

Imperfections in a Crystal

An ideally perfect crystal is one which has the same unit cell and contains the same lattice points throughout the crystal. The term imperfection or defect means the deviation of the ideally perfect crystal from the periodic arrangement of its constituents. There are two types defects

1. Point Defects
2. Line defects.

Point Defects:- If the deviation occurs because of missing atoms, displaced atoms, the imperfection is named as a point defect. This defect is due to the result of imperfect packing during the original crystallisation or arise from thermal vibrations of atoms at elevated temperature because with increase in thermal energy there is increased probability of individual atoms jumping out of their positions of lowest energy.

Schottky Defects. These defects arise if some of the lattice points in a crystal are unoccupied. The points which are unoccupied are called lattice vacancies. The existence of two vacancies, one due to a missing Na^+ ion and the other due to a missing Cl^- ion in a crystal of NaCl. The crystal, as a whole, remains neutral because the number of missing positive and negative ions is the same.

Schottky defects appear generally in ionic crystals in which the positive and the negative ions do not

differ much in size. eg NaCl.

Because of Schottky defects, the crystal is in a position to conduct electricity to a small extent by an ionic mechanism. The existence of vacancies also enables easy movement of atoms or ions in the crystal changing places with one another. This accounts for the phenomenon of diffusion in solids.

Frenkel Defects. These defects arise when an ion occupies an interstitial position between the lattice points. This is shown for the crystal of AgBr. In AgBr crystal, one of the Ag^+ ions occupies a position in the interstitial space rather than its own

appropriate site in the lattice. Though a vacancy is created in the lattice, the crystal remains neutral since the number of positive ions is the same as the number of negative ions. ZnS

is another crystal in which Frenkel defects appear. Zn^{2+} ions are trapped in the interstitial space leaving vacancies in the lattice. Frenkel

defects appear in crystals in which the negative ions are much larger than positive ions. Crystals with Frenkel defects shows conduction of electricity and the phenomenon of diffusion in solids.

Metal Excess Defects. The Colour Centres.

If a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour. This yellow colour is due to the formation of a non-stoichiometric compound of sodium chloride in which there is slight excess of sodium ions. Some sodium metal gets doped into the sodium chloride crystal each atom of which gets ionised into Na^+ and e^- due to crystal energy. This electron occupies a site that would otherwise be occupied by a chloride ion.

The crystal as a whole is neutral but there is an excess of Na^+ ion in the crystal. There are six Na^+ sites adjacent to the vacant site occupied by the electron. The extra electron is thus shared between all the six Na^+ ions which implies that this electron is not localised at the vacant Cl^- site. Also this electron is similar to the delocalised π electrons present in molecules containing conjugate double bonds. Light is absorbed when this delocalised electron makes an easy transition from its ground state to an excited state. As a result, the non-stoichiometric form of sodium chloride appears coloured. Because of this, the sites occupied by the extra electrons are known as colour centres. These are also called F-centres.

Another example of metal excess defects is the formation of magenta coloured non-stoichiometric compound of KCl by exposing the crystals of KCl to K metal vapour.

Metal Deficiency Defects. In this type of defects, one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring two charges instead of one. There is a deficiency of the metal ions although the crystal as a whole is neutral. This type of defect is generally found amongst the compounds of transition metals which can exhibit variable valency. Crystals of FeO, FeS and NiO show this type of defects. The existence of metal deficiency defects in the crystal of FeO is illustrated in the following figure.

All types of point defects result in the creation of vacancies or holes in the lattices of crystals. The presence of holes lowers the density as well as the lattice energy or the stability of the crystals. The presence of too many holes may cause a partial collapse of the lattice.

Line Defects: Dislocations

This type of imperfection occurs when the periodicity of the atomic lattice array is interrupted along certain directions in a crystal. Such interruptions occur along rows of a crystal structure and are called line defects. The most common type of line defect within a crystal is a dislocation. The presence of dislocations results in easy deformation of a crystal under the influence of a shear stress.

Edge dislocations. This type of defect arises when there is a slight mismatch in the orientation of adjacent parts of the growing crystals resulting in the introduction of an extra row of atoms. The edge of the atomic plane terminates within the crystal instead of passing all the way through. Under the impact of the shear, the dislocation moves across the crystal in such a way that the top half of the crystal is displaced one lattice distance with respect to the lower half. The motion of an edge dislocation under shear is shown in the diagram.

Near the edge dislocation, the atoms are pushed together above the edge and pulled apart below the edge. In this way the impurity atoms with larger diameters than the parent atoms tend to concentrate below the edge and the impurity atoms with smaller diameters tend to concentrate above the edge. As a result of binding of ^{the} impurity at the dislocation, it is more difficult to move a dislocation in an impure material. This is the reason why alloys require greater shear force for permanent deformation than do the pure metals.

Screw Dislocations. The formation of a screw dislocation can be visualised by cutting a rubber stopper parallel to its axis and then pushing on one end so that a jog is created on the other end. If initially the stopper contained atoms at regular lattice points, deformation would convert the parallel planes of atoms normal to the axis into a kind of spiral ramp. Such a displacement of the atoms constitutes what is known as screw dislocation. A screw dislocation helps in easy crystal growth because atoms can be added at the step. Screw dislocations result in easy deformation of crystal in the same way as is done by edge dislocations. In practice, real dislocations are mixtures of edge dislocations and screw dislocations. Dislocations provide for preferred sites within a crystal for chemical reactions and physical changes (such as phase transformation, precipitation or etching). The point of emergence of a dislocation at the surface of a crystal is a site of enhanced chemical reactivity.

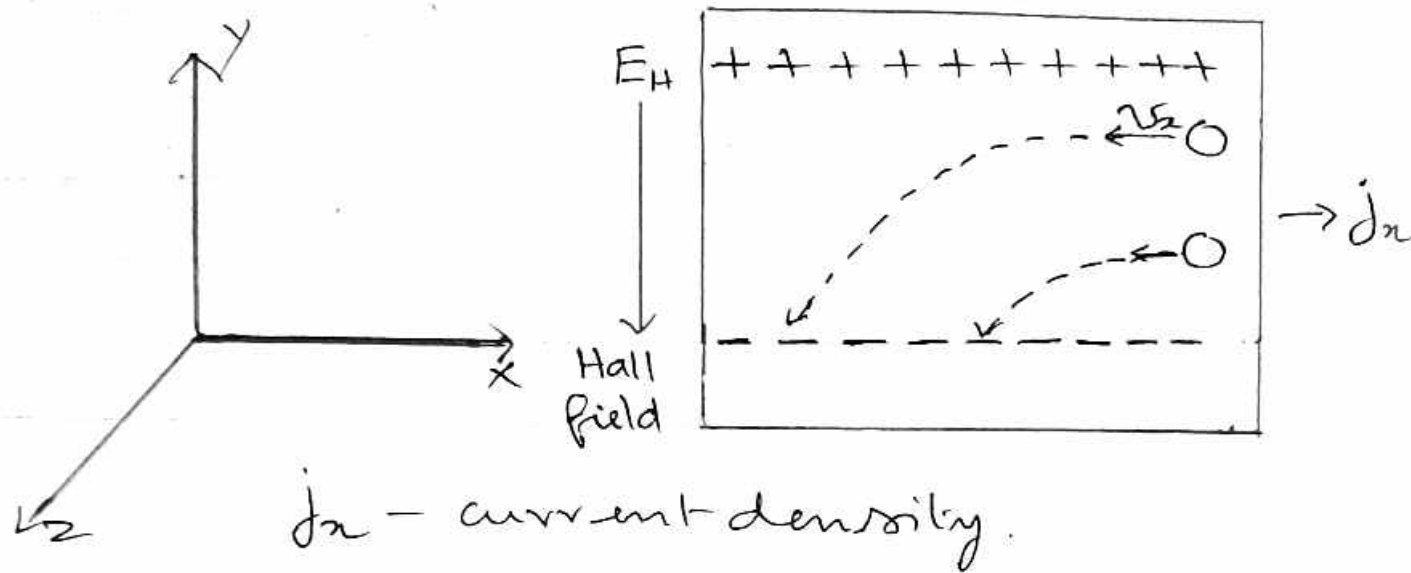
Electrical Properties. Hall effect

If a sample of conducting material is placed in a uniform magnetic field and a current i is passed along the length of the conductor, a voltage is found to develop at right angles to both ^{the} direction of the current flow and that of the magnetic field. This voltage is known as the Hall voltage and its value is found to develop on the magnetic field strength and on the current passed.

Consider a specimen in the form of a rectangular cross-section carrying a current I_x in the x direction. If a uniform magnetic field B_z is applied along the z -axis, it is found that an emf develops along the y -axis (ie) in a direction perpendicular to I_x and B_z . This voltage is called the Hall voltage.

Let us first consider the situation before the magnetic field is introduced. There is an electric current flowing in the positive x -direction, which means that the conduction electrons drifting with a velocity v_x in the negative x -direction. When the magnetic field is introduced, the Lorentz force F_L causes the electrons to bend downward as shown in the fig. As a result, electrons accumulate on the lower surface producing a net

negative charge there. Simultaneously a net positive charge appears on the upper surface, because of the deficiency of electrons there. The combination of positive and negative surface charges creates a down_{ward} field, which is called the Hall field.



Piezoelectricity.

When certain crystals like quartz, Lithium Niobate, Barium Titanate, Rochelle Salt etc are stretched or compressed along certain axis (known as mechanical axis) an electrical potential difference is produced along a perpendicular axis (known as electrical axis). This is known as Piezo-electricity. This type of electricity occurs only in crystals without centre of symmetry. Piezoelectricity is due to net change in polarization that results from mechanical deformation of a crystal.

In the fig the position of the ion A is obviously a centre of symmetry. When the array has been compressed by a mechanical force, the ion B has been moved closer to ion A thus decreasing the BA dipole moment. However, the ion C has also been moved closer to ion A which decreases the CA dipole moment by the same amount in the opposite direction to the decrease in BA moment. Thus no net change in polarisation results from mechanical deformation of a crystal with centre of symmetry.

In a structure without centre of symmetry the dipole moment is determined using an ion plus a fraction of each of its nearest neighbours (here we take one third of each of the charges of the three nearest neighbours). When strained, this structure develops net dipole moments due to each ion and its neighbours.

Photoconductivity

Photoconductivity is an optical and electrical phenomena in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation such as visible light, ultraviolet light, infrared light or gamma radiation. When light is absorbed by a material such as semiconductor, the number of free electron and electron holes increases and raises its electrical conductivity. To cause excitation, the light that strikes the semiconductor must have enough energy to raise electrons across the band gap. When a bias voltage and a load resistor are used in series with the semiconductor, a voltage drop across the load resistor can be measured when the change in electrical conductivity of the material varies the current through the circuit.

Examples

- The conductive polymer - polyvinyl carbazole used in photocopying.
- Lead Sulphide - Used in infrared detection applications.
- Selenium - employed in early television and Xerography.

10
When a photoconductive material is connected as a part of a circuit, it functions as a resistor whose resistance depends on the light intensity. In this context the material is called a photoresistor (also called light dependent or photoconductor)

Negative photoconductivity: Some materials exhibit deterioration in photoconductivity upon exposure to illumination. One prominent example is hydrogenated amorphous silicon (Si-H) in which a metastable reduction in photoconductivity is observable.

Ferroelectricity

Below a certain temperature it is found that some materials spontaneously acquire an electric dipole moment. These materials exhibit a hysteresis curve P versus E and this can be explained by a domain hypothesis

The transition to the ferroelectric state is a cooperative phenomenon which is accompanied by specific heat anomaly or by a latent heat and it appears that at the transition temperature the crystal lattice spontaneously distorts to a more complicated structure which possesses a permanent electric dipole moment.

There are three main types of crystal structure which exhibit ferroelectricity: (1) Rochelle salt structure, typified by Rochelle salt $\text{NaK}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4\text{H}_2\text{O}$ (2) the perovskite group, consisting mainly of titanates and niobates, of which barium titanate, BaTiO_3 is the extensively studied one. (3) the dihydrogen phosphates and arsenates, eg. KH_2PO_4

In ferroelectrics there are large regions which are characterized by the alignment of the electric field. For this reason the electric field turns the whole of such region in the direction of the field

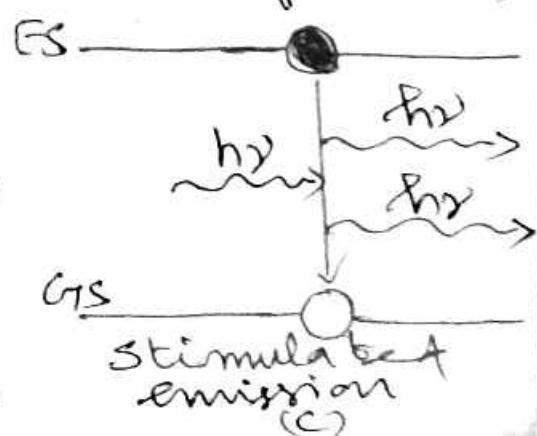
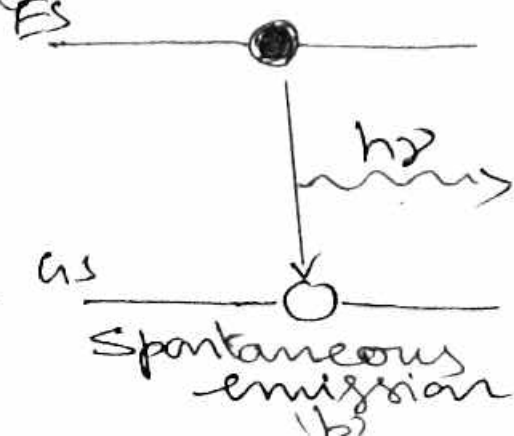
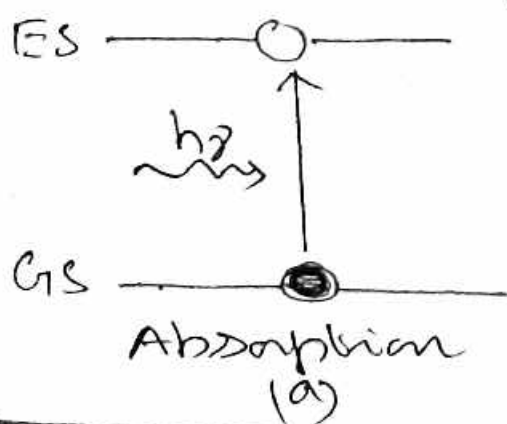
and overcomes the thermal agitation that tends to scatter the electric dipoles in different directions. The aligned electric fields of such regions of ferroelectric combined with the external electric field increasing the flux density thousands of times. The charge of ~~the~~ a condenser is increased the same number of times when a ferroelectric is used instead of air.

When an electric field is applied to a specimen of a ferroelectric crystal, the polarization first rises rapidly with applied field to a value above which the dependence is linear. Linear extrapolation to zero field gives P_s , the saturation or spontaneous polarization. On subsequently reducing the field to zero, remanent (residual) polarization P_r remains. The negative field to reduce the polarization to zero is called the coercive field and represented by E_c . The existence of a dielectric hysteresis loop in a dielectric material implies that the substance possesses a spontaneous polarization and the value of P_s depends upon a number of factors such as the dimensions of the specimen, the temperature, the texture of the crystal, the thermal and electrical properties of the crystal.

The Laser

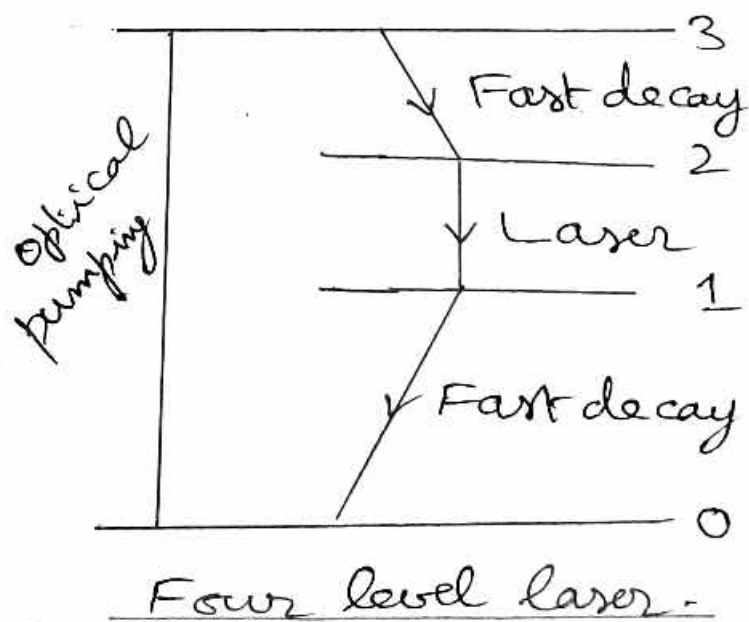
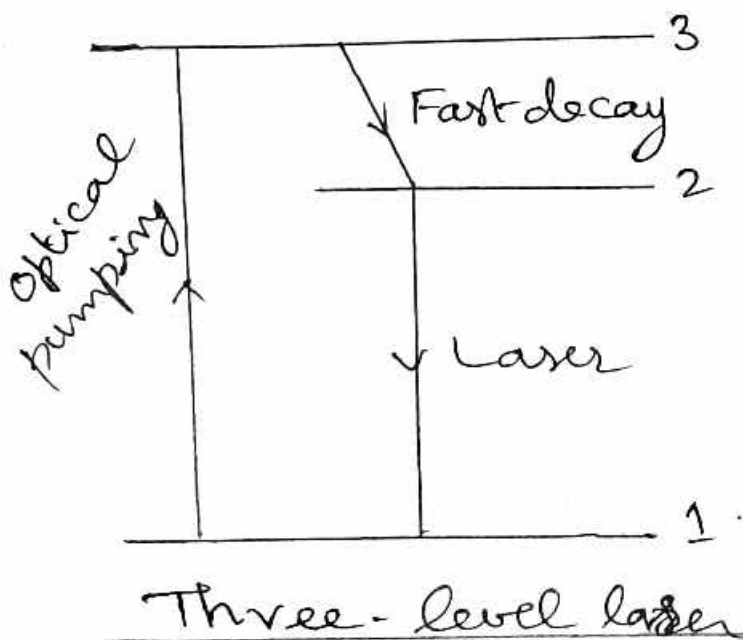
The laser is an acronym for light amplification by stimulated emission of radiation. Laser action involves the increasing the population of the excited state over that of the ground state. called population inversion. The population inversion can be achieved through optical pumping by electrical discharges or by a chemical reaction that produces molecules in the excited state. Once the population inversion has been achieved, the impinging photon has a greater likelihood of encountering an excited state molecule rather than one in the unexcited state. As a consequence, photon emission rather than photon absorption is stimulated. Thus, the emitted photon beam has greater intensity than the incident intensity. This is called laser action.

The laser action can be best understood by considering the following fig. Here the ground state molecule absorbs a photon and is raised to the excited state (Fig a). In fig (b) the excited molecule undergoes spontaneous emission of a photon;



reverting to the ground state. In Fig. (c), the impinging photon encounters a molecule that is already in the excited state. It stimulates the molecule to ~~the~~ revert to the ground state by emitting a second photon. Here laser action has been achieved.

Three types of energies can be delivered to an absorbing system to bring about population inversion. These are radiation energy, collision energy and chemical energy. Population inversion can occur in systems which have three or four energy levels. In a three level system at the correct frequency populates energy level 3, the process being called optical pumping. If the system then rapidly decays to energy level 2, a population inversion is to occur between energy levels 2 and 1.



Population inversion occurs better in system having four energy levels. If such a system is raised to energy level 3 by pumping and there is fast decay to energy level 2, a population inversion occurs between energy levels 2 and 1. The laser beam is highly directional, monochromatic and coherent.

Birefringence

Birefringence is the optical property of a material having a refractive index that depends on the polarization and propagation direction of light. These optically anisotropic materials are said to be birefringent (or birefractive). The birefringence is often quantified as the maximum difference between refractive indices exhibited by the material. Crystals with non-cubic crystal structures are often birefringent, as are plastics under mechanical stress.

Birefringence is responsible for the phenomenon of double refraction whereby a ray of light, when incident upon a birefringent material, is split by polarization into two rays taking slightly different paths

Luminescence: Materials which can absorb photons through their energy levels can also emit them back, and if the radiation lies in visible region the phenomenon is called luminescence. If the time delay between absorption and re-emission is less than 10^{-8} s the material is said to be fluorescent and if longer the material is phosphorescent. In luminescence the exciting photons have greater energy than the emitted photons. For re-emission to take place effectively, producing luminescence phenomenon, there must be suitable energy levels in the band gap and such levels are produced by impurities are called activators and co-activators. Activators have energy levels near the valance band, whereas co-activators have energy levels near the conduction band. For example, in ZnS , Cu is used as the activator and Cl as the co-activator. The activator provides intermediate energy levels for the emitting electrons to fall. The co-activator acts as a trap for the electrons thereby governing the time delay time between absorption and emission process. Luminescence excited by photons is called photoluminescence, when excited by certain chemical reactions it is called chemiluminescence.

Magnetic Properties

The force F acting between two magnetic dipoles of strength m_1 and m_2 separated by a distance R , is given by

$$F = m_1 m_2 / \mu R^2$$

where μ is a constant characteristic of the medium and is called magnetic permeability of the medium. Magnetic permeability measures the tendency of the magnetic lines of force to pass through the medium, compared with their tendency to pass through vacuum for which $\mu = 1$. A substance is said to be diamagnetic when $\mu < 1$ and paramagnetic when $\mu > 1$. Thus a diamagnetic substance is less permeable to the magnetic lines of force than a vacuum. The magnetic lines of force deflect away from a diamagnetic sample whereas they deflect towards a paramagnetic sample.

The magnetic properties of matter are discussed in terms of the magnetic field intensity vector, H and magnetic induction B . When a substance is placed in a magnetic field, the magnetization M i.e. the magnetic moment per unit volume, is related to B and H by the relation

$$B = \mu_0 (H + M) \quad \text{--- (1)}$$

where μ_0 is the permeability of vacuum

$$\text{Also } B = \mu H \quad - (2)$$

From eqns (1) and (2)

$$M = H \left[\frac{\mu}{\mu_0} - 1 \right] = H (\mu_r - 1)$$

where μ_r is the relative permeability of the medium.

A very important quantity, magnetic susceptibility is defined as

$$\chi = \frac{M}{H} = \mu_r - 1$$

For diamagnetic solids, the relative permeability $\mu_r < 1$ so that χ is negative. Also χ is independent of magnetic field intensity and temperature. eg. Copper, graphite, antimony and bismuth. For paramagnetic substances such as Al, Pt $\mu_r > 1$ so that χ is positive. Also χ is independent of magnetic field intensity and decreases with increase in temperature.

For ferromagnetic solids (such as Fe, Co, Ni) μ_r and χ are very high, their values ranging between 200 and 100000. χ depends upon the magnetic field intensity, the temperature and previous history of the sample.

Ferromagnetism and Antiferromagnetism

Some paramagnetic solids at low temperatures undergo a transition to a state in which large domains of spins are aligned parallel to each other ($\uparrow\uparrow\uparrow\uparrow\uparrow$). This cooperative alignment gives rise to very strong magnetization. The ferromagnetic transition occurs at the Curie temperature and results in ferromagnetism. On the other hand, in some other solids, the cooperative effect leads to alternating spin orientations ($\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$) giving rise to low magnetization. The antiferromagnetic transition occurs at the Neel temperature and results in anti-ferromagnetism, when the alignment of magnetic moments is compensatory and the resulting magnetic moment is zero.

Ferrimagnetism

When the magnetic moments are aligned in parallel and antiparallel directions but there is some resultant magnetic moment ($\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow$) they are called ferrimagnetic substances. eg Fe_3O_4 , $MgFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$ etc. All the magnetically ordered solids (ferro, anti-ferro and ferrimagnetic) transfer to paramagnetic state at higher temperature due to randomisation of their spins.