Section-A:

Answer No. -01: (i) b (ii) b (iii) c (iv) b (v) a (vi) a (vii) a (viii) c (ix) d (x) d

Answer No.-02(a):

Intercept along three crystallographic axes:	a/2	b/3	c/4
Division by unit translation	½	1/3	¼
Reciprocals	2	3	4
After clearing fractions	2	3	4

The required Miller indices of the plane are (234).

Answer No.-02(a): We have $\quad p^{-1} : q^{-1} : r^{-1} = h : k : l = 1 : 2 : 3$

Therefore $\qquad p : q : r = 1 : \frac{1}{2} : 1/3$; The ratio of actual lengths of the intercepts are:

$\qquad l_1 : l_2 : l_3 = pa : qb : rc = 1.21/1 : \qquad 1.84/2 : \qquad 1.97/3$

Since l_1 is given as 1.21 Å so $l_2 = 0.92$ Å and $l_3 = 0.657$ Å.

Answer 3(a):

An amorphous solid is a solid in which there is no long range order of the positions of the atoms. Amorphous material can also be produced by additives. An amorphous solid is a solid in which there is no long-range order of the positions of the atoms. (Solids in which there is long-range atomic order are called crystalline solids or morphous). Most classes of solid materials can be found or prepared in an amorphous form. For instance, common window glass is an amorphous ceramic, many polymers (such as polystyrene) are amorphous, and even foods such as cotton candy are amorphous solids. Amorphous materials are often prepared by rapidly cooling molten material. The cooling reduces the mobility of the material's molecules before they can pack into a more thermodynamically favorable crystalline state. Amorphous materials can also be produced by additives which interfere with the ability of the primary constituent to crystallize. For example addition of soda to silicon dioxide results in window glass and the addition of glycols to water results in a vitrified solid. In common terms, the term glass refers to amorphous oxides, and especially silicates (compounds based on silicon and oxygen). Ordinary soda-lime glass, used in windows and drinking containers, is created by the addition of soda and lime (calcium oxide) to silicon dioxide. Some amorphous metallic alloys can be prepared under special processing conditions (such as rapid solidification, thin-film deposition, or ion implantation), but the term "metallic glass" refers only to rapidly solidified materials.

Differences between Crystalline and Amorphous Solids

(i) **Characteristic Geometry:** In *crystalline* solids the particles (atoms, ions, or molecules) are definitely and orderly arranged thus these have characteristic geometry while amorphous solids do not have characteristic geometry.

(ii) **Melting Point:** A crystalline solid has a sharp melting point, i.e., it changes into liquid state at a definite temperature. On the contrary an amorphous solid does not have a sharp melting point. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt or sharp change from solid to liquid state. Therefore, amorphous solids are regarded as "liquids at all temperatures".

(iii) **Cooling curve:** Amorphous solids show smooth cooling curve while crystalline solids show two breaks in cooling curve. In the case of crystalline solids two break points 'a' and 'b' appear.

This is due to the fact that during crystallization process energy is liberated which compensates for the loss of heat, thus the temperature remains constant.

(iv) **Isotropy and Anisotropy:** Amorphous solids differ from crystalline solids and resemble liquids in many respects. The properties of amorphous solids, such as, electrical conductivity, thermal conductivity, mechanical strength, refractive index, coefficient of thermal expansion etc. are same in all directions. Such solids are known as isotropic. Gases and liquids are also isotropic. On the other hand, crystalline solids show these physical properties different in different directions. Therefore crystalline solids are called anisotropic. The anisotropy itself is a strong evidence for the existence of orderly molecular arrangement in crystals. For example, the velocity of light passing through a crystal is different in different directions. A ray of light entering in a crystal may split up into various components.

3(b) <u>primitive Unit cell:</u>   A Unit cell is the geometrical pattern
that forms the smallest unit of space lattice which when repeated
along the direction of the tree basis vectors generates the
space lattice itself.

A primitive unit cell is a unit cell with all the points in it
are at the vertices.

Since the basis vectors could be chosen in many ways,
there is no Uniquenness in the choise of the unit cell for a
given space lattice. Sometimes it becomes a matter of
convenience. For example let us consider a bravais lattice as
shown in figure. For the sake of simplicity we have taken here
in two ~~dimasion~~ dimensions.

we can imagine two ways of
identifying the unit cell in
this structure. One is, with $\vec{a_1}$ and $\vec{b_1}$
as the basis vectors in which case, the
Unit cell will be a parallelogram. Each
of the four points (lattice points) being located
at the vortex (the meeting point of the basis
vectors). Other one in the figure is with
the basis vectors as $\vec{a_2}$ and $\vec{b_2}$ which would
make a rectangle for the unit cell. But in this case, in addition
to the 4 points at the corners, there is one lattice point at the centre
which is not at the meeting points of the basis vector. This is
a nonprimitive cell. we can define primitive unit cell as the
smallest unit cell in volume that can be defined for a given lattice
and the set of linearly independent vectors that define a
primitive unit cell as a primitive basis vectors. The cubic
unit cell for the simple cubic lattice is also a primitive
unit cell because it contains the irreducible minimum one atom
in each such cell. The primitive unit cell for FCC structure
is a trigonal structure with $\alpha = \beta = \gamma = 60°$. A primitive unit
cell contains only one atom is true only in simple structures
which contains atoms of one kind only otherwise it will contain the
number of atoms associated with each basis contains.

The volume of a primitive unit cell is given by $V = [\vec{a} \cdot \vec{b} \times \vec{c}]$

Answer 3(c):

Miller indices form a notation system in crystallography for planes in crystal (Bravais) lattices. In particular, a family of lattice planes is determined by three integers h, k, and ℓ, the *Miller indices*. They are written $(hk\ell)$, and each index denotes a plane orthogonal to a direction (h, k, ℓ) in the basis of the reciprocal lattice vectors. The integers are usually written in lowest terms, i.e. their greatest common divisor should be 1. Miller index (100) represents a plane orthogonal to direction h; index (010) represents a plane orthogonal to direction k; and index (001) represents a plane orthogonal to ℓ.

There are also several related notations:

- The notation $\{hk\ell\}$ denotes the set of all planes that are equivalent to $(hk\ell)$ by the symmetry of the lattice.

  In the context of crystal directions (not planes), the corresponding notations are: $\langle h k l \rangle$ and $[h k l]$.

- $[hk\ell]$, with square instead of round brackets, denotes a direction in the basis of the *direct* lattice vectors instead of the reciprocal lattice; and

- similarly, the notation denotes the set of all directions that are equivalent to $[hk\ell]$ by symmetry $\langle h k l \rangle$.

Miller indices were introduced in 1839 by the British mineralogist William Hallowes Miller. The method was also historically known as the Millerian system, and the indices as Millerian,[2] although this is now rare.

There are two equivalent ways to define the meaning of the Miller indices: via a point in the reciprocal lattice, or as the inverse intercepts along the lattice vectors. Both definitions are given below. In either case, one needs to choose the three lattice vectors a_1, a_2, and a_3 that define the unit cell (note that the conventional unit cell may be larger than the primitive cell of the Bravais lattice, as the examples below illustrate). Given these, the three primitive reciprocal lattice vectors are also determined (denoted b_1, b_2, and b_3).

Then, given the three Miller indices h, k, ℓ, $(hk\ell)$ denotes planes orthogonal to the reciprocal lattice vector:

That is, $(hk\ell)$ simply indicates a normal to the planes in the basis of the primitive reciprocal lattice vectors. Because the coordinates are integers, this normal is itself always a reciprocal lattice vector. The requirement of lowest terms means that it is the *shortest* reciprocal lattice vector in the given direction.

Equivalently, $(hk\ell)$ denotes a plane that intercepts the three points a_1/h, a_2/k, and a_3/ℓ, or some multiple thereof. That is, the Miller indices are proportional to the *inverses* of the intercepts of the plane, in the basis of the lattice vectors. If one of the indices is zero, it means that the planes do not intersect that axis (the intercept is "at infinity").

Considering only $(hk\ell)$ planes intersecting one or more lattice points (the *lattice planes*), the perpendicular distance d between adjacent lattice planes is related to the (shortest) reciprocal

lattice vector orthogonal to the planes by the formula $\rightarrow d = \left[\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{\ell^2}{c^2} \right]^{-\frac{1}{2}}$

The related notation $[hk\ell]$ denotes the *direction*:

That is, it uses the direct lattice basis instead of the reciprocal lattice. Note that $[hk\ell]$ is *not* generally normal to the $(hk\ell)$ planes, except in a cubic lattice, as described below.

Answer NO. 3(d): Reciprocal lattice is a theoretical lattice associated with a crystal lattice. The reciprocal lattice points are obtained by drawing normals to each crystal plane from a common origin and lying at a distance equal to the reciprocal of interplaner spacing.

This reciprocal lattice is itself a Bravais lattice, and the reciprocal of the reciprocal lattice is the original

For an infinite three dimensional lattice, defined by its primitive vectors (a_1, a_2, a_3), its reciprocal lattice

determined by generating its three reciprocal primitive vectors. This method appeals to the definition, and

generalization to arbitrary dimensions. Curiously, the cross product formula dominates introductory mate-

crystallography. The above definition is called the "physics" definition, as the factor of 2π comes natural

the study of periodic structures. Each point (hkl) in the reciprocal lattice corresponds to a set of lattice

(hkl) in the real space lattice. The direction of the reciprocal lattice vector corresponds to the normal to

space planes. The magnitude of the reciprocal lattice vector is given in reciprocal length and is equal

to reciprocal of the interplanar spacing of the real space planes. The reciprocal lattice plays a fundamental

role in most analytic studies of periodic structures, particularly in the theory of diffraction. For Bragg reflec-

neutron and X-ray diffraction, the momentum difference between incoming and diffracted X-rays of a crystal

in reciprocal lattice vector. The diffraction pattern of a crystal can be used to determine the reciprocal vector

lattice. Using this process, one can infer the atomic arrangement of a crystal. consider any given space lattice (a real crystal crystal lattice) and apply the following:

① Form a common origin draw a normal to each crystal plane ② Set the length of each normal equal to or 2π times the reciprocal of the interplaner spacing d_{hkl} (3) Mark a point at the end of each each normal which represents the crystal plane. A collection of points obtain in this way corresponding to various planes forms a lattice array and is known as reciprocal lattice. The relationships between the direct and the reciprocal lattice parameters are given below as:

$$a^* = \frac{2\pi}{d_{100}} = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}\cdot(\vec{b}\times\vec{c})} \ , \quad b^* = \frac{2\pi}{d_{010}} = 2\pi\frac{\vec{c}\times\vec{a}}{\vec{a}\cdot(\vec{b}\times\vec{c})} \ ; \quad c^* = \frac{2\pi}{d_{001}} = 2\pi\frac{\vec{a}\times\vec{b}}{\vec{a}\cdot(\vec{b}\times\vec{c})}$$

Here a^*, b^* and c^* are the primitive translation vectors of reciprocal lattice. Reciprocal of SC lattice is SC lattice. The reciprocal lattice vectors of BCC are just the primitive vectors of FCC lattice.

Answer No-4 :

Matter can exist in solid state only because there are forces of interaction acting between the atoms when they are brought close to each other. From the very existance of solids, one may draw two general conclusions:
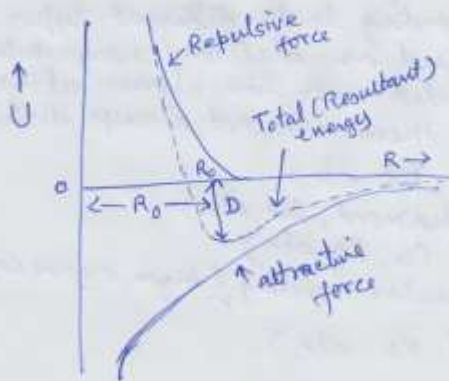
1. There must act attractive forces between the atoms or molecules in solid which keep them together.

2. There must be repulsive forces acting between the atoms or molecules as well, since large external pressure is required to compress a solid to any appreciable extent.

In order to illustrate the importance of both type of forces, let us consider the simplest system in this respect, for example, a single pair of atoms A and B which form a stable chemical compound. Let us assume that the potential ~~energy~~ energy of atom B due to the presence of atom A is given by an expression of the type $\boxed{U(r) = U_{attractive} + U_{repulsive}}$
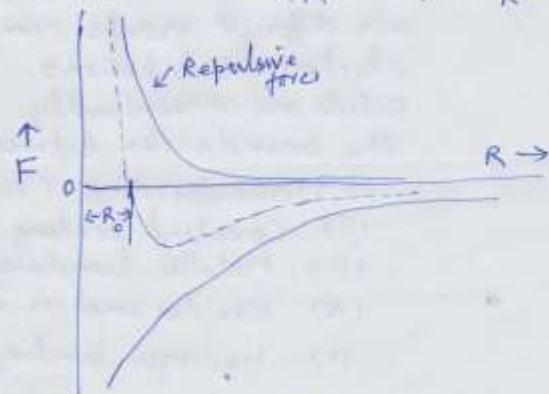
or

$$U(r) = -\frac{A}{R^n} + \frac{B}{R^m}$$ Where R is the distance

between the nuclei of the two atoms; A, B, n and m are constants characteristics of AB compound. The zero of the energy is chosen such that for infinite separation $(R=\infty)$ $U(R) = 0$. The first term which is negative, corresponds to the energy associated with the forces of attraction, the second positive term corresponds to the forces of repulsion. In fact the forces between the two atoms as function of interatomic distance R is given by $F(R) = -\frac{dU(R)}{dR} = -\frac{nA}{R^{n+1}} + \frac{mB}{R^{m+1}}$

Energy

Force

The stable configuration for the system corresponds to the minimum in $U(R)$ curve which occurs for a particular separation $R = R_0$. The corresponding energy is negative ($U(R) = -ve$); thus the positive quantity $D = -U(R)$ is the dissociation energy of compound AB i.e. the energy required to separate the two atoms. Assuming that the energy curve exhibits a minimum one may express the equilibrium distance R_0 and the corresponding __binding__ __energy__ $U(R_0)$ in terms of the constants A, B, n, and m by making use of the condition.

$$\left(\frac{dU}{dR}\right)_{R=R_0} = 0 \quad \text{i.e.} \quad R_0^{m-n} = \left(\frac{m}{n}\right)\left(\frac{B}{A}\right)$$

This condition is equivalent to the requirement that the attractive and repulsive forces are equal i.e. $F(R_0) = 0$.

Now
$$U(R_0) = -\frac{A}{R_0^n} + \frac{B}{R_0^m} = -\left(\frac{A}{R_0^n}\right)\left(1 - \frac{n}{m}\right)$$

Although the attractive and repulsive ~~energies~~ forces are equal in equilibrium, the attractive and repulsive energies are not equal since $m \neq n$. However if $m \gg n$, the total binding energy is essentially determined by the energy of attraction.

The forces acting between the atoms in solids are electrostatic in nature; they are determined essentially by the way in which the outer electron of the composing atoms are distributed in space. The physical properties of solids are determined to a large extent by the electron distribution and it is thus possible on an empirical basis to divide solids into different groups corresponding to the different types of electrons distributions. Based on electron/charge distribution solids are conveniently divided into five classes although the boundaries between them are not always distinct.

(i) Ionic bonding (NaCl, KF etc)
(ii) Covalent bonding (diamond, SiC etc)
(iii) Metallic bonding (Cu, Ag etc)
(iv) Van der waal or molecular bonding (Argon, organic crystals)
(v) Hydrogen bonding (ice etc)

Calculation of Cohesive energy:

The cohesive energy of ionic crystals is mainly due to electrostatic interaction and can be calculated on the basis of point charge model. The cohesive energy (U) of a crystal containing oppositely charged ions with charges z_1 and z_2 is sum of two terms; one due to attraction and the other due to repulsion as:

$$U = - \frac{A z_1 z_2 e^2}{4\pi\epsilon_0 R} + B \exp(-R/\rho) ;$$ Here A is known as

the Madelung constant and depends only on geometrical arrangement of ions in the crystal; B is repulsion constant; ρ is repulsion exponent and R is distance between two oppositely charged ions. The repulsion term accounts for the stability of ionic crystal without collapsing & areses from the fact that the ions with closed electron shells resist overlap of their electron clouds with neighbouring ions. The constant B and ρ are a measure of the strength and range of repulsive force.

For uni-univalent crystal (NaCl) $z_1 = z_2 = 1$

$$U = - \frac{A e^2}{4\pi\epsilon_0 R} + B \exp(-R/\rho)$$

Total energy per mole $$U = N \left[- \frac{A e^2}{4\pi\epsilon_0 R} + B \exp(-R/\rho) \right]$$

The potential energy at equilibrium separation (R_0) is given by

$$\boxed{U_0 = - \frac{A e^2 N}{4\pi\epsilon_0 R_0} \cdot \left(1 - \rho/R_0 \right)}$$

This equation gives us the cohesive energy (also lattice energy) of an ionic solid like NaCl. This is the amount of energy released during formation of NaCl crystal or the energy spent to separate the solid ionic crystal into its constituent ions. The value of ρ/R_0 for the alkali halides can be obtained experimentally from compressibility measurements of solids. The value of $R_0/\rho = \frac{18 R_0^4}{A e^2} \beta + 2$ where β is Bulk modulus.

The final expression for cohesive energy becomes

$$U = - \frac{N A e^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{1}{n} \right)$$ where n is known as Born exponent.

However, for an accurate calculations, the modified expression for the cohesive/lattice energy of MX-type solids is

$$U_c = \left[- \frac{A e^2}{4\pi\epsilon_0 R_0} + B \exp(-R_0/\rho) - \left(\frac{C}{R_0^6} + \frac{D}{R_0^8} \right) + \frac{9}{4} h \nu_{max} \right]$$

Answer No-05 :

The atoms in real crystal are not at rest indefinitely but they vibrate under the influence of a suitable thermal gradient or thermal energy. The internal energy of a solid increases by thermal (heat) energy. This is manifested mainly as - (i) the increase in the vibration of atoms (lattice vibrations) about their mean positions (actual lattice site) and (ii) the increase in the kinetic energy of free electrons. The lattice vibrations under influence of thermal energy is assumed as a series of superimposed sound waves or strain (elastic) waves or lattice waves with a frequency spectrum determined by the elastic properties of the crystal. The smallest unit of energy of a vibration corresponding this wave (a quantum of sound wave) is phonon. This quantum of energy of an elastic wave is called phonon in analogy with the photon which is the quantum of an electromagnetic wave. The sound wave or lattice wave is usually thought of as a wavelike disturbance that requires a medium (gas, liquid or solid) to propagate. A phonon is a packet of sound waves which behave live a massless particle with energy $h\nu$ and momentum h/λ where ν is the frequency of vibration and λ is the wavelength. The product of the wavelength and the frequency $\nu\lambda = \upsilon$ is the velocity of the sound wave. The important characteristics of phonons are as follows: (1) Phonons have dual nature ie wave and particle (wave particle duality which apply to photon also).
(2) phonons (like photons) are bosons and are not conserved; they can be either created or destroyed during collisions.
(3) phonons are indistinguishable particles and these particles obey Bose-Einstein statistics. The energy of a phonon is $h\nu$.
(4) The total energy of phonons which they acquire at finite temperature is actually the thermal energy of the solid because at this temperature, the solid is presumed to be full of phonons.
(5) Acoustic and optical phonons are two types of phonons which are associated with acoustic and optical mode of vibrations respectively.
(6) The phonon interaction is assumed as a scattering collision when the lattice vibrations is involved in an interaction not only is its energy always an integral multiple of $h\nu$, but also, at a time only a single phonon is excited or absorbed.

The acoustic and optical modes of lattice vibrations are already discussed in many text books and is a mathematical

ANSWER No- 6 (a)   **Hydrogen Bonding**

A hydrogen bond is the electromagnetic attractive interaction between polar molecules in which hydrogen (H) is bound to a highly electronegative atom, such as nitrogen (N), oxygen (O) or fluorine (F). The name *hydrogen bond* is something of a misnomer, as it is not a true bond but particularly strong dipole-dipole attraction, and should not be confused with a covalent bond.

These hydrogen-bond attractions can occur between molecules (*intermolecular*) or within different parts of a single molecule (*intramolecular*).[1] The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. This type of bond can occur in inorganic molecules such as water and in organic molecules like DNA and proteins.

Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C) compared to the other group 16 hydrides that have no hydrogen bonds. Intramolecular hydrogen bonding is partly responsible for the secondary and tertiary structures of proteins and nucleic acids. It also plays an important role in the structure of polymers, both synthetic and natural.

A hydrogen atom attached to a relatively electronegative atom is a hydrogen bond donor.[5] This electronegative atom is usually fluorine, oxygen, or nitrogen. An electronegative atom such as fluorine oxygen, or nitrogen is a hydrogen bond acceptor, whether it is bonded to a hydrogen atom or not. A example of a hydrogen bond donor is ethanol, which has a hydrogen bonded to oxygen; an example of hydrogen bond acceptor which *does not* have a hydrogen atom bonded to it is the oxygen atom on diethyl ether. A hydrogen attached to carbon can also participate in hydrogen bonding when the carbon atom is bound to electronegative atoms, as is the case in chloroform, $CHCl_3$.[6][7] The electronegative atom attract the electron cloud from around the hydrogen nucleus and, by decentralizing the cloud, leaves the atom with a positive partial charge. Because of the small size of hydrogen relative to other atoms and molecules, the resulting charge, though only partial, represents a large charge density. A hydrogen bond results when this strong positive charge density attracts a lone pair of electrons on another heteroatom, which becomes the hydrogen-bond *acceptor*.

The hydrogen bond is often described as an electrostatic dipole-dipole interaction. However, it also has some features of covalent bonding: it is directional and strong, produces interatomic distances shorter than sum of van der Waals radii, and usually involves a limited number of interaction partners, which can be interpreted as a type of valence. These covalent features are more substantial when acceptors bind hydrogens from more electronegative donors.

The partially covalent nature of a hydrogen bond raises the following questions: "To which molecule of atom does the hydrogen nucleus belong?" and "Which should be labeled 'donor' and which 'acceptor'? Usually, this is simple to determine on the basis of interatomic distances in the X–H Y system: X–F distance is typically ≈110 pm, whereas H Y distance is ≈160 to 200 pm. Liquids that display hydrogen bonding are called **associated liquids**. Hydrogen bonding is a special type of dipole-dipole attraction between molecules, not a covalent bond to a hydrogen atom. It results from the attractive force between hydrogen atom covalently bonded to a very electronegative atom such as a N, O, or F atom and anothe very electronegative atom. Hydrogen bond strengths range from 4 kJ to 50 kJ per mole of hydrogen bonds.
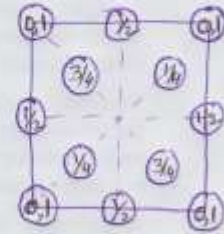
Answer No - 6(b)   Crystal Structure of diamond:

The crystal structure of diamond can be derived from the fcc lattice although the structure itself is not a closed packed one. Formally it may be described as being built up from two interpenetrating fcc lattices which are displaced with respect to one another along the body diagonal of the cube by one quarter of the length of the diagonal. One sublattice has its origin at the point (0 0 0) and the other at a point quarter of the way along the body diagonal (at the point $a/4, a/4, a/4$).

The diamond cubic structure is loosely packed, since each atom has only four nearest neighbours. If an atom is imagined to be at the centre of a regular tetrahedron, then its neighbours are on the four corners.

Diamond Structure

Positions of atoms from one face.

Answer No - 6(C):

The response of materials to temperature is known as thermal properties. The specific heat, thermal conductivity etc. are some important thermal properties of materials. The knowledge of lattice vibrations and related aspects are very important in understanding various thermal properties of materials. In general, specific heats of solids is measured at constant volume i.e. $C_v = \left(\frac{dE}{dT}\right)_v$ where E is the internal energy and T is the temperature. When some heat is supplied to a solid its temperature rises and its internal energy is increased. The increase in internal energy is manifested mainly as (i) an increase in the kinetic energy of free electrons and (ii) an increase in the vibration of atoms about their mean position. The corresponding specific heats are known as the lattice specific heat and the electronic specific heat respectively.

Thermal conductivity is a process in which heat is transferred from one part of the body to another as a result of temperature gradient. If the gradient is uniform, then the amount of thermal energy crossing a unit area in unit time is directly proportional to the temperature gradient:

$Q \propto \frac{dT}{dx}$ or $Q = k\left(\frac{dT}{dx}\right)$ Where proportionality constant k is known as thermal conductivity. In general transfer of heat both by $\bar{e}$ and phonons. Thermal conductivity $k = \frac{1}{3} v \lambda C_v$ where v is average velocity of electrons, λ is mean free path and C_v is specific heat.
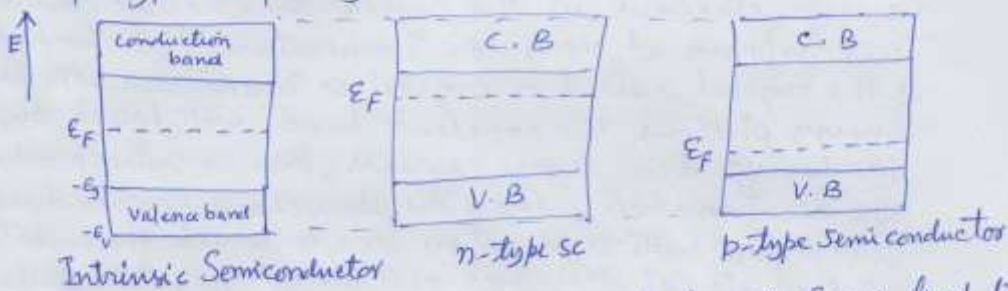
Answer NO- 6(d): Intrinsic Semiconductors are very pure materials free from impurity atoms; defects etc and crystallize in a manner that there are very few free electrons or holes at low temperature. These materials are in fact insulators at 0K. Since such a pure materials are rare, for all practical purposes very pure crystals are considered as intrinsic Semiconductors. Silicon and Germanium are two widely used elemental semiconductor having diamond structure. The atomic arrangement is such that each atom has four nearest neighbours and in tetrahedral bonding. The bonding is covalent and saturated leaving no free electrons in the crystal for electric conduction. This happens at very low temperature. If the temperature of the crystal raised or crystal is illuminated with high energy photons, the covalent bonds will break and thereby producing free-charge carriers; this is called production of electron-hole pair. The free charge carrier density increases with temperature due to which the resistance of the material decreases and we get negative temperature coefficient of resistance (NTCR). In case of intrinsic sc the energy gap is small ($Si = 1.1$ eV; $Ge = 0.68$ eV) and at very low temperature the conduction band is empty.

In an intrinsic Semiconductor the number of holes created in the valence band is equal to the number of electrons in the conduction band. In an intrinsic semiconductor the density of electrons (n) and holes (p) is equal and is n_i. If μ_e and μ_p are the electron and hole mobilities, the conductivity of intrinsic semiconductor is $\boxed{\sigma = |e| n_i (\mu_e + \mu_p)}$.

The Fermi level of an intrinsic semiconductor lies at the middle of the energy gap.

Let a few Ge and Si atoms be replaced by atoms of group-V elements (P, As ...). such atoms in the host crystal are called impurity atoms. When group-V, impurity atoms are in crystal lattice each atom will contribute four electrons towards the formation of covalent bonds, while the fifth electron will be loosely bound to the nucleus and therefore, can be ionized easily. As the impurity atoms can donate electrons to the conduction band, the impurity is called "donor type impurity and or simply donor impurity and the semiconductor is called as n-type Semiconductor.

However, if the impurity atoms belong to group III elements (Al, Ga, In) the covalent bonds will remain unsaturated i.e. the impurity atoms could provide three electrons per atom, Although for saturation of bonds four electrons per atom is necessary. The absence of an electron in the valence band means the presence of a hole in the valence band. The thermal energy may help in breaking saturated bonds. Impurity atoms capture the electrons, freed in the process and the hole will move from atom to atom. This kind of impurity atoms can accept electrons and therefore, called acceptor-type impurity or p-type impurity.

Intrinsic Semiconductor   n-type sc   p-type Semiconductor

In intrinsic n- and p-type semiconductors, the Fermi level lies halfway between E_c and E_d and between E_a and E_v, respectively at low temperature. For n-type of semiconductor, the position of Fermi level in the low temperature range is

$$E_{F_n} = \frac{E_d + E_c}{2} + \frac{KT}{2} \ln \frac{N_D}{N_c}$$ whereas in case of

p-type semiconductor $E_{F_p} = \frac{E_a + E_v}{2} + \frac{KT}{2} \ln \frac{N_A}{N_v}$ where N_A and N_D
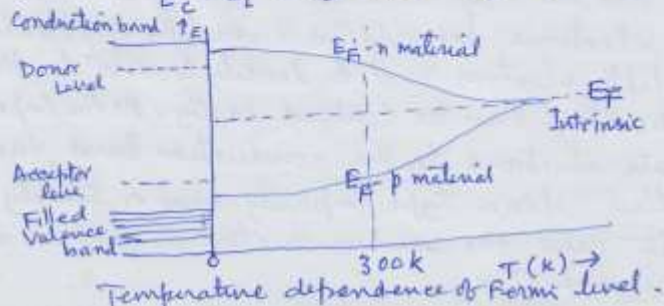
being the density of donors and acceptors respectively.

Expression for electron concentration in n-type semiconductors

is $$n = \sqrt{2 N_D} \left(\frac{2\pi m_e^* KT}{h^2} \right)^{3/2} \exp\left(- E_d / 2KT \right)$$ and expression

for hole concentration in p-type semiconductors is

$$p = \sqrt{2 N_A} \left(\frac{2\pi m_h^* KT}{h^2} \right)^{3/2} \exp\left(- E_a / 2KT \right)$$ where

$E_c - E_i = E_d$ and $E_i - E_v = E_a$.

Temperature dependence of Fermi level.
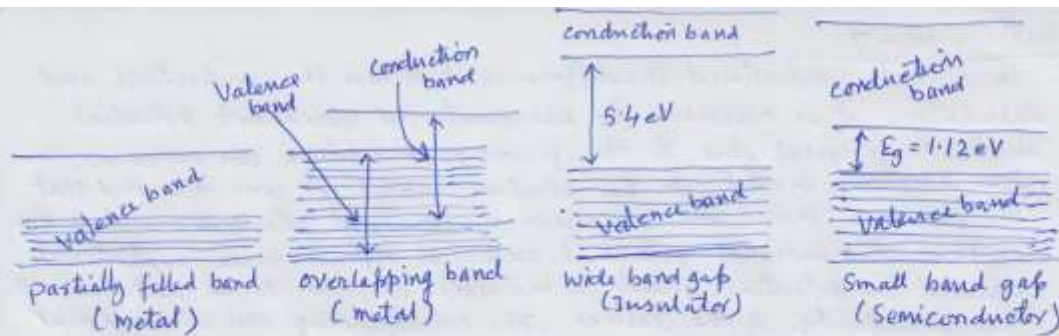
Answer No - 7

In order to understand the difference between the conductors and insulators, it is necessary to incorporate the variation of potential inside the crystal due to the presence of positive ion cores in the free electron model. In free electron model, it was assumed that the electrons move in a region of constant potential inside a one or three dimensional potential well. It appears more realistic to assume the potential inside a metallic crystal to be periodic with the periodicity of the lattice, The corresponding one dimensional Schrodinger equation can be written as:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}[E - V(x)]\psi = 0 \quad \text{where } V(x) = V(x+a); \quad \begin{array}{l} a = \text{lattice} \\ \text{constant} \end{array}$$

According to Bloch, the one dimensional solution of the schrodinger equation takes the form $\psi(x) = \exp(ikx) U_k(x)$. This represents the free electron wave modulated by the periodic function $U_k(x)$ where $U_k(x)$ is periodic with the periodicity of the crystal lattice. Making use of Bloch theorem and Kronig-Penney Model, the energy spectrum of the electron is found to comprise a set of contineous bands, separated by regions of forbidden energies which are called Energy gaps.

Motion of electrons in a periodic potential such as Kronig-Penney type gives rise to an energy spectrum which consists of allowed and forbidden bands. Each allowed energy band was found to contain a limited number of energy levels. Further, in compliance with the Pauli's exclusion principle, each energy level must be occupied with/by no more than two electrons. However, with a limited number of electrons in the atoms of a solid, it is expected that only the lower energy bands will be filled. The outermost energy band that is completely or partially filled is called the valence band in solids. The band that is above the valence band and is empty at 0K, is called the conduction band. Hence, according to nature of band occupation by electrons, all solids can classified broadly into two groups.

The first group includes solids in which there is a partially filled bands immediately above the uppermost filled (valence) band. This is possible in two ways. In first case, the valence band is only partially filled. In the second case, a completely filled valence band overlaps the partially filled conduction band.

The second group includes solids with empty bands lying above completely filled bands. The solids of this group are conventionally subdivided into insulators (dielectrics) and semiconductors depending on the width of the forbidden band. Insulators include solids with relatively wide forbidden bands. For typical insulators the band gap $E_g > 3$ eV. Diamond with $E_g = 5.4$ eV, boron nitride with $E_g = 4.6$ eV, Al_2O_3 with $E_g = 7.0$ eV etc are some typical examples of insulators having wide band gaps.

| partially filled band (metal) | overlapping band (metal) | wide band gap (Insulator) | small band gap (Semiconductor) |

On the otherhand, semiconductors include solids with relatively narrow (small) forbidden bands. For typical semiconductors $E_g \leq 1$ eV. Germanium (Ge) with $E_g = 0.7$ eV, Silicon with $E_g = 1.12$ eV, Indium antimonide with $E_g = 0.17$ eV, gallium arsenide (GaAs) with $E_g = 1.43$ eV etc. are some typical examples of important semiconductors.

The examples of half filled valence band solids are monovalent metals such as Lu, Ag and Au have one electron in the outermost shell. On the other hand, the divalent metals such as Be, Mg, Ca etc have overlapping valence and conduction bands. The band structure of trivalent metals such as Al, Ga etc is similar to that of monovalent metals.

Thus, the concept of energy bands in solids provides view points that are useful in formulating the distinction between metals, insulators and semiconductors.

Electrical conductivity of semiconductors:

The electrical conductivity of a pure and perfect semiconductor (Intrinsic Semiconductors) crystal at any temperature is due to intrinsic charge carriers ie. electrons and holes. This statement is not valid at very low temperatures because intrinsic semiconductor will behave like an insulator at very low temperature. Electrical conductivity due to electrons and holes in a pure and perfect semiconductor crystals is termed as Intrinsic conductivity. For a intrinsic Semiconductor $n = p = n_i$. So the intrinsic conductivity is given by $\sigma_i = n_i \cdot e \, (\mu_e + \mu_h)$ where μ_e and μ_h are mobilities of electron and hole. (Mobility is defined as the average drift velocity per unit electric field). so using expressions given in other parts of answers, we get

$$\sigma_i = 2e \left(\frac{2\pi k T}{h^2} \right)^{3/2} (m_e^* \cdot m_h^*)^{3/4} \exp\left(-\frac{E_g}{2kT}\right) (\mu_e + \mu_h)$$

at higher temperatures, when the semiconductor is intrinsic, the scattering is dominated by phonons. In this case, mobility is proportional to $T^{-3/2}$, we get $\sigma_i = \sigma_i(0) \exp(-E_g/2kT)$ where

$$\sigma_i(0) = 2e \left(\frac{2\pi k T}{h^2} \right)^{3/2} (m_e^* \cdot m_h^*)^{3/4} (\mu_e + \mu_h)$$

This pre-exponential constant $(\sigma_i(0))$ is practically independent of temperature. As $T \to \propto \Rightarrow \sigma_i \to \sigma_i(0)$. Taking the logarithm, we obtain.

$$\ln \sigma_i = \ln \sigma_i(0) - \frac{Eg}{2kT}$$

By plotting $\ln \sigma_i$ with inverse of temperature, one can determine the band gap (Eg).

In an extrinsic semiconductor, either n- or p-type impurity is present. Let us consider n-type semiconductor, the carrier concentration is given by

$$n = \sqrt{2N_D} \left(\frac{2\pi m_e^* kT}{h^2} \right)^{3/2} \exp\left(-\frac{Eg}{2kT}\right).$$

In n-type semiconductors, majority charge carriers of electrons and electrical conduction is due to flow of electrons when electric field is applied to it, is given by

$$\sigma_e = \frac{J}{E} = \frac{neV}{E} = ne\mu_e$$

So

$$\sigma_e = \sqrt{2N_D} \, e \left[\frac{2\pi m_e^* kT}{h^2} \right]^{3/2} \mu_e \exp\left(-\frac{Ed}{2kT}\right)$$

or

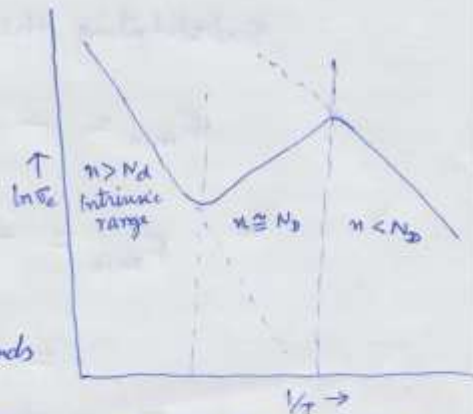$$\sigma_e = \sigma_e(0) \exp\left(-\frac{Ed}{2kT}\right)$$ Where $\sigma_e(0)$ is pre-exponential constant and

is very weakly dependent on temperature as compared to the exponential term. The mobility of n-type semiconductors $(n \ll N_D)$ at low temperatures is due to ionized impurities and is proportional to $T^{3/2}$. Taking logarithm we get, $\boxed{\ln \sigma_e = \ln \sigma_e(0) - \frac{Ed}{2kT}}$.

In most of the semiconductors, both the phonon scattering and the impurity ionization scattering take place. The former is dominates at higher temperatures and latter at low temperatures. However, in the intermediate temperature range neither mechanism is strong. This is the saturation region and corresponds to $n \simeq N_D$.

Similarly, we can derive expression for p-type semiconductors also.

A plot of σ_e as a function of $1/T$ for an n-type semiconductor.

Answer No - 08:

Given $R_0 = 3 A° = 3 \times 10^{-10}$ m, $D = -U_e = 4 \times 1.6 \times 10^{-19}$ J, $n = 2$, $m = 10$

At equilibrium $F = 0 = -\left(\frac{dU}{dR}\right)$ or $\frac{nA}{R_0^{n+1}} = \frac{mB}{R_0^{m+1}}$

or $R_0 = \left(\frac{mB}{nA}\right)^{\frac{1}{m-n}}$ or $A = \frac{5 R_0^2}{4} \times D = 7.2 \times 10^{-38}$ J m^2

Further, we know that at eq^m separation, the net force is zero

$$F = -\left(\frac{dU}{dR}\right)_{R=R_0} = -\frac{2A}{R_0^3} + \frac{10B}{R_0^{11}} = 0$$

or $B = \frac{A \times (R_0)^8}{5} = \frac{7.2 \times 10^{-38} \times (3 \times 10^{-10})^8}{5} = 9.44 \times 10^{-115}$ J m^{10}

Further, we know that $F(R) = -\frac{dU}{dR} = 0$ will be minimum or maximum when $\frac{dF}{dR} = 0$ and $R = R_c$ (at critical separation). Thus

$$\frac{dF}{dR} = \frac{d^2U}{dR^2} = +\frac{6A}{R_c^4} - \frac{110B}{R_c^{12}} = 0$$

Substituting the value of B/A from above and simplifying this we have

$$R_c = \left(\frac{22}{6}\right)^{1/8} \times R_0 = 3.53 A°$$

Now, $F(R) = -\frac{dU}{dR} = -\frac{2A}{R^3} + \frac{10B}{R^{11}}$ is minimum when $R = R_c$

therefore

$$F_{min} = -\frac{2A}{R_c^3} + \frac{10B}{R_c^{11}} = -\frac{2A}{R_c^3}\left[1 - \frac{10B}{2AR_c^8}\right]$$

Substituting the value of (B/A) in above eq^n, we get

$$F_{min} = -\frac{2A}{R_c^3}\left[1 - \left(\frac{R_0}{R_c}\right)^2\right]$$

So

$$F_{min} = -\frac{2 \times 7.2 \times 10^{-38}}{(3.53 \times 10^{-10})^3}\left[1 - \left(\frac{3}{3.53}\right)^8\right]$$

$$= -0.238 \times 10^{-8} \text{ J/m}$$

$$F_{min} = -0.238 \times 10^{-8} \text{ N}$$

This is the force needed to dissociate the molecule.

— x —