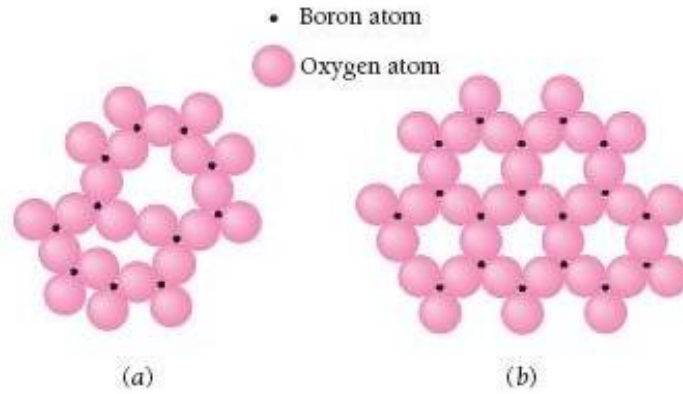# Chapter 8 Solid States

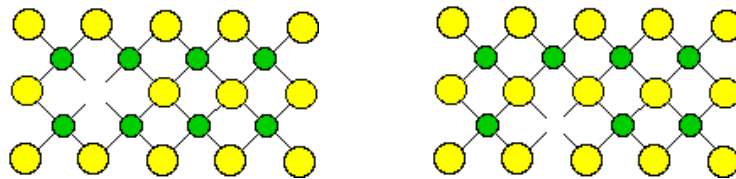## 8-1 Crystalline and Amorphous Solids

Two-dimensional representation of B_2O_3. (a) Amorphous B_2O_3 exhibits only short-range order. (b) Crystalline B_2O_3 exhibits long-range order as well.

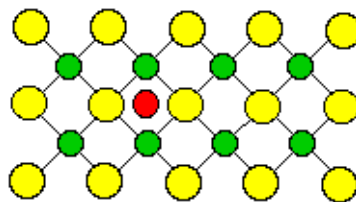**Crystal:** Crystalline solids exhibit long-range order.

Amorphous Solid: Crystalline solids exhibit short-range order.
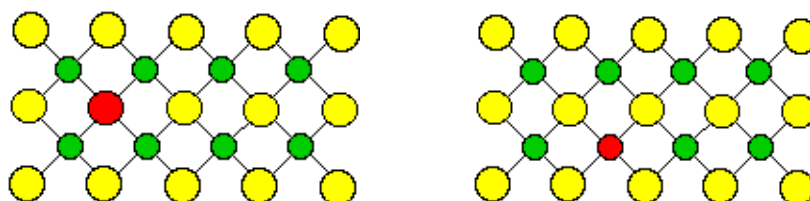
Crystal defects:

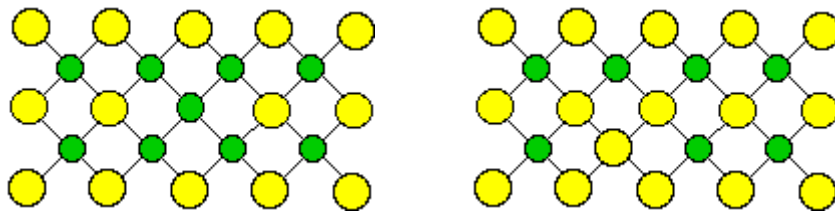Vacancy:

Interstitial impurity:
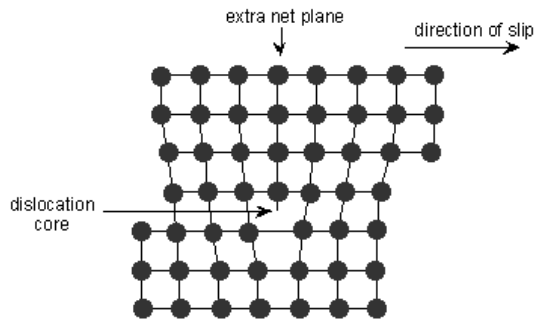

Substitution:

Antisite defect:

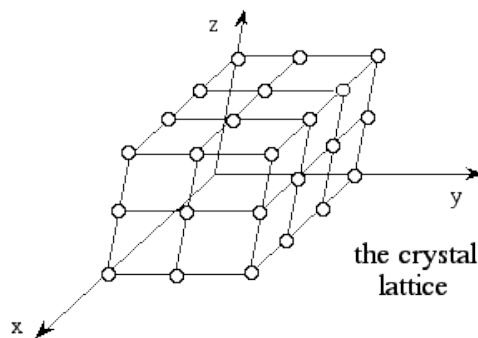Edge dislocation: Skew dislocation:

Lattice: A periodical structure of atoms. Due to the periodicity of the lattice, we have

$\varepsilon(\vec{r} + \vec{R}) = \varepsilon(\vec{r})$. Furthermore, $\varepsilon(-\vec{r}) = \varepsilon(\vec{r})$ and there exist several axes and planes

of symmetry.

the crystal
lattice

Primitive vectors: $\vec{a}_1 = \vec{a}, \ \vec{a}_2 = \vec{b}, \ \vec{a}_3 = \vec{c}$

Translation vector: $\vec{R} = \alpha_1 \vec{a}_1 + \alpha_2 \vec{a}_2 + \alpha_3 \vec{a}_3$, where $\alpha_1, \ \alpha_2, \ \alpha_3 = 0, \pm 1, \pm 2, \pm 3, \ldots.$

r = 0a + 2b + 1c
[021]

Real space
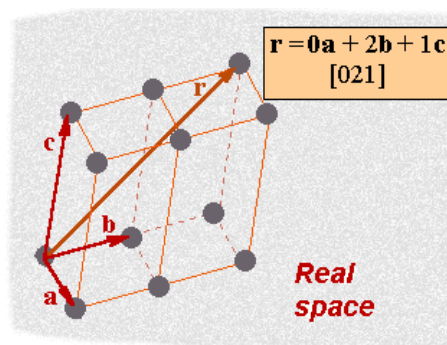
Primitive cell: The parallel hexagonal region composed of $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$.
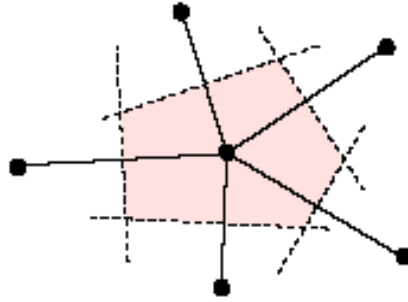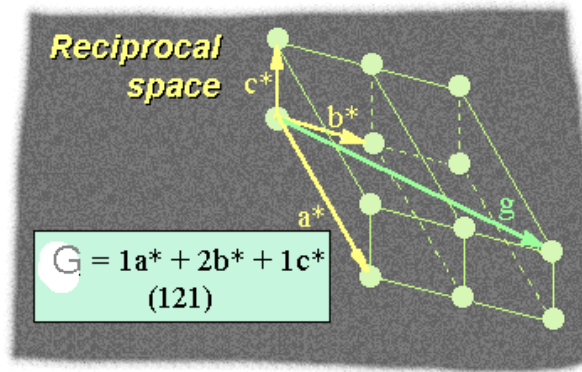
Wigner-Seitz cell: The region bounded by bisecting line of two adjacent atoms.

Reciprocal lattice: The Fourier domain of original lattice by optical diffraction or electron beam diffraction.

Reciprocal lattice primitive vectors: $\vec{b}_1 = \vec{a}*,\ \vec{b}_2 = \vec{b}*,\ and\ \vec{b}_3 = \vec{c}*$.

Translation vector in the reciprocal lattice: $\vec{G} = \beta_1 \vec{b}_1 + \beta_2 \vec{b}_2 + \beta_3 \vec{b}_3$, where
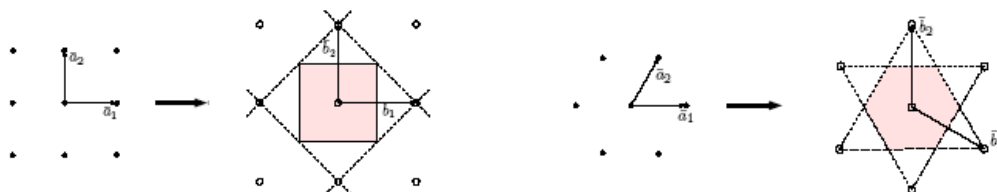
$\beta_1,\ \beta_2,\ \beta_3 = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ldots.$

$$\because \varepsilon(\vec{r} + \vec{R}) = \varepsilon(\vec{r}),\quad \therefore \varepsilon(\vec{r}) = \sum_{\vec{G}} \bar{\varepsilon}(\vec{G}) e^{i\vec{G}\cdot\vec{r}} = \varepsilon(\vec{r} + \vec{R}) = \sum_{\vec{G}} \bar{\varepsilon}(\vec{G}) e^{i\vec{G}\cdot(\vec{r}+\vec{R})}$$

$\Rightarrow$ **Bragg's diffraction law:** $\vec{G} \cdot \vec{R} = 2n\pi$. It implies $\vec{b}_j \cdot \vec{a}_i = 2\pi \delta_{ij}$.

Let $\vec{b}_1 = k(\vec{a}_2 \times \vec{a}_3)$, $\vec{b}_1 \cdot \vec{a}_1 = 2\pi \Rightarrow k = \dfrac{2\pi}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \Rightarrow \vec{b}_1 = \dfrac{2\pi(\vec{a}_2 \times \vec{a}_3)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

Similarly, $b_2 = 2\pi \dfrac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}$ and $b_3 = 2\pi \dfrac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$

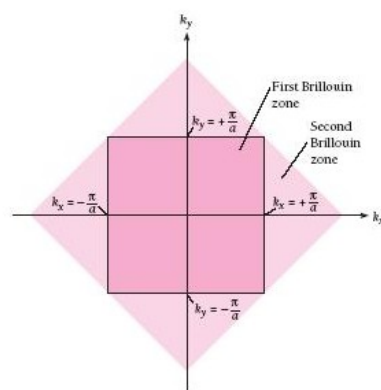| Square lattice	$\bar{a}_1 = a\hat{x}$	$\bar{b}_1 = 2\pi/a\,\hat{x}$
	$\bar{a}_2 = a\hat{y}$	$\bar{b}_2 = 2\pi/a\,\hat{y}$
Triangular lattice	$\bar{a}_1 = a\hat{x}$	$\bar{b}_1 = 2\pi/a\,(\hat{x} - \sqrt{3}/3\,\hat{y})$
	$\bar{a}_2 = (\hat{x} + \sqrt{3}\hat{y})$	$\bar{b}_2 = 2\pi/a\,2\sqrt{3}/3\,\hat{y}$

Table   Definition of $\bar{a}$ and $\bar{b}$ vectors for square and triangular (or hexagonal) lattice.
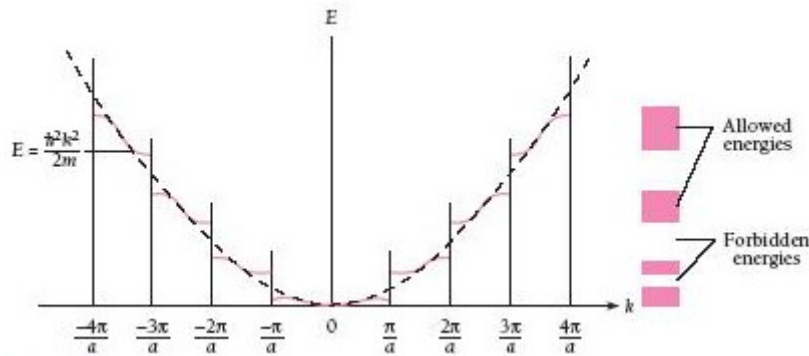
Brillouin Zones: Wigner-Seitz cells in the reciprocal lattice.

The first and second Brillouin zones of a two-dimensional square lattice.
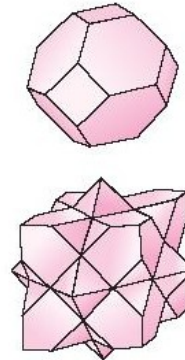
First and second Brillouin zones in a face-centered crystal.

**Band diagram:** Describe the relation between the energy and the momentum.

In quantum mechanics, the energy of n photons is $E_{\text{photon}}=nh\nu = n\hbar\omega$ ($\propto \omega$ or ν), the energy of n phonons is $E_{\text{phonon}}=(n+1/2)h\nu = (n+1/2)\hbar\omega$, where h is the Plank's constant, ν is the frequency, $\hbar = h/2\pi$, and $\omega=2\pi\nu$. The downward transition of an electron between energy levels or bands may emit photons or phonons. The upward transition between energy levels or bands can absorb photons or phonons.

On the other hand, quantum mechanics shows that the momentum of an electron is $p=m\nu=h/\lambda = \hbar k \propto k$, where $k=2\pi/\lambda$ is the wavenumber of matter wave.

We can depict the relation of the energy **E** (or **ω)** of electrons in a crystal versus **k** (or **p**). It is called *E-k* diagram or band diagram.
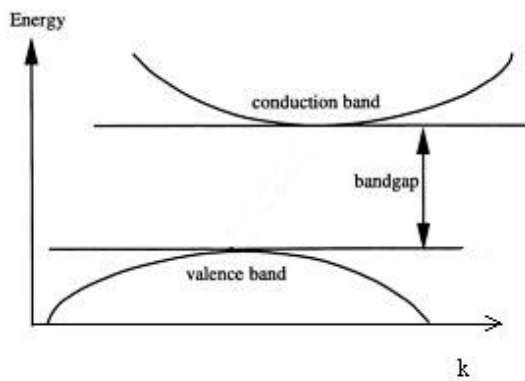
Eg. Two examples of band diagrams.

**Direct bandgap: Eg. GaAs, Ga_xAl_{1-x} As.**
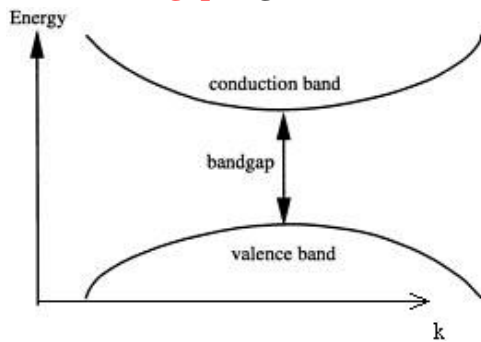
The downward transition of an electron in a crystal of the **direct bandgap** can emit photons. ($\because \triangle k = \triangle p = 0$, $\therefore$ no variation in lattice momentum. All loss of energy due to downward transition must become radiation of photons).

Indirect bandgap: Eg. Crystalline Si.

The downward transition of an electron in a crystal of the **indirect bandgap** can not emit photons, but it can cause lattice vibration and then generate heat or acoustic waves, etc. ($\because \triangle k \neq 0$, i. e., $\triangle p \neq 0$, There exists variation in lattice momentum. The loss of energy due to downward transition can become phonon radiation).

8-2 Ionic Crystals
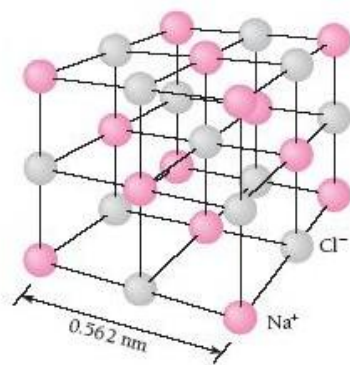
The face-centered cubic structure of NaCl. The coordination number (the number of nearest neighbors about each ion) is 6.
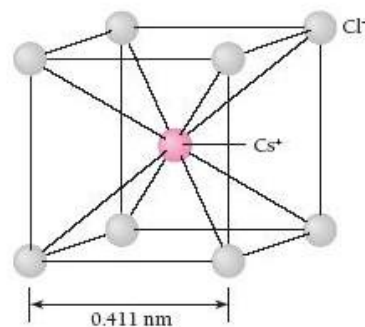
The body-centered cubic structure of CsCl. The coordination number is 8.

Ionic bonds: Ionic bonds between the atoms of two elements can be form when one atom becomes positive ion and the other element has a high electro affinity.

The Coulomb energy of ionic crystal is $V_{\text{coulomb}} = -\alpha \dfrac{e^2}{4\pi\varepsilon_0 r}$ and the potential energy

due to repulsive force is $V_{\text{rep}} = \dfrac{B}{r^n}$, $\therefore$ Total $V = -\alpha \dfrac{e^2}{4\pi\varepsilon_0 r} + \dfrac{B}{r^n}$

$\because$ At equilibrium, V is the minimum, $\therefore$ $dV/dr = 0 \Rightarrow B = \dfrac{\alpha e^2 r_0^{\,n-1}}{4\pi\varepsilon_0 n}$

$\Rightarrow$ Lattice energy is $V = -\dfrac{\alpha e^2}{4\pi\varepsilon_0 n}(1 - \dfrac{1}{n})$, where average $n \approx 9$.

Eg. In a NaCl crystal, the equilibrium distance r_0 between ions is 0.281nm. Find the cohesive energy in NaCl.

(Sol.) $\alpha = 1.748$, $n \approx 9$, $V = -\dfrac{\alpha e^2}{4\pi\varepsilon_0 n}(1 - \dfrac{1}{n}) = -1.27\times10^{-18}J = -7.96eV$

Eg. (a) The total potential energy in an ionic crystal is given by the equation: $U = -\alpha \dfrac{e^2}{4\pi\varepsilon_0 r} + \dfrac{B}{r^n}$. Please show graphically the potential energy of this equation and explain the origin of these two terms. (b) Please calculate the value of the constant n for the NaCl molecule. (The binding energy of this molecule is 7.95 eV/molecule. The equilibrium distance between Na$^+$ and Cl$^-$ ions is 2.8 $\overset{o}{A}$ and Madelung constant for the NaCl crystal is $\alpha = 1.75$. [台大電研]
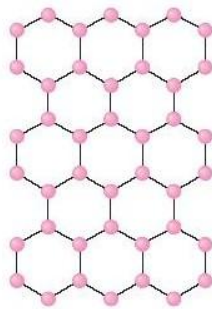
8-3 Covalent Crystals

Covalent bonds: Shared electrons results in the strongest bonds.

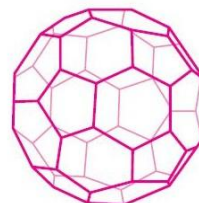**Eg. Three crystalline structures of carbon: diamond, graphite, and bulkyball. And a diamond is the hardest material in nature.**
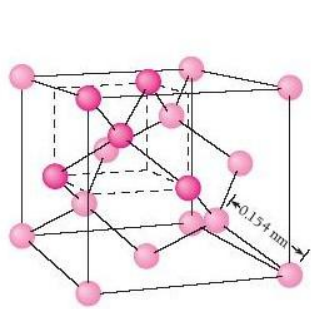
The tetrahedral structure of diamond. The coordination number is 4.

Graphite consists of layers of carbon atoms in hexagonal arrays, with each atom bonded to three others. The layers are held together by weak van der Waals forces.

In a buckyball, carbon atoms form a closed cagelike structure in which each atom is bonded to three others. Shown here is the C_{60} buckyball that contains 60 carbon atoms. The lines represent carbon-carbon bonds; their pattern of hexagons and pentagons closely resembles the pattern made by the seams of a soccer ball. Other buckyballs have different numbers of carbon atoms.
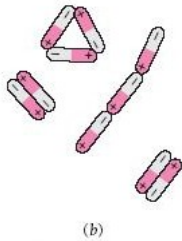
8-4 Van Der Waal Force and Ketallic Bonds

Van Der Waal Force: The force is a weak and short-range attraction among all molecules and atoms, due to polar molecules or polarized molecules.
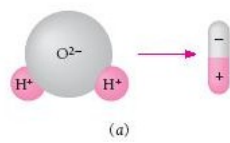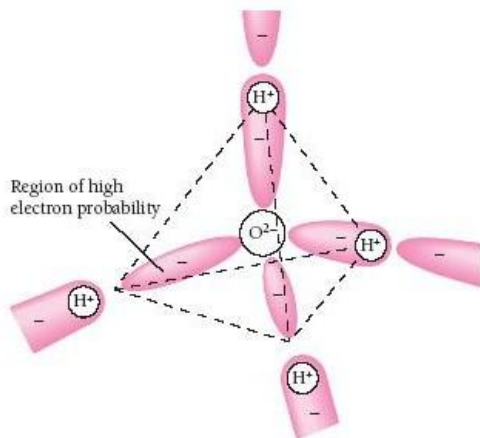
The dipole electric field is $\vec{E}=\dfrac{1}{4\pi\varepsilon_0}[\dfrac{\vec{p}}{r^3}-\dfrac{3(\vec{p}\bullet\vec{r})}{r^5}\vec{r}]$ and the

(a)

induced dipole moment is $\vec{p}'=\alpha\vec{E}$. The interaction energy is

$$U=-\vec{p}'\cdot\vec{E}=\dfrac{-\alpha}{4\pi\varepsilon_0}(1+3\cos\theta)\dfrac{p^2}{r^6}$$

And the Van Der Waal's force=$-dU/dr \propto r^{-7}$

(b)

Region of high electron probability

In an H_2O molecule, the four pairs of valence electrons around the oxygen atom (six electrons contributed by the O atom and one each by the H atoms) preferentially occupy four regions that form a tetrahedral pattern. Each H_2O molecule can form hydrogen bonds with four other H_2O molecules.
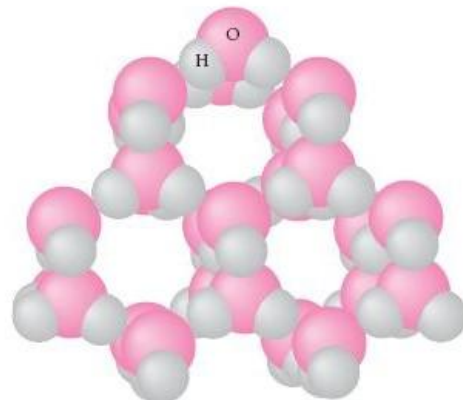
The structure of an ice crystal, showing the open hexagonal arrangement of the H_2O molecules. There is less order in liquid water, which allows the molecules to be closer together on the average than they are in ice. Thus the density of ice is less than that of water, and ice floats.

Metallic bond: Metallic ions are surrounded by a gas of free electrons.

**Comparison of various bonds:**

Table Types of Crystalline Solids. The cohesive energy is the work needed to remove an atom (or molecule) from the crystal and so indicates the strength of the bonds holding it in place.

Type	Ionic	Covalent	Molecular	Metallic
Lattice	Negative ion / Positive ion	Shared electrons	Instantaneous charge separation in molecule	Metal ion / Electron gas
Bond	Electric attraction	Shared electrons	Van der Waals forces	Electron gas
Properties	Hard; high melting points; may be soluble in polar liquids such as water; electrical insulators (but conductors in solution)	Very hard; high melting points; insoluble in nearly all liquids; semi-conductors (except diamond, which is an insulator)	Soft; low melting and boiling points; soluble in covalent liquids; electrical insulators	Ductile; metallic luster; high electrical and thermal conductivity
Example	Sodium chloride, NaCl $E_{cohesive}=3.28$ eV/atom	Diamond, C $E_{cohesive}=7.4$ eV/atom	Methane, CH_4 $E_{cohesive}=0.1$ eV/molecule	Sodium, Na $E_{cohesive}=1.1$ eV/atom

8-5 Band Theory of Semiconductor Devices


(a) Metal

(b) Semiconductor

(c) Insulator
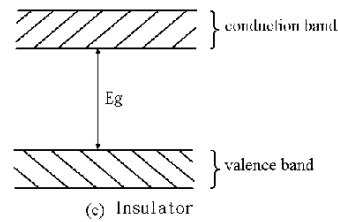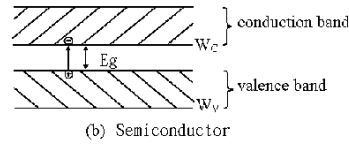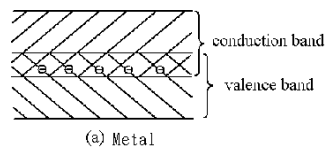
(a) **Metal:** The conduction band and the valence band may overlap. (b) Semiconductor: The bandgap between the conduction band and the valence band is very small. The electron can be easily excited into the conduction band to become a free electron. (c) Insulator: The bandgap between the conduction band and the valence band is very large. The electron is hardly excited into the conduction band to become a free electron.

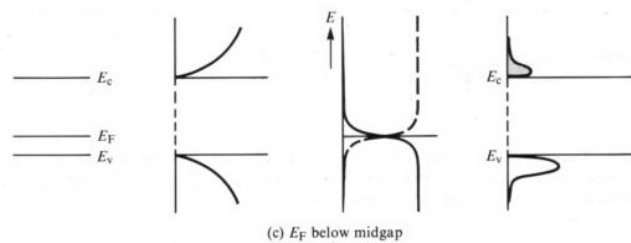(b) E_F near midgap
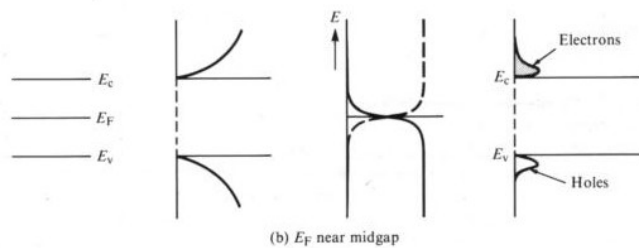
Intrinsic semiconductor:

$$E_F \approx \frac{1}{2}(E_v + E_c)$$

(a) E_F above midgap
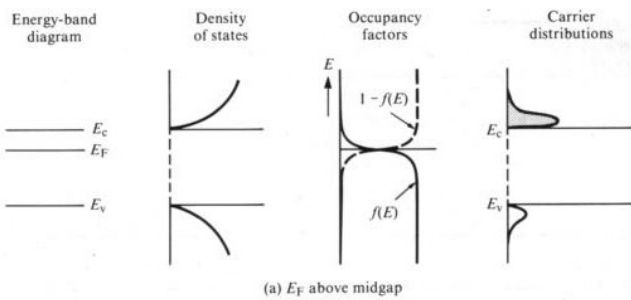
The *n*-type semiconductor:

E_F is near E_c.

(c) E_F below midgap

The *p*-type semiconductor:

E_F is near E_v.
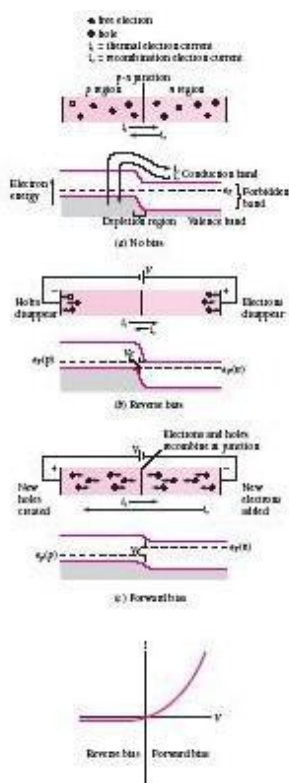
Bandgap theory of diode:

Fig. (a) No bias: $E_F(p)=E_F(n)$

Fig. (b) Reverse bias: $E_F(p)>E_F(n)$, entrance of electrons becomes more difficult than the case of no bias. ∴ Current ceases.
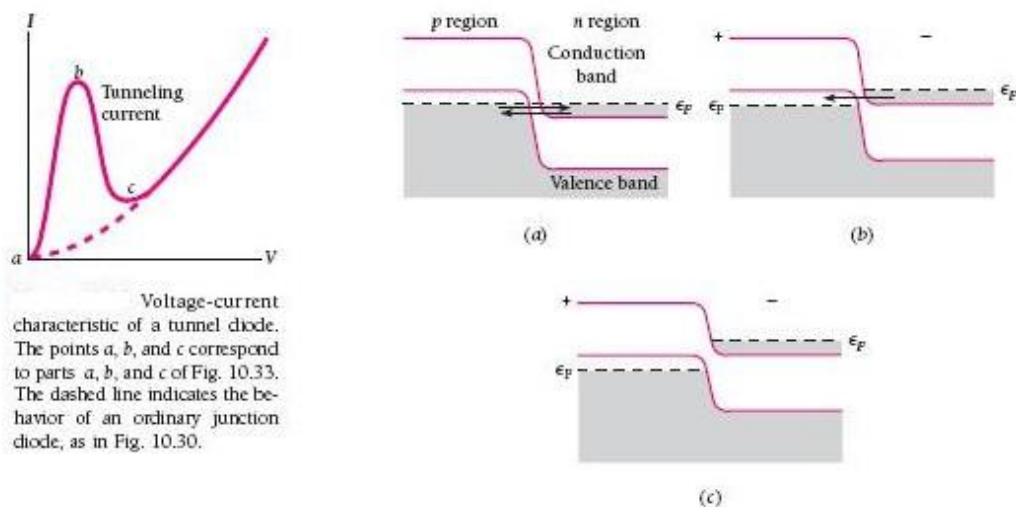
Fig. (c) Forward bias: $E_F(p)<E_F(n)$, entrance of electrons becomes easier than the case of no bias. ∴ Current increases as the forward bias voltage.

Bandgap theory of tunnel diode: The both *p*- and *n*-regions of the tunnel diode are **heavily doped**. And the depletion region is very narrow.
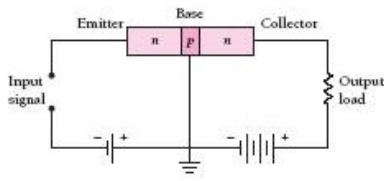
Fig. (a) No bias: $E_F(p)=E_F(n)$, electrons tunnel in both direction are equal.

Fig. (b) Small forward bias (From point *a*→*b*→*c* of *I-V* curve): Electrons tunnel from *n*-region to *p*-region only, because the filled lower part of *n*-region conduction band is opposite the empty upper part of the *p*-region valence band.

Fig. (c) Larger forward bias: The two bands no longer overlap. The tunnel current therefore cease. From now on the tunnel diode behaves exactly like an ordinary junction diode.

Voltage-current characteristic of a tunnel diode. The points a, b, and c correspond to parts a, b, and c of Fig. 10.33. The dashed line indicates the behavior of an ordinary junction diode, as in Fig. 10.30.

Bandgap theory of *n-p-n* transistor:

The transistor is given a forward bias across the emitter-base junction and a reverse bias across the base-collector junction. The emitter is more heavily doped than base, so nearly all the current across the emitter-base junction consists of electrons moving from left to right.
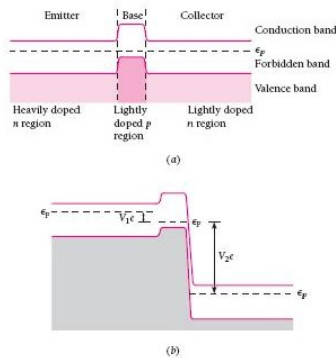

Fig. (a) No bias: E_F(emitter)=E_F(base)=E_F(collector)

Fig. (b) Small forward bias across the emitter-base junction and large reverse bias across the base-collector junction:

∵ The base is very thin and V_2e is small, electrons can pass through it from the emitter to the collector without recombining with holes there.

∴ Most of electrons can reach the collector. Once the electrons arrive at the collector, they lose energy due to collisions. And then they can not return to base because the potential hill V_2e is too high.
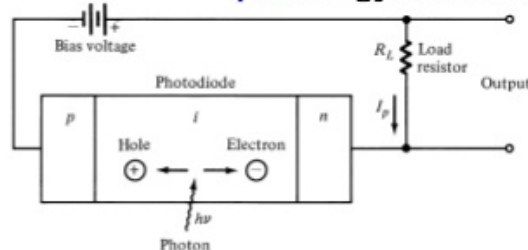
Bandgap theory of *pin* photodiode

The *pin* photodiode is given a reverse bias across the diode. The intrinsic layer (*i*) is lightly *n*-doped.

The *pin* Photodiode
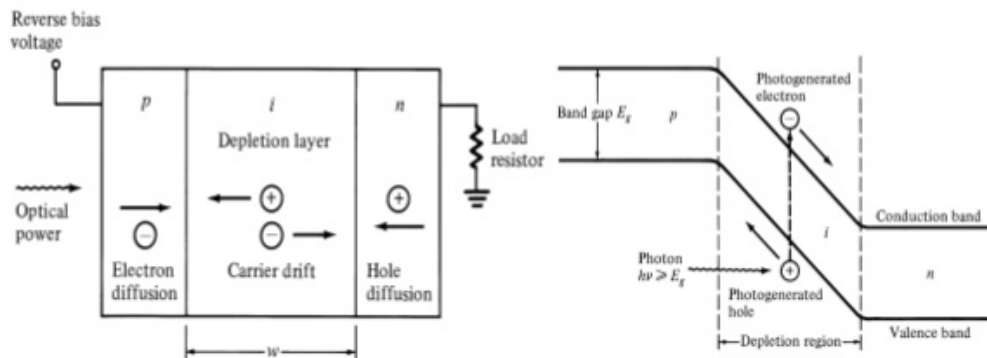
❑ *pin* photodiode circuit

❑ *pin* energy-band diagram

By Anurodh

Field-Effect (FET) transistor: FET is like a switch. It utilizes the gate voltage to control the channel current.