

나노소재합성개론

2025-2

2. Structure and Bonding

2. Structure and Bonding

2.1 Introduction to Structure and Bonding

Matter (materials) is composed of atoms and molecules

Gases, liquids and solids are different states of matter (there can be some other states also under some extreme conditions of matter)

→ Phase diagram

: depending upon their stability at different pressure, temperature or variation of both

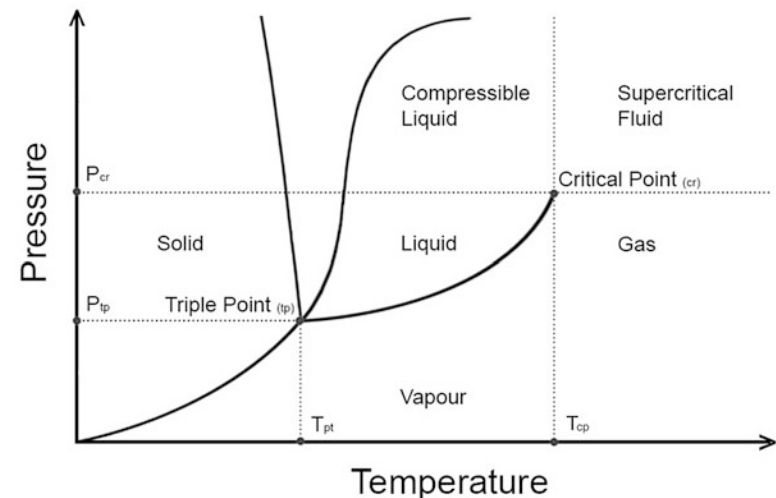
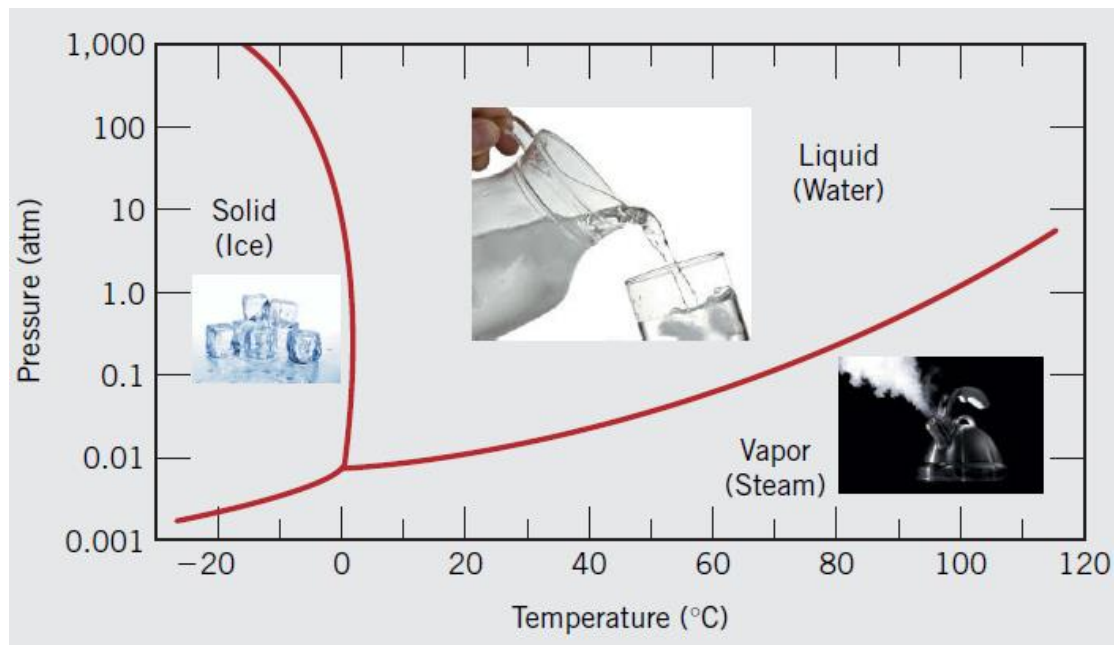


Fig. 2.1 Phase diagram showing different states of matters, which depend upon pressure and temperature

2. Structure and Bonding

2.1 Introduction to Structure and Bonding

Water molecule (H_2O) can be in gaseous state (vapour), liquid state (water) or solid state (ice) depending on the temperature and pressure



Three phases for the H_2O system are shown in this photograph:
Ice (the iceberg)
water (the ocean or sea),
vapor (the clouds).
These three phases are not in equilibrium with one another.

2. Structure and Bonding

2.1 Introduction to Structure and Bonding

Density and atomic distance

Density of gas is usually very low 10^{19} atoms/cc,
whereas that of solids and liquids is high viz 10^{23} atoms/cc

Between atoms (or molecules)

In gases; 3 to 4 nm

In solids and liquids; 0.2–0.4 nm



an order of magnitude

the density and distances between the atoms or molecules for both liquids and solids are comparable

- **A liquid** does not have a particular shape and takes the shape of its container. Atoms or molecules in a liquid, as in a gas, are under a state of continuous, random motion known as Brownian motion
- **Solid:** There the atoms and molecules also are in a state of motion, but the motion is about their fixed positions. Atoms and molecules vibrate about their fixed positions with some characteristic frequencies.

2. Structure and Bonding

2.1 Introduction to Structure and Bonding

Crystalline structure on materials properties

Example: Solid Al_2O_3

appear as a transparent, opaque or translucent even without change of its chemical formula or presence of impurities

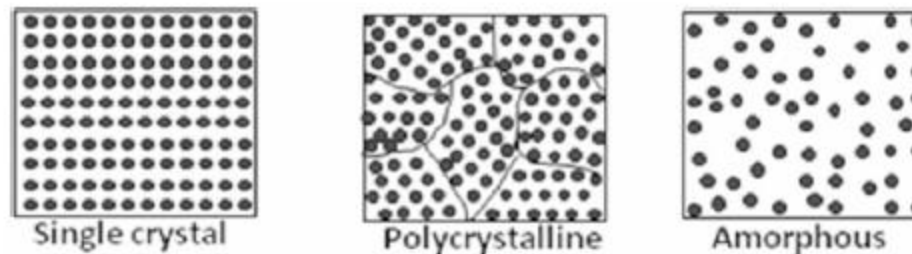


Fig. 2.2 Different types of solids

‘Single crystal’ there is almost infinitely long arrangement of atoms or molecules with certain symmetry characteristics of the material

‘Polycrystalline’ solid, there are some ‘grain boundaries’. Size of the grain can depend upon the processing and typically can be few μm . Each grain itself is a ‘single crystal’ but the orientations of these different crystals are different or random. Each grain also has a kind of ‘grain wall’ in which atoms may be more or less randomly distributed

2. Structure and Bonding

2.1 Introduction to Structure and Bonding

Crystalline structure on materials properties



Fig. 2.2 Different types of solids

The thickness of such walls is often very crucial in determining the various properties of materials such as mechanical, optical or electrical. At the grain boundary the long range periodicity of the solid is broken.

‘Amorphous’ solid: each grain in the material becomes too small, comparable to the distance between the atoms or molecules

→ the grain boundaries disappear

the arrangement between nearest or even next nearest atoms may look similar for most of the atoms, they lack long-range order as in a poly or single crystal.

2. Structure and Bonding

2.1 Introduction to Structure and Bonding

Crystalline structure on materials properties

with same type of atoms or molecules even different single crystals can be formed with altogether different properties

Diamond vs. Graphite

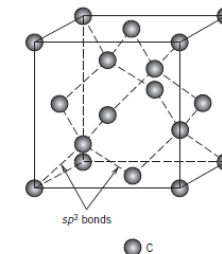


Figure 12.16 A unit cell for the diamond cubic crystal structure.

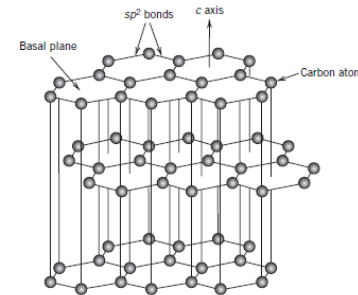


Figure 12.17 The structure of graphite.

Properties	Graphite	Diamond
Crystal system and form	Hexagonal; substantial lamellar veins and earthy masses	Isometric; cubes and octahedrons
Specific Gravity	2.2	3.5
Density (g/cm ³)	2.25	3.52
Color/Appearance	Grey black, Black silver, opaque shiny	Variable-pale yellows, browns, grays, and also white, blue, black, reddish, greenish, colorless and sparkling
Hardness (Mohs)/Field indicator	1–2; Soft, slippery, soapy, greasy luster, density and streak	10; Very Hard (a hardest substance known)
Luster	Metallic to dull	Adamantine to waxy
Cleavage	Perfect in 1 direction	Perfect in 4 directions forming octahedrons
Transparency	Crystals are opaque	Crystals are transparent to translucent in rough crystals
Fracture	Flaky	Conchoidal
Electrical and Heat conductivity (E&H)	Good conductor of both E&H	Poor electrical conductor; good thermal conductor
Burning in the air	At about 700 °C	Most readily at about 900 °C

2. Structure and Bonding

2.2 Arrangement of Atoms

Crystalline

A **crystalline** material is one in which the atoms are situated in a repeating or periodic array over large atomic distances

- long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest neighbor atoms.

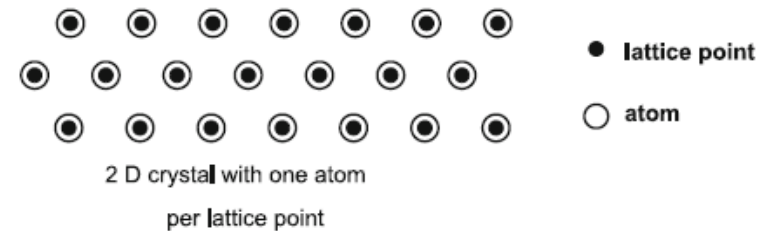


Fig. 2.4 A lattice + atom makes a solid or crystal

Lattice

Arrangement of points repeated in one, two or three directions making it a one dimensional, two dimensional or three dimensional lattice.



Fig. 2.3 A periodic arrangement of points in two dimensions makes a lattice

2. Structure and Bonding

2.2 Arrangement of Atoms

Unit Cell

The structure into small repeat entities called **unit cells**
the unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within

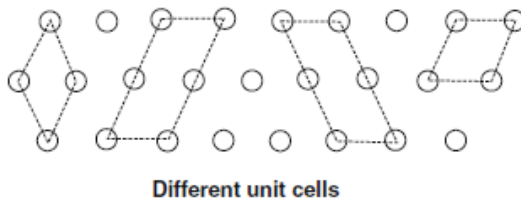
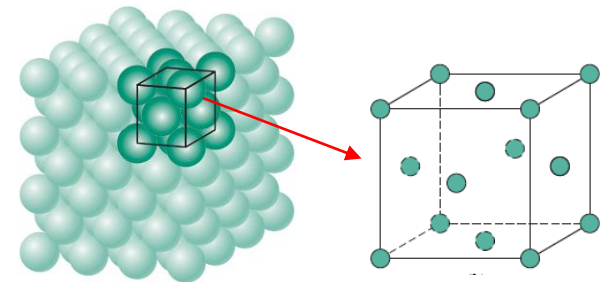


Fig. 2.5 Different unit cells in the same arrangement of atoms



Primitive Cell

Unit cell with smallest volume is known as '*primitive cell*'
unit cell vectors which define the boundaries or edges of unit cell. It can be seen that in direction of **a**, if we translate the cell by '**a**' unit, the cell is repeated. Same is true for **b**. Thus **a** and **b** are translation vectors.

Translation vectors of primitive or smallest unit cell are known as 'primitive vectors'

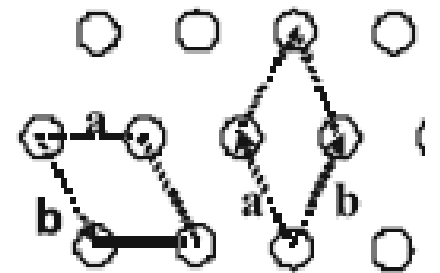


Fig. 2.6 primitive cells

2. Structure and Bonding

2.2 Arrangement of Atoms

Symmetry

Symmetry transformation about **a point** is the one which leaves the system invariant or without any change even after some operation

Rotational Symmetry

Circle is a perfectly symmetric object which can be rotated about an axis through its centre by any angle θ without it appearing as if it was rotated.

Thus by rotating through any angle we make an invariant transformation for a circle or a sphere.

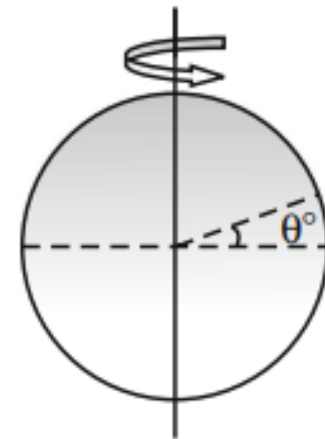


Fig. 2.7 A circle can be rotated around an axis passing through its centre through any angle and would appear as if unmoved

2. Structure and Bonding

2.2 Arrangement of Atoms

Rotational Symmetry

Square: a lower symmetry object

rotate it by 90° about an axis passing through **its midpoint** which appears as if it has not been rotated

This can be done only four times successively in any direction (clockwise or anticlockwise)

➡ a fourfold symmetry

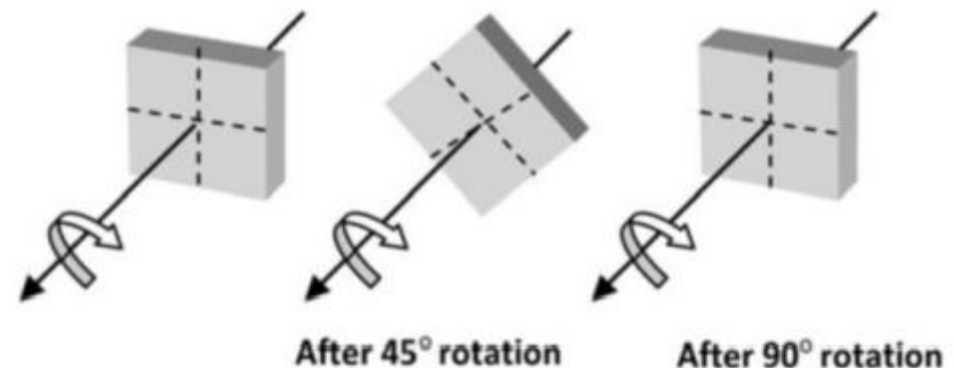


Fig. 2.8 Point symmetry of a square

2. Structure and Bonding

2.2 Arrangement of Atoms

Rotational Symmetry

Rectangle: a lower symmetry object

rotate it through 90° , you see the difference as shown in Fig. 2.9, but if you rotate it through 180° it looks similar to the original state.

This you can do twice.

➡ Twofold symmetry

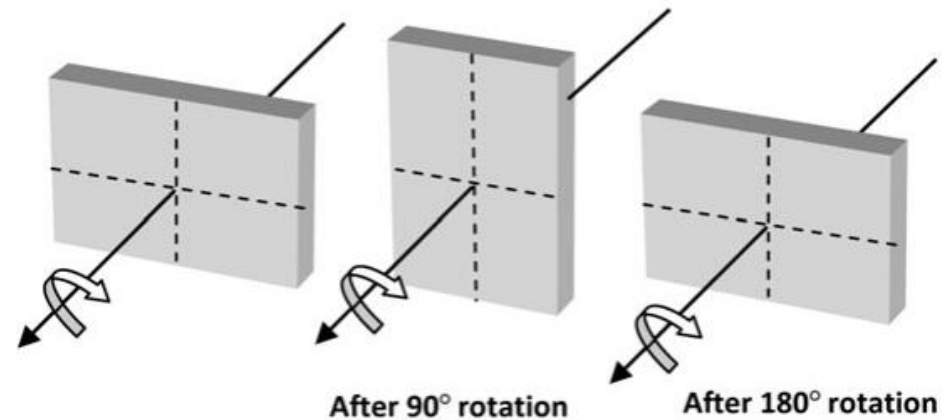


Fig. 2.9 Point symmetry of a rectangle

2. Structure and Bonding

2.3 Two Dimensional Crystal Structures

Only five types of units or Bravais lattices

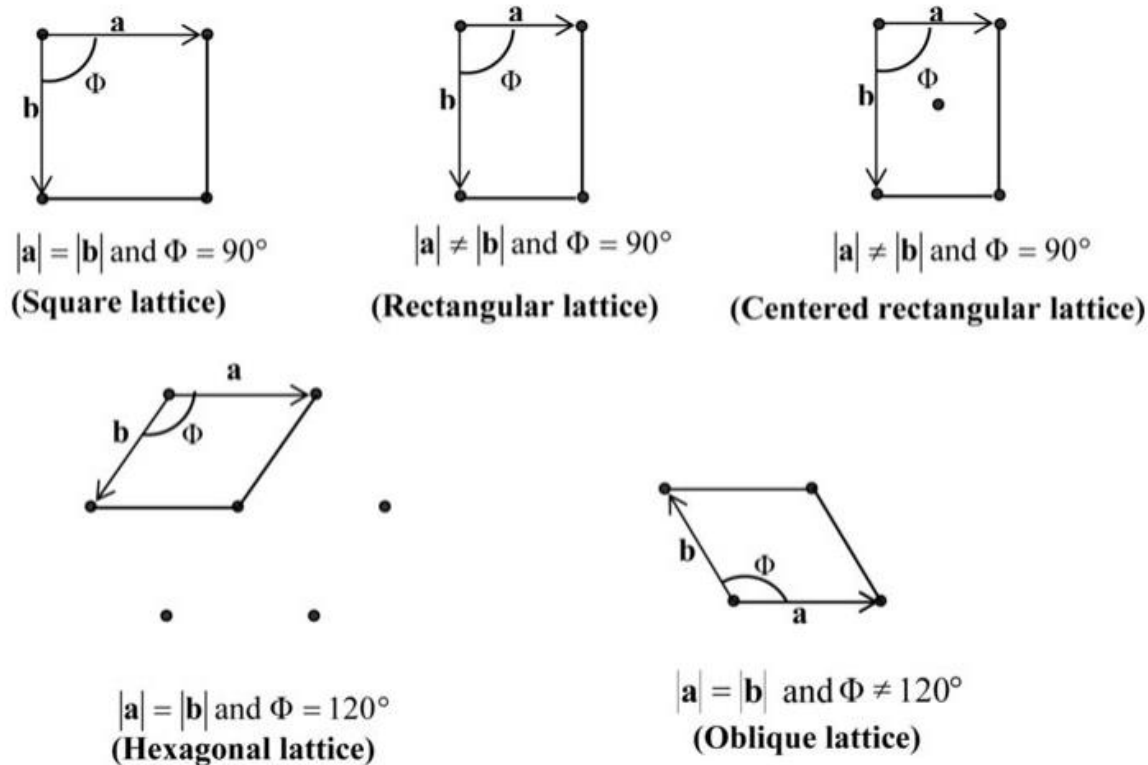


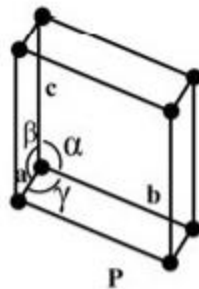
Fig. 2.10 Five two-dimensional Bravais lattices

2. Structure and Bonding

2.4 Three Dimensional Crystal Structures

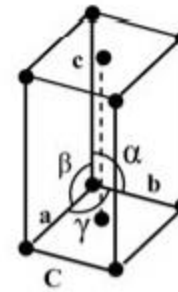
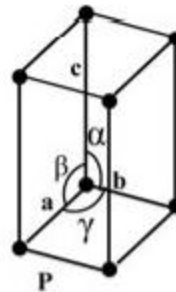
Three dimensional solids are divided into seven crystal systems and fourteen Bravais lattices

1. Triclinic



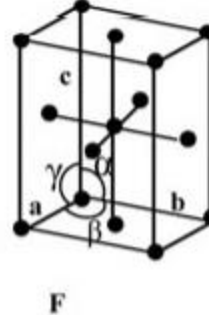
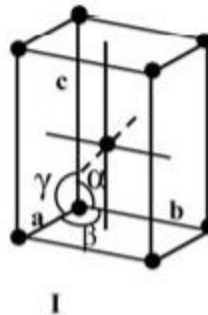
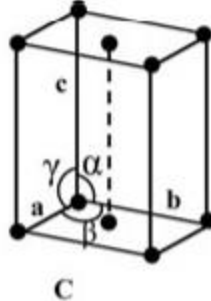
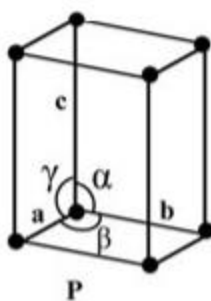
$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma$$

2. Monoclinic



$$a \neq b \neq c$$
$$\alpha = \beta = 90^\circ \neq \gamma$$

3. Orthorhombic



$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$

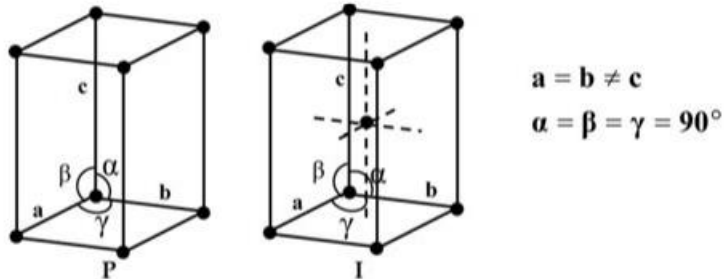
Fig. 2.11 Fourteen Bravais lattices in three dimensions (**P** Primitive cell, **I** Body centred cell, **F** Face centred cell, **C** Base centred cell)

2. Structure and Bonding

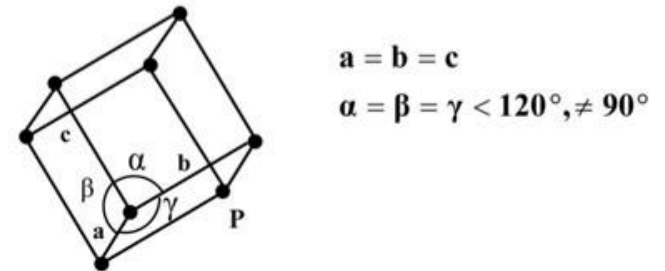
2.4 Three Dimensional Crystal Structures

Three dimensional solids are divided into seven crystal systems and fourteen Bravais lattices

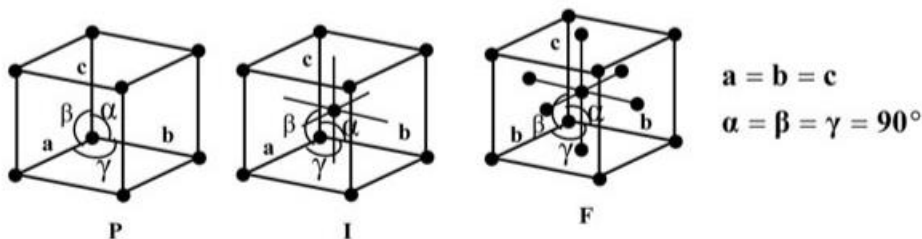
4. Tetragonal



6. Triagonal



5. Cubic



7. Hexagonal

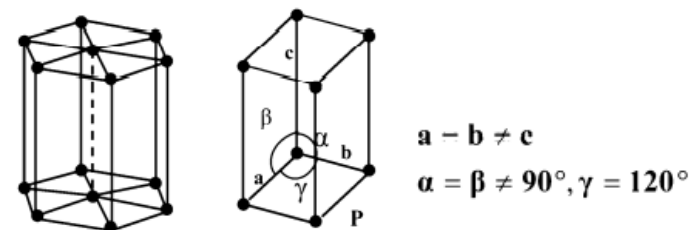


Fig. 2.11 Fourteen Bravais lattices in three dimensions (**P** Primitive cell, **I** Body centred cell, **F** Face centred cell, **C** Base centred cell)

2. Structure and Bonding

2.5 Some Examples of Three Dimensional Crystals

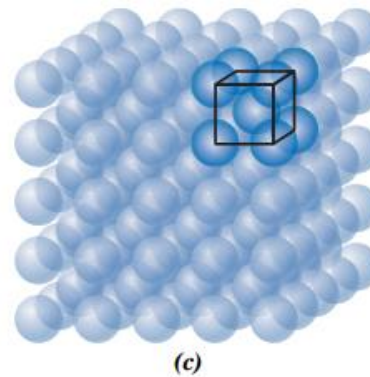
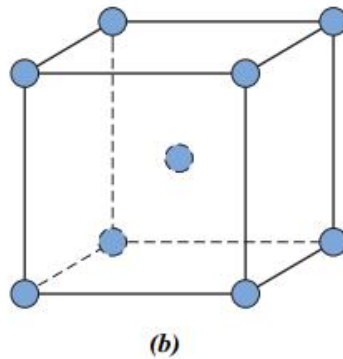
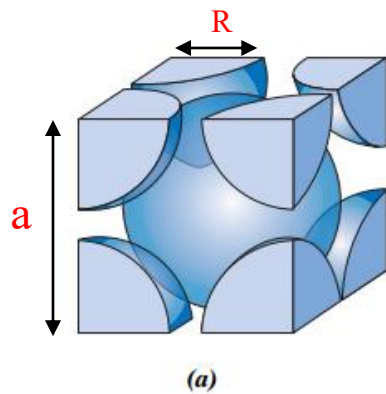
2.5.1 Body Centred Cube (bcc)

The Body-Centered Cubic Crystal Structure

a cubic unit cell with atoms located at all eight corners and a single atom at the cube center.

Center and corner atoms touch one another along cube diagonals, and unit cell length **a** and atomic radius **R** are related through

$$a = \frac{4R}{\sqrt{3}}$$



The number of atoms per BCC unit cell

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$
$$= 1 + 0 + \frac{8}{8} = 2$$

N_i = the number of interior atoms

N_f = the number of face atoms

N_c = the number of corner atoms

Fig. For the body-centered cubic crystal structure, (a) a hard-sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atom

2. Structure and Bonding

2.5 Some Examples of Three Dimensional Crystals

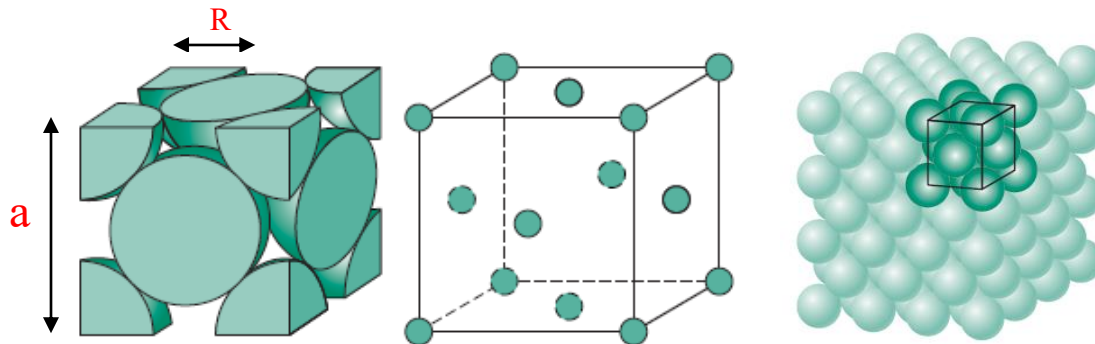
2.5.2 Face Centred Cube (fcc)

The Face-Centered Cubic Crystal Structure

a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces.

spheres or ion cores touch one another across a face diagonal; the cube edge length **a** and the atomic radius **R** are related through

$$a = 2R\sqrt{2}$$



The number of atoms per FCC unit cell

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

$$N = 0 + \frac{6}{2} + \frac{8}{8} = 4$$

Fig. For the face-centered cubic crystal structure, (a) a hard-sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atom

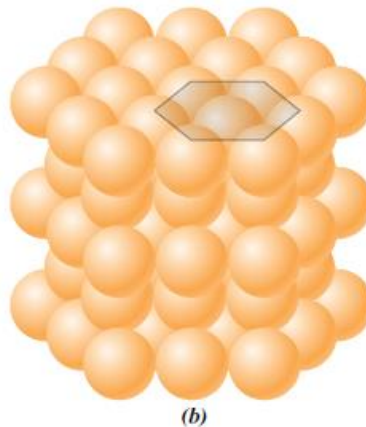
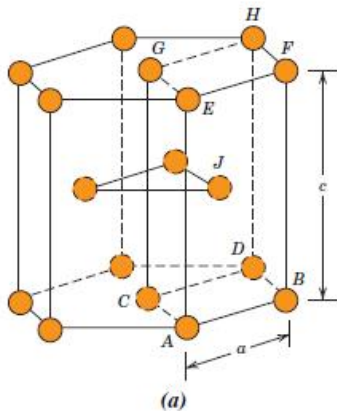
2. Structure and Bonding

2.5 Some Examples of Three Dimensional Crystals

2.5.3 hexagonal close-packed (HCP)

The Hexagonal Close-Packed Crystal Structure

The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes.



The number of atoms per unit cell for the HCP crystal structure

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{6}$$

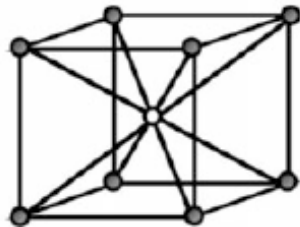
$$N = 3 + \frac{2}{2} + \frac{12}{6} = 6$$

Fig. For the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell (a and c represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms.

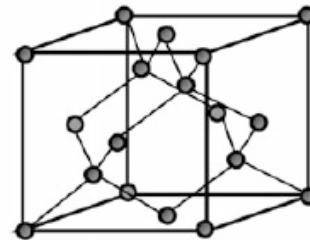
2. Structure and Bonding

2.5 Some Examples of Three Dimensional Crystals

CsCl: Body Centred Cubic (bcc), Cs^+ ion at (000), two atoms/cell, Cl^- ion at $(1/2, 1/2, 1/2)$ co-ordinates. It is a conventional unit cell.

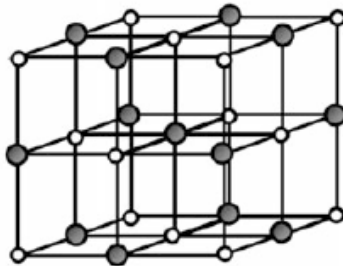


Diamond: Cubic, interpenetrating cubes, eight atoms/cell

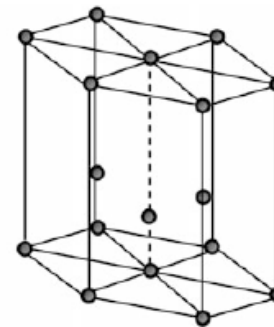


● Carbon

NaCl: Face Centred Cubic (fcc), alternate arrangement of Na^+ and Cl^- ions in x , y and z directions. It is a conventional unit cell.



Graphite: Hexagonal hcp ABAB... $c/a = 1.633$



● Carbon

2. Structure and Bonding

2.6 Point Coordinates

three point coordinate indices: q , r , and s .

These indices are fractional multiples of a , b , and c unit cell edge lengths—that is, q is some fractional length of a along the x axis, r is some fractional length of b along the y axis, and similarly for s ; or

qa = lattice position referenced to the x axis

rb = lattice position referenced to the y axis

sc = lattice position referenced to the z axis

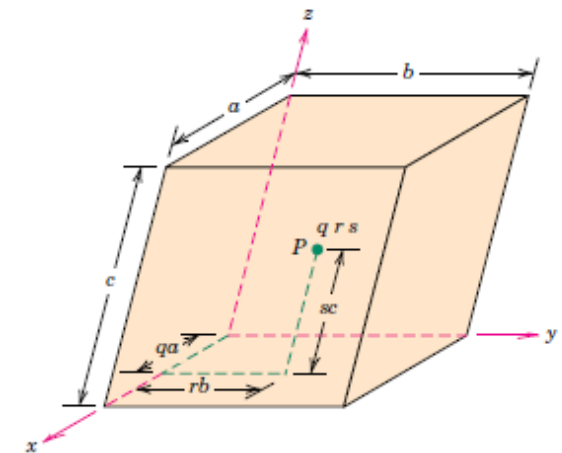


Fig. The manner in which the q , r , and s coordinates at point P within the unit cell are determined. The q coordinate (which is a fraction) corresponds to the distance qa along the x axis, where a is the unit cell edge length. The respective r and s coordinates for the y and z axes are determined similarly.

the x - y - z coordinate system with its origin located at a unit cell corner, and the lattice site located at point P . Note how the location of P is related to the products of its q , r , and s coordinate indices and the unit cell edge lengths

2. Structure and Bonding

2.6 Point Coordinates

Specify coordinate indices for all numbered points of the unit cell in the illustration

Point 1 is located at the origin of the coordinate system, and, therefore, its lattice position indices referenced to the x , y , and z axes are **0a**, **0b**, and **0c**

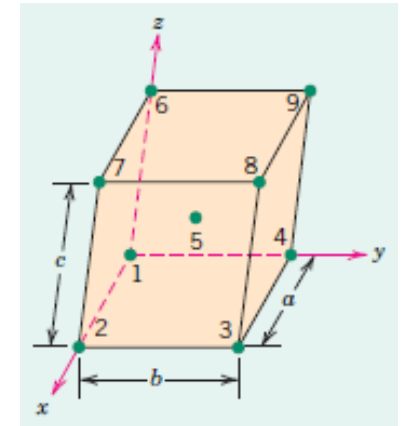
lattice position referenced to the x axis = $0a = qa$
lattice position referenced to the y axis = $0b = rb$
lattice position referenced to the z axis = $0c = sc$

$$q = \frac{0a}{a} = 0 \quad r = \frac{0b}{b} = 0 \quad s = \frac{0c}{c} = 0 \quad \Rightarrow \quad \text{this is the } \mathbf{0\ 0\ 0} \text{ point}$$

Point 2 is located at the origin of the coordinate system, and, therefore, its lattice position indices referenced to the x , y , and z axes are **a**, **0b**, and **0c**

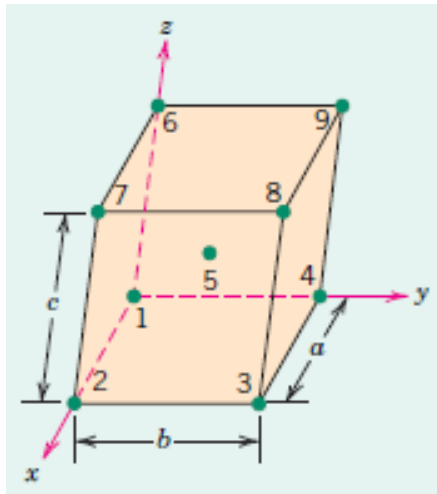
lattice position referenced to the x axis = $a = qa$
lattice position referenced to the y axis = $0b = rb$
lattice position referenced to the z axis = $0c = sc$

$$q = \frac{a}{a} = 1 \quad r = \frac{0b}{b} = 0 \quad s = \frac{0c}{c} = 0 \quad \Rightarrow \quad \text{this is the } \mathbf{1\ 0\ 0} \text{ point}$$



2. Structure and Bonding

2.6 Point Coordinates



<i>Point Number</i>	<i>q</i>	<i>r</i>	<i>s</i>
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1

2. Structure and Bonding

2.7 Crystallographic Directions

A *crystallographic direction* is defined as a line directed between two points, or a vector.

1. A right-handed x - y - z coordinate system is first constructed. As a matter of convenience, its origin may be located at a unit cell corner.
2. The coordinates of two points that lie on the direction vector (referenced to the coordinate system) are determined—for example, for the vector tail, point 1: x_1 , y_1 , and z_1 ; whereas for the vector head, point 2: x_2 , y_2 , and z_2 .
3. Tail point coordinates are subtracted from head point components—that is, $x_2 - x_1$, $y_2 - y_1$, and $z_2 - z_1$.
4. These coordinate differences are then normalized in terms of (i.e., divided by) their respective a , b , and c lattice parameters—that is,
$$\frac{x_2 - x_1}{a} \quad \frac{y_2 - y_1}{b} \quad \frac{z_2 - z_1}{c}$$
5. If necessary, these three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
6. The three resulting indices, not separated by commas, are enclosed in square brackets, thus: $[uvw]$. The u , v , and w integers correspond to the normalized coordinate differences referenced to the x , y , and z axes, respectively.

2. Structure and Bonding

2.7 Crystallographic Directions

A *crystallographic direction* is defined as a line directed between two points, or a vector.

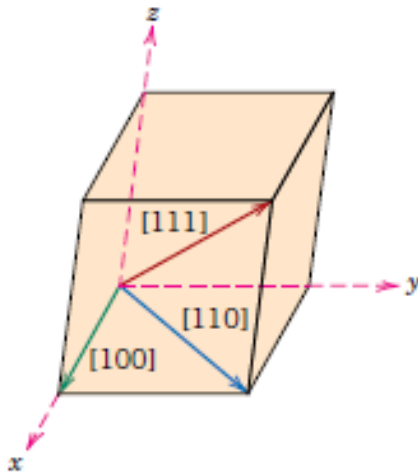


Fig. The [100], [110], and [111] directions within a unit cell.

For each of the three axes, there are both **positive** and **negative** coordinates.

Thus, negative indices are also possible, which are represented by a bar over the appropriate index.

For example, the $[1\bar{1}1]$ direction has a component in the y direction.

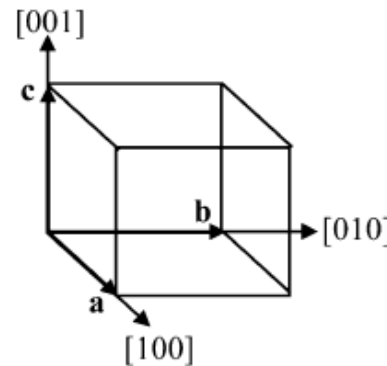


Fig. 2.15 Crystallographic directions

Homework #1: How to define Directions in Hexagonal Crystals

Please make sure uploading the homework file on LMS system at “Report (레포트)” by 7th October)

2. Structure and Bonding

2.8 Crystallographic Planes

Miller indices

crystallographic planes are specified by three **Miller indices** as (hkl)

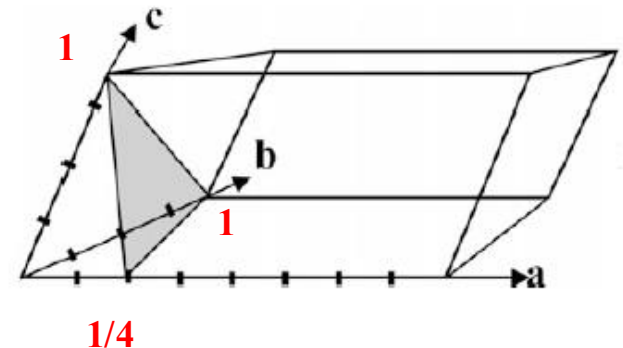
Consider the intercepts on **a**, **b**, **c** (the primitive axes or non-primitive axes of unit cell).

For example as in Fig. 2.13, let the axial lengths be 0.8, 0.4 and 0.4 nm along **a**, **b** and **c** respectively.

Let the intercepts be 0.2, 0.4 and 0.4 nm respectively.

Fractional intercepts would be $\frac{1}{4}$, 1 and 1. Miller indices of the plane would be 4, 1 and 1 or conventionally written as (411). Miller indices are written in the round brackets.

Fig. 2.13 Plane having Miller indices (411)



2. Structure and Bonding

2.8 Crystallographic Planes

Miller indices

The procedure used to determine the h , k , and l index numbers is as follows:

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.
2. At this point, the crystallographic plane either intersects or parallels each of the three axes. The coordinate for the intersection of the crystallographic plane with each of the axes is determined (referenced to the origin of the coordinate system). These intercepts for the x , y , and z axes will be designed by A , B , and C , respectively.
3. The reciprocals(역수) of these numbers are taken. A plane that parallels an axis is considered to have an infinite intercept and therefore a zero index.
4. The reciprocals of the intercepts are then normalized in terms of (i.e., multiplied by) their respective a , b , and c lattice parameters. That is, $\frac{a}{A} \quad \frac{b}{B} \quad \frac{c}{C}$
5. If necessary, these three numbers are changed to the set of smallest integers by multiplication or by division by a common factor.
6. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (hkl) . The h , k , and l integers correspond to the normalized intercept reciprocals referenced to the x , y , and z axes, respectively.

$$h = \frac{na}{A}$$

$$k = \frac{nb}{B}$$

$$l = \frac{nc}{C}$$

n is the factor that may be required to reduce h , k , and l to integers

2. Structure and Bonding

2.8 Crystallographic Planes

Miller indices

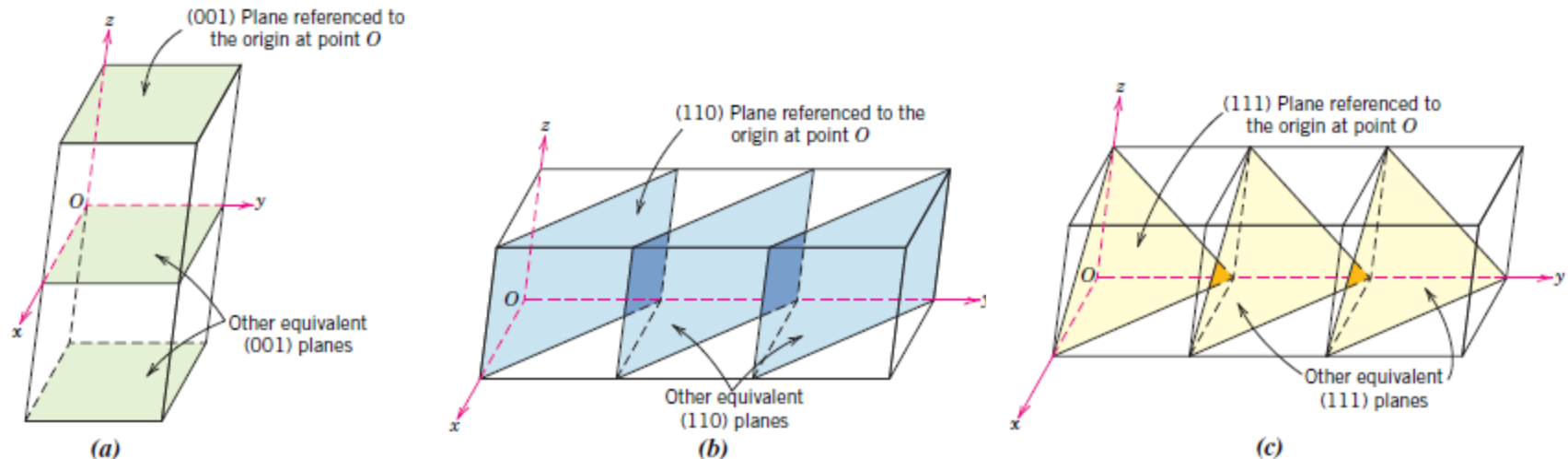


Fig. Representations of a series each of the (a) (001) , (b) (110) , and (c) (111) crystallographic planes.

*One interesting and unique characteristic of cubic crystals is that planes and directions having the same indices are perpendicular to one another

2. Structure and Bonding

2.9 Reciprocal Lattice

Using X-rays, electrons or neutrons having wavelength ~ 0.1 to 0.2 nm, length comparable to distance between atoms or planes in a solid, it is possible to obtain a diffraction pattern



Analysis of diffraction patterns leads to the determination of crystal structure

Diffraction pattern is obtained in the *reciprocal space*.

Points in the reciprocal space are related to real space.

Each point in the reciprocal space represents a set of planes in real lattice.

It is therefore often convenient to use the concept of reciprocal lattice to deal with the crystals.

Reciprocal Lattice Vectors **A**, **B** and **C** are defined in terms of the vectors **a**, **b** and **c** in real lattice as

$$\mathbf{A} = \frac{2\pi (\mathbf{b} \times \mathbf{c})}{(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})}$$

$$\mathbf{B} = \frac{2\pi (\mathbf{c} \times \mathbf{a})}{(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})}$$

$$\mathbf{C} = \frac{2\pi (\mathbf{a} \times \mathbf{b})}{(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})}$$

In the resulting network of reciprocal points, position vector **G** can be written as

$$\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$$

where h, k, l are Miller indices of the planes

2. Structure and Bonding

2.10 Quasi Crystals

As far as point symmetry is concerned, $360/5D72_1$ is a possible rotation. However if one tries to translate a pentagon in two dimensional space, it cannot fill the space completely as can be seen from the Fig. 2.16.

➡ Therefore fivefold rotation does not satisfy the criterion viz. rotation plus translation symmetry to make a crystal

However there are now evidences after the experimental work by Dan Shechtman in 1982 that in some crystalline matter fivefold symmetry does exist. Indeed in some alloys like Al-Mn, Al-Pd-Mn and Al-Cu-Co, fivefold, eightfold or tenfold symmetries have been observed.

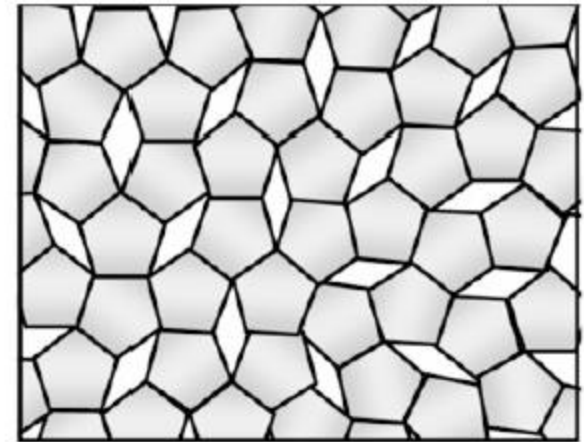


Fig. 2.16 Five-fold pattern

The credit for it goes to astrophysicist Penrose and is known as '*penrose tiling*'

What Penrose suggested is that instead of using a single unit cell for the translation, use two-unit cells like a thin and a fat rhombus or a kite and a dart as shown in Fig. 2.17.

2. Structure and Bonding

2.10 Quasi Crystals

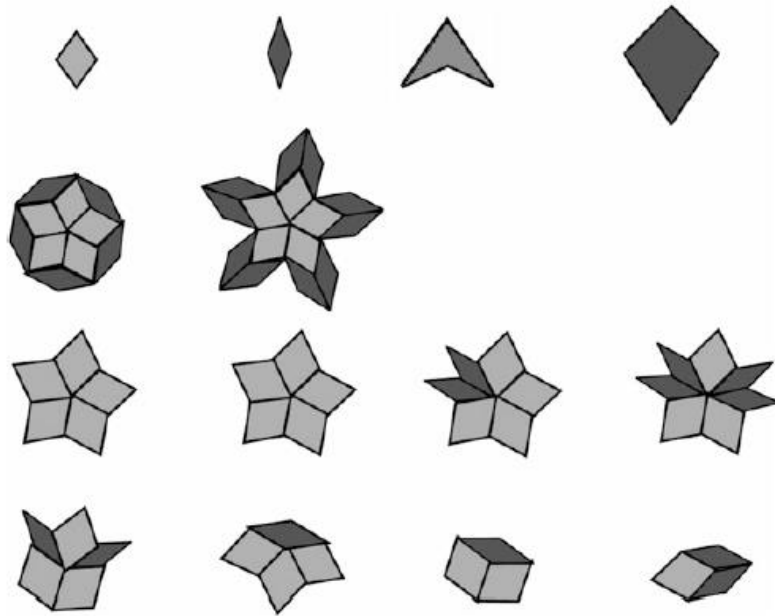


Fig. 2.17 Penrose tiles (*first line*) and various motifs generated using them

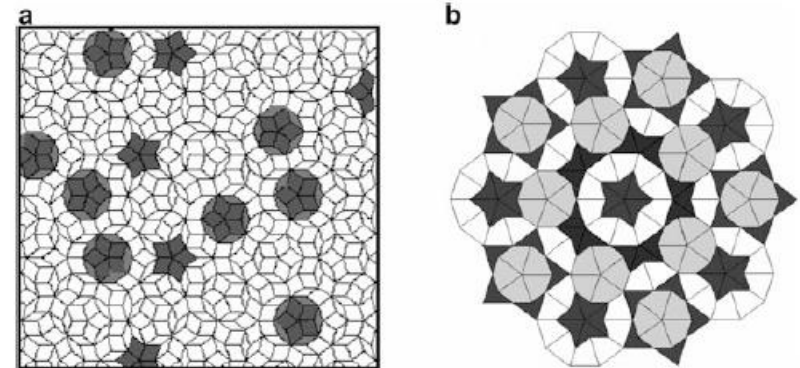


Fig. 2.18 Penrose tiling: (a) using fat and thin rhombus and (b) using kite and dart

Such aperiodic materials which exhibit X-ray diffraction patterns are known as *quasi crystals*.

Properties of such alloys are quite interesting. For example they are poor heat and electricity conductors. They also do not get rusted easily

2. Structure and Bonding

2.11 Liquid Crystals

Similar to quasicrystals, **liquid crystal** is another class of unconventional crystals.

Friedrich Reinitzer noticed that the cholesteryl benzoate, when heated, became a cloudy liquid at 145 °C and clear liquid at 179 °C.

Otto Lehman looked into more details and not only confirmed Reinitzer's results but also gave the name liquid crystals in 1889 to it and similarly behaving materials. He found that some molecules before melting pass through a (liquid) phase in which they flow like liquids.

Many molecules have rod-like shapes and are the candidates of different types of liquid crystals like nematic, cholesteric, smectic and discotic

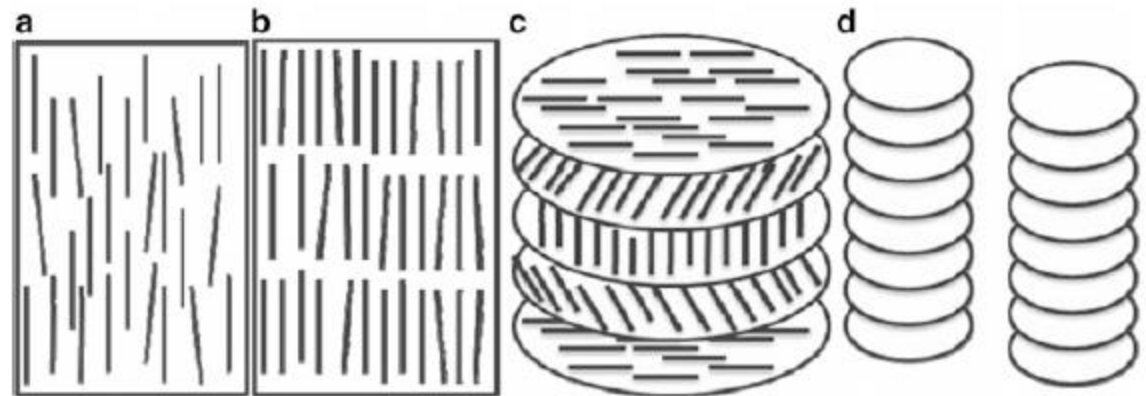


Fig. 2.19 (a) Nematic (b) Smectic (c) Cholesteric (d) Discotic liquid crystals

2. Structure and Bonding

2.11 Liquid Crystals

Nematic crystals the molecules are almost parallel to each other in the vertical direction but their positions are random

➡ orientation order like in a crystal but positional disorder like in a liquid

Smectic crystals are characterized by slabs of oriented molecules which are disordered with respect to each other

Cholesteric (also called chiral nematic) the molecules are oriented in the same direction as in a nematic crystal in a single plane but there is rotation of molecules from plane to plane like twisting

Discotic liquid crystals: disc-like molecules which arrange themselves randomly in a plane but form vertical stacks to form

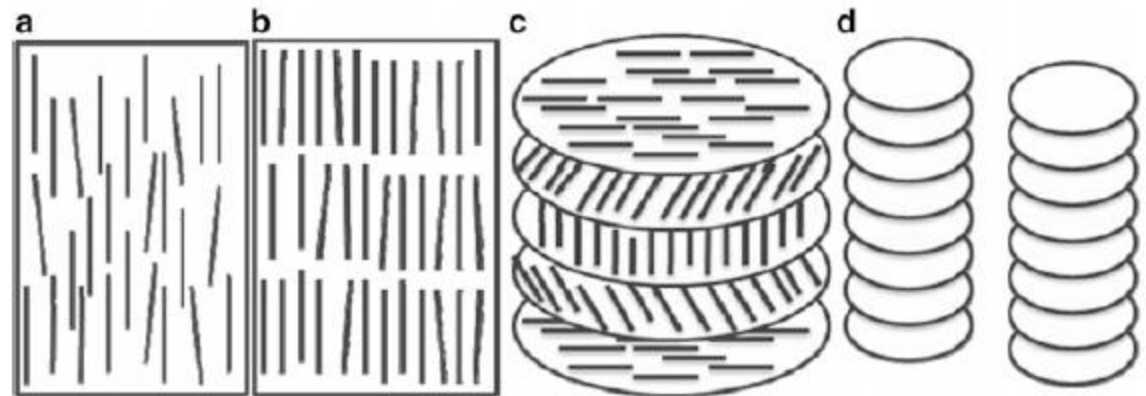


Fig. 2.19 (a) Nematic (b) Smectic (c) Cholesteric (d) Discotic liquid crystals

2. Structure and Bonding

2.12 Bonding in Solids

Bonding forces and Energies

the principles of atomic bonding are best illustrated by considering how two isolated atoms interact as they are brought close together from an infinite separation.

At large distances:

interaction negligible

At small separation distances:

attractive (F_A) and repulsive (F_R), and the magnitude of each depends on the separation or interatomic distance (r)

The origin of an **attractive force** (F_A) depends on the particular type of bonding that exists between the two atoms, as discussed shortly.

Repulsive forces (F_R) arise from interactions between the negatively charged electron clouds for the two atoms and are important only at small values of r as the outer electron shells of the two atoms begin to overlap

➡ The net force (F_N) between the two atoms

$$F_N = F_A + F_R$$

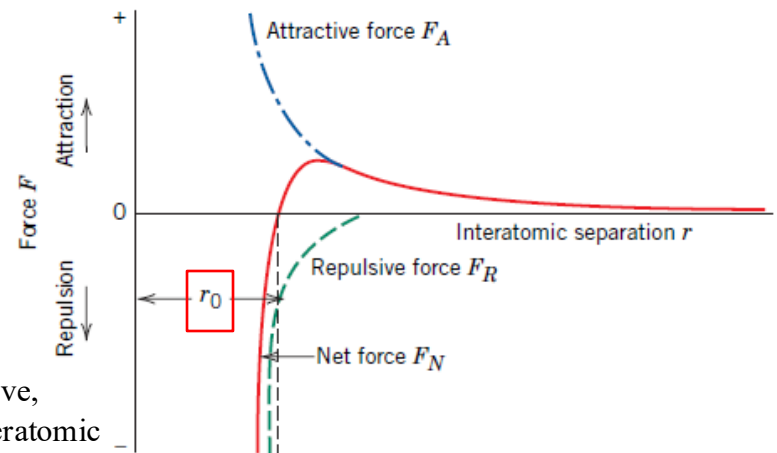


Fig. The dependence of repulsive, attractive, and net forces on interatomic separation for two isolated atoms.

2. Structure and Bonding

2.12 Bonding in Solids

Bonding forces and Energies

At equilibrium state

F_A and F_R are equal in magnitude but opposite in sign $F_A + F_R = 0$

The centers of the two atoms remain separated by the equilibrium spacing r_0 ,

The potential energies between two atoms instead of forces

$$\begin{aligned} E &= \int F dr \\ E_N &= \int_r^\infty F_N dr \\ &= \int_r^\infty F_A dr + \int_r^\infty F_R dr \\ &= E_A + E_R \end{aligned}$$

E_N , E_A , and E_R are, respectively, the net, attractive, and repulsive energies for two isolated and adjacent atoms

The minimum in the net energy curve corresponds to the equilibrium spacing, r_0 .

➡ **Bonding energy** for these two atoms, E_0 , corresponds to the energy at this minimum point

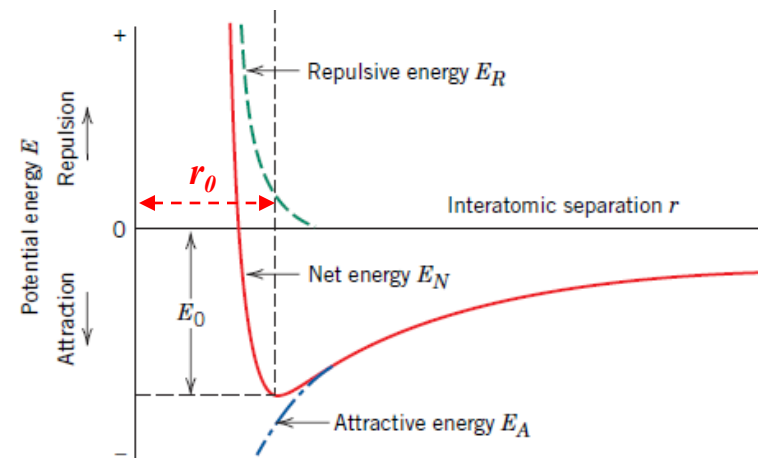


Fig. The dependence of repulsive, attractive, and net potential energies interatomic separation for two isolated atoms..

2. Structure and Bonding

2.12 Bonding in Solids

Bonding forces and Energies

The magnitude of this bonding energy and the shape of the energy–versus–interatomic separation curve vary from material to material, and they both depend on the type of atomic bonding.

➡ Material properties depend on E_0 , the curve shape, and bonding type

For example

materials having **large bonding energies** typically also have high melting temperatures; at room temperature, solid substances are formed for large bonding energies, **whereas for small energies**, the gaseous state is favored; liquids prevail when the energies are of intermediate magnitude

The mechanical stiffness (or modulus of elasticity) of a material is dependent on the shape of its force–versus–interatomic separation curve

Primary bonds

Different types of bonds as: (1) Covalent bond, (2) Ionic bond, (3) Metallic bond,
(4) Mixed bond and (5) Secondary bond

2. Structure and Bonding

2.12 Bonding in Solids

Covalent Bond

Covalent bonding, is found in materials whose atoms have small differences in electronegativity

When two atoms form a molecule by sharing some of their valence electrons, a covalent bond is established.

*The hydrogen atom has a single 1s electron. Each of the atoms can acquire a helium electron configuration (two 1s valence electrons) when they share their single electron

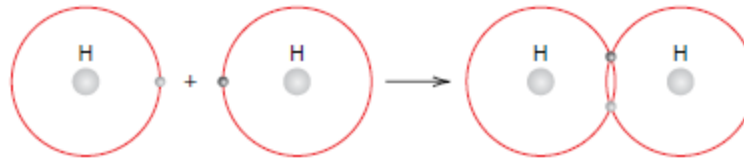


Fig. Schematic representation of covalent bonding in a molecule of hydrogen (H_2).

Many nonmetallic elemental molecules (e.g., Cl_2 , F_2), as well as molecules containing dissimilar atoms, such as CH_4 , H_2O , HNO_3 , and HF , are covalently bonded

Bond	Bond length (nm)	Bond energy (eV)
H-H	0.07414	4.5
O-O	0.12074	1.4
P-P	0.18931	2.2
Cl-Cl	0.19879	2.5
C-C	0.12425	3.6
Si-Si	0.2246	1.8
Ge-Ge	0.2403	1.6

2. Structure and Bonding

2.12 Bonding in Solids

Covalent Bond

Covalent bonding of carbon

Often associated with the covalent bonding of carbon (as well other nonmetallic substances) is the phenomenon of hybridization—the mixing (or combining) of two or more atomic orbitals with the result that more orbital overlap during bonding results. For example, consider the electron configuration of carbon: $1s^2 2s^2 2p^2$.

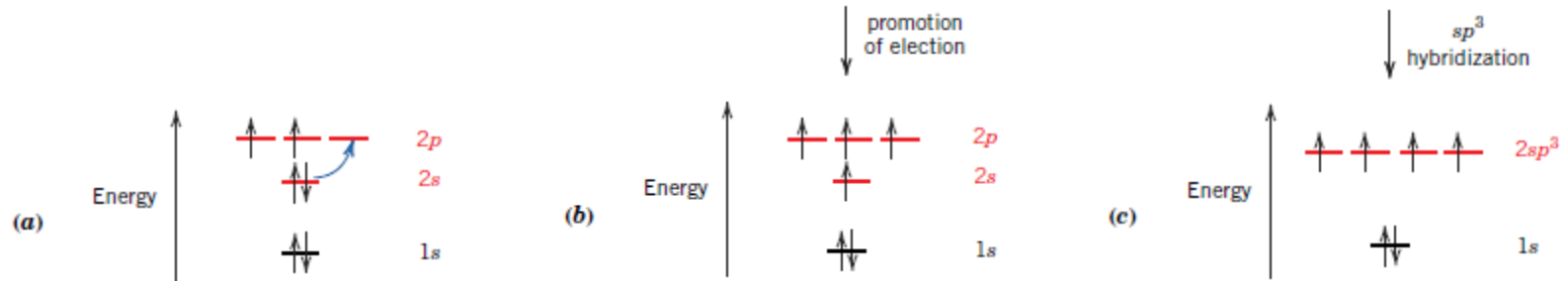
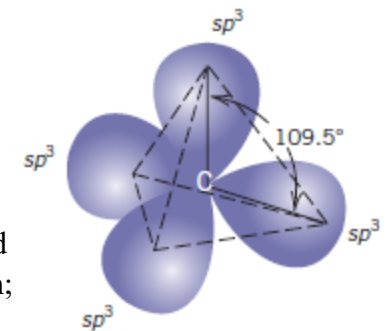


Fig. Schematic diagram that shows the formation of sp^3 hybrid orbitals in carbon. (a) Promotion of a 2s electron to a 2p state; (b) this promoted electron in a 2p state; (c) four $2sp^3$ orbitals that form by mixing the single 2s orbital with the three 2p orbitals.

Fig. Schematic diagram showing four sp^3 hybrid orbitals that point to the corners of a tetrahedron; the angle between orbitals is 109.5°



2. Structure and Bonding

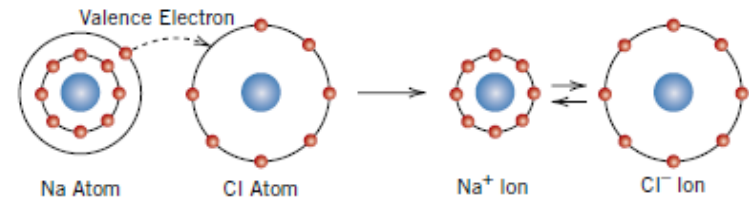
2.12 Bonding in Solids

Ionic Bond

This type of chemical bond is formed when atoms are in the vicinity and electron(s) from one atom is transferred to another

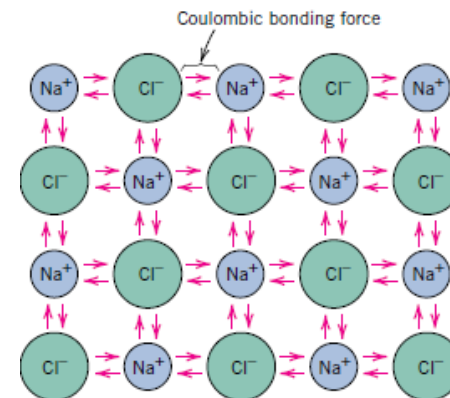
It is always found in compounds composed of both metallic and nonmetallic elements, elements situated at the horizontal extremities of the periodic table.

The one able to transfer the electron or electrons is termed as electropositive and the one which has a tendency to accept electron or electrons is known as electronegative. The ions thus formed are called **cations** and **anions** respectively.



The attractive bonding forces are **coulombic** positive and negative ions, by virtue of their net electrical charge, attract one another

Ionic bonding is termed *nondirectional*—that is, the magnitude of the bond is equal in all directions around an ion. It follows that for ionic materials to be stable, all positive ions must have as nearest neighbors negatively charged ions in a three-dimensional scheme, and vice versa.



2. Structure and Bonding

2.12 Bonding in Solids

Ionic Bond

Bonding energies, which generally range between 600 and 1500 kJ/mol, are relatively large, as reflected in high melting temperatures

Interatomic bonding is typified by ceramic materials, which are characteristically hard and brittle and, furthermore, electrically and thermally insulative

<i>Substance</i>	<i>Bonding Energy (kJ/mol)</i>	<i>Melting Temperature (°C)</i>
Ionic		
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF ₂	1548	1418
Covalent		
Cl ₂	121	−102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830
Metallic		
Hg	62	−39
Al	330	660
Ag	285	962
W	850	3414
van der Waals^a		
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH ₄	18	−182
Cl ₂	31	−101
Hydrogen^a		
HF	29	−83
NH ₃	35	−78
H ₂ O	51	0

2. Structure and Bonding

2.12 Bonding in Solids

Metallic Bond

Atoms like Na, K, Cu, Au, Ag, Fe, Co and Ca in which there are one or more electrons which can be easily removed (valence electrons) from them form metals and the bond that holds the crystal together is known as **metallic bond**

The loose electrons are able to move quite easily from one atom to another and cannot be localized to a particular atom or the other.

Such electrons form what is known as an *electron gas* (of free electrons) and are responsible for the *metallic bond* which is an electrostatic interaction between the positive ions of atoms that have lost the electrons and are unable to move themselves (however, ions vibrate about their mean positions) in the crystal.

The metals are thus ductile. The free electrons in metals respond to electric or magnetic field quite easily making them electrically or thermally good conducting materials.

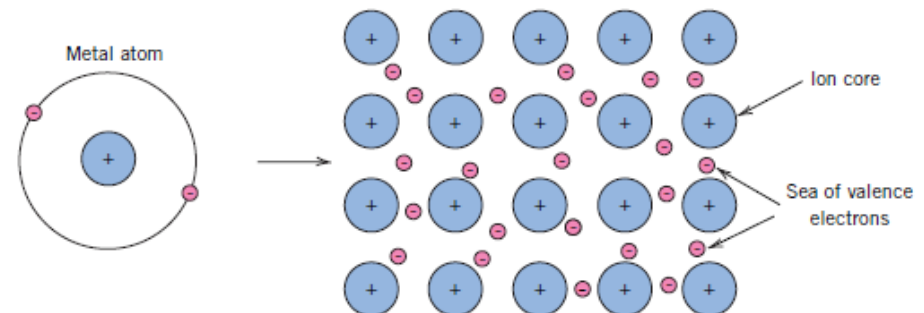


Fig. Schematic illustration of metallic bonding.

2. Structure and Bonding

2.12 Bonding in Solids

Secondary Bonding or Van Der Waals Bonding

Secondary bonds, or **van der Waals** (physical) **bonds**, are weak in comparison to the primary or chemical bonds; bonding energies range between about 4 and 30 kJ/mol.

Secondary bonding forces arise from atomic or molecular **dipoles**

- The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one

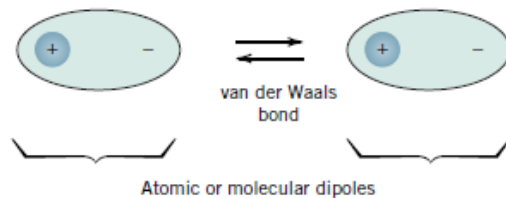


Fig. Schematic illustration of van der Waals bonding between two dipoles.

Permanent dipoles on them which can then interact with each other. Molecules with permanent dipoles on them are known as *polar molecules*. (water molecule H_2O)

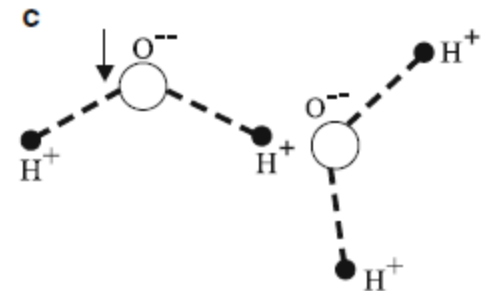


Fig. Dipole-dipole interaction

2. Structure and Bonding

2.13 Electronic structure of Solids

A qualitative picture representing metal, insulator and semiconductors

A **metal** would have its outermost electron filled band (valence band) overlapping with empty band (conduction band).

If the gap is larger, the material is an **insulator**. by introducing small amount of dopant (atoms different compared to those in the host material), some localized energy states can be introduced in the energy gap.



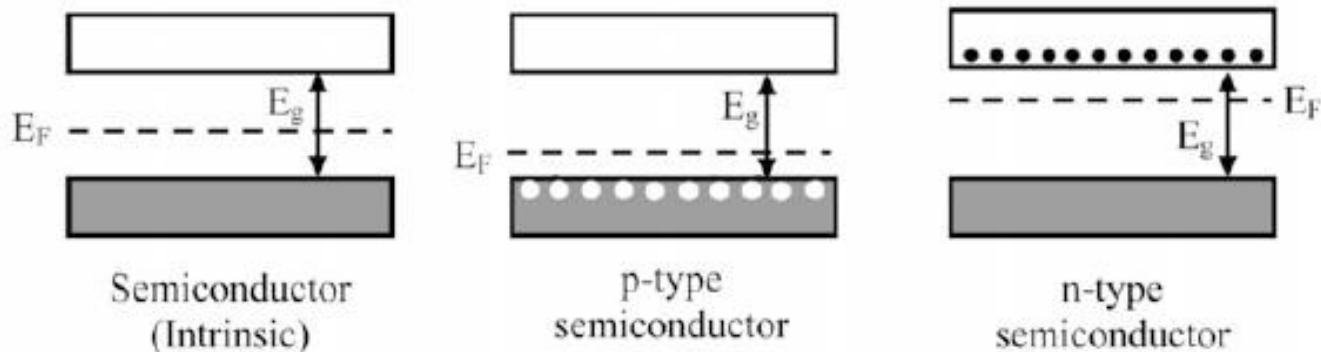
2. Structure and Bonding

2.13 Electronic structure of Solids

A qualitative picture representing metal, insulator and semiconductors

If there is a small gap between valence and conduction band (upto 2–3 eV) then it is a **semiconductor**.

- Depending upon whether such levels are close to valence band or close to conduction band, semiconductor becomes *p* or *n* type semiconductor. The electrical conductivity in many semiconductor devices is controlled by such dopants.



2. Structure and Bonding

2.13 Electronic structure of Solids

Electronic properties of materials

How do we know the electrical properties materials?

Resistance: R

$$R = V / I \quad \text{From Ohm's law}$$

the current I flowing through a bar of homogeneous material with uniform cross section when a voltage V is applied across it, we can find its resistance R

Resistivity: ρ

$$\rho = R \frac{A}{L}$$

is related to the resistance of the bar by a geometric ratio where L and A are the length and cross-sectional area of the sample

2. Structure and Bonding

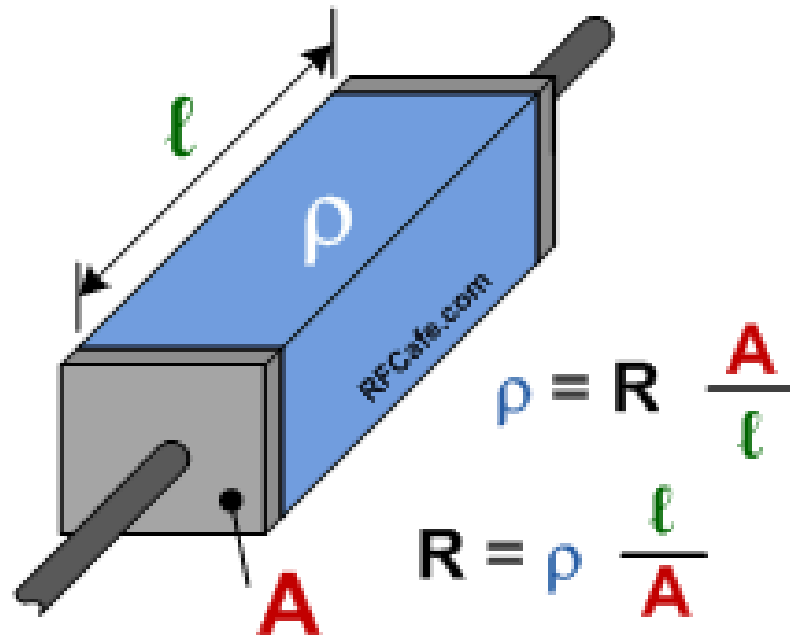
2.13 Electronic structure of Solids

Electronic properties of materials

How do know the electrical properties materials?

Resistance: R

Resistivity: ρ



2. Structure and Bonding

2.13 Electronic structure of Solids

Resistivity

The resistivity of common materials used in solid-state devices cover a wide range
An example is the range of resistivities encountered at room temperature for the materials used to fabricate typical silicon integrated circuits

Resistivities of $10^{-6} \Omega\text{-cm}$ at room temperature

: very low-resistivity materials, connect elements of the integrated circuit;
aluminum and copper

Resistivities of $10^{16} \Omega\text{-cm}$ at room temperature

: the resistivity scale are insulating materials such as silicon dioxide, which
serve to isolate portions of the integrated circuit

Resistivities of $10^{18} \Omega\text{-cm}$ at room temperature

: the resistivity of the plastics often used to encapsulate integrated circuits

2. Structure and Bonding

2.13 Electronic structure of Solids

Classification by resistivity

Materials are generally classified according to their resistivities (ρ)

Conductor

: Resistivities less than $10^{-2} \Omega\text{-cm}$

Insulator

: Resistivities greater than $10^5 \Omega\text{-cm}$

Semiconductor

: Intermediate resistivities region

→ resistivities can be varied by design and precisely controlled

→ can be made to conductor by one of two types of current carriers (electron / hole)

2. Structure and Bonding

2.13 Electronic structure of Solids

Physics of Semiconductor Materials

An understanding of the physics of electrons in solid

: achieved by first considering electrons in an isolated atom

→ resistivities can be varied by design and precisely controlled

Considering allowed energies of electron influenced by an isolated atom

In solid materials (many atoms system)

→ we have to look at the effect of bringing other atoms near the first atom

→ Study the effect of the atomic core in crystal on the behavior of the associated electron

→ Investigate the effect on the electron of applied electric field to the solid materials

 *Energy band model / Crystal-bonding model*

2. Structure and Bonding

2.13 Electronic structure of Solids

Energy band in solids

There are discrete energy levels in the case of an isolated atom

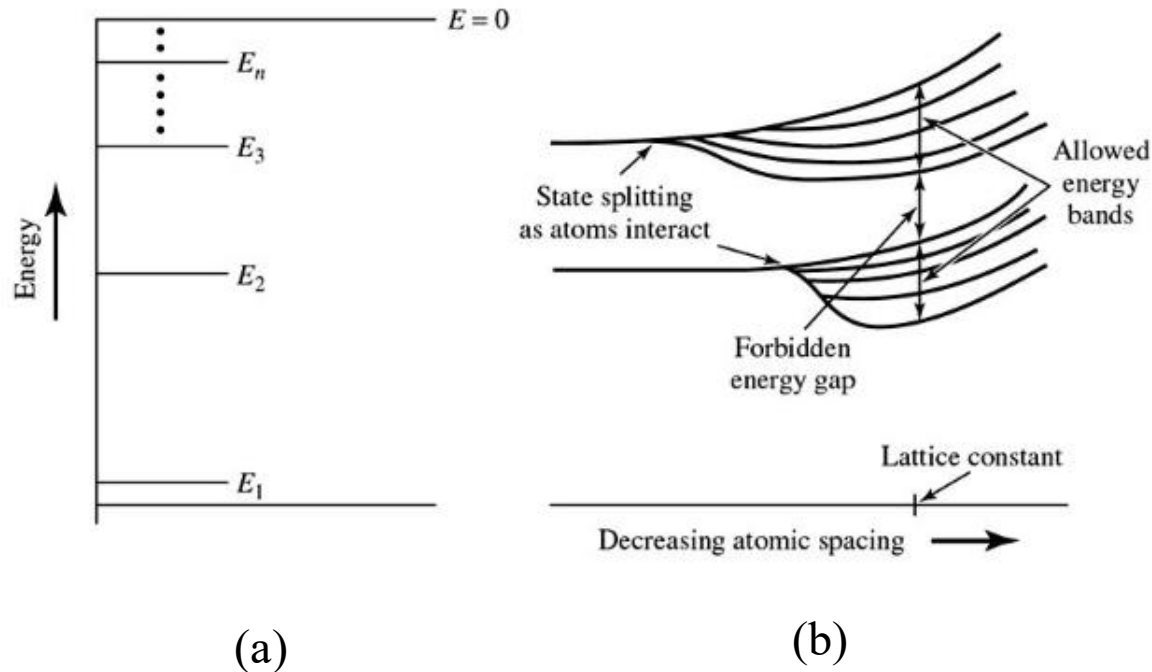


Figure 1.1 (a) Allowed energy levels of an electron acted on by the Coulomb potential of an atomic nucleus (b) splitting of the energy state into allowed bands separated by a forbidden energy gap as the atomic spacing decreases; the electrical properties of a crystalline material correspond to specific allowed and forbidden energies associated with an atomic separation related to the lattice constant of the crystal.

2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Case 1: Isolated atom

Allowed series of energy level that electron can occupy

$$E_n = -\frac{me^4}{8\epsilon_o^2 h^2} \left(\frac{Z^2}{n^2} \right)$$

See on page 2~3 of the text book

Case 2: More than one electron are associated

The electrons filled the allowed levels starting with the lowest energies.

→ By the Pauli exclusion principle, at most two electrons (of opposite spins) can occupy any energy level.

If two atoms approach on another (atoms are close together)

→ the atomic core of the first atom exerts a force on the second electron, changing the potential the determines the energy levels of the electron

→ All allowed energy levels for the electron are consequently modified

2. Structure and Bonding

2.13 Electronic structure of Solids

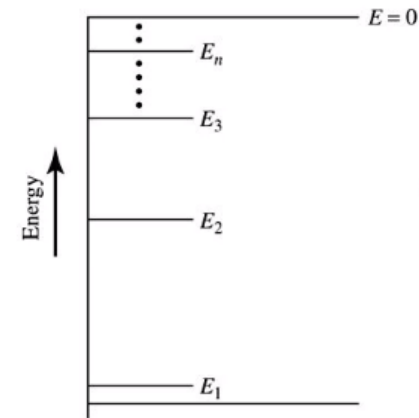
Band model of solids

Two atom system with two electron

Isolated (separated) two atoms

An energy level, E_n

Contain at most two electrons of opposite spin, total system contain at most four electrons

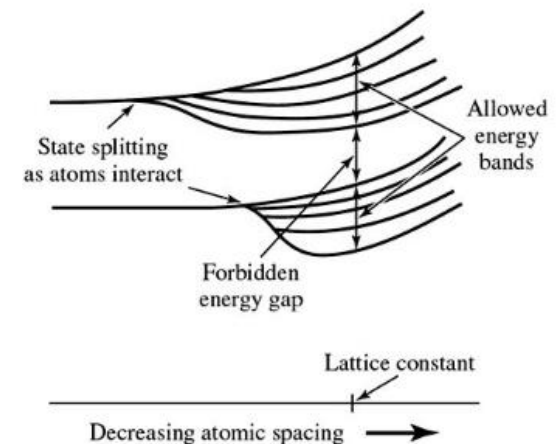


When the isolated two atoms are brought together to form one system

Bringing two atoms close together

- slightly perturbs each energy level of the isolated atom
- splits each of the energy levels of the isolated atoms into two slightly separated energy levels

→ As two atoms are brought closer together, stronger interaction are expected and the splitting increases



2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Many atoms form a crystalline structure

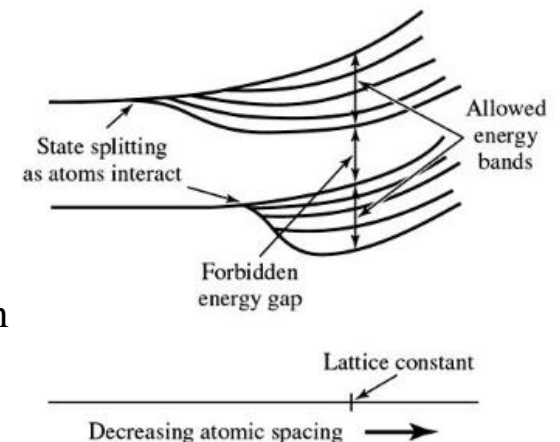
the forces encountered by each electron are altered further, and additional changes in the energy levels occur

→ Pauli exclusion principle demands that each allowed electron energy level have a slightly different energy so that many distinct, closely spaced energy levels characterize the crystal.

When N atoms are included in the system

the original *energy level* E_n splits into N different allowed levels, forming an *energy band*, which may contain at most $2N$ electrons (because of spin degeneracy)

→ the discrete energies that characterize isolated atoms split into multiple levels as the atomic spacing decreases. When the atomic spacing equals the crystal-lattice spacing



2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Bohr radius r_n associated with the n th energy level:

$$r_n = \frac{n^2 \epsilon_0 h^2}{Z \pi m_0 q^2} = \frac{n^2}{Z} \times 0.0529 \text{ nm}$$

For higher energy levels (larger n) the electron is less tightly bound and can wander farther from the atomic core.

If the electron is less tightly confined, it comes closer to the adjacent atoms and is more strongly influenced by them.

This greater interaction causes a larger change in the energy levels so that the wider energy bands correspond to the higher energy electrons of the isolated atoms.

2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

The formation of energy bands from discrete levels occurs whenever the atoms of any element are brought together to form a solid.

Consider first an alkali metal composed of N atoms, each with one valence electron in the outer shell. When the atoms are brought close together, an energy band forms from this energy level. In the simplest case this band has space for $2N$ electrons. The N available electrons then fill the lower half of the energy band and there are empty states just above the filled states.

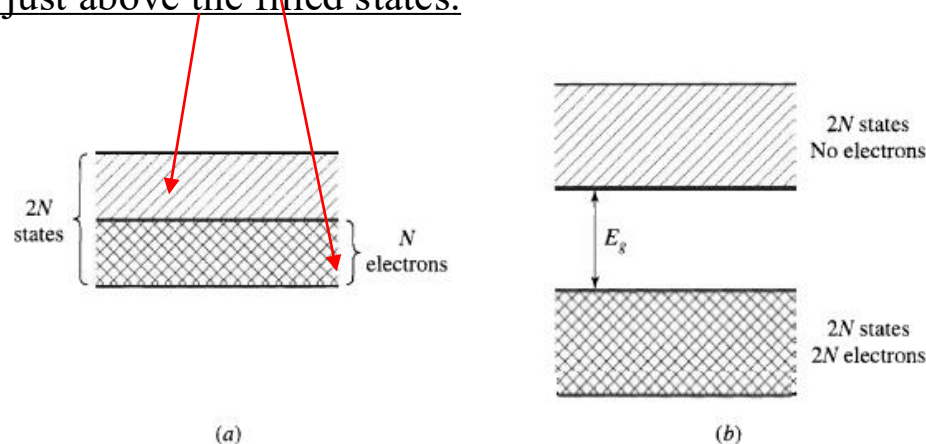


FIGURE 1.3 Energy-band diagrams: (a) N electrons filling half of the $2N$ allowed states, as can occur in a metal. (b) A completely empty band separated by an energy gap E_g from a band whose $2N$ states are completely filled by $2N$ electrons, representative of an insulator.

2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Band structure of metal

The electrons near the top of the filled portion of the band can easily gain small amounts of energy from an applied electric field and move into these empty states.

→ partially fill electrons behave almost as free electrons and can be transported through the crystal by an externally applied electric field



(a)

2. Structure and Bonding

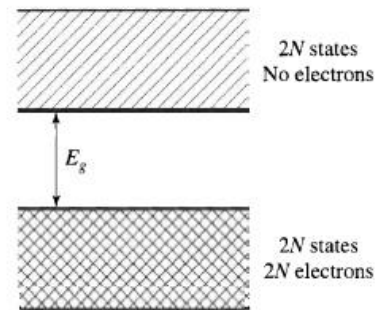
2.13 Electronic structure of Solids

Band model of solids

Band structure of insulator

the valence (outermost shell) electrons completely fill an allowed energy band and there is an energy gap to the next higher band

the closest allowed band above the filled band is completely empty at low temperatures



The lowest-energy empty states are separated from the highest filled states by the energy gap E_g .

In insulating material, E_g is generally greater than 5 eV ($\sim 8\text{-}9$ eV for SiO_2), much larger than typical thermal or field-imparted energies (tenths of an eV or less).

→ no electrons close to empty allowed states and, therefore, no electrons can gain small energies from an externally applied field. Consequently, no electrons can carry an electric current, and the material is an insulator.

2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Electron motion in metal and insulator

Metal

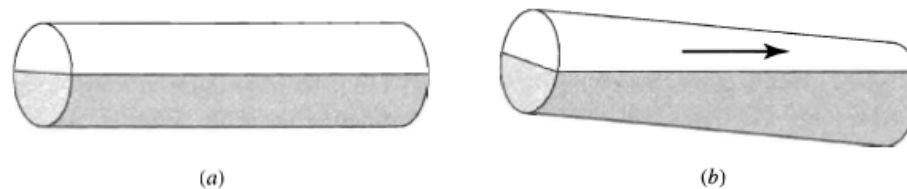


FIGURE 1.4 Electron motion in an allowed band is analogous to fluid motion in a glass tube with sealed ends; the fluid can move in a half-filled tube just as electrons can move in a metal.

→ When a force (gravity in this case) is applied by tipping the tube, the fluid can easily move along the tube.

Insulator

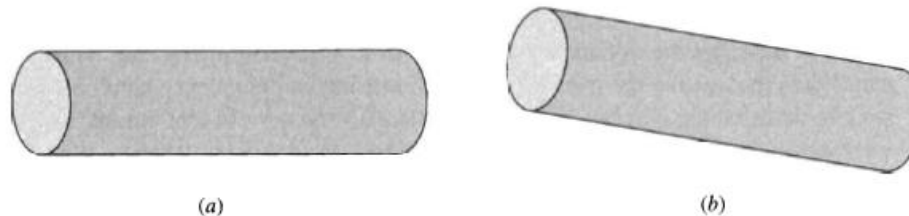


FIGURE 1.5 No fluid motion can occur in a completely filled tube with sealed ends.

→ When the filled tube is tipped, the fluid cannot flow because there is no empty volume into which it can move; that is, there are no empty allowed states.

2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Band structure of semiconductor

Both electrical insulators and semiconductors have similar band structures.

The electrical difference between insulators and semiconductors arises from the size of the forbidden-energy gap and the ability to populate a nearly empty band by adding conductivity enhancing impurities to a semiconductor.

e.g. the energy gap separating the highest band that is filled at absolute zero temperature from the lowest empty band is typically of the order of 1 eV

Silicon (Si): 1.1 eV

Germanium (Ge): 0.7 eV

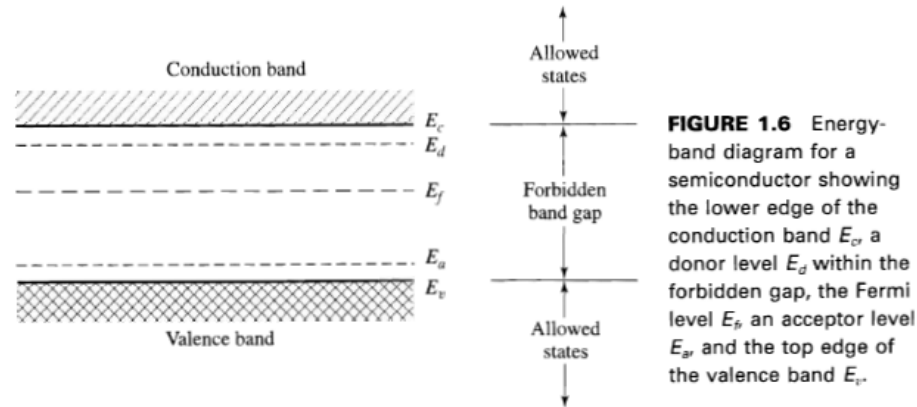
Gallium arsenide (GaAs): 1.4 eV

2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Band structure of semiconductor



At any temperature above absolute zero, the valence band is not entirely filled because a small number of electrons possess enough thermal energy to be excited across the forbidden gap into the next allowed band.

- The smaller the energy gap and the higher the temperature, the greater the number of electrons that can jump between bands. The electrons in the upper band can easily gain small amounts of energy and can respond to an applied electric field to produce a current.
- This band is called the *conduction band* because the electrons that populate it are conductors of electricity.

2. Structure and Bonding

2.13 Electronic structure of Solids

Band model of solids

Band structure of semiconductor

Current flow in the conduction band

$$J_{cb} = \frac{I}{A} = \sum_{cb} (-q) v_i$$

summing the charge $(-q)$ times the net velocity (v_i) of each electron populating the band

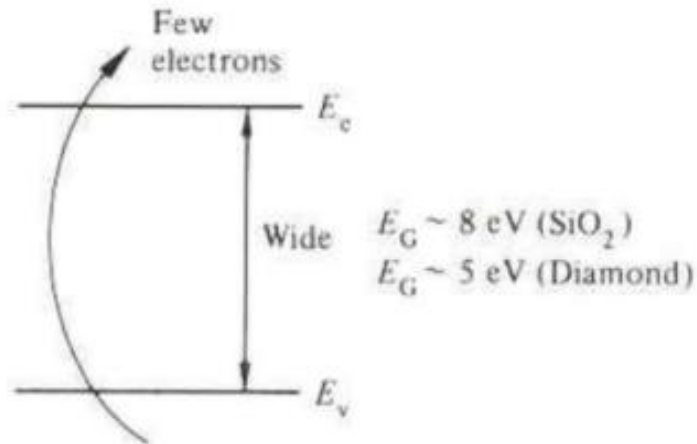
Current density at conduction band

2. Structure and Bonding

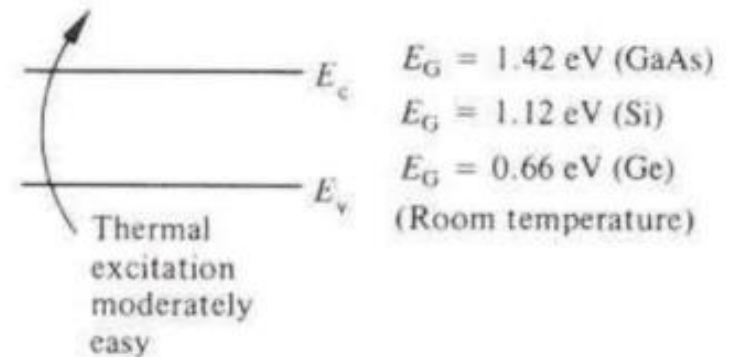
2.13 Electronic structure of Solids

Band model of solids

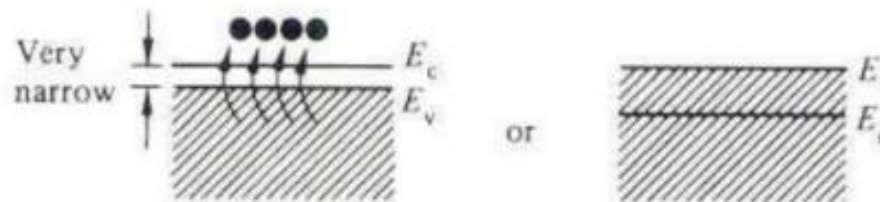
Band structure of insulator, semiconductor, metal



(a) Insulator



(b) Semiconductor



(c) Metal

2. Structure and Bonding

2.13 Electronic structure of Solids

Holes

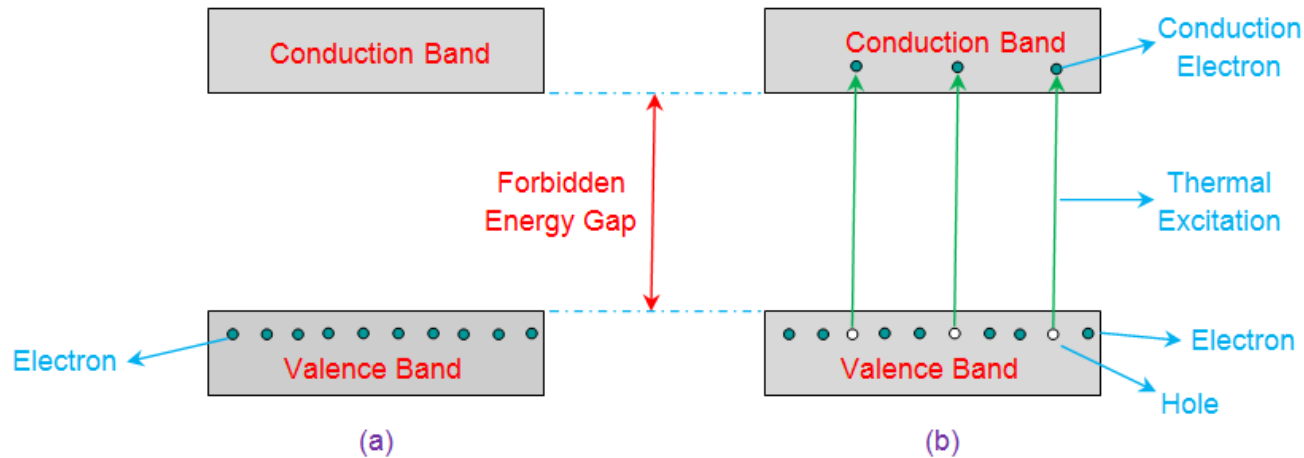


Figure 2 Energy Band Diagram of Intrinsic Semiconductor at (a) 0K (b) Temperature > 0K

When electrons are excited into the conduction band, empty states are left in the valence band.

If an electric field is then applied, nearby electrons can respond to the field by moving into these empty states to produce a current

2. Structure and Bonding

2.13 Electronic structure of Solids

Holes

Current flow in the valence band

$$J_{vb} = \sum_{vb} (-q) v_i$$

summing the motion of all electrons in the valence band of a unit volume of the material.

Mathematically, we can describe the current in the valence band as the current that would flow if the band were completely filled minus that associated with the missing electrons.

$$J_{vb} = \sum_{vb} (-q) v_i = \sum_{\text{Filled band}} (-q) v_i - \sum_{\text{Empty states}} (-q) v_i$$

since no current can flow in a completely filled band

the current in the valence band

$$J_{vb} = 0 - \sum_{\text{Empty states}} (-q) v_i = \sum_{\text{Empty states}} q v_i$$

the motion of charge in the valence band in terms of the vacant states by treating the states as if they were particles with **positive charge; “hole”**

2. Structure and Bonding

2.13 Electronic structure of Solids

Holes

Current flow in the valance band

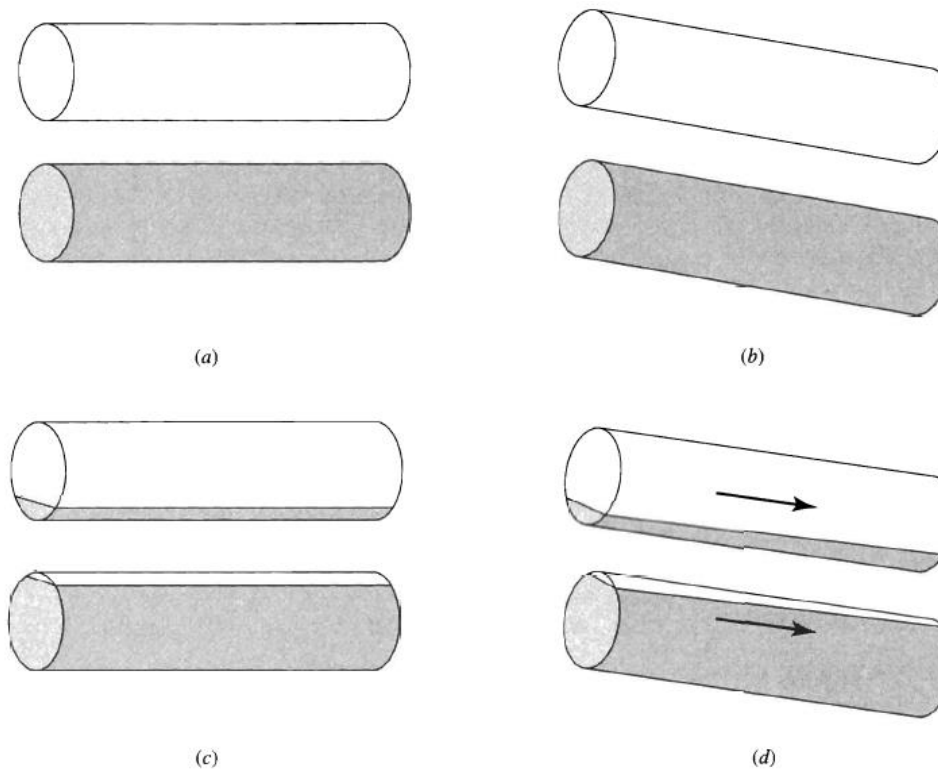


FIGURE 1.7 Fluid analogy for a semiconductor. (a) and (b) No flow can occur in either the completely filled or completely empty tube. (c) and (d) Fluid can move in both tubes if some of it is transferred from the filled tube to the empty one, leaving unfilled volume in the lower tube.

2. Structure and Bonding

2.13 Electronic structure of Solids

Bond Model

Free holes and electrons in semiconductors can also be phrased in terms of the behavior of completed and broken electronic bonds in a semiconductor crystal

→ Hard to account for important quantum mechanical constraints on the behavior of electrons in crystals, but **useful qualitative concepts**.

Consider diamond-type crystal structure

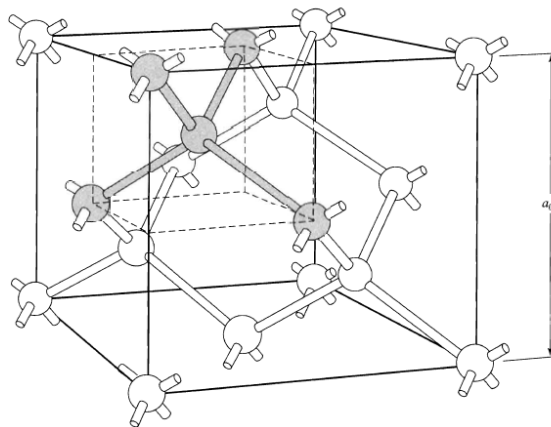


FIGURE 1.8 The diamond-crystal lattice characterized by four covalently bonded atoms. The lattice constant, denoted by a_0 , is 0.356, 0.543 and 0.565 nm for diamond, silicon, and germanium, respectively. Nearest neighbors are spaced $(\sqrt{3}a_0/4)$ units apart. Of the 18 atoms shown in the figure, only 8 belong to the volume a_0^3 . Because the 8 corner atoms are each shared by 8 cubes, they contribute a total of 1 atom; the 6 face atoms are each shared by 2 cubes and thus contribute 3 atoms, and there are 4 atoms inside the cube. The atomic density is therefore $8/a_0^3$, which corresponds to 17.7 , 5.00 , and $4.43 \times 10^{22} \text{ cm}^{-3}$, respectively. (After W. Shockley: *Electrons and Holes in Semiconductors*, Van Nostrand, Princeton, N.J., 1950.)

2. Structure and Bonding

2.13 Electronic structure of Solids

Bond Model

Consider diamond-type crystal structure

→ each atom has covalent bonds with its four nearest neighbors

two tightly bound electrons associated with each bond—one from each atom

At absolute zero temperature,
all electrons are held in these bonds, and
therefore none are free to move about the
crystal in response to an applied electric field.

At higher temperatures,
thermal energy breaks some of the bonds and
creates nearly free electrons, which can then
contribute to the current under the influence of
an applied electric field

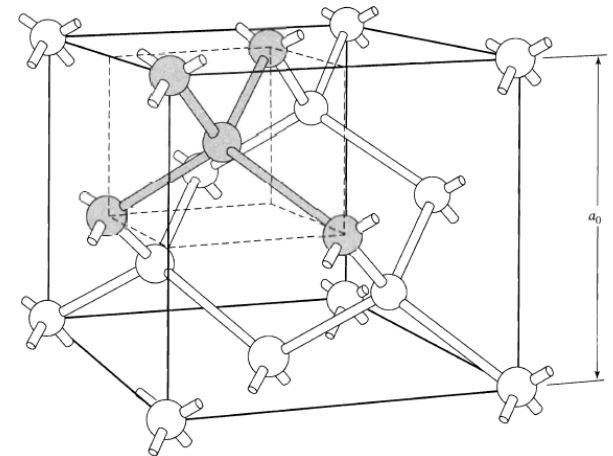


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2. Structure and Bonding

2.13 Electronic structure of Solids

Bond Model

At higher temperatures,
thermal energy breaks some of the bonds and creates nearly free electrons

- freed electron moves away, an empty bond is left behind
- An electron from an adjacent bond can then jump into the vacant bond, leaving a vacant bond behind
- The vacant bond, therefore, moves in the opposite direction to the electrons.

If a net motion is imparted to the electrons by an applied field, the vacant bond can continue moving in the direction opposite to the electrons as if it had a positive charge.

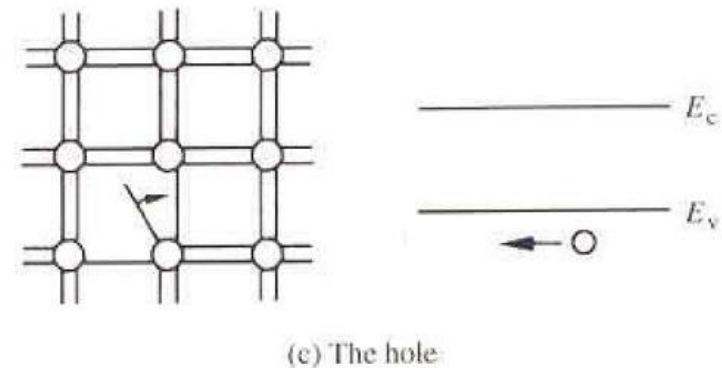
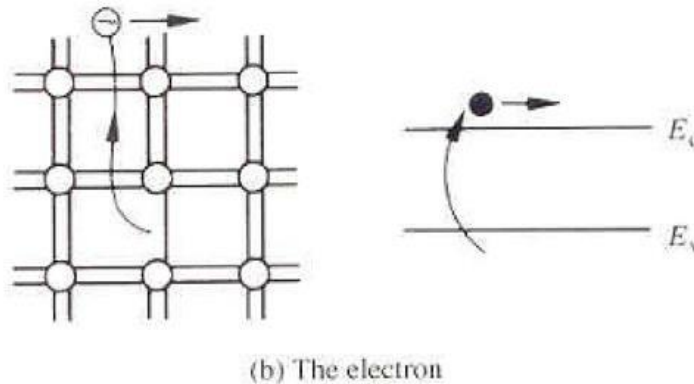
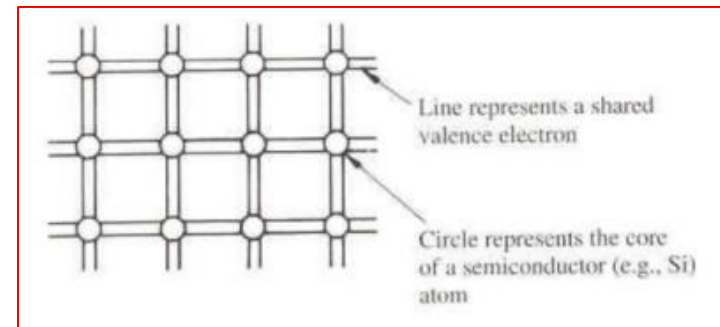
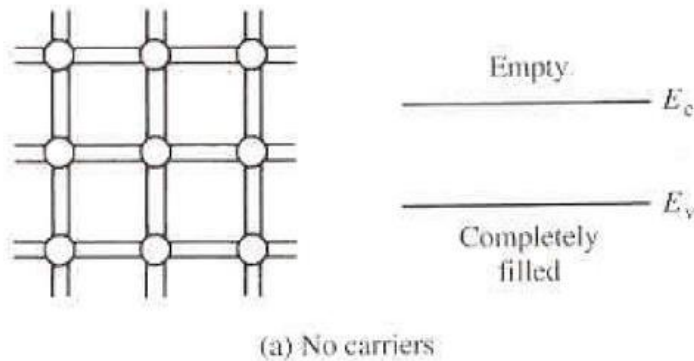
- This vacant bond corresponds to the hole associated with the valence band in the energy-band picture.

2. Structure and Bonding

2.13 Electronic structure of Solids

Bond Model

Band vs. Bond model for electronic band structure



2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

Pure semiconductor material (*intrinsic* semiconductor)

each electron excited into the conduction band leaves a vacant state in the valence band

The number of negatively charged electrons n in the conduction band
= the number of positively charged holes p in the valence band

n_i : the densities of electrons (carriers cm^{-3})

p_i : the densities of holes (carriers cm^{-3})

subscript “ i ” means *intrinsic*

→ The most useful means for controlling the number of carriers in a semiconductor is by incorporating *substitutional impurities*; that is, *impurities* that occupy lattice sites in place of the atoms of the pure semiconductor

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

Donors

substitutional group V impurities *donate electrons to the silicon*

if we replace one silicon atom (four valence electrons) with an impurity atom from group V in the periodic table, such as phosphorus (five valence electrons), then four of the valence electrons from the impurity atom fill bonds between the impurity atom and the adjacent silicon atoms.

The fifth electron, however, is not covalently bonded to its neighbors; it is only weakly bound to the impurity atom by the excess positive charge on the nucleus.

→ Only a small amount of energy is required to break this weak bond so its the fifth electron can wander about the crystal and contribute to electrical conduction.

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

Types of Dopants in Extrinsic Semiconductors

Doping : **impurities** that occupy lattice sites in place of the atoms of the pure semiconductor

Crystals of [Silicon](#) and Germanium are doped using two types of dopants:

Pentavalent (valency 5)

; Arsenic (As), Antimony (Sb), Phosphorous (P), etc.

Trivalent (valency 3);

Indium (In), Boron (B), [Aluminum](#) (Al), etc.

IIB	IIIA	IVA	VA	VIA
			⁷ N Nitrogen	⁸ O Oxygen
	¹³ Al Aluminum	¹⁴ Si Silicon	¹⁵ P Phosphorus	¹⁶ S Sulfur
³⁰ Zn Zinc	³¹ Ga Gallium	³² Ge Germanium	³³ As Arsenic	³⁴ Se Selenium
⁴⁸ Cd Cadmium	⁴⁹ In Indium		⁵¹ Sb Antimony	⁵² Te Tellurium
⁸⁰ Hg Mercury				

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

Donors

the amount of energy needed to break the bond to a donor atom,

The energy binding the electron to the core

$$E = \frac{m_n^* q^4}{8h^2 \epsilon_0^2 \epsilon_r^2} = \frac{13.6}{\epsilon_r^2} \frac{m_n^*}{m_0} \text{ eV}$$

where ϵ_r is the relative permittivity of the semiconductor and m_n^* is the effective mass of the electron in the semiconductor conduction band

For silicon with $\epsilon_r = 11.7$ and $m_n^* = 0.26 m_0$, $E = 0.03$ eV, which is only about 3% of the silicon bandgap energy (1.1 eV)

More detailed calculations and measurements indicate that the binding energy for typical donors is somewhat higher: 0.044 eV for phosphorus, 0.049 eV for arsenic, and 0.039 eV for antimony

→ much easier to break the weak bond connecting the fifth electron to the donor than to break the silicon-silicon bonds.

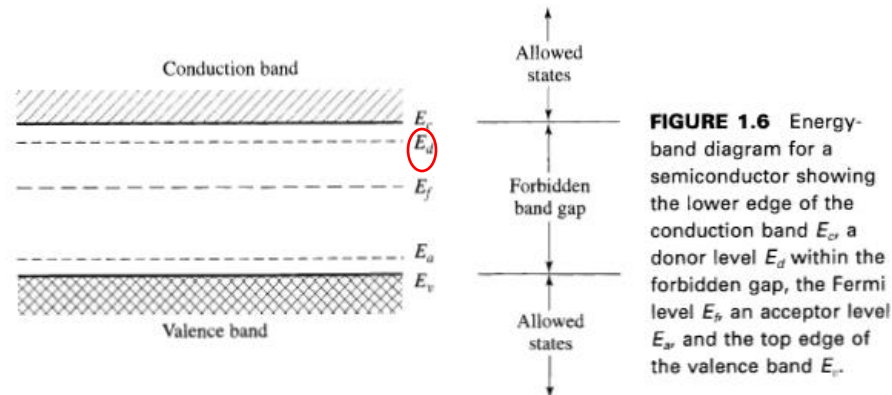
2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

N-type semiconductor

According to the energy-band model, it requires only a small amount of energy to excite the electron from the donor atom into the conduction band, while a much greater amount of energy is required to excite an electron from the valence band to the conduction band



the state corresponding to the electron when bound to the donor atom by a level E_d about 0.05 eV below the bottom of the conduction band E_c

The density of donors (atoms cm^{-3}); N_d

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

N-type semiconductor

Most impurities are of the donor type

→ the number of electrons in the conduction band is much greater than the number of holes in the valence band

Electron: *majority carriers*

Holes: *minority carrier*

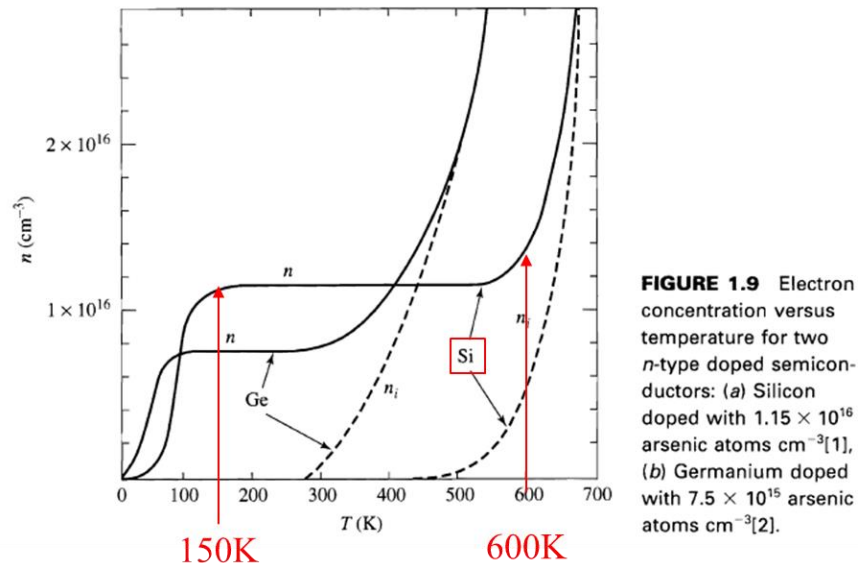
n-type semiconductor; because most of the current is carried by the *negatively charged* electrons.

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

Conduction electron concentration vs. temperature (N-type semiconductor)



the hole density is at most equal to n_i

n_i : the densities of electrons (carriers cm^{-3})

Electrons are far more numerous than holes when the temperature is in the range sufficient to ionize the donor atoms (about 150 K) but not adequate to free many electrons from silicon-silicon bonds (about 600 K).

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

p-type semiconductor

Similarly, an impurity atom with three valence electrons, such as boron, can replace a silicon atom in the lattice.

- The three electrons fill three of the four covalent silicon bonds, leaving one bond vacant
- If another electron moves to fill this vacant bond from a nearby bond, the vacant bond is moved, carrying with it positive charge and contributing to hole conduction

Just as a small amount of energy was necessary to initiate the conduction process in the case of a donor atom, only a small amount of energy is needed to excite an electron from the valence band into the vacant bond caused by the trivalent impurity

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

p-type semiconductor

This energy is represented by an energy level E_a slightly above the top of the valence band E_v

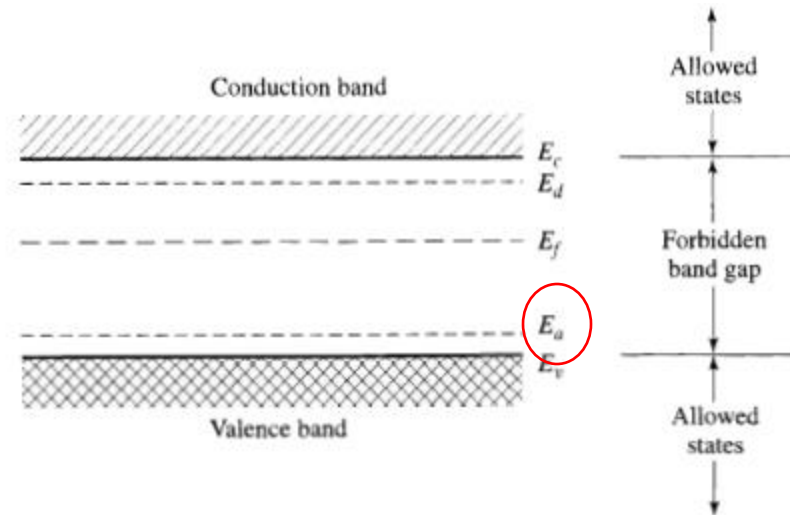


FIGURE 1.6 Energy-band diagram for a semiconductor showing the lower edge of the conduction band E_c , a donor level E_d within the forbidden gap, the Fermi level E_f , an acceptor level E_a , and the top edge of the valence band E_v .

An impurity that contributes to hole conduction is called an *acceptor impurity* because it leads to vacant bonds, which easily accept electrons. The acceptor concentration (atoms cm^{-3}) is denoted as N_a .

If most of the impurities in the solid are acceptors, the material is called a *p-type* semiconductor because most of the conduction is carried by *positively charged* holes.

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

p-type semiconductor

Semiconductors in which conduction results primarily from carriers contributed by impurity atoms are said to be *extrinsic*.

→The donor and acceptor impurity atoms, which are intentionally introduced to change the charge-carrier concentration, are called *dopant atoms*.

2. Structure and Bonding

2.13 Electronic structure of Solids

Donors and Acceptors

Parameter	P-Type	N-Type
Impurity doped	Trivalent impurity	Pentavalent impurity
Also known as	Acceptor atom because of presence of additional hole.	Donor atom due to the existence of additional electron.
Doped group	Group III elements. For eg - boron, gallium, indium, aluminium etc.	Group V elements. for eg - arsenic, antimony, bismuth, phosphorus etc.
Majority carriers	Holes	Electrons
Minority carriers	Electrons	Holes
Conductivity	Due to presence of holes.	Due to presence of electrons.
Presence of fermi level	Fermi level appears closer to the valence band than the conduction band.	Fermi level is present nearer to the conduction band than the valence band.
Concentration of electrons	Low	Very high as compared to p type semiconductor
Concentration of holes	High	Comparatively less than p type semiconductor.

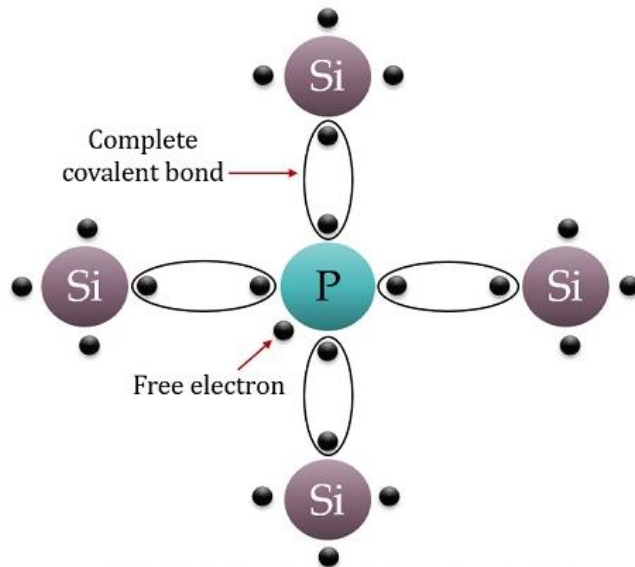
2. Structure and Bonding

2.13 Electronic structure of Solids

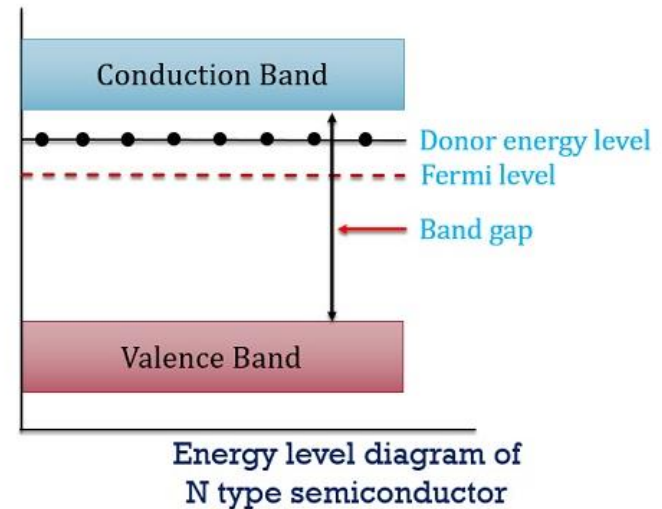
Donors and Acceptors

n-type semiconductor

N-type extrinsic semiconductors are formed when **group V** elements like phosphorus, antimony, bismuth etc. are doped to a pure semiconductor crystal.



- Si = Intrinsic semiconductor atom
- P = Pentavalent impurity atom



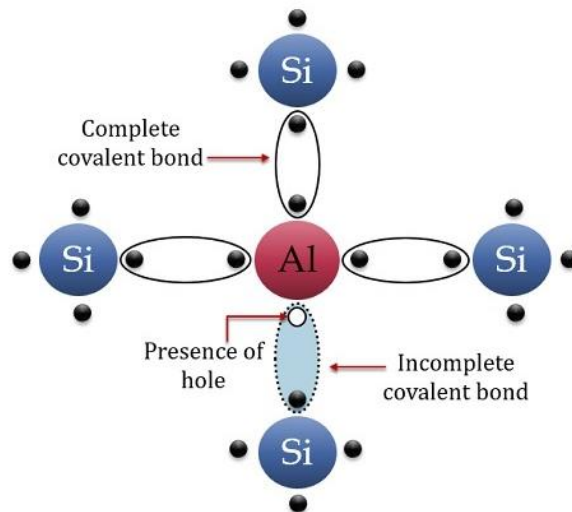
2. Structure and Bonding

2.13 Electronic structure of Solids

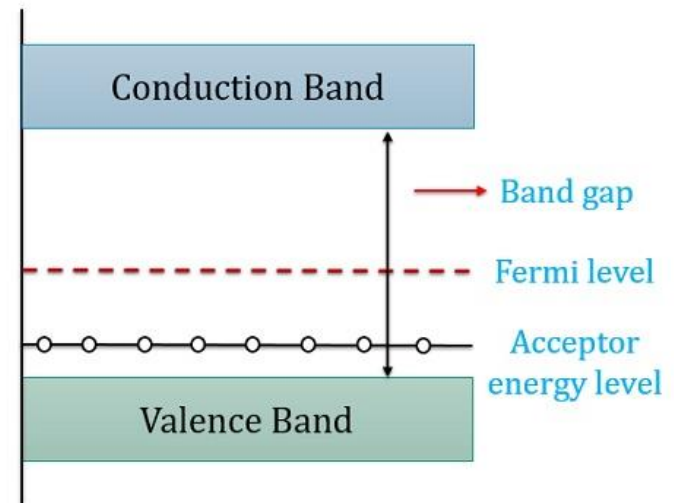
Donors and Acceptors

P-type semiconductor

When a pure or intrinsic semiconductor is doped with **group III** elements of periodic table like **boron, gallium, aluminum** etc. that these are known as the p-type extrinsic semiconductor.



- Si = Intrinsic semiconductor atom
- Al = Trivalent impurity atom



Energy level diagram of P type semiconductor

2. Structure and Bonding

2.13 Electronic structure of Solids

Key Differences between P-Type and N-Type Semiconductor

1. A p-type semiconductor is formed when **group III** elements are doped to a pure semiconductor material. As against, an n-type semiconductor is formed when **group V** elements are doped to an intrinsic semiconductor.
2. As elements like boron, gallium, indium etc. are doped to form p-type semiconductor thus it produces an additional hole hence also known as **acceptor atom**.
On the contrary, elements like arsenic, antimony, bismuth etc. are doped in order to have n-type semiconductor hence it produces an additional electron thus also termed as **donor atom**.
3. Another factor that generates a key difference between p-type and n-type semiconductor is that in case of p-type semiconductor holes are the majority carriers. While in case of n-type semiconductor electrons act as majority carriers.
4. The minority carriers in case of the p-type semiconductor are electrons whereas in that of n-type semiconductor these are holes.
5. As we know that the conductivity of the device depends on the majority carriers. Thus in the p-type semiconductor, **holes are responsible for current conduction**. On the contrary, in case of an n-type semiconductor, **electrons are responsible for current conduction**.
6. The **fermi-level** in case of p-type semiconductor appears closer to valence band than that of the conduction band. As against, the Fermi level in case of n-type semiconductor exists near the conduction band.
7. The concentration of holes is more than electrons in case of p-type semiconductor material. While in n-type semiconductors the concentration of electrons is greater than holes.

Next

3. Synthesis of Nanomaterials (Physical Methods)