, it really has to jump as no continuous energy is available. As atoms come close to each other and eventually form a solid, they form an energy continuum (bands). Within the bands, available energy levels are continuous.



Energy levels inside a molecule made up of n-number of Na atoms

Q. Decide whether any d orbitals on titanium in TiO (with the rock-salt structure) can overlap to form a band.

Answer: It is to decide whether there are d orbitals on neighboring metal atoms that can overlap with one another. Figure 3.66 shows one face of the rock-salt structure with the d*xy* orbital drawn in on each of the Ti atoms. The lobes of these orbitals point directly towards each other and will overlap to give a band. In a similar fashion the d*zx* and d*yz* orbitals overlap in the directions perpendicular to the *xz* and *yz* faces.

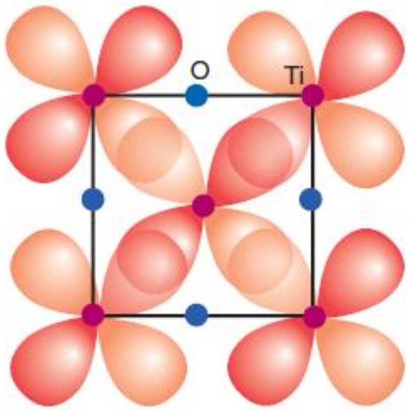
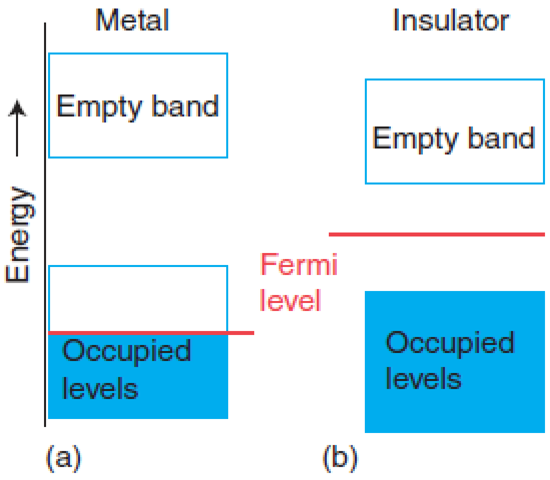


**Figure 3.66** One face of the TiO rock-salt structure showing how orbital overlap can occur for the $d_{xy}$, $d_{yz}$, and $d_{zx}$ orbitals.

Q. Which d orbitals can overlap in a metal having a primitive structure?

# Fermi level

- At $T = 0$, electrons occupy the individual MOs of the bands (as per building-up principle)
- The highest occupied orbital at $T = 0$ is called **Fermi level**; lies near the center of the band.
- When the band is not completely full, the electrons close to the Fermi level can easily be promoted to nearby empty levels. As a result, they are mobile and can move relatively freely through the solid, and the substance is an electrical conductor.
- Solid is a *metallic* conductor; the electrical conductivity α 1/T
- An atom vibrating vigorously at a site is equivalent to an impurity that disrupts the orderliness of the orbitals. This decrease in uniformity reduces the ability of the electron to travel from one edge of the solid to the other, so the conductivity of the solid is less than at $T = 0$.
- Electrons moving through the solid are scattered by atomic vibration. Rise in temperature increases the lattice vibration thereby increasing the carrier scattering & causing the inverse temperature dependence of the conductivity of metals.

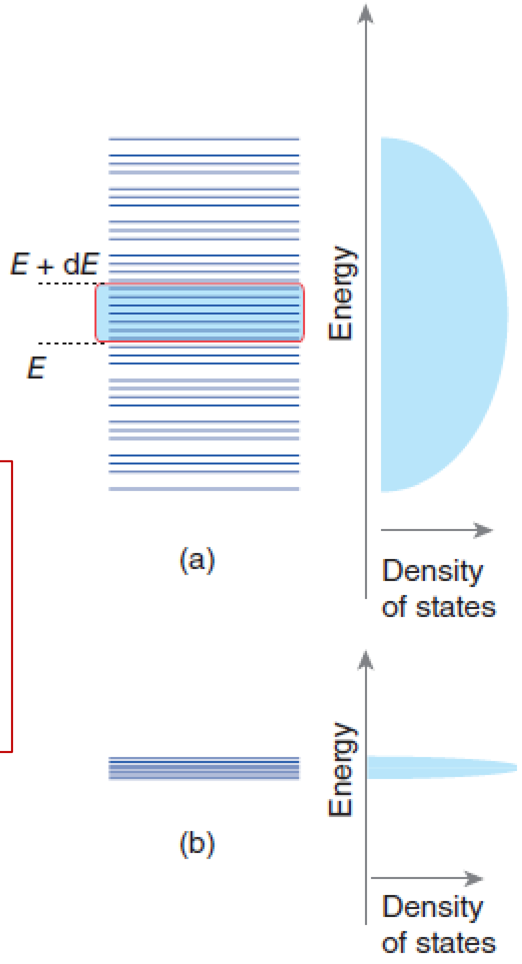


(a) Typical band structure for a metal showing the Fermi level; if each of the *N* atoms supplies one s electron, then at *T* = 0 the lower ½ *N* orbitals are occupied and the Fermi level lies near the center of the band. (b) Typical band structure for an insulator with the Fermi level midway in the band gap.

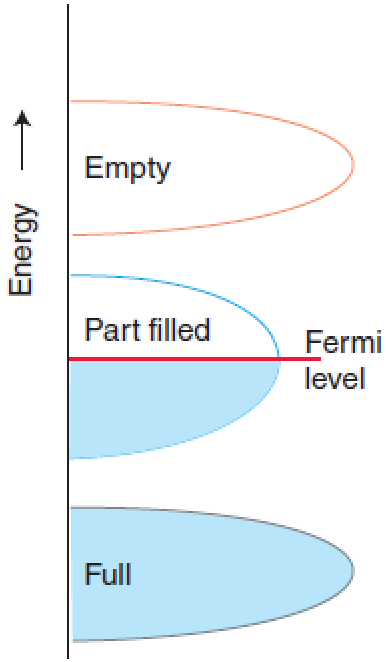
# Density of states and width of bands

- The number of energy levels in an energy range divided by the width of the range is called the **density of states (DOS)**, *ρ* (a).
- 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.
- The DOS near the center of the band is maximum and at the edge it is in minimum (c).
- This can be attributed to the number of ways of producing a particular LCAOs. There is only one way of forming a fully bonding MO (the lower edge of the band) and a fully antibonding MO (the upper edge). But, there are many ways (in 3D) of forming a MO with an energy corresponding to the interior of a band.
- The number of orbitals contributing to a band determines the total number of states (the area enclosed by the DOS curve).
- Large numbers of contributing AOs which have strong overlap produce broad (in energy terms) bands with a high density of states while relatively few atoms contribute to a narrow band with only a few states & these are well separated in the solid (b)

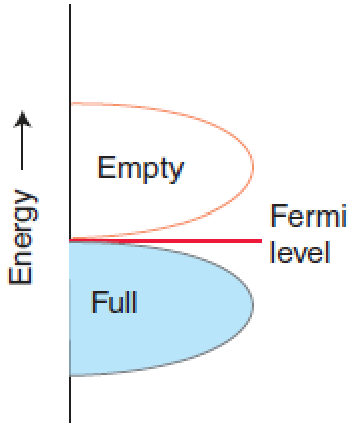
- The density of states is zero in the band gap itself i.e., there is no energy level in the gap
- In certain cases, a full band and an empty band might coincide in energy but with a zero density of states at their conjunction (d). Solids with this band structure are called **semimetals**. Graphite is a semimetal in directions parallel to the sheets of C-atoms.



(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.



(c) Density of states diagram for a three-dimensional metal.

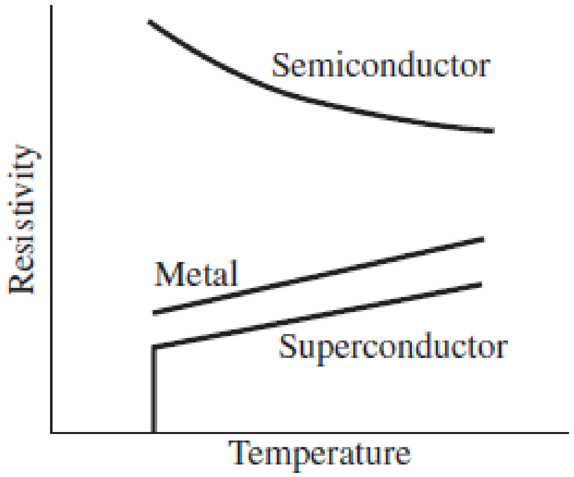


(d) The density of states in semimetal.

# Electrical Properties

- The electrical properties of materials depend on whether they are conductors or dielectrics (insulators)
- If conductor, whether the current carriers are electrons or ions.
- Electronic conductivity occurs to varying extents and by different mechanisms in a wide variety of materials.
- It is responsible for the characteristic electrical properties of metals, superconductors and semiconductors
- Conductivities increase with increase in temperature for all materials except metals and superconductors. In superconductors, the conductivity is independent of temperature since the resistance is zero and = in metals, the conductivity decreases gradually with increase in temperature
- Dielectric materials, or insulators, are characterized by the complete absence of electrical conductivity (both electronic and ionic). Their bonding may be strongly ionic (MgO), strongly covalent (diamond) or strongly polar covalent ($SiO_2$)

- 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.
- The criterion for distinguishing between a metallic conductor and a semiconductor is the temperature dependence of the electric conductivity. Metallic conductivity at room temperature is usually higher than that of semiconductors (not always)
- A solid **insulator** is a substance with a very low electrical conductivity. Conductivity of an insulator is found to increase with temperature, like that of a semiconductor.
- **Superconductors** have zero electrical resistance below a critical temperature.



## Metallic conductivity

- Considerable outer shell or valence electrons are free to move throughout the structure and are completely delocalised.
- Collisions between these electrons and *phonons* (lattice vibrations) are responsible for the residual resistance to current flow and associated heat losses.
- Metallic bonding and conductivity are described using band theory.

## Ionic conductivity

- Ionic conductivity occurs in solid electrolytes, superionic conductors or fast ion conductors
- These have a rigid framework structure within which one set of ions forms a mobile sublattice.
- Conductivities as high as $1\Omega^{-1}cm^{-1}$ are mobile.
- The structural requirements for high ionic conductivity are (i) there must be available empty sites for ions to hop into and (ii) the energy barrier for ions to hop between sites is small.
- High level of ionic conduction are rare but modest level is common, especially in non-stoichiometric/doped materials.

## Semiconductivity

- It is associated with a limited degree of electronic conduction.
- It is intermediate between metallic conduction (significant number of outer shell electrons are free to move) and insulating behavior (the valence electrons are either tightly bound to individual atoms or localized in bonds between atoms)
- It either may be regarded as an electron hopping process, or may be described using band theory, depending on the particular material.
- The number of electrons involved depends on temperature and impurity level, in contrast to metallic conductivity.

## Superconductivity

- Valence shell electrons again appear to be delocalized.
- The electrons move cooperatively, perhaps as loosely coupled pairs.
- No electron-phonon collisions occur, there is no heat loss and there is no resistance to current flow

# Insulators

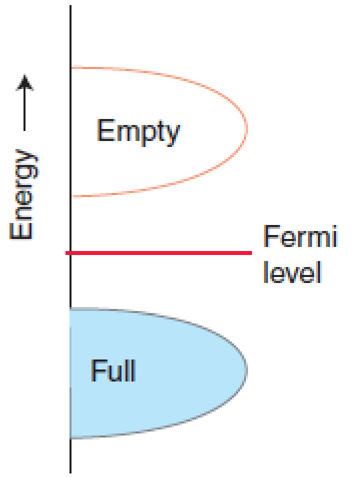


**Figure 3.71** The structure of a typical insulator: there is a significant gap between the filled and empty bands.

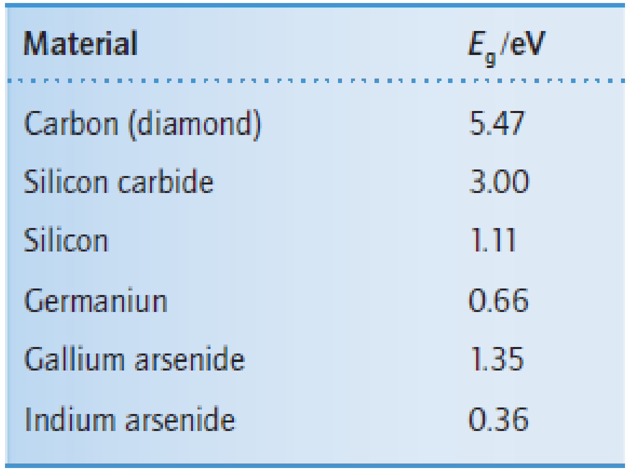
- A solid is an insulator if enough electrons are present to fill a band completely and there is a considerable energy gap before an empty orbital and its associated band become available.
- An insulator is a solid with a large band gap (> 4.0 eV).
- In an insulator the band of highest energy that contains 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**.

**Insulating nature of NaCl**

- 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. The band gap is about 7 eV
- A total of 8 electrons are to be accommodated (7 from Cl + 1 from Na). These electrons enter the lower chlorine band, fill it, and leave the sodium band empty. The energy of thermal motion available at room temperature is $kT \approx 0.03$ eV quite low and so very few electrons have enough energy to occupy the orbitals of the sodium band.

# Semiconductor

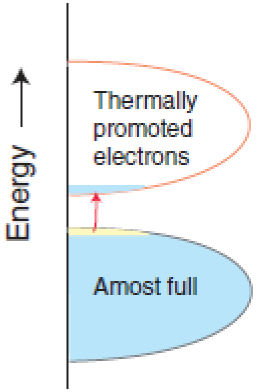
- In a semiconductor, the gap between the conduction band and the valence band is very less; therefore, whenever sufficient energy is provided, electrons jump from the valence band to the conduction band.
- The characteristic physical property of a semiconductor is that its electrical conductivity increases with increasing temperature. Conductivity within the range $10^{-6}$ to $10^{-4}$ $(\Omega m)^{-1}$
- At room temperature, its conductivity is in between those of metals and insulators.
- The dividing line between insulators & semiconductors is a matter of the size of the band gap (for semiconductor < 4.0 eV)
- Semiconductor materials are essential components of all modern electronic circuits and some devices based on them



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

# Intrinsic semiconductors

- 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.
- 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.
- An intrinsic 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.
- These type of materials are known as undoped or intrinsic semiconductors. Example: Silicon, Germanium.



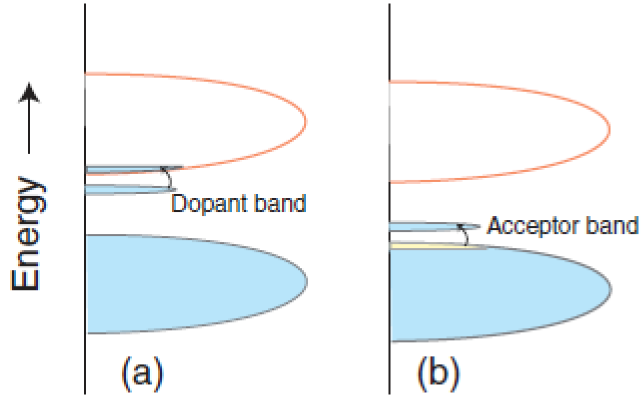
In an intrinsic semiconductor, the band gap is so small that the Fermi distribution results in the population of some orbitals in the upper band.

- The strong, increasing temperature dependence of the conductivity follows from the exponential Boltzmann-like temperature dependence of the electron population in the upper band.
- The conductivity of a semiconductor should show an Arrhenius-like temperature dependence of the form $\sigma = \sigma_o \exp[-E_g/2kT]$; where $E_g$ is the width of the band gap ($E_a \approx \frac{1}{2} E_g$).

# Extrinsic semiconductors

- An **extrinsic semiconductor** is a substance whose semiconductivity is primarily attributed to the presence of intentionally added impurities/dopants (Gr13 and 15 elements).
- The number of electron carriers can be increased if atoms with more electrons than the parent element can be introduced by doping.
- Significantly low levels of dopant concentration are needed (only about one atom per $10^9$ of the host material), very high purity of the parent element is essential.
- If As-atoms are introduced into a Si crystal, one additional electron will be available for each dopant (the dopant takes the place of a Si atom). If the donor atoms (As) are far apart from each other, their electrons will be localized and the donor band will be very narrow.
- 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, thermal excitation will lead to the transfer of an electron from an As-atom into the empty orbitals on a neighboring Si-atom

- Electrons will then able to migrate through the structure in the band formed by Si–Si overlap. This process gives rise to **n-type semiconductivity** (n for negative charged charge carriers).
- An alternative substitutional procedure is to dope the Si crystal with atoms of an element with fewer valence electrons on each atom, such as Ga.
- A dopant atom of this kind effectively introduces holes into the solid. The dopant atoms form a very narrow, empty **acceptor band** that lies above the full Si band.
- At $T = 0$ the acceptor band is empty but at higher temperatures it can accept thermally excited electrons from the Si valence band.
- It introduces holes into the latter & allows the remaining electrons in the band to be mobile.
- The charge carriers are effectively positive holes in the lower band, and hence is called **p-type semiconductivity**.



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

- d-metal oxides such as ZnO and $Fe_2O_3$ are n-type semiconductors.
- This is due to small variations in stoichiometry and a small deficit (vacancy) of O atoms. The electrons to be in localized O atomic orbitals (giving a very narrow oxide band) occupy a previously empty conduction band formed by the metal orbitals.
- The conductivity decreases on heating with oxygen and cooling slowly back to room temperature (deficit of O atoms is partly minimized and electrons are withdrawn from the conduction band to form oxide ions).
- At high temperatures the conductivity of ZnO increases because further oxygen is lost from the structure, so increasing the number of electrons in the conduction band.

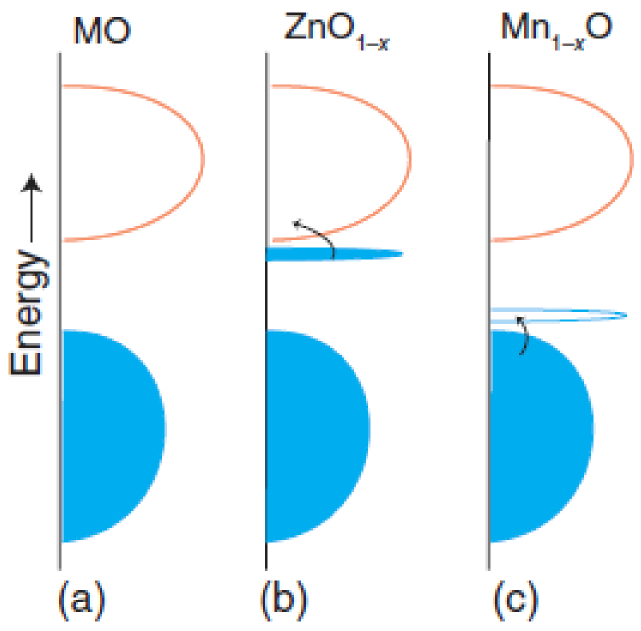


**Figure 3.74** The band structure in (a) a stoichiometric oxide, (b) an anion-deficient oxide, and (c) an anion-excess oxide.

n-type semiconductivity occurs in oxides with metals in higher OS, as the metal can be reduced to a lower oxidation state by occupation of a conduction band formed from the metal orbitals ($Fe_2O_3$, $MnO_2$ & CuO)

- p-type semiconduction is observed for low oxidation number d-metal chalcogenides and halides such as $Cu_2O$, FeO, MnO, $Cr_2O_3$, FeS, CuI.
- Here, 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 for FeS and halogen for CuI) because more holes are formed in the metal band as oxidation progresses.

Which of the oxides $WO_3$, MgO, and CdO are likely to show p- or n-type extrinsic semiconductivity?

Answer: The type of semiconductivity 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 semiconductivity 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 semiconductivity is expected. Thus, $WO_3$, with tungsten present in the high oxidation state W(VI), is readily reduced and accepts electrons from the $O^{2-}$ ions, which escape as elemental oxygen. The excess electrons enter a band formed from the W d-orbitals, resulting in n-type semiconductivity. Similarly, CdO, like ZnO, readily loses oxygen and is predicted to be an n-type semiconductor. In contrast, $Mg^{2+}$ ions are neither easily oxidized nor reduced, so MgO does not lose or gain even small quantities of oxygen and is an insulator.

Q. Predict p- or n-type extrinsic semiconductivity for $V_2O_5$ and CoO.

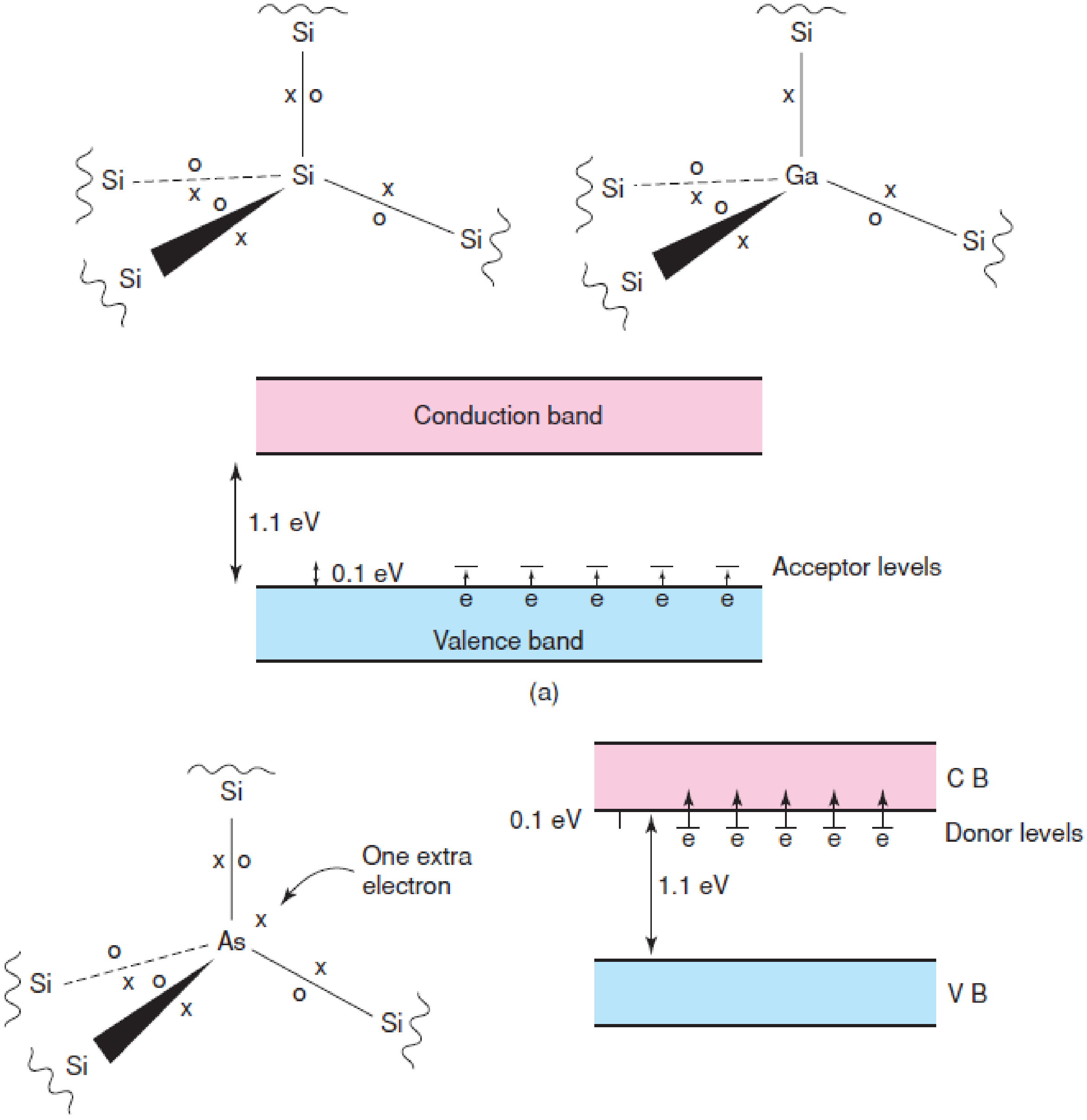
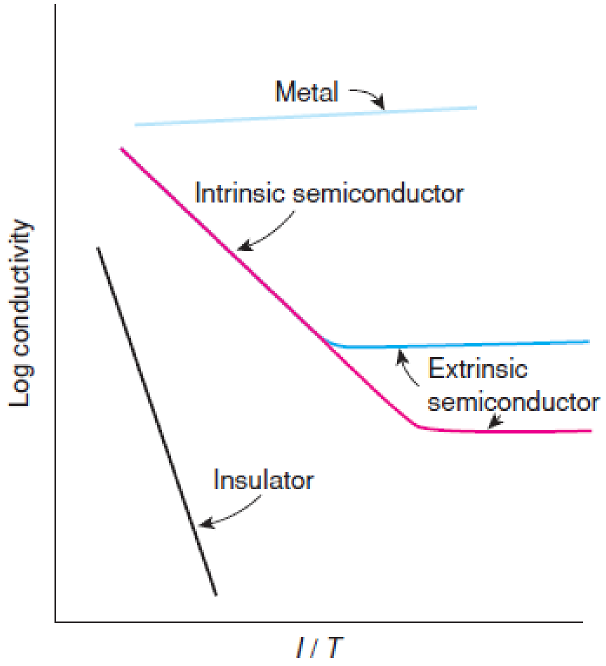
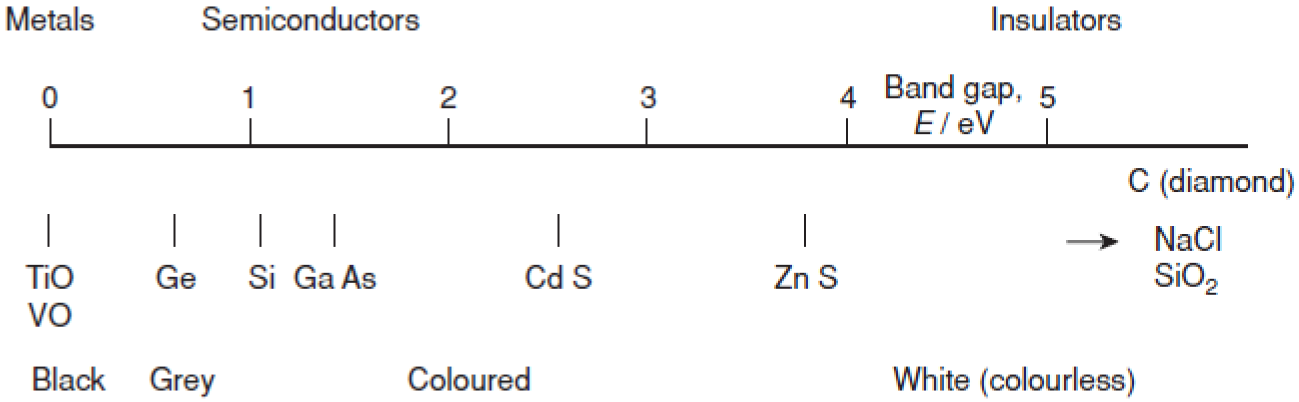


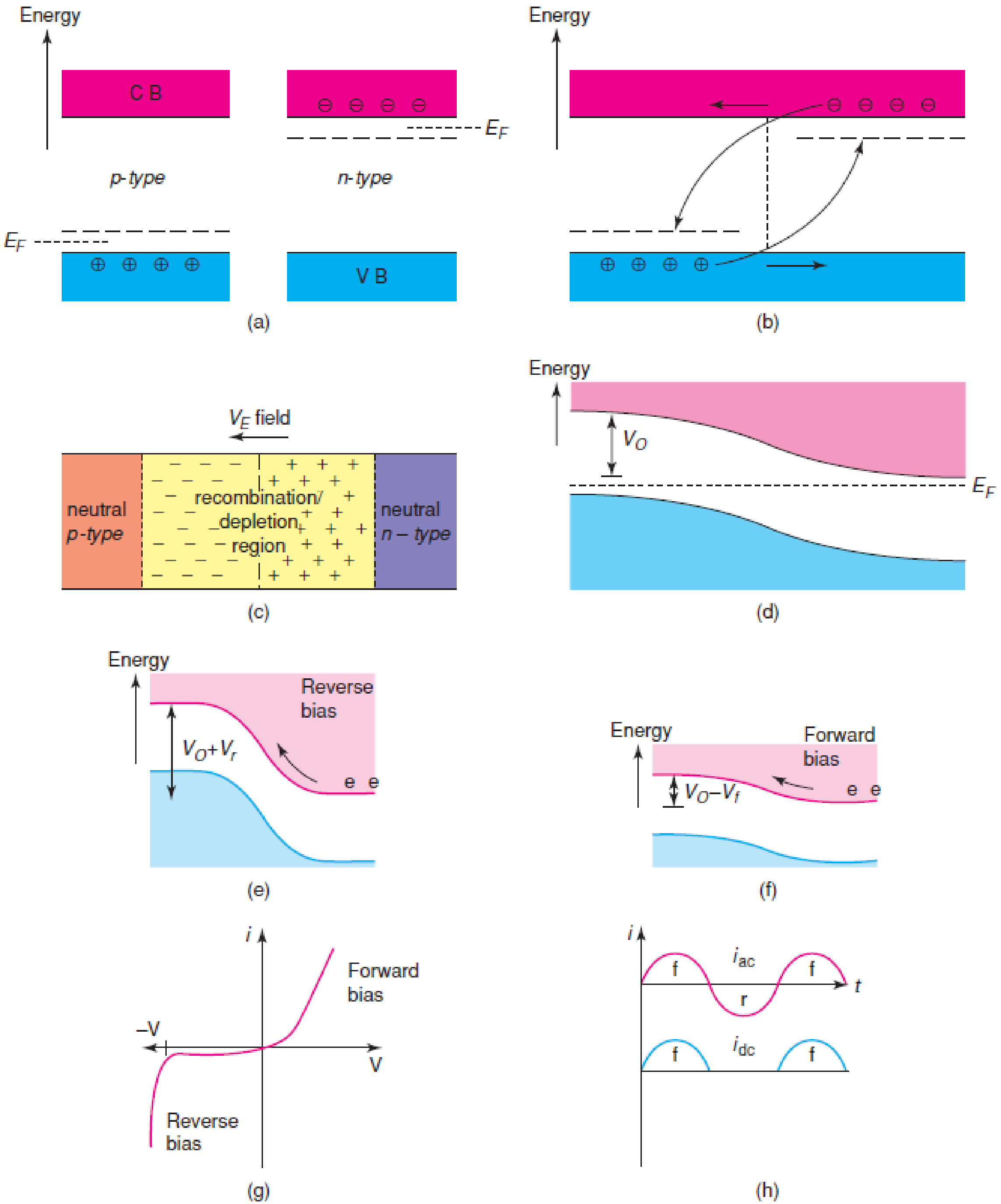
*Figure 8.12* ***(a) p-Type semiconductivity in gallium-doped silicon; (b) n-type semiconductivity in arsenic-doped silicon.***



'0 *Conductivity of metals, semiconductors and insulators.*



11 *Relation between electronic properties and magnitude of the band gap with typical examples.*



A p–n junction. (a) Energy levels in p-type and n-type semiconductor; (b) p- and n-type regions in contact leading to (c) creation of a charge depletion region by spontaneous diffusion and (d) equalization of EF across the p–n junction. The resulting band bending is (e) increased in reverse bias and (f) decreased in forward bias. (g) Voltage–current characteristics as a function of bias leading to (h) current rectification.

# Superconductor

- The conductivity of some metals changes abruptly near liquid helium temperatures (below 10 K) and they become **superconductors**
- A superconductor has zero or almost zero electrical resistance. It can carry an electric current without loosing energy and flow of electrons, and currents started in a loop will continue to flow indefinitely
- There is a critical temperature (Tc) at which the resistance drops sharply and superconduction occurs
- **Meissner Effect**: Some superconducting materials do not permit a magnetic field to penetrate their bulk (the exclusion of a magnetic field). This phenomenon was discovered by Meissner and Ochsenfeld. This is now known as Meissner Effect, and results a magnet to float over give the superconductor. This originates from the mutual repulsion between a permanent magnet and a superconductor.
- Moreover, superconductor also expels all internal magnetic field arising from unpaired electron and becomes diamagnetic.
- Meissner effect is being explored in many areas, including magnetic levitation of trains

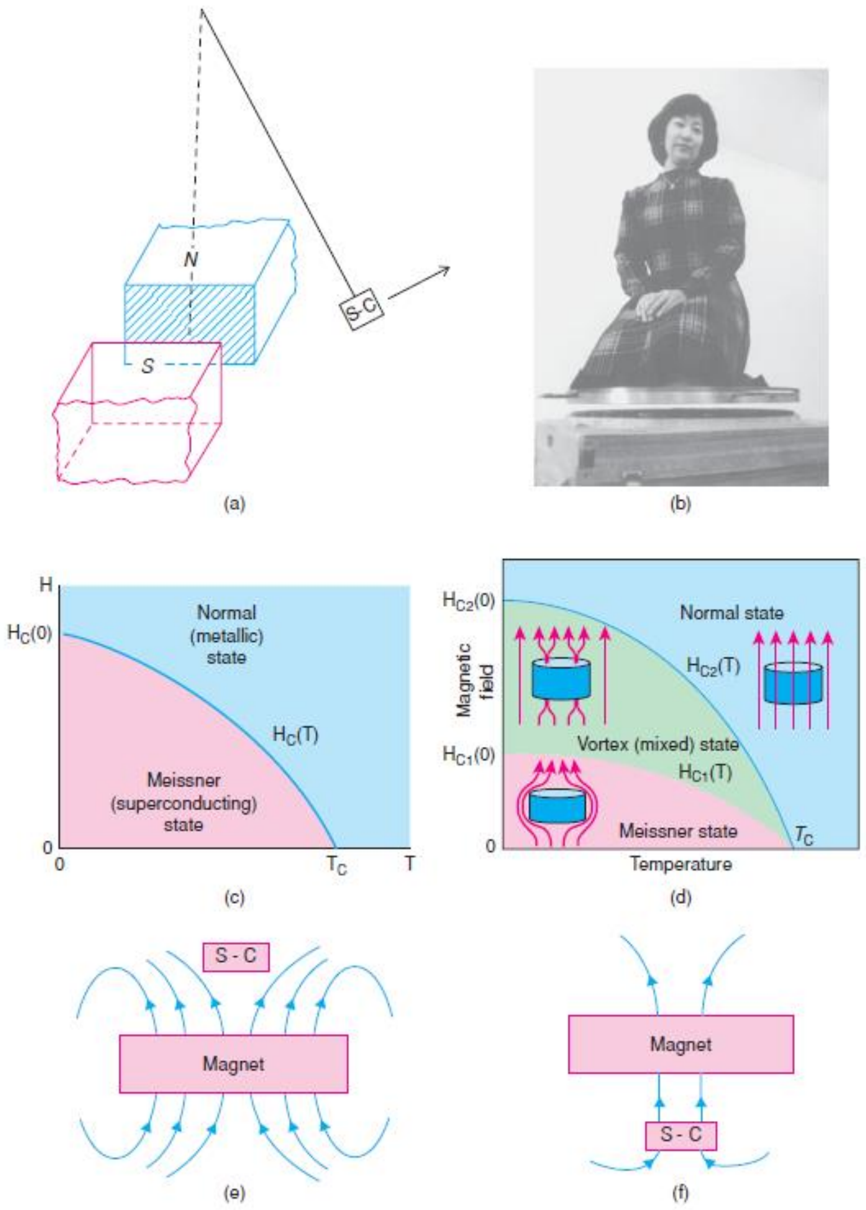


*Figure 8.5 (a) The Meissner effect showing repulsion of a superconductor, S-C, by a magnetic field. (b) Levitation in action: the Japanese lady is kneeling on a magnet that is floating above a bed of superconducting melt-processed $YBa_2Cu_3O_7$. Photograph courtesy of Dr M. Murakami, ISTEC, Japan. (c) A type I and (d) a type II superconductor. Distribution of flux lines in a demonstration of (e) levitation and (f) suspension by vortex pinning.*

# Low-Temperature Superconducting Alloys

- In 1911, superconductivity was discovered by Kammerling Onnes in Hg below 4.2 K temperature and in Pb near absolute zero temperature.

- Most of these superconducting materials are alloys of niobium (Nb-Ti alloy), although superconductivity are also found in many oxides and sulfides

- Two types of superconductors are known.

- **Type I** superconductors have the additional property of expelling all magnetic flux when cooled below the critical temperature (Tc). This abrupt change is called the *Meissner effect*. It prevails until the magnetic field reaches a critical value (Hc), at which point the applied field destroys the superconductivity. This temperature-dependent change is sudden rather than gradual. The highest *Tc* found for niobium alloys is 23.3 K for $Nb_3Ge$

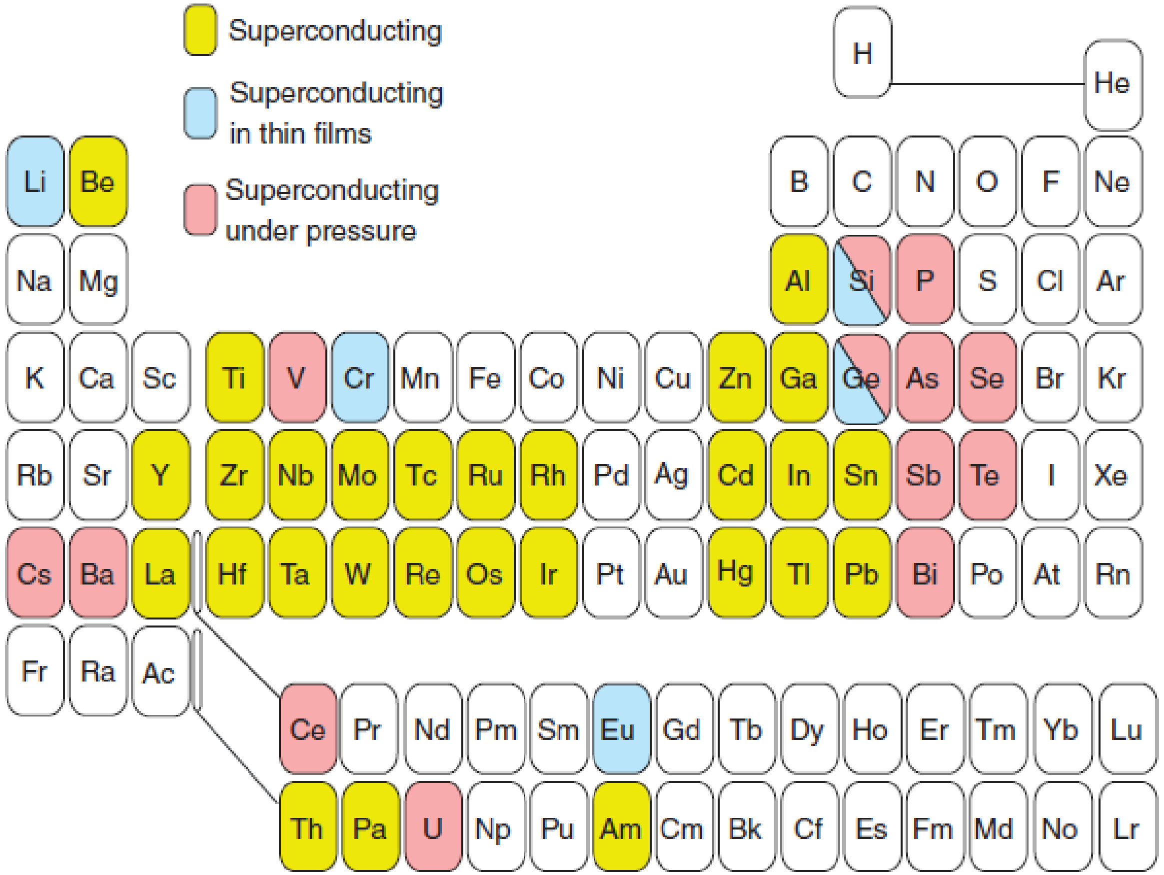
- **Type II** superconductors have a more complicated field dependence. Below a given critical temperature they exclude the magnetic field completely. In the intermediate temperature region, these materials exhibit a mixture of superconducting & normal conductance behavior

# Theory of Superconductivity (Cooper Pairs)

- Bardeen, Cooper, and Schrieffer (BCS) - theory to explain superconductivity.
- The theory postulated that electrons travel through a material in pairs, in spite of their mutual electrostatic repulsion, as long as the two have opposite spins (*Cooper pairs*).
- The formation of these *Cooper pairs* is assisted by small vibrations of the atoms in the lattice; as one electron moves past, the nearest positively charged atoms are drawn very slightly toward it. This increases the positive charge density, which attracts the second electron.
- This effect then continues through the crystal, analogous to a sports crowd doing the wave.
- The attraction between the two electrons is small, and they change partners frequently, but the overall effect is that the lattice helps them on their way rather than interfering.
- If the temperature rises above *Tc*, the thermal motion of the atoms is sufficient to overcome the slight attraction between the electrons, & superconductivity ceases.

# High-Temperature Superconductors (HTSC)

- Bednorz and Müller (1986) discovered that the ceramic oxide $La_2CuO_4$ was superconducting above 30 K when doped with Ba, Sr, or Ca to form compounds such as $(La_{2-x}Sr_x)CuO_4$.
- There is a degree of periodicity in the elements that exhibit superconductivity. Ferromagnetic metals Fe, Co, Ni, alkali metals or the coinage metals Cu, Ag, and Au do not exhibit superconductivity



- In 1987, $YBa_2Cu_3O_{7-\delta}$ ($\delta$ is very small) was discovered and have higher *Tc*, 93 K
- HTSC allows cooling with inexpensive liquid nitrogen (bp 77 K, quite fascinating)
- This material is called ‘123’ for the stoichiometry of the metals in it or YBCO (ib-co), is a Type II superconductor
- It expels magnetic flux at low fields, but allows some magnetic field lines to enter at higher fields, and consequently ceases to be superconducting at high fields.
- **Preparation**: pH adjusted precipitation and high temperature decomposition of carbonates is the most typically used method for preparation of 123 semiconductor.

$$2Y^{3+} + HCO_3^- \xrightarrow{-H+} Y_2(CO_3)_3$$

$$Ba^{2+} + HCO_3^- \xrightarrow{-H+} BaCO_3$$

$$Cu^{2+} + HCO_3^- \xrightarrow{-H+} CuCO_3$$

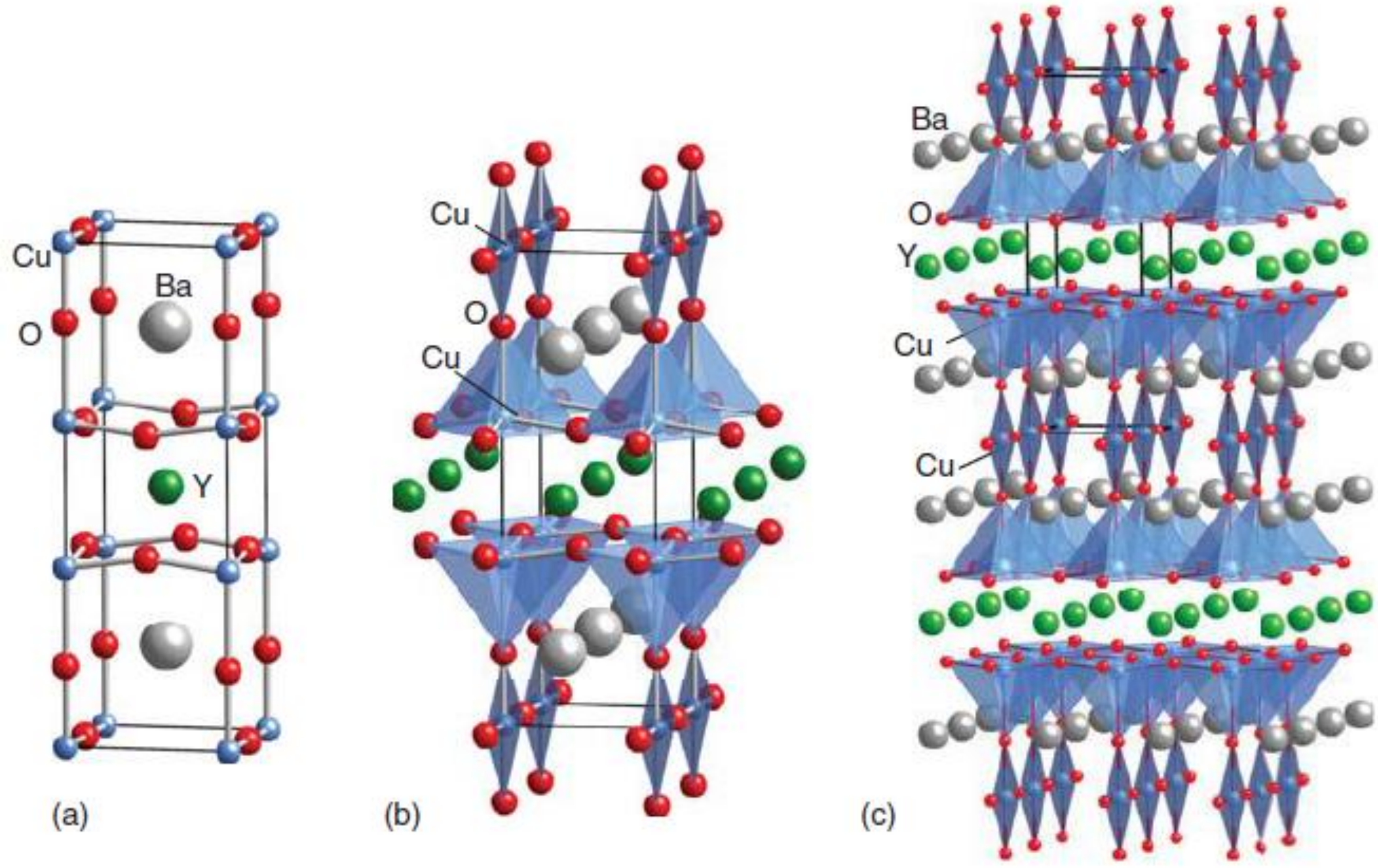
$$Y_2(CO_3)_3 + 4BaCO_3 + 6CuCO_3 \xrightarrow{-950\ ^{\circ}C} 2YBa_2Cu_3O_{7-\delta} + 13CO_2$$

The rate and condition of cooling are also important

- Other procedures starts with oxides or mixture of oxides and carbonates

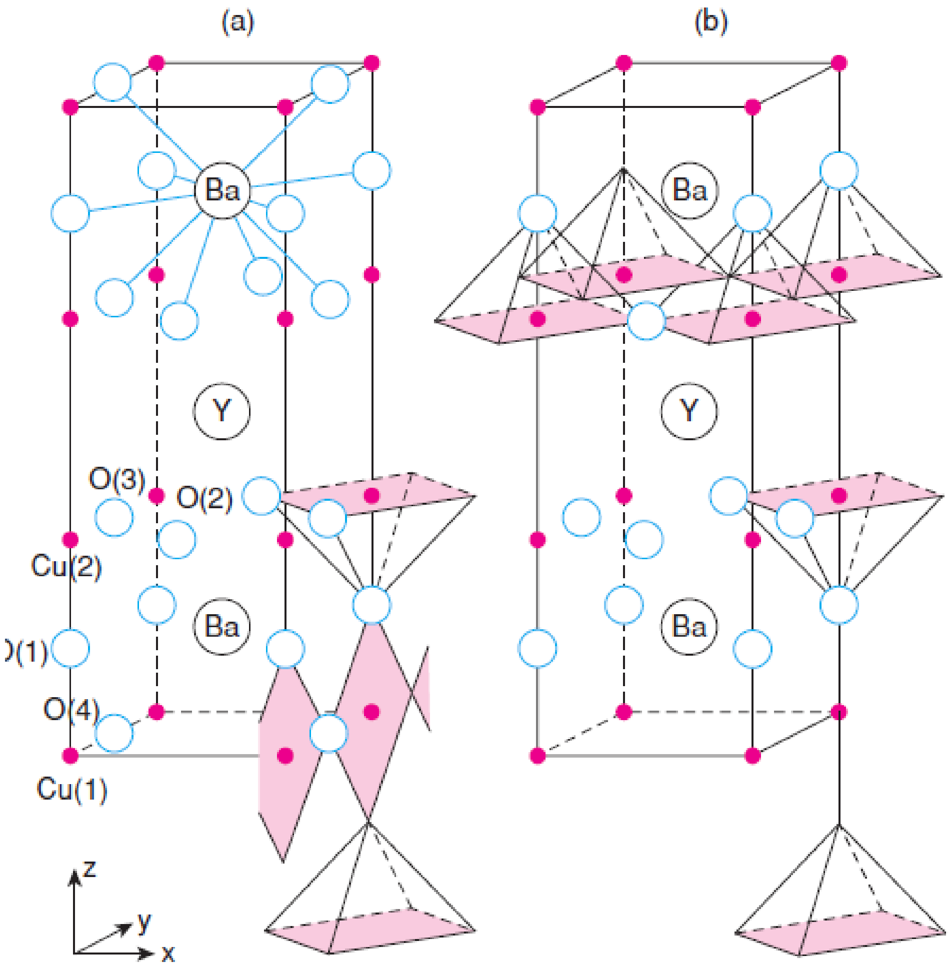
# Structure

- The 123 superconductor has a perovskite like structure.
- Its unit cell consists of three cubic perovskite units stacked vertically with Y and Ba and Cu atoms, giving an elongated (tetragonal) unit cell.
- The 123 superconductor unit cell has a large number of systematic O-atom vacancies in the Y-atom plane.
- Some Cu-atoms have five O-atoms neighbors in a square-pyramidal $CuO_5$ arrangement and some have only four, as square-planar $CuO_4$ units.
- Y and Ba in the unit cell have less than 12-coordination. The compound $YBa_2Cu_3O_7$ readily loses oxygen from some sites within the $CuO_4$ square planes, forming $YBa_2Cu_3O_{7-\delta}$
- Vacancies between Cu atoms in the Cu-O planes lying between the planes of Ba-atoms.
- It is a mixed oxidation state material character with $Cu^{2+}$ and $Cu^{3+}$ ions. The $YBa_2Cu_3O_{7-\delta}$ material formally contains some $Cu^{3+}$ until $\delta$ increases above 0.5



Structure of the $YBa_2Cu_3O_7$ superconductor: (a) the unit cell and (b) oxygen polyhedra around the copper ions; (c) showing the layers formed from linked $CuO_5$ square pyramids and chains formed from corner-linked $CuO_4$ square planes

Several lanthanides including Sm, Eu, Nd, Dy and Yb have been substituted for Y in 123 structure (Tc upto 93 K), known as warm superconductors



a = 3.817, b = 3.882, c = 11.671 Å
Ba : ½ ½ 0.18; ½ ½ 0.82
Y : ½ ½ ½
Cu(1) : 0 0 0
Cu(2) : 0 0 0.35; 0 0 0.65
O(1) : 0 0 0.16; 0 0 0.84
O(2) : ½ 0 0.38; ½ 0 0.62
O(3) : 0 ½ 0.38; 0 ½ 0.62
O(4) : 0 ½ 0

a = b = 3.8, c = 11.8 Å
fractional coordinates :
as for (a), but with
O(4) unoccupied

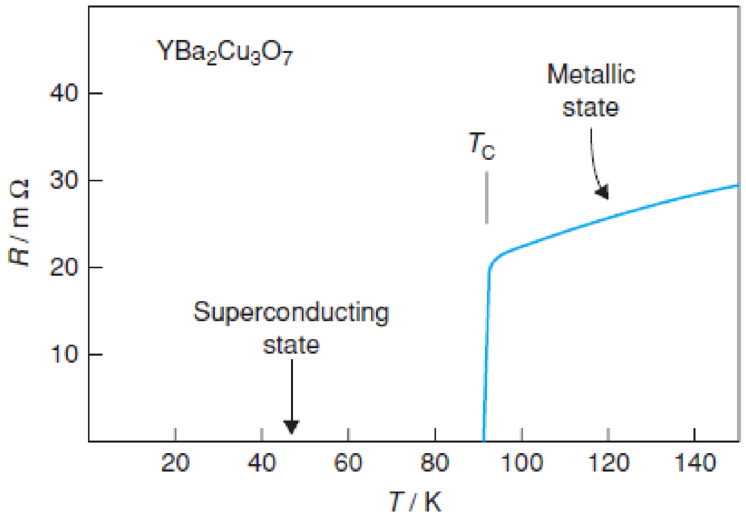
- Alternatively, the number of electrons in $YBa_2Cu_3O_{7-\delta}$ indicates the presence of partially filled band which is consistent with the high electrical conductivity and metallic behavior of this oxide at room temperature.
- If this band is considered to be constructed from 3d-orbitals of Cu, then the partial filling is a result of holes in this level (corresponding to $Cu^{3+}$).
- Square-planar $CuO_4$ units in $YBa_2Cu_3O_{7-\delta}$ are arranged in chains and the $CuO_5$ units link together to form infinite sheets.
- The stoichiometry of an infinite sheet of vertex sharing $CuO_4$ square planes is $CuO_2$. The addition of one or two apical O-atoms link the layers maintains the $CuO_2$ sheet. Superconductivity occurs in the $CuO_2$ layers. This structural feature is also seen in all other oxocuprate HTSCs and predicted to be an important component of the mechanism of superconduction in these materials.
- $Tl_2Ba_2Ca_2Cu_3O_{10}$ can be considered as having three perovskite layers based on Cu, O, and Ca separated by double layers of a rock-salt structure built from Tl and O; the Ba lie between the rock-salt and perovskite layers.
- $Tl_2Ba_2Cu_3O_{10}$ superconductor has the highest critical temperature of 125K

# Some generalizations for all HTSCs

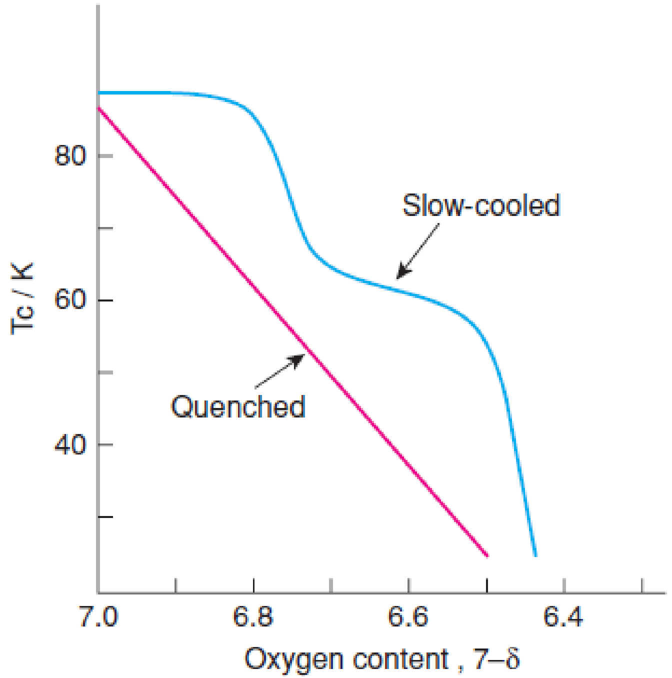
- The structures can be derived by stacking different amounts and sequences of rock salt & perovskite-like layers of metal and oxygen
- Superconductivity occurs in the $CuO_2$ layers
- The similarity in energy between Cu 3d and oxygen 2p level causes them to mix extensively in the electronic band at Fermi level
- The non $CuO_2$ layers furnish electron density at tunes the electronic state of the $CuO_2$ layers

**Origin of superconductivity**

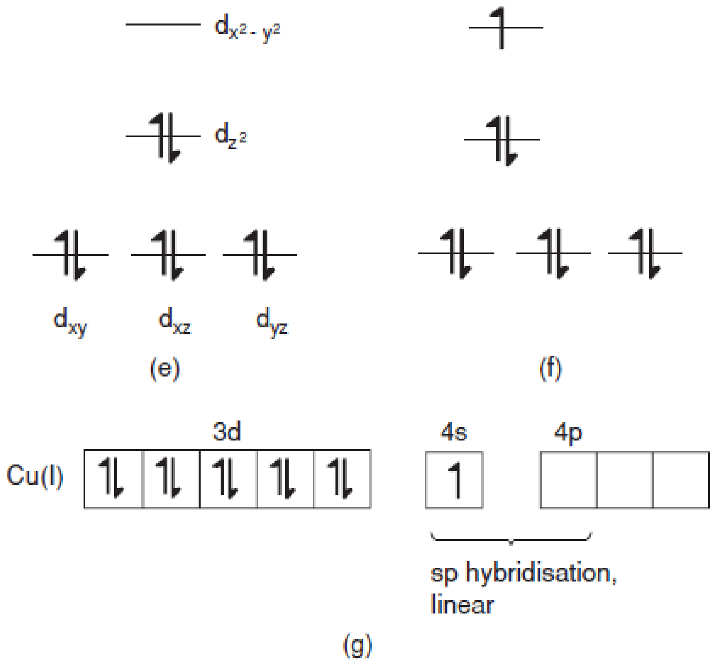
- It is believed that the movement of pairs of electrons, known as ‘Cooper pairs’ and responsible for conventional superconductivity, is also important in the high-temperature materials, but the mechanism for pairing is questionable.
- Superconductivity in is thought to be associated with the ready transfer of electrons between Cu(I), Cu(II) and Cu(III)



*Electrical resistance of $YBa_2Cu_3O_7$ as a function of temperature.*



Tc versus oxygen content δ for YBa2Cu3Oδ showing the importance, also, of sample history (i.e. cooling rate after synthesis).



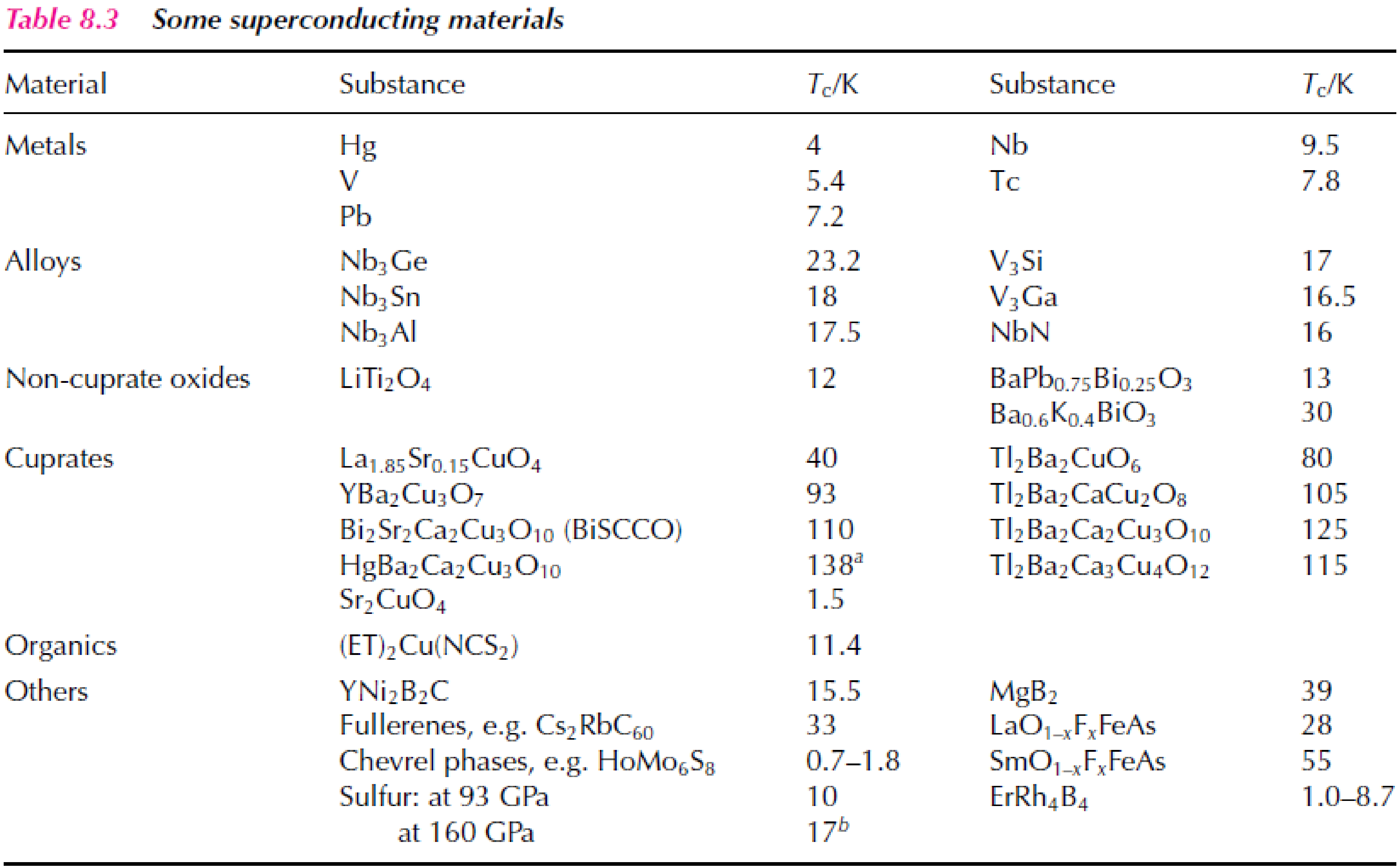


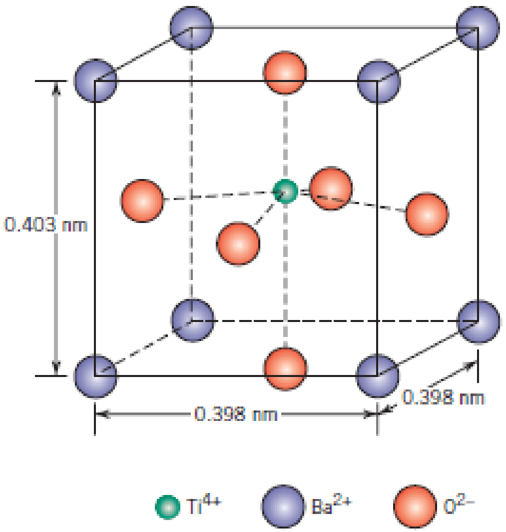
*Table 8.3* ***Some superconducting materials***

| Material | Substance | $T_c$/K | Substance | $T_c$/K |
|---|---|---|---|---|
| Metals | Hg | 4 | Nb | 9.5 |
| | V | 5.4 | Tc | 7.8 |
| | Pb | 7.2 | | |
| Alloys | $Nb_3Ge$ | 23.2 | $V_3Si$ | 17 |
| | $Nb_3Sn$ | 18 | $V_3Ga$ | 16.5 |
| | $Nb_3Al$ | 17.5 | NbN | 16 |
| Non-cuprate oxides | $LiTi_2O_4$ | 12 | $BaPb_{0.75}Bi_{0.25}O_3$ | 13 |
| | | | $Ba_{0.6}K_{0.4}BiO_3$ | 30 |
| Cuprates | $La_{1.85}Sr_{0.15}CuO_4$ | 40 | $Tl_2Ba_2CuO_6$ | 80 |
| | $YBa_2Cu_3O_7$ | 93 | $Tl_2Ba_2CaCu_2O_8$ | 105 |
| | $Bi_2Sr_2Ca_2Cu_3O_{10}$ (BiSCCO) | 110 | $Tl_2Ba_2Ca_2Cu_3O_{10}$ | 125 |
| | $HgBa_2Ca_2Cu_3O_{10}$ | 138[a] | $Tl_2Ba_2Ca_3Cu_4O_{12}$ | 115 |
| | $Sr_2CuO_4$ | 1.5 | | |
| Organics | $(ET)_2Cu(NCS_2)$ | 11.4 | | |
| Others | $YNi_2B_2C$ | 15.5 | $MgB_2$ | 39 |
| | Fullerenes, e.g. $Cs_2RbC_{60}$ | 33 | $LaO_{1-x}F_xFeAs$ | 28 |
| | Chevrel phases, e.g. $HoMo_6S_8$ | 0.7–1.8 | $SmO_{1-x}F_xFeAs$ | 55 |
| | Sulfur: at 93 GPa | 10 | $ErRh_4B_4$ | 1.0–8.7 |
| | at 160 GPa | 17[b] | | |

# Other Electrical Characteristics of Materials

## Ferroelectricity

- The group of dielectric materials called **ferroelectrics** exhibit spontaneous polarization that is, polarization in the absence of an electric field.
- Spontaneous polarization of this group of materials results as a consequence of interactions between adjacent permanent dipoles wherein they mutually align, all in the same direction.
- Ferroelectrics have extremely high dielectric constants at relatively low applied field frequencies.
- Consequently, capacitors made from these materials can be significantly smaller than capacitors made from other dielectric materials.
- When barium titanate is heated above its *ferroelectric Curie temperature* (120ºC), the unit cell becomes cubic, and all ions assume symmetric positions within the cubic unit cell and the ferroelectric behavior ceases



**Ferroelectricity has the following characteristics**:

(a) It is intermediate between solid electrolyte behavior, in which ions migrate over long distances, and dielectric behavior, in which there is no net displacement of ions from their regular lattice sites.

(b) These limited atomic displacements lead to a net polarization and creation of a dipole moment.

(c) Ferroelectricity occurs in a small group of materials: e.g. in perovskite, $BaTiO_3$, at room temperature, Ti atoms are displaced towards one corner of the $TiO_6$ octahedra because Ti is slightly too small for a regular octahedral site.

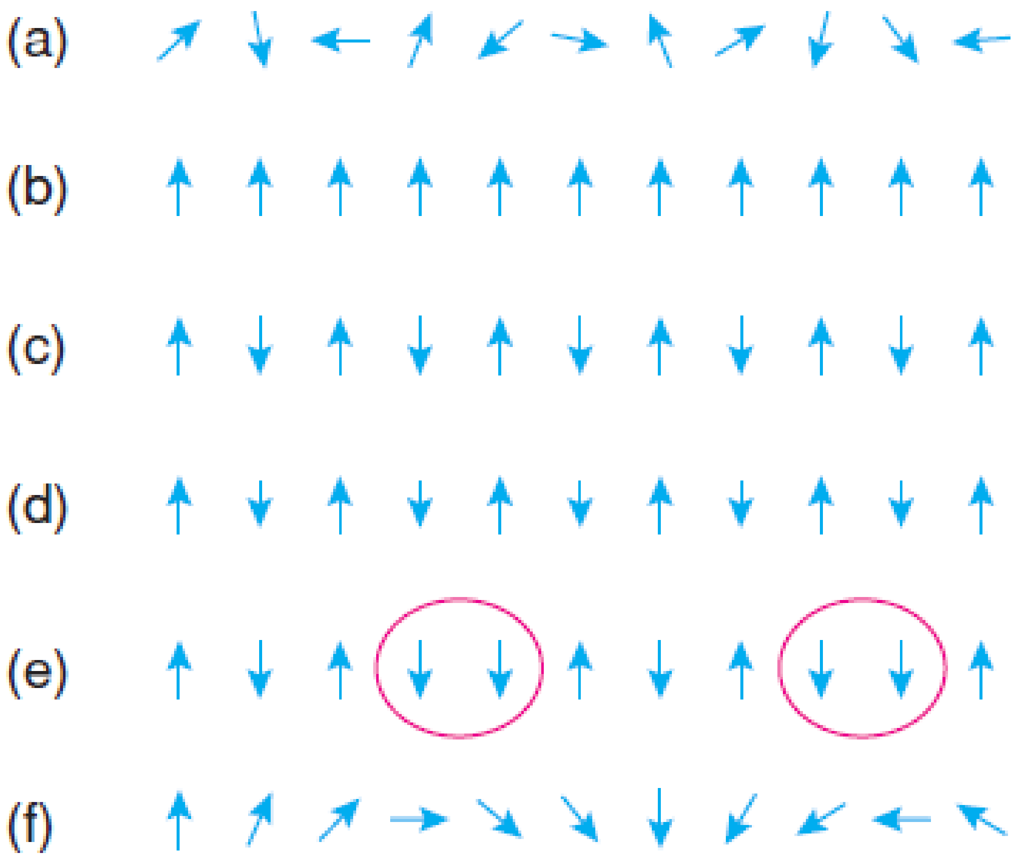
**Piezoelectricity**

- An unusual property exhibited by a few ceramic materials is piezoelectricity: polarization is induced and an electric field is established across a specimen by the application of external forces.
- Reversing the sign of an external force (i.e., from tension to compression) reverses the direction of the field.
- The piezoelectric behavior of a polycrystalline specimen may be improved by heating above its Curie temperature and then cooling to room temperature in a strong electric field.
- Piezoelectric materials are used in transducers, which are devices that convert electrical energy into mechanical strains, or vice versa
- In pyroelectricity, ionic displacements occur spontaneously and vary with temperature; in piezoelectricity, the displacements also occur spontaneously but vary under an applied pressure; in ferroelectricity, the spontaneous displacements may be reversed in an applied electric field, giving rise to hysteresis

# Magnetic Properties

- Inorganic solids exhibit magnetic effects other than *diamagnetism (*property of all substances), have some unpaired electrons in their outer valence shells
- The unpaired electrons can have both spin and orbital motion, which together generate a magnetic moment associated with the electrons.
- Magnetic behavior is thus restricted mainly to compounds of transition metals and lanthanoids.
- Atomic nuclei also possess magnetic moments, but these are several orders of magnitude smaller than electron magnetic moments.
- The unpaired electron spins may be oriented at random on the different atoms, the material is *paramagnetic* (a)
- The unpaired electron may interact with each other leading to *cooperative magnetic phenomena*.
- The spins may be aligned parallel, the material possesses an overall magnetic moment & is *ferromagnetic* (b)
- The unpaired electron or they may be aligned antiparallel, giving zero overall magnetic moment & is *antiferromagnetic* (c)

- If the alignment is antiparallel but with unequal numbers in the two orientations, a net magnetic moment results and the behavior is *ferrimagnetic* (d).
- *Spin glass behavior* is observed in certain cases where the prime ordering tendency is antiferromagnetic but full antiferromagnetic order is not able to propagate through the structure; instead, it is blocked by an arrangement where pairs of spins are ordered ferromagnetically (e).
- In *helimagnetic* behavior, spins are not confined to be simply parallel or antiparallel but show a gradual angular rotation between adjacent spins, giving a helical magnetic structure (f).



| Properties | Description | Alignment of magnetic dipoles | Examples | Application |
|---|---|---|---|---|
| Diamagnetic | They are weakly repelled by the magnetic fields | All the electrons in the orbitals are paired and are completely filled. | NaCl, Benzene | Behaves like an insulator |
| Paramagnetic | They are weakly attracted by the magnetic fields. | Contains at least one unpaired electron in the orbital. | $O_2$, $Cu^{2+}$ etc | Electronic appliances |
| Ferromagnetic | Strongly attracted by the magnetic field. It can be magnetized permanently | Consists of unpaired electrons, all having the same direction | Co, Ni, $CrO_2$ etc. | $CrO_2$ is commonly used in making cassette recorder |
| Antiferromagnetic | Net magnetic moment is zero. | Dipole moments are arranged in a compensatory way | NiO, MnO, $V_2O_3$ etc | - |
| Ferrimagnetic | Possess small net magnetic moments | Unequal number of parallel and antiparallel arrangement of magnetic moments | $Fe_3O_4$ | - |

# Behavior of substances in a magnetic field

- When a substance is placed in a magnetic field, H, the density of lines of force in the sample, known as the magnetic induction or magnetic flux density, B, is related to H by the permeability, μ

  $B = \mu H$ (1) $B = \mu_o H + \mu_o M$ (2)

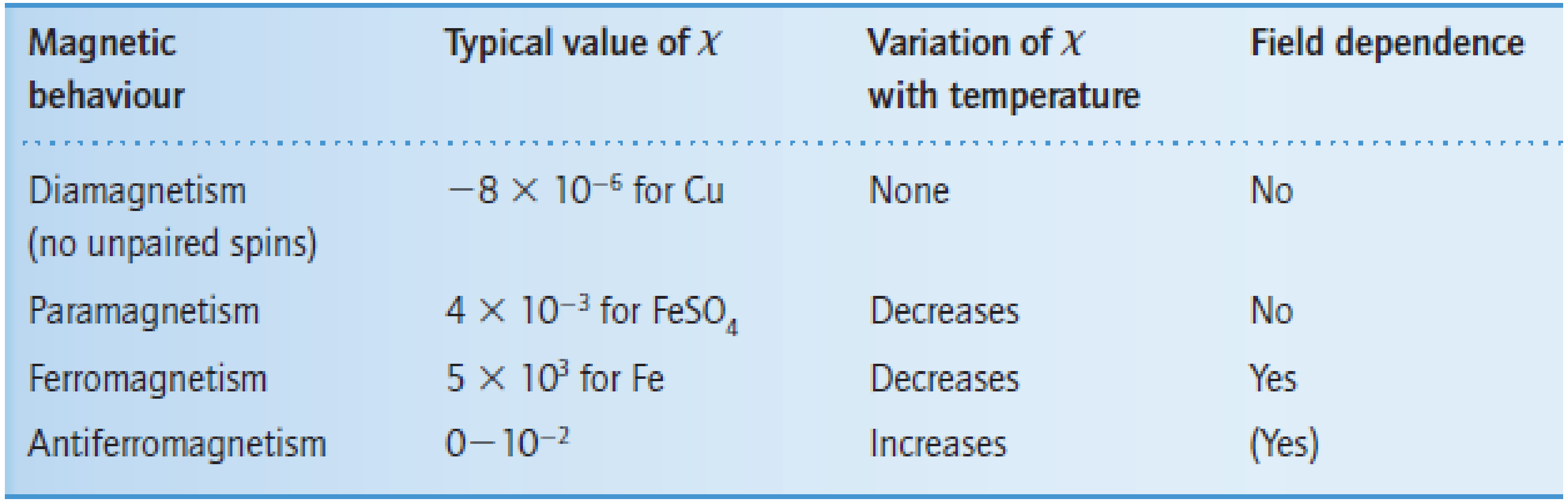
  where $\mu_o$ is the *permeability of free space*, $4\pi\times10^{-7}$ $\mathrm{Hm}^{-1}$ (*H* is the symbol for henry) and *M* is the *magnetization* or *magnetic moment* of the sample. $\mu_o H$ is the induction generated by the field alone and $\mu_o M$ is the additional induction contributed by the sample.

- The SI unit of magnetic field is amps per meter, $\mathrm{Am}^{-1}$, since magnetic fields are produced whenever an electric current flows in a wire or coil; the unit of *B* is the tesla, T.

- The *magnetic susceptibility*, χ, is defined as the ratio of magnetization to field:

  $\chi = M/H$ (3) and thus $\mu = \mu_o(1 + \chi)$ (4)

- The ratio $\mu/\mu_o$, which equals $1 + \chi$, is known as the *relative permeability*, $\mu_r$, and is unitless. The susceptibility, which is also unitless, is the main parameter that is usually considered in the characterization of magnetic properties and basically provides a measure of the response of a sample to an applied magnetic field. It is somewhat analogous to permittivity and polarizability, which refer to the responses in an electrical field.



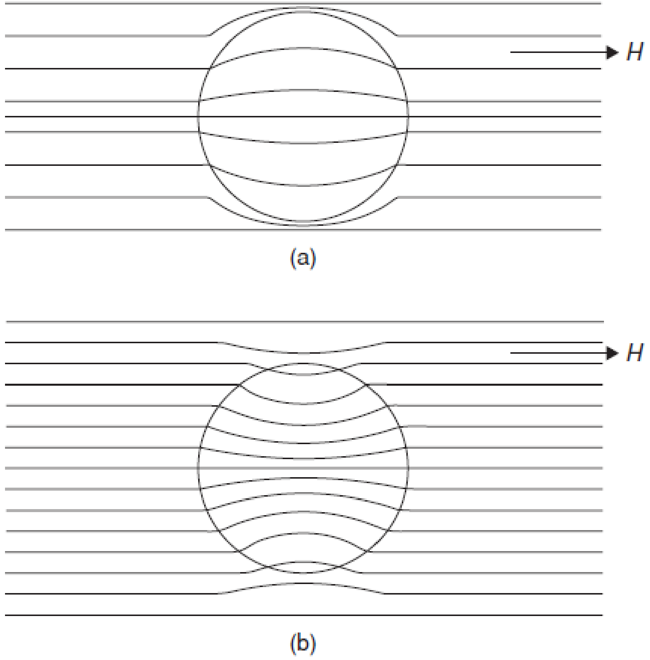
| Magnetic behaviour | Typical value of $\chi$ | Variation of $\chi$ with temperature | Field dependence |
|---|---|---|---|
| Diamagnetism (no unpaired spins) | $-8 \times 10^{-6}$ for Cu | None | No |
| Paramagnetism | $4 \times 10^{-3}$ for $FeSO_4$ | Decreases | No |
| Ferromagnetism | $5 \times 10^{3}$ for Fe | Decreases | Yes |
| Antiferromagnetism | $0-10^{-2}$ | Increases | (Yes) |

- The different kinds of magnetic behavior may be distinguished by the values of $\chi$ and $\mu$r and by their temperature and field dependences.

- For *diamagnetic* substances, $\chi$ is very small and slightly negative. Diamagnetism is associated with orbital motion of electrons in atoms. This orbital motion generates a small electric field and in the presence of an external field, the orbital motion is modified slightly to give a magnetic moment that opposes the applied field leading to a slight repulsion effect which is explained by Lenz’s law of electromagnetism.

- Superconductors represent a special, extreme type of diamagnetism since they repel magnetic fields completely. Since $B$ inside a superconductor is zero, then, from equation 2, $H = –M$. and from equation 3 , $\chi = –1$.

- For *paramagnetic* substances, $\chi$ is small and positive. Thus, when placed in a magnetic field, the number of lines of force passing through a substance is greater if it is paramagnetic and slightly less if it is diamagnetic than would pass through a vacuum. Consequently, paramagnetic substances are attracted by a magnetic field whereas diamagnetic substances experience a slight repulsion. Since superconductors show perfect diamagnetism, they expel magnetic fields completely, leading to the Meissner effect and applications in levitation.
- In *ferromagnetic* substances, $\chi < 1$ and such materials are strongly attracted to a magnetic field.
- In *antiferromagnetic* substances, $\chi$ is positive and comparable to or somewhat less than that for paramagnetic substances.



Variation of flux density or number of lines of force in (a) diamagnetic and (b) paramagnetic substances in a magnetic field

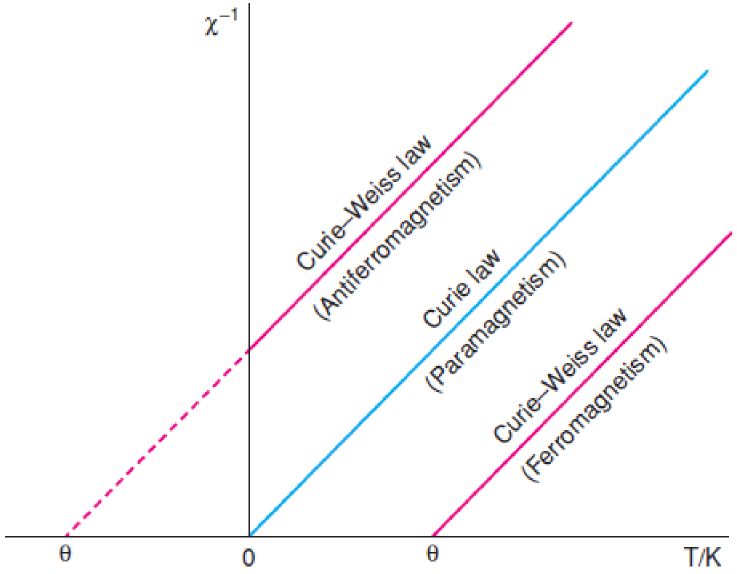
# Effects of temperature: Curie and Curie-Weiss laws

- The susceptibilities of different kinds of magnetic material are distinguished by both their temperature dependences and their absolute magnitudes
- Ordered magnetic structures, whether ferro-, ferri-, antiferro-, heli-magnetic or spin glass, lose their ordered structures above a temperature known as either the Curie temperature, $T_c$ (ferro- and ferri-magnets), or the Neel point, $T_N$ (antiferro- and heli-magnets); the spins become disordered and the materials are therefore paramagnetic.
- At these transition temperatures, there is a balance between thermal energy, which tends to randomize the orientation of the magnetic moments, and internal exchange interactions, which try to maintain the cooperative aligned structures.
- At $T_c$ and $T_N$, an order-disorder transition occurs, therefore, as the structures transform from an ordered structure to the disordered paramagnetic structure.
- Paramagnetic substances may obey the simple Curie law, which states that magnetic susceptibility ($\chi$) is inversely proportional to temperature, $\chi = C/T$

  where $C$ is the Curie constant. Such a Curie response occurs when there is no spontaneous interaction between adjacent unpaired electrons. They do tend to align in a magnetic field, but with increasing temperature this alignment is more difficult and $\chi$ decreases (above eqn).

- When there is some spontaneous interaction between adjacent spins, which may develop into an ordered magnetic structure at low temperatures, a better fit to the high-temperature behavior in the paramagnetic region is often provided by the Curie-Weiss law $\chi = C/T - \theta$ where $\theta$ is the Weiss constant.
- These two types of behavior are shown in $\chi$ −1 vs $T$ plot.
- For paramagnetic substances that show no tendency to magnetic order, the plot extrapolates to 0 K. For paramagnetic substances that show a tendency to ferromagnetic order, there is already some local alignment of spins and $\chi$ is higher than for the simple paramagnetic case. Also, $\chi$ becomes infinite ($\chi$−1→0) at a positive value of $\theta$ which coincides approximately with the *ferromagnetic Curie temperature*, $T$c, below which the sample is ferromagnetic.
- In paramagnetic substances that show a tendency to antiferromagnetic order, the $\chi$ values may be lower than in the simple paramagnetic case. This has the effect of displacing the Curie-Weiss plot to lower temperatures and the extrapolated value of $\theta$ is below 0 K. Obviously, such temperatures can never be reached; instead, on cooling, antiferromagnetism develops below $T_N$ and departure from Curie-Weiss behavior occurs

- The behavior shown is for paramagnetic substances or for ferro-, ferri- and antiferro-magnetic substances in the paramagnetic state above *T*c and $T_N$; it is somewhat idealized and departures from ideality do occur in practice. Below *T*c and $T_N$, Curie–Weiss behavior is not observed.
- Ferromagnetic substances show very large susceptibilities at low temperatures, which decrease increasingly rapidly on heating towards *T*c.
- For antiferromagnetic substances, $\chi$ is very small at low temperatures in well-ordered structures but increases with increase in temperature (unlike for ferromagnets) as some thermally induced disorder is introduced into the antiferromagnetic state; $\chi$ passes through a maximum at *T*N and then decreases at higher temperatures, following Curie-Weiss behavior.



Reciprocal of susceptibility versus temperature for substances that are paramagnetic but may show magnetic ordering at low temperatures

# Magnetic moments

- Magnetic properties are expressed in terms of the magnetic moment ($\mu$) since it relates directly to the number of unpaired electrons.
- The magnetic properties of unpaired electrons arise from two causes, electron spin and electron orbital motion. Of most importance is the spin component. An electron may usefully be visualized as a bundle of negative charge spinning on its axis. The magnitude of the resulting spin moment, $\mu_s$, is 1.73 BM (Bohr magneton); the Bohr magneton is defined as 1BM = eh/4πmc where *e* is the electron charge, *h* is Planck's constant, *m* is the electron mass and *c* is the velocity of light.
- $\mu_s$ for a single electron is $\mu_s = g\sqrt{[s(s + 1)]}$ where s is the spin quantum number, 1/2, and g is the gyromagnetic ratio, ~2.00.
- For atoms or ions that contain more than one unpaired electron, the overall spin moment is given by $\mu_S = g\sqrt{[S(S + 1)]}$ where *S* is the sum of the spin quantum numbers of the individual unpaired electrons
- Substituting for *s* and *g* gives $\mu_s = 1.73$ BM for a single electron. For high-spin $Fe^{3+}$, containing five unpaired 3*d* electrons, $S = 5/2$ and $\mu_s = 5.92$ BM

- The motion of an electron around the nucleus may, in some materials, especially those containing heavy metal ions such as the lanthanoids, give rise to an *orbital moment* which contributes to the overall magnetic moment. In cases where the orbital moment makes its full contribution, $\mu_{S+L} = \sqrt{[4S(S + 1) + L(L + 1)]}$ where $L$ is the orbital angular momentum quantum number for the ion.

The equation may not hold because the orbital angular momentum is either wholly or partially *quenched* in cases where the electric fields on the surrounding atoms or ions restrict the orbital motion of the electrons. In such cases, therefore, the observed moments are similar to or somewhat larger than the calculated, spin-only values

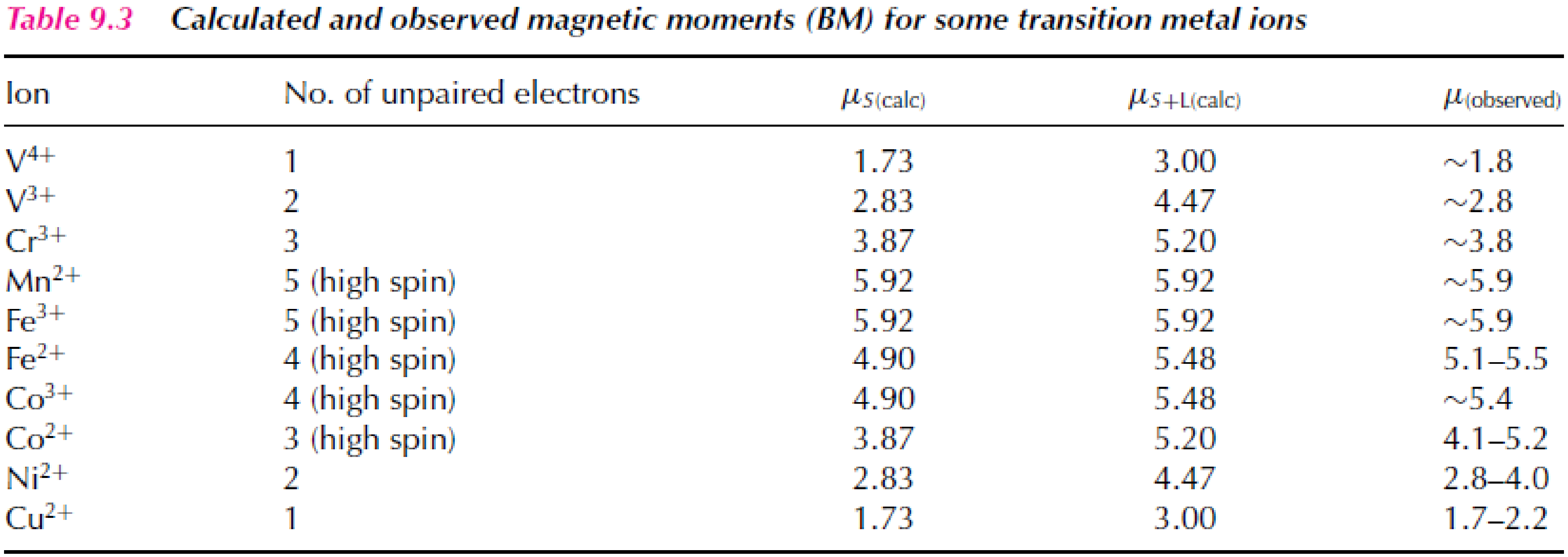


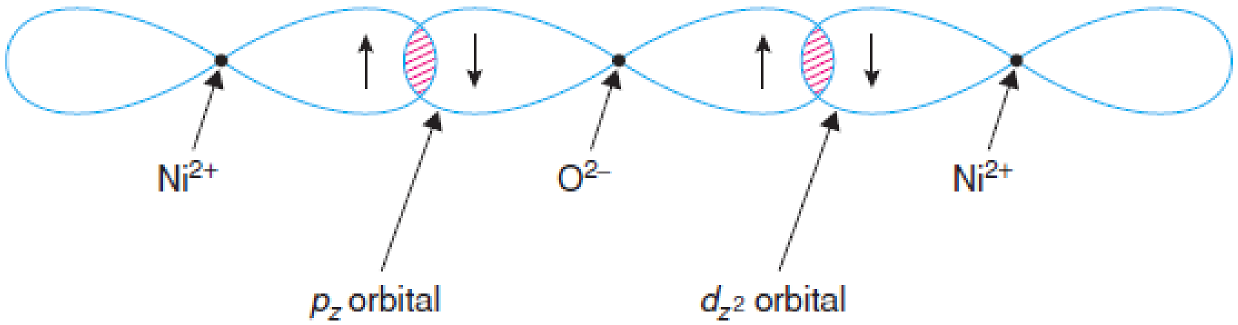
*Table 9.3 Calculated and observed magnetic moments (BM) for some transition metal ions*

| Ion | No. of unpaired electrons | $\mu_{S(\mathrm{calc})}$ | $\mu_{S+\mathrm{L}(\mathrm{calc})}$ | $\mu_{(\mathrm{observed})}$ |
|---|---|---|---|---|
| $V^{4+}$ | 1 | 1.73 | 3.00 | ~1.8 |
| $V^{3+}$ | 2 | 2.83 | 4.47 | ~2.8 |
| $Cr^{3+}$ | 3 | 3.87 | 5.20 | ~3.8 |
| $Mn^{2+}$ | 5 (high spin) | 5.92 | 5.92 | ~5.9 |
| $Fe^{3+}$ | 5 (high spin) | 5.92 | 5.92 | ~5.9 |
| $Fe^{2+}$ | 4 (high spin) | 4.90 | 5.48 | 5.1–5.5 |
| $Co^{3+}$ | 4 (high spin) | 4.90 | 5.48 | ~5.4 |
| $Co^{2+}$ | 3 (high spin) | 3.87 | 5.20 | 4.1–5.2 |
| $Ni^{2+}$ | 2 | 2.83 | 4.47 | 2.8–4.0 |
| $Cu^{2+}$ | 1 | 1.73 | 3.00 | 1.7–2.2 |

# Mechanisms of ferro- and antiferromagnetic ordering: superexchange

- In the paramagnetic state, individual magnetic moments of ions containing unpaired electrons are oriented at random. Partial alignment occurs only on application of a magnetic field. The energy of interaction between dipoles and a magnetic field may be calculated readily. It is generally greater than the thermal energy, $kT$, possessed by the ions or dipoles.
- In the ferro- and antiferromagnetic states, alignment of magnetic dipoles occurs spontaneously. There must therefore be some positive energy of interaction between neighboring spins that allows this to occur, either parallel or antiparallel. The origin of this coupling of spins or cooperative interaction is quantum mechanical.
- One process, by which spins couple to give antiferromagnetism is *superexchange*

- For example, in case of NiO, $Ni^{2+}$ ion has eight *d*-electrons. In an octahedral environment, two of these occupy singly the $e_g$ orbitals, $dz^2$ and $dx^2{-}y^2$ . These orbitals are oriented parallel to the axes of the unit cell and therefore point directly at adjacent oxide ions. The unpaired electrons in these $e_g$ orbitals couple with electrons in the *p* orbitals of the $O^{2-}$ ions. This coupling may involve the formation of an excited state in which the electron transfers from the $e_g$ orbital of $Ni^{2+}$ to the oxygen *p* orbital. Or it may be regarded as partial covalent bond formation involving pairing of electrons between adjacent Ni and O atoms. The *p* orbitals of the $O^{2-}$ ion contain two electrons each, which are also coupled antiparallel. Hence, provided that $Ni^{2+}$ and $O^{2-}$ ions are sufficiently close that coupling of their electrons is possible, a chain coupling effect may occur which propagates through the crystal structure. The net effect is that neighboring $Ni^{2+}$ ions, separated by intervening $O^{2-}$ ions, are coupled antiparallel.



*Antiferromagnetic coupling of spins of d electrons on $Ni^{2+}$ ions through p electrons of oxide ions.*

## Domains and Hysteresis

- Below its Curie temperature, a ferromagnetic or ferrimagnetic material is composed of domains - small-volume regions wherein all net dipole moments are mutually aligned and the magnetization is saturated (Figure 20.11).

- The total magnetization of the solid is just the appropriately weighted vector sum of the magnetizations of all these domains.

- As an external magnetic field is applied, domains having magnetization vectors oriented in the direction of the field grow at the expense of domains that have unfavourable magnetization orientations (Figure 20.13).

- At total saturation, the entire solid is a single domain and the magnetization is aligned with the field direction.

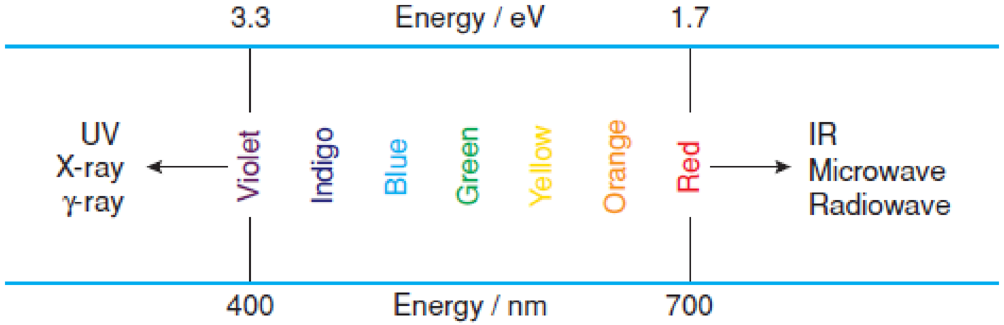
- The change in domain structure with increase or reversal of a magnetic field is accomplished by the motion of domain walls. Both hysteresis (the lag of the $B$ field behind the applied $H$ field) as well as permanent magnetization (or remanence) result from the resistance to movement of these domain walls.

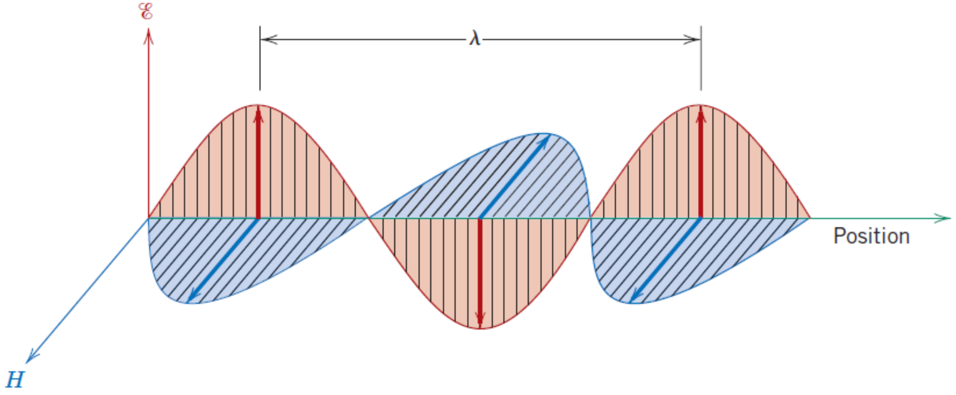
- From a complete hysteresis curve for a ferromagnetic/ferrimagnetic material the following may be determined: Remanence value of the $B$ field when $H$  0 ($Br$, Figure 20.14), Coercivity value of the $H$ field when $B$  0 ($Hc$, Figure 20.14)

# Optical Properties

## Electromagnetic Radiation

- The optical behavior of a solid material is a function of its interactions with electromagnetic radiation having wavelengths within the visible region of the spectrum (about 400 to 700 nm).
- From a quantum-mechanical perspective, electromagnetic radiation may be considered to be composed of photons - groups or packets of energy that are quantized, that is, they can have only specific values of energy.
- Photon energy is equal to the product of Planck’s constant and radiation frequency, E=hν

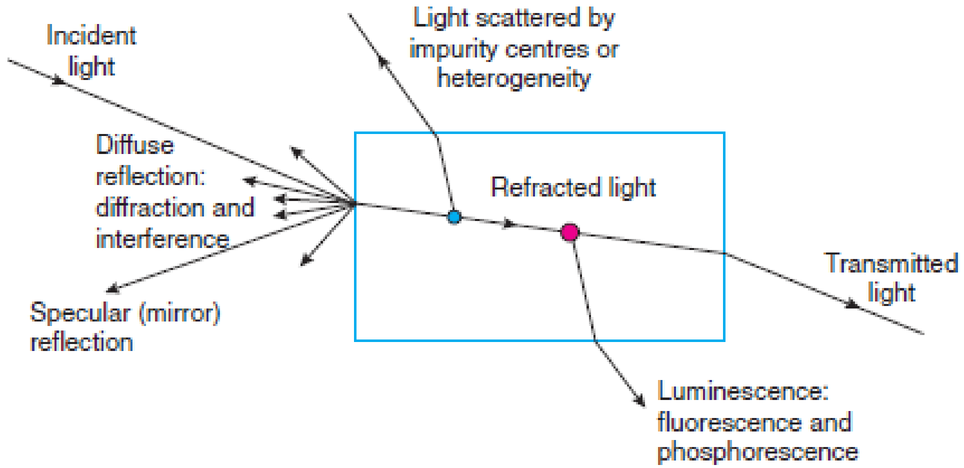




## Light interactions with solids

- The light can be reflected, transmitted, scattered or absorbed. The appearance of the solid depends on which of these interactions occur.
- The intensity $I_o$ of the beam incident to the surface of the solid medium must equal the sum of the intensities of the transmitted, absorbed, and reflected beams, denoted as $I_T$, $I_A$, and $I_R$, respectively i.e., $I_o = I_T + I_A + I_R$

  Alternatively, $T + A + R = 1$ where $T$, $A$, and $R$ represent, respectively, the transmissivity $(I_T/I_o)$, absorptivity $(I_A/I_o)$, and reflectivity $(I_R/I_o)$, or the fractions of incident light that are transmitted, absorbed, and reflected by a material; their sum must equal unity, because all the incident light is either transmitted, absorbed, or reflected.



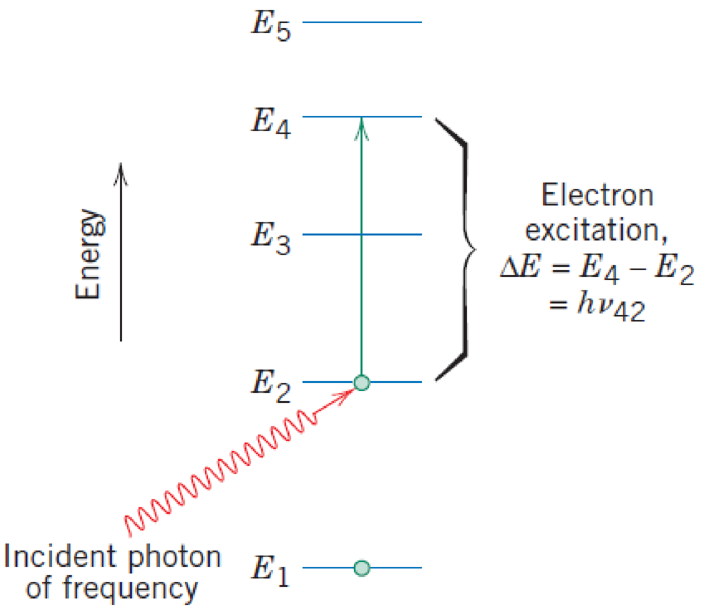
The interaction of light with a solid

- Regarding degree of light transmissivity, materials are classified as follows

- **Transparent -** light is transmitted through the material with very little absorption and reflection.
- **Translucent -** light is transmitted diffusely; there is some scattering within the interior of the material.
- **Opaque** - virtually all light is scattered or reflected, none is transmitted through the material.

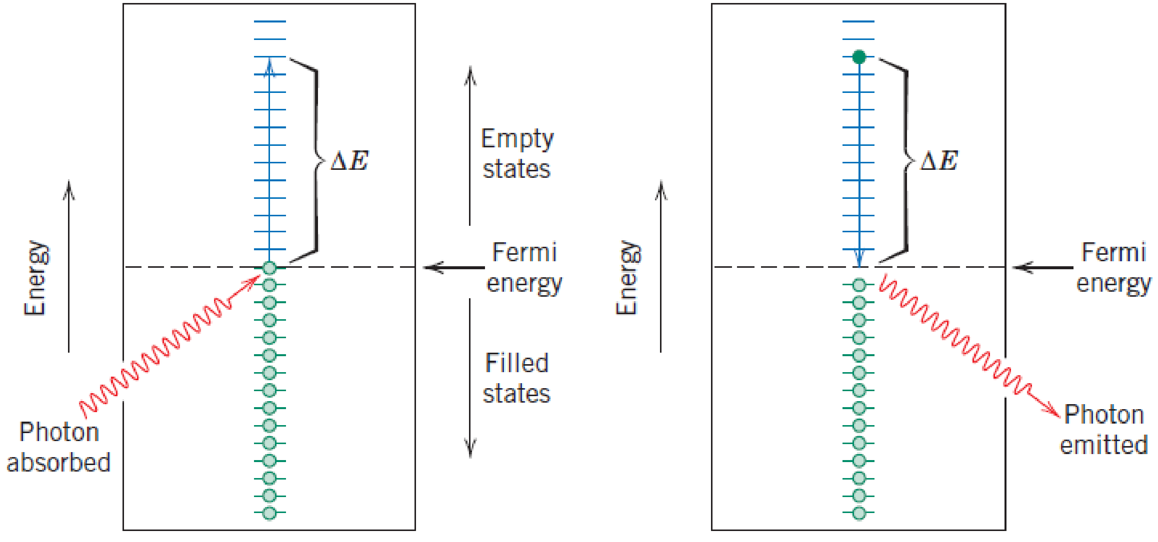
## Atomic and electronic interactions

- One possible interaction between electromagnetic radiation and matter is electronic polarization - the electric field component of a light wave induces a shift of the electron cloud around an atom relative to its nucleus.
- Two consequences of electronic polarization are absorption and refraction of light.
- Electromagnetic radiation may be absorbed by causing the excitation of electrons from one energy state to a higher state.



## Optical Properties of Metals

- Metals appear opaque as a result of the absorption and then reemission of light radiation within a thin outer surface layer.
- Absorption occurs via the excitation of electrons from occupied energy states to unoccupied ones above the Fermi energy level. Reemission takes place by decay electron transitions in the reverse direction.
- The perceived color of a metal is determined by the spectral composition of the reflected light



(*a*)

(*b*)

(*a*) Schematic representation of the mechanism of photon absorption for metallic materials in which an electron is excited into a higher-energy unoccupied state. The change in energy of the electron $E$ is equal to the energy of the photon. (*b*) Reemission of a photon of light by the direct transition of an electron from a high to a low energy state.

## Refraction

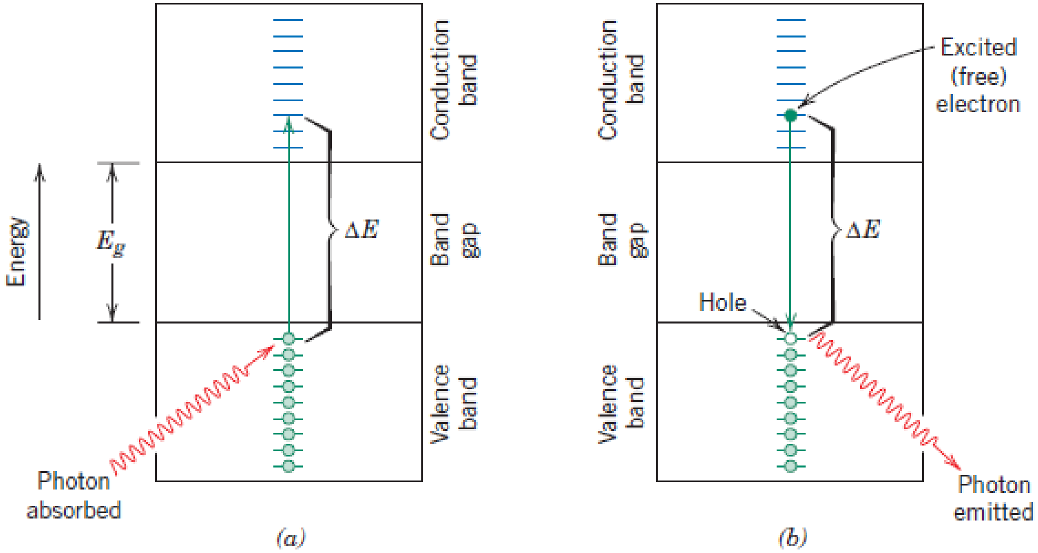
- Light radiation experiences refraction in transparent materials; that is, its velocity is retarded and the light beam is bent at the interface.
- The phenomenon of refraction is a consequence of electronic polarization of the atoms or ions. The larger an atom or ion, the greater the index of refraction.
- The index of refraction *n* of a material is defined as the ratio of the velocity in a vacuum *c* to the velocity in the medium v or $n = c/v$
- The magnitude of *n* (or the degree of bending) will depend on the wavelength of the light.

## Reflection

- When light passes from one transparent medium to another having a different index of refraction, some of it is reflected at the interface.
- The degree of the reflectance depends on the indices of refraction of both media, as well as the angle of incidence.
- For normal (perpendicular) incidence (to the interface), reflectivity may be calculated using $R=(n_2-n_1)^2/(n_2+n_1)^2$ where where $n_1$ and $n_2$ are the indices of refraction of the two media

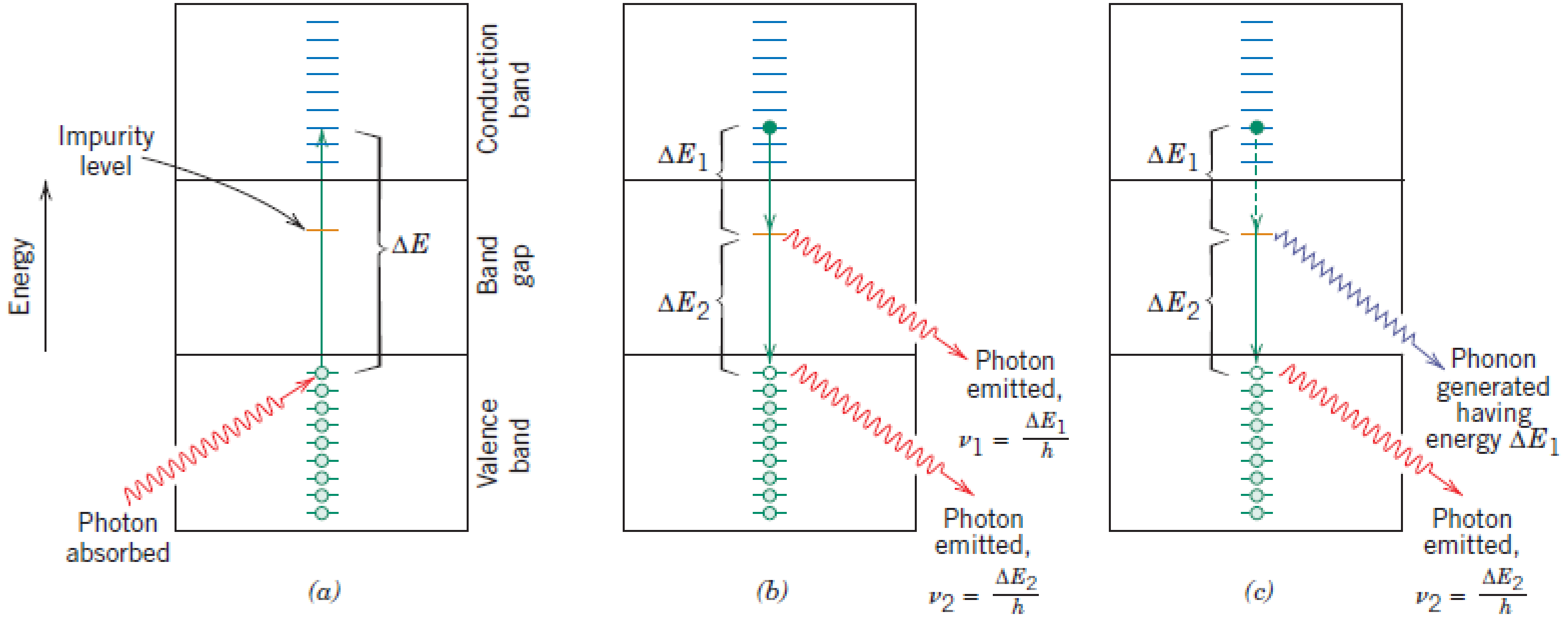
# Absorption

- Pure nonmetallic materials are either intrinsically transparent or opaque. Opacity results in relatively narrow band-gap materials ($E_g$ =1.8 eV) as a result of absorption whereby a photon’s energy is sufficient to promote valence band - conduction band electron transitions.
- Transparent nonmetals have band gaps greater than 3.1 eV.
- For nonmetallic materials that have band gaps between 1.8 and 3.1 eV, only a portion of the visible spectrum is absorbed; these materials appear coloured.
- Some light absorption occurs in even transparent materials as a consequence of electronic polarization.



(*a*) Photon absorption for non-metallic materials in which an electron is excited across the band gap, leaving behind a hole in the valence band. The energy of the photon absorbed is *E*, which is necessarily greater than the band gap energy $E_g$, (*b*) Emission of a photon of light by a direct electron transition across the band gap.

- For wide-band-gap insulators that contain impurities, decay processes involving excited electrons to states within the band gap are possible with the emission of photons having energies less than the band gap energy.



(*a*) Photon absorption via a valence band–conduction band electron excitation for a material that has an impurity level that lies within the band gap. (*b*) Emission of two photons involving electron decay first into an impurity state, and finally to the ground state. (*c*) Generation of both a phonon and a photon as an excited electron falls first into an impurity level and finally back to its ground state.

## Color

- Transparent materials appear colored as a consequence of specific wavelength ranges of light that are selectively absorbed (usually by electron excitations).
- The color discerned is a result of the distribution of wavelength ranges in the transmitted beam.

## Opacity and Translucency in Insulators

- Normally transparent materials may be made translucent or even opaque if the incident light beam experiences interior reflection and/or refraction.
- Translucency and opacity as a result of internal scattering may occur

  (1) in polycrystalline materials that have anisotropic indices of refraction;

  (2) in two-phase materials;

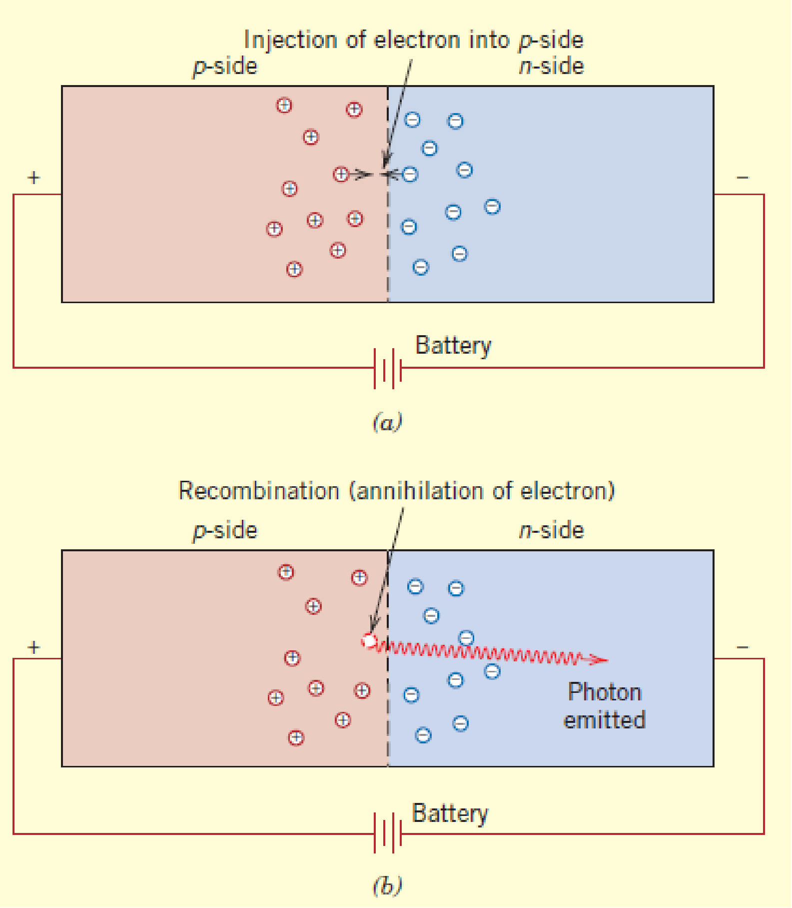
  (3) in materials containing small pores; and

  (4) in highly crystalline polymers.

# Applications of Optical Phenomena

## Luminescence

- With luminescence, energy is absorbed as a consequence of electron excitations, which is subsequently reemitted as visible light.
- Caused by chemical or biochemical reactions, activity of subatomic particles, radiation or stress on a crystal
- When light is reemitted in less than a second after excitation, the phenomenon is called *fluorescence*.
- For longer reemission times, the term *phosphorescence* is used.
- *Electroluminescence* is the phenomenon in which light is emitted as a result of electron–hole recombination events that are induced in a forward-biased diode.
- The device that experiences electroluminescence is light-emitting diode (LED).



Schematic diagram of a forward-biased semiconductor *p*–*n* junction showing (*a*) the injection of an electron from the *n*-side into the *p*-side, and (*b*) the emission of a photon of light as this electron recombines with a hole.

- *Crystalloluminescence* - Light is made during crystallization and it is theorized that the light comes from small fractures in the crystal

**Fluorescence**

- Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation.
- In most cases, the emitted light has a longer wavelength, and therefore a lower photon energy, than the absorbed radiation.
- A perceptible example of fluorescence occurs when the absorbed radiation is in the UV-region of the spectrum (invisible), while the emitted light is in the visible region; this gives the fluorescent substance a distinct color that can only be seen when exposed to UV light.
- Fluorescent materials cease to glow nearly immediately when the radiation source stops.
- Fluorescence has many practical applications, including mineralogy, gemology, medicine, chemical sensors (fluorescence spectroscopy), fluorescent labelling, dyes, biological detectors, cosmic-ray detection, vacuum fluorescent displays, and cathode-ray tubes.

- Its most common everyday application is in (gas-discharge) fluorescent lamps and LED lamps, in which fluorescent coatings convert UV or blue light into longer-wavelengths resulting in white light which can even appear indistinguishable from that of the traditional but highly inefficient incandescent lamp.
- Fluorescence also occurs frequently in nature in some minerals and in many biological forms across all kingdoms of life. The latter may be referred to as biofluorescence, indicating that the fluorophore is part of or is extracted from a living organism (rather than an inorganic dye or stain).
- Since fluorescence is due to a specific chemical, which can also be synthesized artificially in most cases, it is sufficient to describe the substance itself as fluorescent

**Phosphorescence**

- Phosphorescence is a type of photoluminescence related to fluorescence.
- When exposed to light (radiation) of a shorter wavelength, a phosphorescent substance will glow, absorbing the light and reemitting it at a longer wavelength.

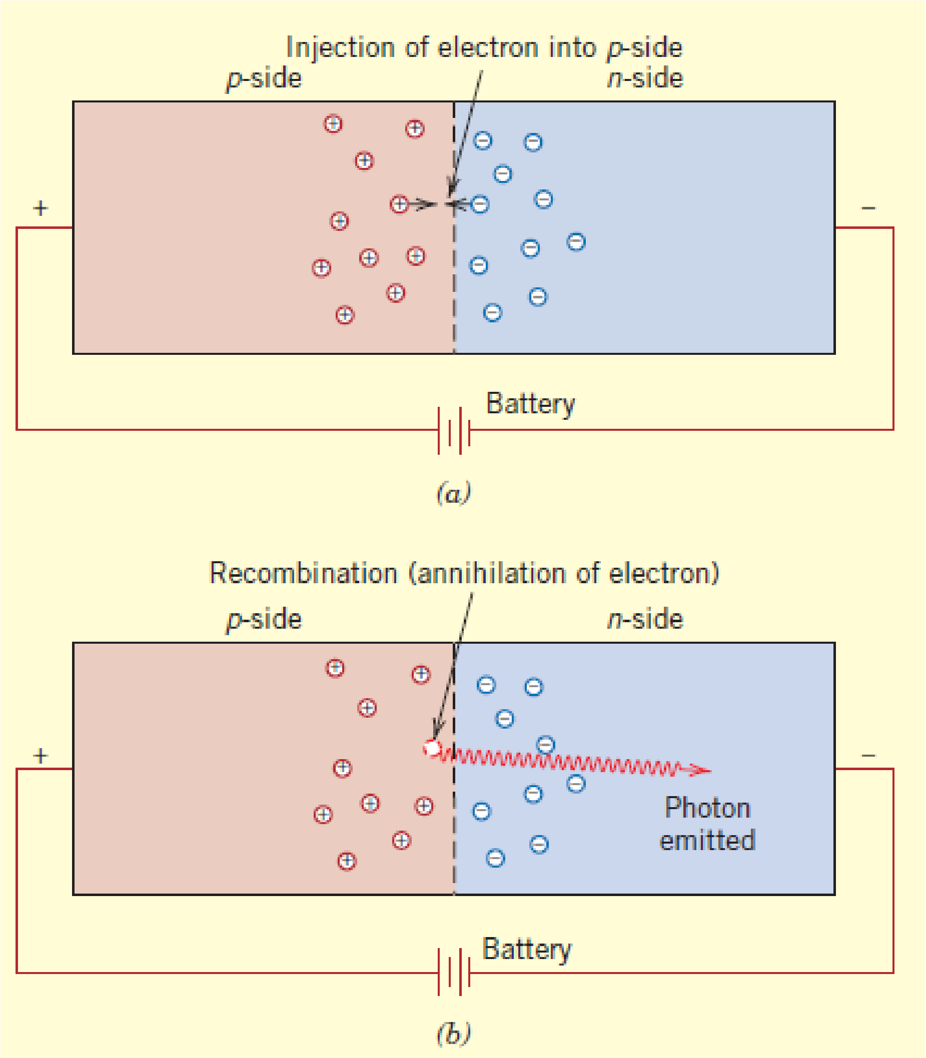
- Phosphorescent material does not immediately reemit the radiation it absorbs. Instead, a phosphorescent material absorbs some of the radiation energy and reemits it for a much longer time after the radiation source is removed.
- Usually, there is no distinct boundary between the emission times of fluorescence and phosphorescence (if a substance glows under a black light it is generally considered fluorescent, and if it glows in the dark it is called phosphorescent).
- Fluorescent materials stop emitting light within nanoseconds after the excitation radiation is removed while phosphorescent materials may continue to emit radiation after the excitation is removed.
- There are two separate mechanisms that may produce phosphorescence, called triplet phosphorescence (or phosphorescence) and persistent phosphorescence (or persistent luminescence).
- Triplet phosphorescence occurs when an atom absorbs a high-energy photon, and the energy becomes locked in the spin multiplicity of the electrons, generally changing from a fluorescent "singlet state" to a slower emitting "triplet state".
- The slower timescales of the reemission are associated with "forbidden" energy state transitions in quantum mechanics.

- Persistent phosphorescence occurs when a high-energy photon is absorbed by an atom and its electron becomes trapped in a defect in the lattice of the crystalline or amorphous material.
- A defect such as a missing atom (vacancy defect) can trap an electron like a pitfall, storing that electron's energy until released by a random spike of thermal (vibrational) energy.
- Everyday examples of phosphorescent materials are the glow-in-the-dark toys, stickers, paint, wristwatch and clock dials that glow after being charged with a bright light such as in any normal reading or room light.
- Typically, the glow slowly fades out, sometimes within a few minutes or up to a few hours in a dark room.
- The study of phosphorescent materials led to the discovery of radioactive decay.

- **Photoluminescence -** This is a process where a substance absorbs photons and then re-emits them. The electromagnetic energy is absorbed at a certain wavelength and is emitted at a different wavelength which is most commonly longer.
- **Radioluminescence -** Light from this process is made from using radiation or high energy particles to bombard a substance. This is used in medical physics and radar screens.
- **Sonoluminescence -** This produces light from bubbles that are hitting one another when sound waves passed through the liquid. The sound waves cause bubbles which emit light when popped.
- **Thermoluminescence -** Light comes from using heat to release of electrons that were trapped in a substance. This process is used in archaeological dating.
- **Triboluminescence -** In this process, the light coming from the substance is made by friction, like rubbing, crushing, or scratching. The friction pulls apart chemical bonds, thus causing electrical charges.

# Light-Emitting Diodes

- The conversion of electrical energy into light energy is termed as electroluminescence, and the device that produces it is termed as light-emitting diode (LED).
- The forward-biased potential attracts electrons on the *n*-side toward the junction, where some of them pass (inject) into the *p*-side (a). Here, the electrons are minority charge carriers and therefore "recombine" with, or are annihilated by, the holes in the region near the junction, where the energy is in the form of photons of light (b)
- Analogous process occurs on the *p*-side-holes travel to the junction and recombine with the majority electrons on the *n*-side.
- The elemental semiconductors (Si & Ge) are not suitable for LEDs due to the detailed natures of their band gap structures. Some of the Gr. III-V semiconducting compounds such as GaAs, InP and their alloys are frequently used.
- The wavelength (color) of the emitted radiation is related to the band gap of the semiconductor (normally the same for both *n*- and *p*-sides of the diode)

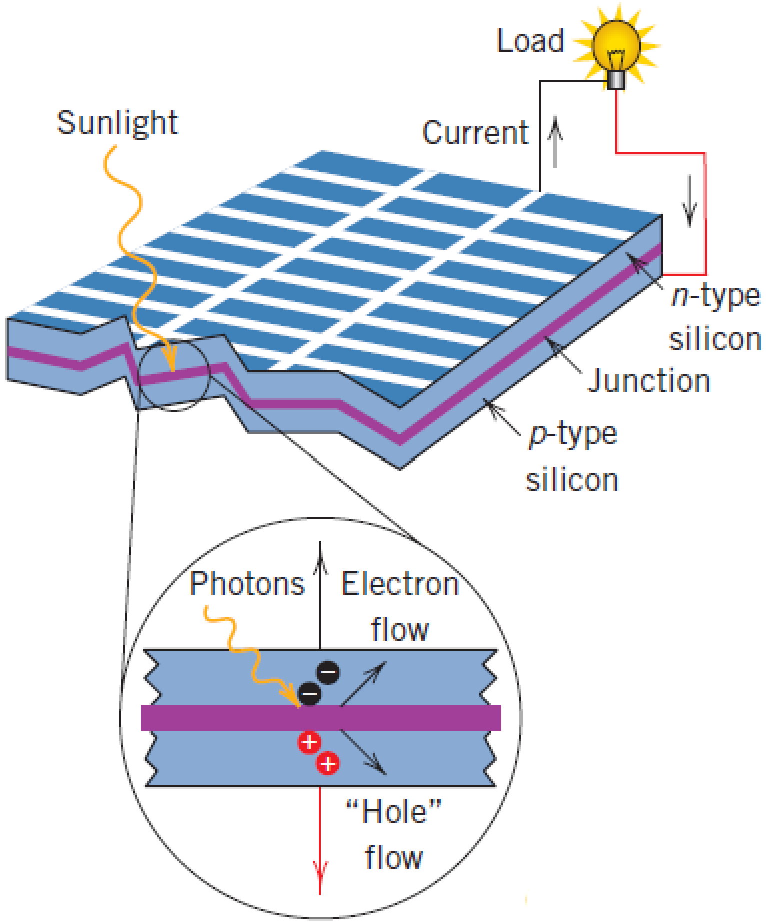


Schematic diagram of a forward-biased semiconductor *p*–*n* junction showing (*a*) the injection of an electron from the *n*-side into the *p*-side, and (*b*) the emission of a photon of light as this electron recombines with a hole.

- Several important applications for semiconductor LEDs include digital clocks and illuminated watch displays, optical mice (computer input devices), and film scanners.
- Electronic remote controls (for televisions, DVD players) also employ LEDs that emit an infrared beam; this beam transmits coded signals that are picked up by detectors in the receiving devices.
- In addition, LEDs are now being used for light sources. They are more energy efficient than incandescent lights, generate very little heat, and have much longer lifetimes (because there is no filament that can burn out). Most new traffic control signals use LEDs instead of incandescent lights
- Some polymeric materials may be semiconductors (both *n*- and *p*-type). As a consequence, light-emitting diodes made of polymers are possible, of which there are two types: (1) *organic light-emitting diodes* (or *OLED*s), which have relatively low molecular weights; and (2) the high-molecular-weight *polymer light-emitting diodes* (or *PLED*s).

## Photoconductivity

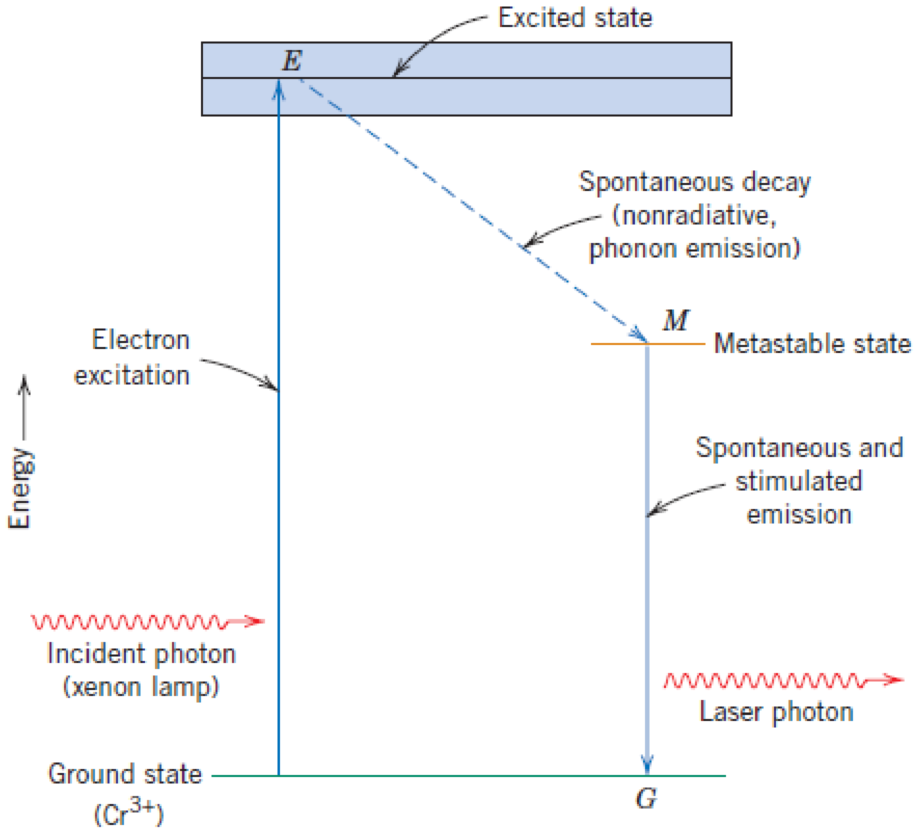
- Photoconductivity is the phenomenon whereby the electrical conductivity of some semiconductors may be enhanced by photo-induced electron transitions, whereby additional free electrons and holes are generated.
- When a specimen of a photoconductive material is illuminated, the conductivity increases. This phenomenon is used in photographic light meters.
- A photoinduced current is measured, and its magnitude is a direct function of the intensity of the incident light radiation, or the rate at which the photons of light strike the photoconductive material.
- Visible light radiation must induce electronic transitions in the photoconductive material; cadmium sulfide is commonly used in light meters.
- Sunlight may be directly converted into electrical energy in solar cells, which also employ semiconductors.
- The operation of these devices is, in a sense, the reverse of that for the light-emitting diode.
- A *p*–*n* junction is used in which photoexcited electrons and holes are drawn away from the junction, in opposite directions, and become part of an external current



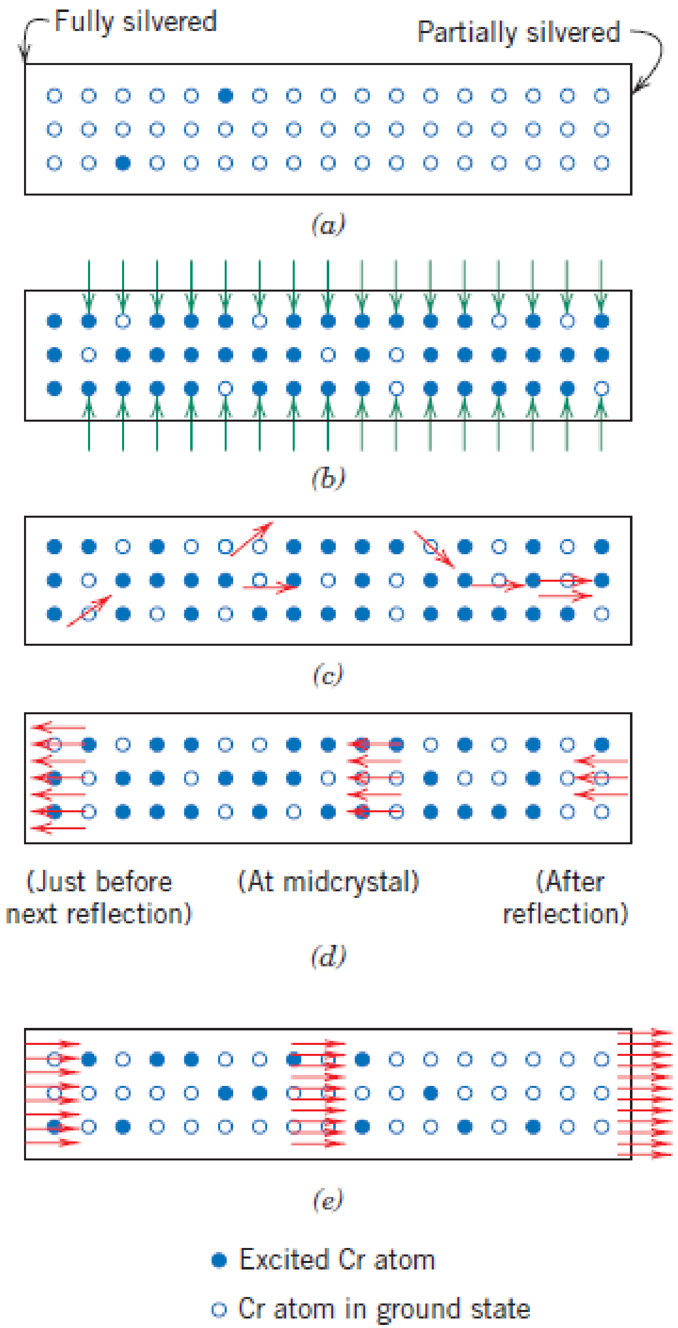
Schematic diagram illustrating the operation of a photovoltaic solar cell. The cell itself is made of polycrystalline silicon that has been fabricated to form a *p*–*n* junction. Photons of sunlight excite electrons into the conduction band on the *n* side of the junction, create holes on the *p* side.

## Lasers

- Coherent and high-intensity light beams are produced in lasers by stimulated electron transitions.
- Laser is just the acronym for light amplification by stimulated emission of radiation.
- Although there are several different varieties of laser, the principles of operation are explained using the solid-state ruby laser.
- With the ruby laser, a beam is generated by electrons that decay back into their ground Cr(III) states from metastable excited states.
- The beam from a semiconducting laser results from the recombination of excited electrons in the conduction band with valence band holes.



Schematic energy diagram for the ruby laser, showing electron excitation and decay paths.



Schematic representations of the stimulated emission and light amplification for a ruby laser. (*a*) The chromium ions before excitation. (*b*) Electrons in some chromium ions are excited into higher energy states by the xenon light flash. (*c*) Emission from metastable electron states is initiated or stimulated by photons that are spontaneously emitted. (*d*) Upon reflection from the silvered ends, the photons continue to stimulate emissions as they traverse the rod length. (*e*) The coherent and intense beam is finally emitted through the partially silvered end.

- For the semiconductor laser, schematic representations of the stimulated recombination of excited electrons in the conduction band with holes in the valence band that gives rise to a laser beam.

(a) One excited electron recombines with a hole; the energy associated with this recombination is emitted as a photon of light

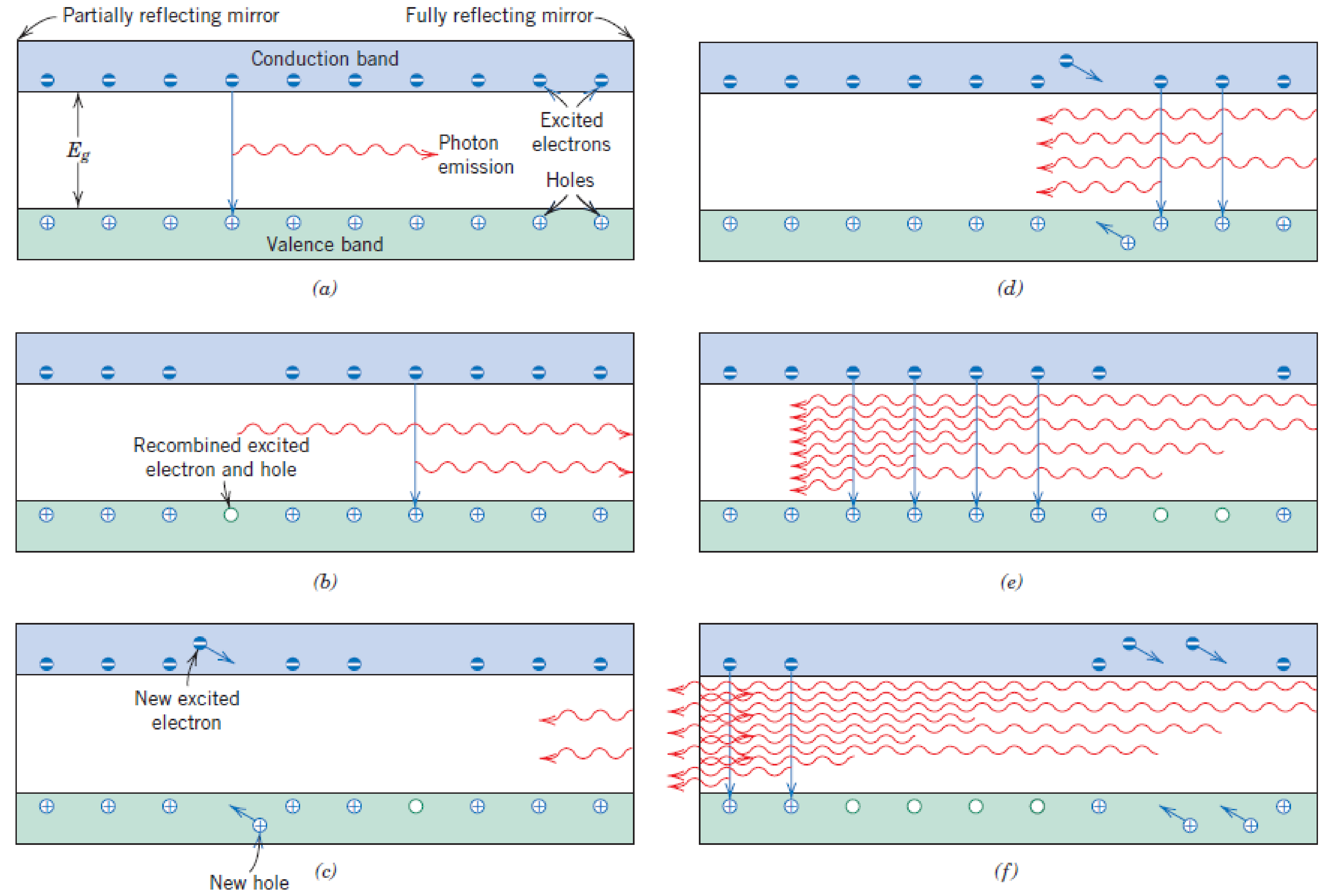
(b) The photon emitted in (*a*) stimulates the recombination of another excited electron and hole, resulting in the emission of another photon of light.

(c) The two photons emitted in (*a*) and (*b*), having the same wavelength and being in phase with one another, are reflected by the fully reflecting mirror back into the laser semiconductor.

(d) In addition, new excited electrons and new holes are generated by a current that passes through the semiconductor

(e) In proceeding through the semiconductor, more excited electron–hole recombinations are stimulated, which give rise to additional photons of light that also become part of the monochromatic and coherent laser beam.

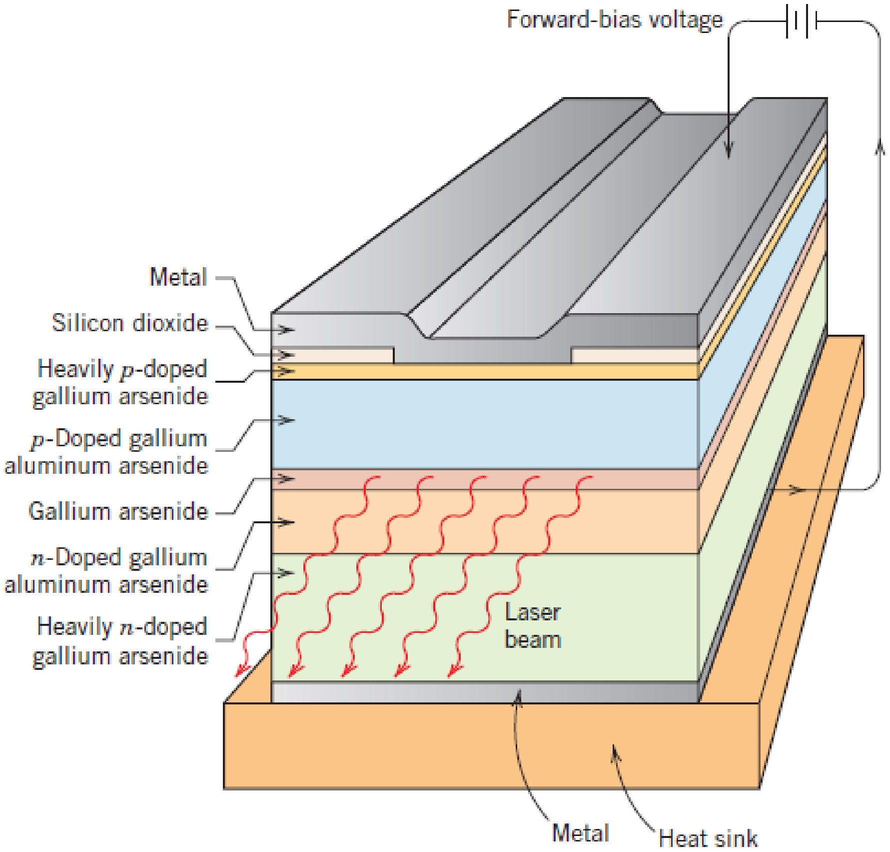
(f) Some portion of this laser beam escapes through the partially reflecting mirror at one end of the semiconducting material.


Partially reflecting mirror
Fully reflecting mirror
Conduction band
$E_g$
Photon emission
Excited electrons
Holes
Valence band
(a)
Recombined excited electron and hole
(b)
New excited electron
New hole
(c)
(d)
(e)
(f)

# Semiconducting Laser

- Semiconducting materials such as gallium arsenide may also be used as lasers that are employed in compact disc players and in the modern telecommunications industry.

- One requirement of these semiconducting materials is that the wavelength associated with the band gap energy $E_g$ must correspond to visible light $\lambda = hc/E_g$ the value of must lie between 0.4 and 0.7 m.



Schematic diagram showing the layered cross section of a GaAs semiconducting laser. Holes, excited electrons, and the laser beam are confined to the GaAs layer by the adjacent *n*- and *p*-type GaAlAs layers.

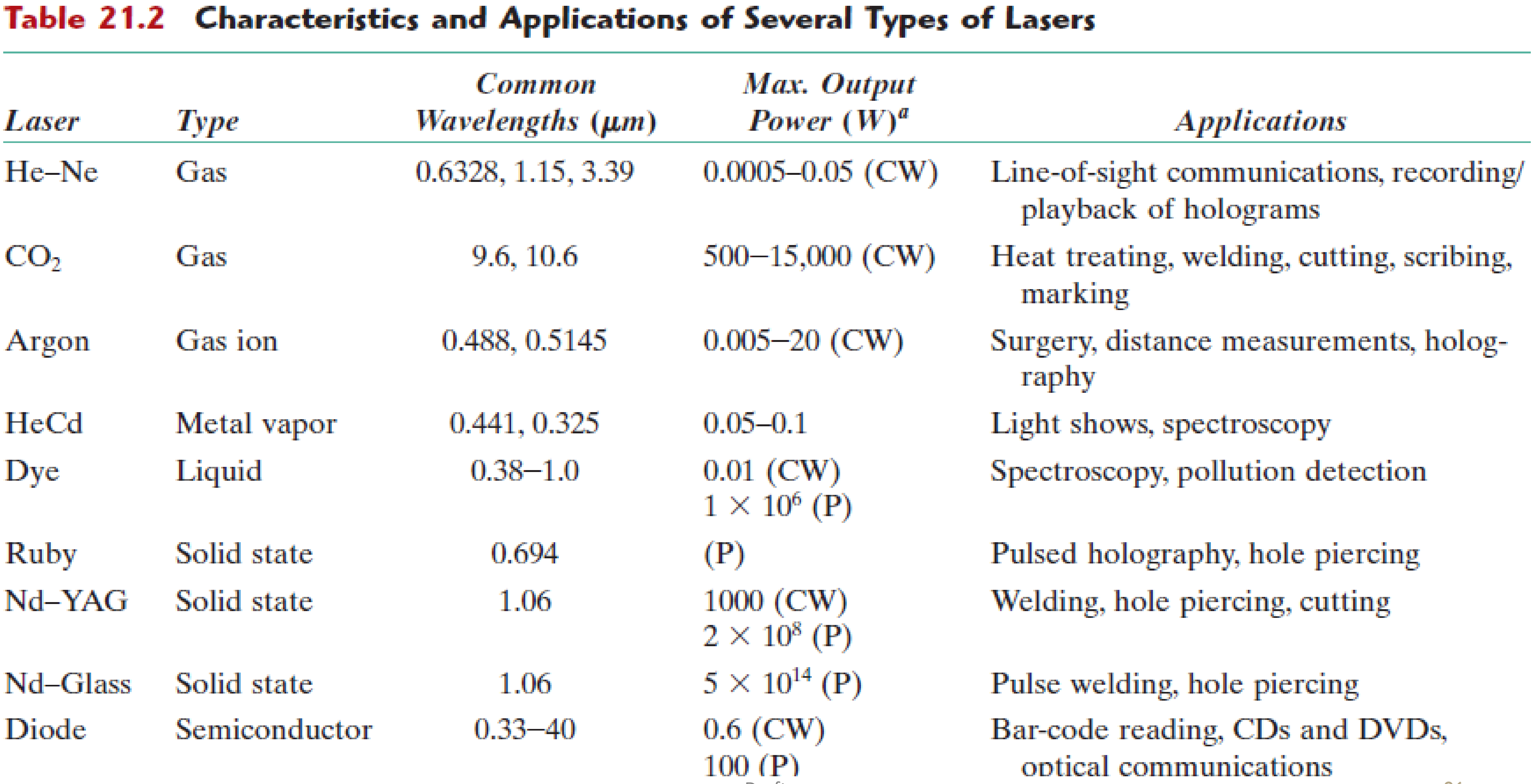
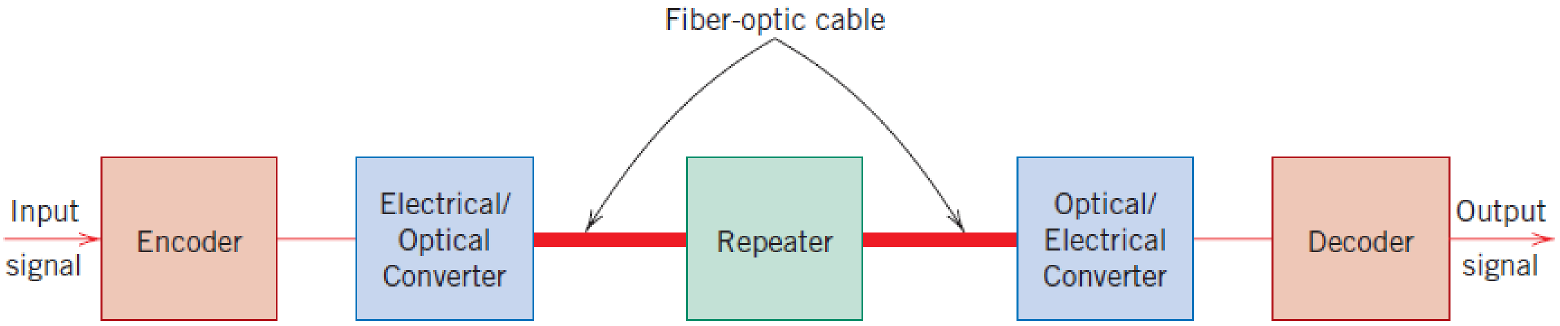


**Table 21.2** Characteristics and Applications of Several Types of Lasers

| *Laser* | *Type* | *Common Wavelengths (μm)* | *Max. Output Power (W)*[a] | *Applications* |
|---|---|---|---|---|
| He–Ne | Gas | 0.6328, 1.15, 3.39 | 0.0005–0.05 (CW) | Line-of-sight communications, recording/playback of holograms |
| $CO_2$ | Gas | 9.6, 10.6 | 500–15,000 (CW) | Heat treating, welding, cutting, scribing, marking |
| Argon | Gas ion | 0.488, 0.5145 | 0.005–20 (CW) | Surgery, distance measurements, holography |
| HeCd | Metal vapor | 0.441, 0.325 | 0.05–0.1 | Light shows, spectroscopy |
| Dye | Liquid | 0.38–1.0 | 0.01 (CW)<br>$1 \times 10^6$ (P) | Spectroscopy, pollution detection |
| Ruby | Solid state | 0.694 | (P) | Pulsed holography, hole piercing |
| Nd–YAG | Solid state | 1.06 | 1000 (CW)<br>$2 \times 10^8$ (P) | Welding, hole piercing, cutting |
| Nd–Glass | Solid state | 1.06 | $5 \times 10^{14}$ (P) | Pulse welding, hole piercing |
| Diode | Semiconductor | 0.33–40 | 0.6 (CW)<br>100 (P) | Bar-code reading, CDs and DVDs, optical communications |

## Optical Fibers in Communications

- Use of fiber-optic technology in our modern telecommunications provides for the transmission of information that is interference free, rapid, and intense.
- An optical fiber is composed of the following elements:
  - A core through which the pulses of light propagate
  - The cladding, which provides for total internal reflection and containment of the light beam within the core
  - The coating, which protects the core and cladding from damage



Schematic diagram showing the components of an optical-fiber communications system

- The information (i.e., telephone conversation) in electronic form must first be digitized into bits, that is, 1s and 0s; this is accomplished in the encoder.
- It is next necessary to convert this electrical signal into an optical (photonic) one, which takes place in the electrical-to-optical converter. This converter is normally a semiconductor laser, which emits monochromatic and coherent light.
- The output from this laser converter is in the form of pulses of light. These photonic pulse signals are then fed into and carried through the fiber-optic cable to the receiving end. For long transmissions, *repeaters* may be required; these are devices that amplify and regenerate the signal.
- Finally, at the receiving end the photonic signal is reconverted to an electronic one and then decoded (undigitized).
- The heart of this communication system is the optical fiber. It must guide these light pulses over long distances without significant signal power loss (i.e., attenuation) and pulse distortion.