4.DEFECTS IN CRYSTALS

Introduction: In actual crystals, imperfections or defects are always present and their nature and effects are important in understanding the properties of crystals.

The properties of materials which are not affected by the presence of defects in crystals are termed as the structure-insensitive properties. Ex: stiffness, density and electrical conductivity.

The properties of materials which are affected by the presence of defects in crystals are termed as the structure-sensitive properties. Ex: mechanical strength, crystal growth, magnetic hysteresis, dielectric strength, conduction in semiconductors, e.t.c.

The structural imperfections can be classified on the basis of their geometry as point, line, surface and the volume imperfections. The common types of point defects in solid materials can be divided into 3 classes:

(1) lattice site defects such as vacancies and interstitial defects
(2) compositional defects and
(3) electronic defects

Line defects may be classified as

(1) edge dislocation and
(2) screw dislocation

Surface defects may be classified as

(1) external surface defect represented by the discontinuity at the surface and
(2) internal surface defect like grain boundaries, tilt boundaries, twin boundaries and stacking fault etc.

Volume defects occur due to the presence of air bubbles, internal cracks and empty spaces in crystals.

Thermal Vibrations: Mathematically, atoms in a perfect lattice should occupy exactly the sites to which they are attached. No crystal is perfectly rigid, since it can be deformed by finite forces. It is possible to displace the atoms from their ideal sites with a finite expenditure of energy due to thermal vibrations. The frequency of vibration is almost independent of temperature, but the amplitude increases with increasing temperature. When the vibrations become strong enough the atoms may break the bonds between them. Since the atoms interact with one another they tend to vibrate in synchronism. The thermal vibration of atoms of a solid, does not seriously disturb the perfect structure of the crystal.

Point Defects: point imperfections are lattice errors at isolated lattice points. They are imperfect point-like regions in the crystal and, therefore, they may be referred to as zero-dimensional imperfections. A point imperfection arises because of the absence of a matrix atom(an atom that would be present in a perfect crystal), the presence of an impurity atom or a matrix atom in the wrong place.

Vacancy Defect: It is the simplest point defect in a crystal. This refers to a missing atom or vacant atomic site. Such defects may arise either from imperfect packing during the original crystallization or from thermal vibration of the atoms at high temperatures. When thermal energy due to vibration is increased there is an increased probability that individual atoms will jump out of their positions of lowest energy. Vacancies may be single or two.

Interstitialcies: In a closely packed structure, if the atomic packing factor is low, an extra atom may be lodged or introduced within the crystal structure. This is known as interstitial. An atom can enter the interstitial void or space between the regularly positioned atoms only when it is substantially smaller than the parent atoms, otherwise it will produce atomic distortions. Interstitials may be single, di and tri interstitials.

Schottky Defect and Frenkel Defect: In non-metallic crystals, the formation of a vacancy involves a local readjustment of charge in the surrounding crystal such that charge neutrality is maintained in the crystal. If in an ionic crystal there is a vacancy in a positive-ion site, charge neutrality may be achieved by creating vacancy in a neighbouring negative-ion site. Such a pair of vacant sites is called schottky defect.

On the other hand, if the charge neutrality is maintained by having a positive ion in an interstitial position, the pair constitutes a Frenkel defect.

Close-packed structures have fewer interstitials and Frenkel defects than vacancies and Schottky defects, as additional energy is required to force the atoms in their new positions.

As a result of thermal fluctuations, vacancies are produced and destroyed constantly in crystal. As a result the disorder increases resulting in an increase in the entropy. In thermal equilibrium, a certain number of lattice vacancies are always present which can be estimated as follows:

Let E_v be the energy required to take an atom from the lattice site.

$n E_v$ – increase in energy associated with the generation of n isolated vacant sites.

Total number of ways in which n-atoms can be picked up from the crystal consisting of N atoms is given by

$$P = N ! / (N – n) ! n ! \quad \text{----------(1)}$$

Since disorder increases due to the creation of n vacancies the increase in entropy is given by

$$S = K_B \log P$$

$$= K_B \log [N ! / (N – n) ! n !] \quad \text{----------(2)}$$

Increase in entropy further produces a change in free energy F.

$$F = U – T S$$

$$= n E_v - K_B T \log [N ! / (N – n) ! n !] \quad \text{----------(3)}$$

According to Sterling's approximation,

$$\text{Log } x ! = x \log x - x \quad \text{----------(4)}$$

Using eq (4) in eq (3),we get

$$F = n E_v - K_B T [N \log N - N - \{ (N - n) \log (N - n) - (N - n) \} - \{ n \log n - n \}]$$

$$= n E_v - K_B T [N \log N - N - (N - n) \log (N - n) + N - n - n \log n + n]$$

$$= n E_v - K_B T [N \log N - (N - n) \log (N - n) - n \log n]$$

Free energy in thermal equilibrium at constant volume must be minimum w.r.to change in n,

$$[\partial F / \partial n]_T = 0 = E_v + K_B T [- (N - n) \{ 1 / (N - n) \} - \log (N - n) + n (1 / n) + \log n]$$

$$= E_v + K_B T [- 1 - \log (N - n) + 1 + \log n]$$

$$= E_v - K_B T [\log (N - n) - \log n]$$

$$= E_v - K_B T \log [(N - n) / n]$$

$$\therefore \quad E_v = K_B T \log [(N - n) / n]$$

$$E_v / K_B T = \log [(N - n) / n]$$

$$(N - n) / n = e^{E_v / K_B T}$$

$$n = (N - n) / e^{E_v / K_B T} = (N - n) e^{-(E_v / K_B T)}$$

If $n << N$, we can neglect n in (N – n) , so that

$$n \cong N e^{-(E_v / K_B T)} \quad \text{----------(5)}$$

Therefore n represents the number of vacancies created in the crystal.

If $n E_v = 1$ eV and T = 1000K, then $n/N = e^{-11.6} = 9.1 \times 10^{-6} \cong 10^{-5}$

The equilibrium concentration of vacancies decreases as the temperature decreases.

Equilibrium Concentration Of Schottky defect: In ionic crystals, the formation of paired vacancies is most favoured ie, an equal number of positive and negative ion vacancies are produced. The formation of pairs makes it possible to keep the surface of the crystal electrostatically neutral.

The different ways in which n separated pairs can be formed are

$$P = [N ! / (N - n) ! n !]^2 \quad \text{----------(1)}$$

Increase in entropy is given by

$$S = K_B \log P$$

$$= K_B \log [N ! / (N – n) ! n !]^2 \quad \text{----------(2)}$$

Increase in entropy further produces a change in free energy F.

$$F = U – T S$$

$$= n E_P - K_B T \log [N ! / (N – n) ! n !]^2 \quad \text{----------(3)}$$

where E_P is the energy of formation of a pair

According to Sterling's approximation,

$$\log x ! = x \log x – x \quad \text{----------(4)}$$

Using eq (4) in eq (3),we get

$$F = n E_P –2 K_B T [N \log N – N -\{ (N – n) \log (N – n) – (N – n) \}- \{ n \log n – n \}]$$

$$= n E_P – 2 K_B T [N \log N – N - (N – n) \log (N – n) + N – n - n \log n + n]$$

$$= n E_P – 2 K_B T [N \log N – (N – n) \log (N – n) – n \log n]$$

Free energy in thermal equilibrium at constant volume must be minimum w.r.to change in n,

$$[\partial F / \partial n]_T =0= E_P +2K_B T [(N – n) \{ -1 / (N – n) \}- \log (N – n) + n (1 / n) + \log n]$$

$$= E_P + 2 K_B T [- 1 – \log (N – n) + 1 + \log n]$$

$$= E_P - 2K_B T [\log (N – n) – \log n]$$

$$= E_P - 2K_B T \log [(N – n) / n]$$

$$\therefore \quad E_P = 2 K_B T \log [(N – n) / n]$$

$$E_P / 2K_B T = \log [(N – n) / n]$$

$$(N – n) / n = e^{Ep / 2 K_B T}$$

$$n = (N – n) / e^{Ep / 2 K_B T} = (N – n) e^{-(Ep / 2 K_B T)}$$

If $n << N$, we can neglect n in (N – n) , so that

$$n \cong N e^{-(Ep / 2 K_B T)} \quad \text{----------(5)}$$

Equilibrium Concentration Of Frenkel defects:

Let in a perfect crystal,

E_i be the energy required to displace an atom from a regular lattice site to an interstitial position

N_i be the number of interstitial atoms

N be the number of atoms

The total number of ways in which n Frenkel defects can be formed can be given by

$$P = [N ! / (N – n) ! n !] \times [N_i ! / (N_i – n) ! n !] \quad \text{----------(1)}$$

Since disorder increases due to the creation of Frenkel defects, the increase in entropy is given by

$$S = K_B \log P$$

$$= K_B \log [\{ N ! / (N – n) ! n ! \} x \{ N_i ! / (N_i – n) ! n ! \}] \quad \text{----------(2)}$$

Increase in entropy further produces a change in free energy F.

$$F = U – T S$$

$$= E_i - K_B T \log [\{ N ! / (N – n) ! n ! \} x \{ N_i ! / (N_i – n) ! n ! \}] \quad \text{------(3)}$$

According to Sterling's approximation,

$$\text{Log } x ! = x \log x – x \quad \text{----------(4)}$$

Using eq (4) in eq (3),we get

$$F = E_i - K_B T [N \log N – N -\{ (N – n) \log (N – n) – (N – n) \}- \{ n \log n – n \}+ N_i \log N_i – N_i -\{ (N_i – n) \log (N_i – n) – (N_i – n)\}- \{n \log n – n \}]$$

$$= E_i - K_B T [N \log N – N - (N – n) \log (N – n) -N + n - n \log n + n + N_i \log N_i – N_i - (N_i – n) \log (N_i – n) + N_i – n - n \log n + n]$$

$$= E_i - K_B T [N \log N – (N – n) \log (N – n) + N_i \log N_i - (N_i – n) \log (N_i – n) – 2 n \log n]$$

Free energy in thermal equilibrium at constant volume must be minimum w.r.to change in n,

$$[\partial F / \partial n]_T = 0 = E_i - K_B T \log [(N – n) (N_i - n) / n^2]$$

$$= E_i - K_B T \log [(N – n) (N_i - n) / n^2]$$

$$\therefore \quad E_i = K_B T \log [(N - n) (N_i - n) / n^2]$$

$$E_i / K_B T = \log [(N - n) (N_i - n) / n^2]$$

If $n << N$ and $n << N_i$,

$$\text{then } E_i \cong K_B T \log (N N_i / n^2)$$

Thus $E_i \cong K_B T [\log (N N_i) - 2 \log n]$

$$\log n = \tfrac{1}{2} \log (N N_i) - E_i / 2K_B T$$

$$n = (N N_i)^{1/2} \exp (- E_i / 2K_B T)$$

Therefore n should be proportional to $(N N_i)^{1/2}$.

Line Imperfections: If a plane of atoms lies only partway through a crystal, the edge of such a plane is a defect in the form of a line, and is known as dislocation. There are two types of dislocation (1) Edge dislocation and (2) Screw dislocation.

In a perfect crystal, atoms are arranged in both vertical and horizontal planes parallel to the side faces full length, but ends in between, within the crystal then it is called edge dislocation. Because of dislocation, just above the discontinuity, atoms are squeezed and are in a state of tension. The distorted configuration extends all along the edge into the crystal. Thus as the region of maximum distortion is centered around the edge of the incomplete plane, this distortion represents a line imperfection called an edge dislocation.

If the extra plane of atoms is from top of the crystal, this dislocation is called as positive dislocation and is represented by ‘ ⊥ ‘ . If the extra plane of atoms is from bottom of the crystal, this dislocation is called as negative dislocation and is represented by ‘ T ‘ .

Burgers Vector: The magnitude and the direction of the displacement are defined by the vector called the Burgers vector. To determine the Burger vector, Burger circuit has to be constructed.

FIG.

Let us consider one perfect crystal and another crystal with edge dislocation. In the perfect crystal, starting from the point P, we go up by 6 steps, then move towards right by 5 steps, and move down by 6 steps and finally move towards left by 5 steps to reach the starting point P, the Burger circuit gets closed. When the same operation is performed on the dislocated crystal, we end up at Q instead of the starting point P. In order to close the Burger’s circuit an

extra step **QP** has to be made. The magnitude and the direction of the step defines the Burgers vector. The Burgers vector is perpendicular to the edge dislocation line.

Screw Dislocation: Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line.

FIG.

In screw dislocation, the Burger vector **b** is parallel to the dislocation line.