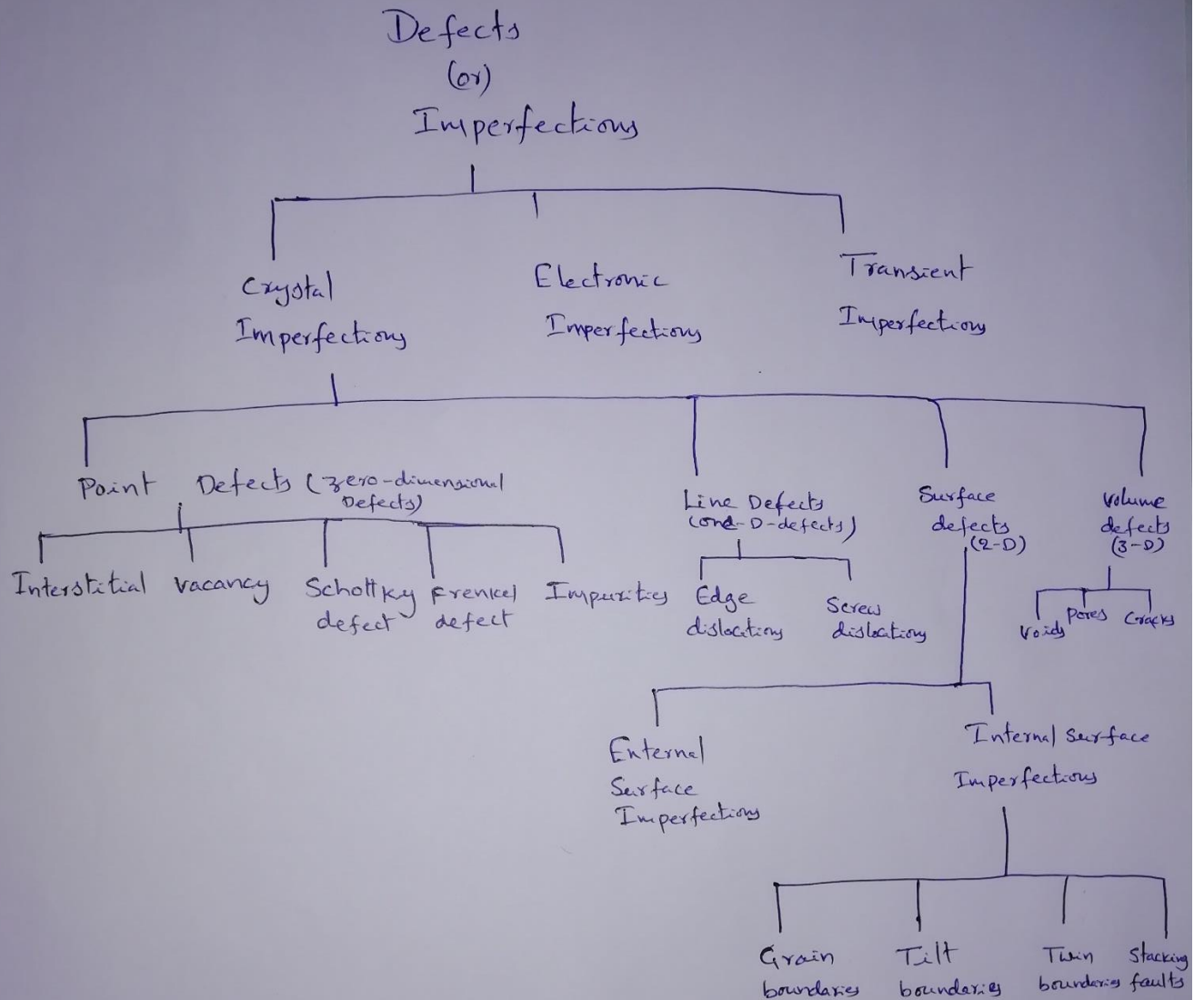
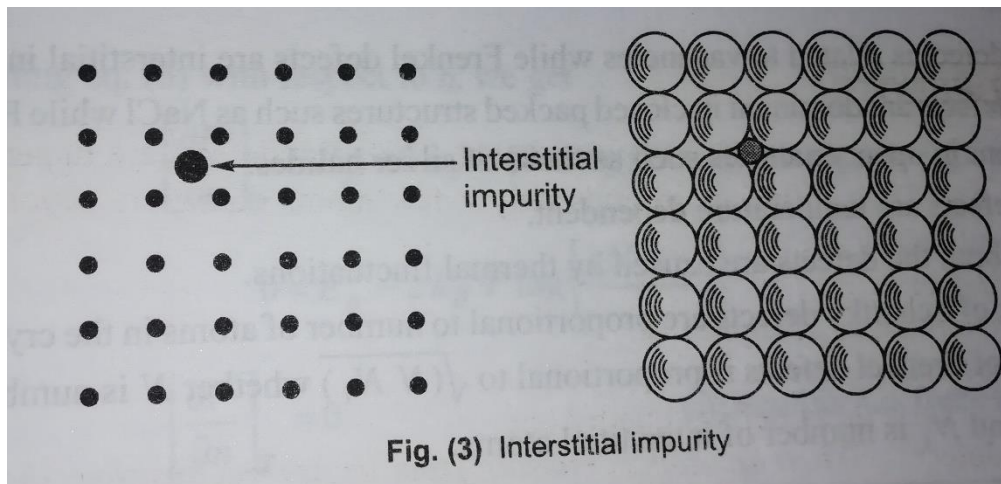
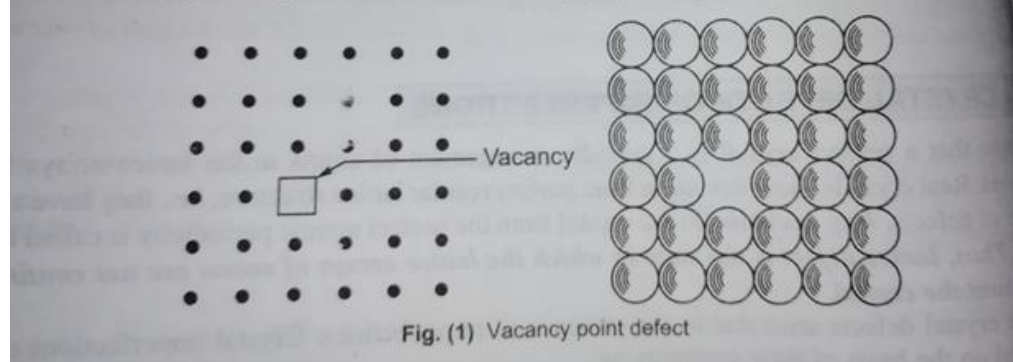


Defects in crystals  
(or)  
Imperfections in crystals

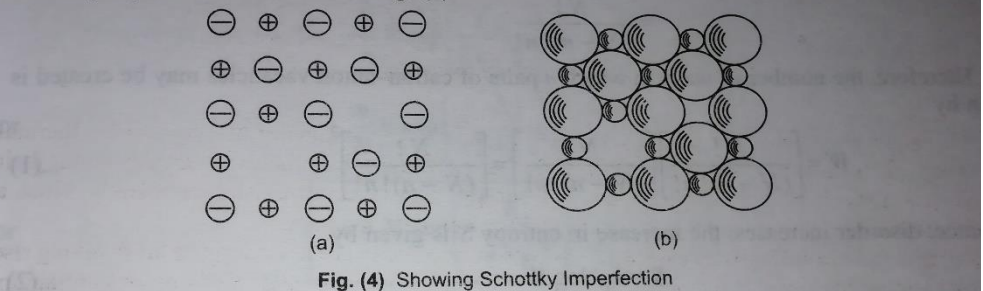




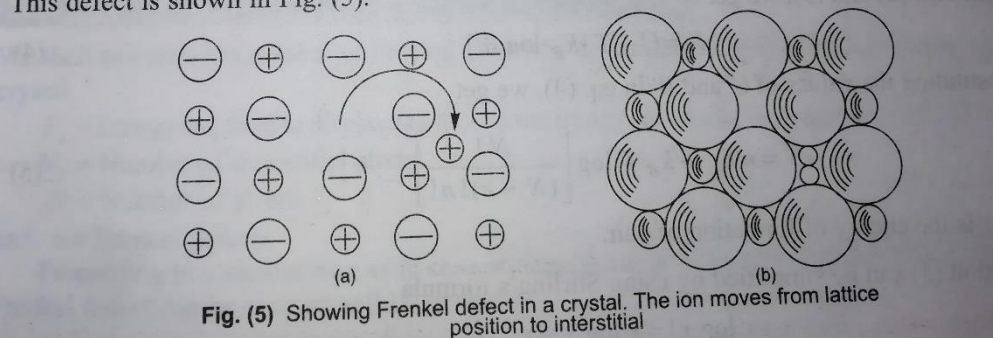
(a) Vacancy defect: When an atom is missing from its normal position, then the defect is called as vacancy point defect. This is shown in Fig. (1).



crystal as a whole. Thus, if there is a vacancy in a positive ion-site, the charge neutrality may be achieved by creating vacancy in neighbouring negative-ion site. Such a pair of vacant sites is called **Schottky defect**. This is shown in Fig. (4).



When an atom is transferred from its regular lattice site to an interstitial position (void between atoms, i.e., the position not normally occupied by an atom) is called as **Frenkel defect**. This defect is shown in Fig. (5).



vacancy is created, this vacancy is called

**(b) Substitutional impurity defect:** A foreign atom may replace a regular atom giving rise to substitutional impurity. Pentavalent or trivalent impurity atoms doped in silicon or germanium are also substitutional impurities in the crystal. The substitutional impurity is shown in Fig.

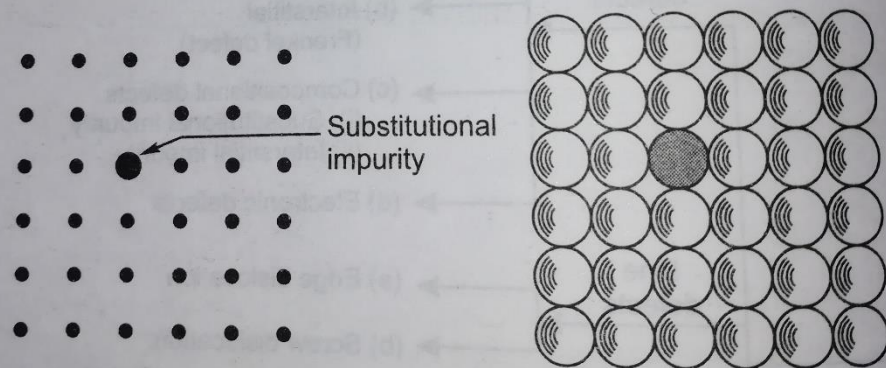
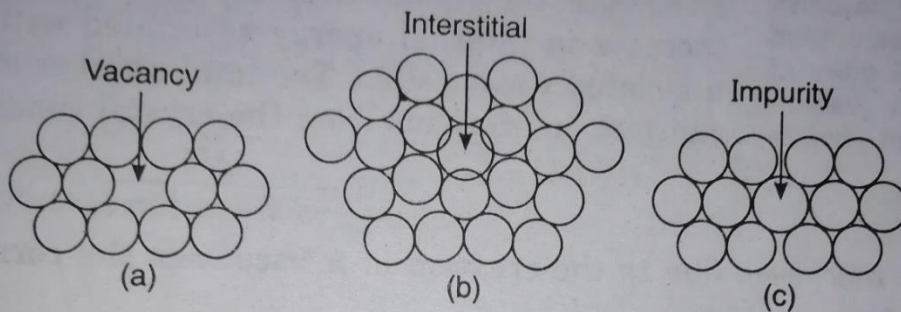
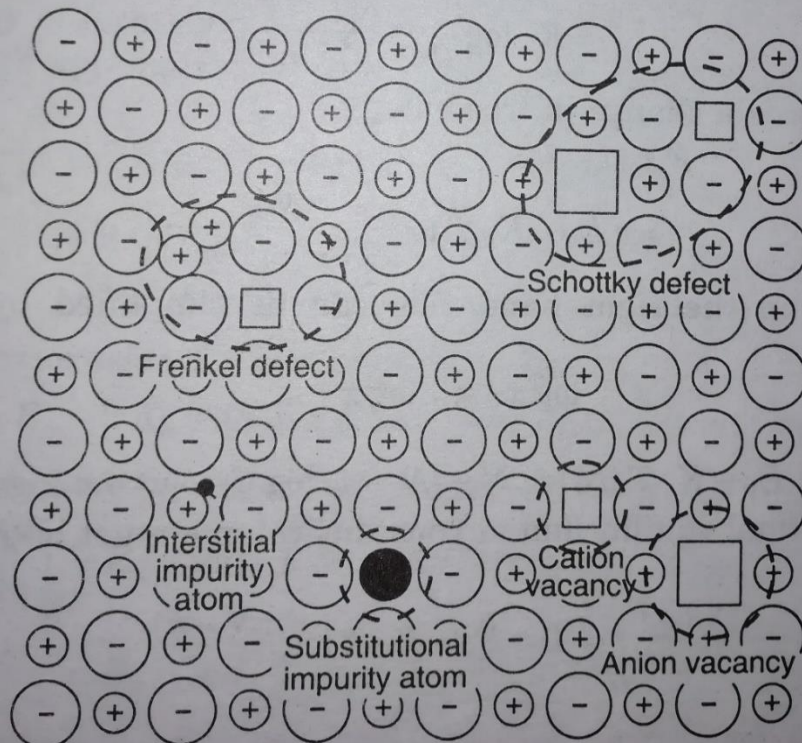


Fig. (2) Substitutional impurity



Three common point defects. (a) vacancy, (b) interstitial, (c) impurity.





Consider a perfect crystal composed of equal numbers of positively and negatively charged ions. In order for a cation vacancy to occur, a positive ion must somehow migrate out of its proper position in the structure to the crystal's exterior. If only positive ions migrate out of the crystal and collect on its surface, the surface will become positively charged. This positive surface charge opposes the migration of additional positive ions out of the crystal's interior. Simultaneously, the excess negative charge created inside the crystal is conducive to the formation of negative vacancies. In the absence of external forces, therefore, the number of oppositely charged vacancies inside a crystal tends to be equal.

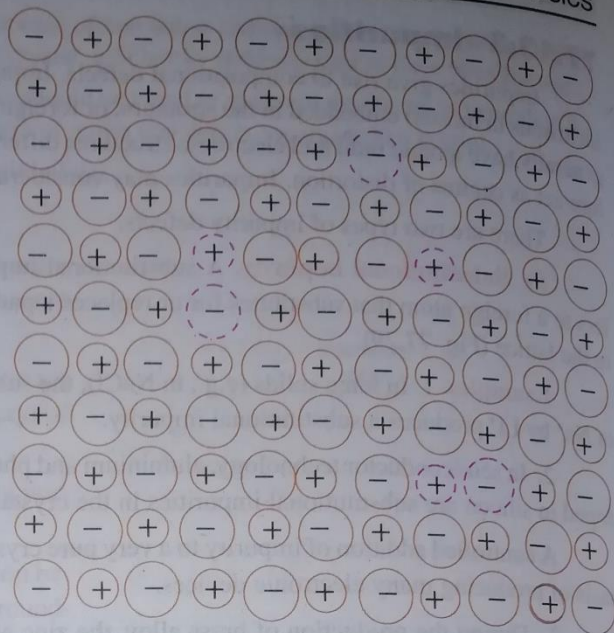


Fig. 77.31

Suppose that the crystal contains a total of  $N$  atoms.

Suppose that  $n$  Schottky defects are produced by removing  $n$  cations and  $n$  anions from the crystal's interior.

The different ways in which each kind of ion can be removed is given by

$$\frac{N(N-1)(N-2)\dots(N-n+1)}{n!} = \frac{N!}{(N-n)!n!} \quad \dots(1)$$

The number of cation and anion vacancies are equal.

So different ways in which  $n$  Schottky defects can be formed is obtained by squaring the expression in Eq. (1).

$$\therefore P = \left[ \frac{N!}{(N-n)!n!} \right]^2 \quad \dots(2)$$

The creation of  $n$  Schottky defects increases the crystal's entropy, according to the Boltzmann relation, by an amount

$$S = k \ln \left[ \frac{N!}{(N-n)!n!} \right]^2 \quad \dots(3)$$

Let  $E_p$  be the energy required to remove a pair of atoms from the crystal's interior to the surface.

Total change in internal energy =  $E = nE_p$ .

Here,  $n$  is the number of vacancy pairs.

This, in turn, produces a change in Helmholtz free energy

$$\begin{aligned} F &= E - TS \\ &= nE_p - kT \ln \left[ \frac{N!}{(N-n)!n!} \right]^2 \end{aligned} \quad \dots(4)$$

The logarithmic term in Eq. (4) containing factorials can be simplified by using Stirling's formula,  $\ln x! \approx x \ln x - x$ .

$$\begin{aligned}
 \ln \left[ \frac{N!}{(N-n)!n!} \right]^2 &\approx 2[\ln N! - \ln(N-n)! - \ln n!] \\
 &= 2[N \ln N - N - (N-n) \ln(N-n) + (N-n) - n \ln n + n] \\
 &= 2[N \ln N - (N-n) \ln(N-n) - n \ln n]. \quad \dots(5)
 \end{aligned}$$

When equilibrium is attained at a given temperature  $T$ , the Helmholtz free energy is constant and its first derivative is, therefore, equal to zero.

$$\begin{aligned}
 \left( \frac{\partial F}{\partial n} \right)_T &= 0 = E_p - 2kT [\ln(N-n) - \ln n] \\
 &= E_p - 2kT \ln \frac{N-n}{n} \quad \dots(6)
 \end{aligned}$$

Here the partial differentiation is with respect to  $n$  since the total number of atomic positions in the crystal  $N$  is not altered.

$$E_p = 2kT \ln \frac{N-n}{n} \quad \dots(7)$$

$$\frac{N-n}{n} = e^{E_p/2kT} \quad \dots(8)$$

or

The number of Schottky defects in a crystal is much smaller than the number of atoms; that is,  $n \ll N$  and  $N-n \approx N$ .

Eq. (8) reduces to

$$n \approx N e^{-E_p/2kT} \quad \dots(9)$$

Eq. (9) is used to determine the approximate number of defects present at any temperature.

**Derivation of an Expression for the Number of Frenkel Defects**

Eq. (9) is used to determine the approximate number of defects present at any temperature. ... (9)

# **15 To Derive an Expression for the Number of Frenkel Defects at a given Temperature**

In Frenkel defect, an atom is transferred from a lattice site to an interstitial position, a position normally occupied by an atom (Fig. 77.32).

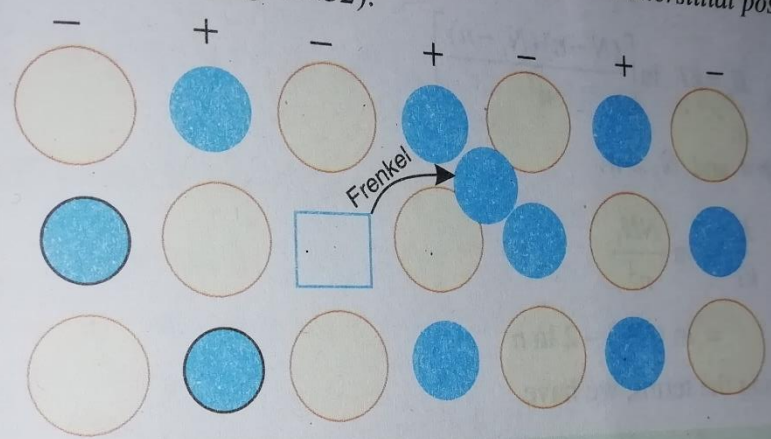


Fig. 77.32

In a perfect crystal, the energy required to displace an atom from its proper position to an interstitial position is  $E_i$ .

Suppose there are  $N$  atoms in the crystal and  $N_i$  interstitial positions in its structure.

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



$$P = \frac{N!}{(N-n)!n!} \frac{N_i!}{(N_i-n)!n!}$$

The corresponding increase in entropy due to the creation of Frenkel defects is given by ... (1)

$$S = k \ln \left\{ \left[ \frac{N!}{(N-n)!n!} \right] \times \left[ \frac{N_i!}{(N_i-n)!n!} \right] \right\}$$

The amount of energy required to produce  $n$  Frenkel defects is

$$E = nE_i$$

The change in the Helmholtz free energy produced by the creation of  $n$  Frenkel defects is

$$F = E - TS$$

$$\therefore F = nE_i - kT \ln \frac{N!}{(N-n)!n!} \frac{N_i!}{(N_i-n)!n!} \quad \dots (2)$$

The factorial terms are simplified by using Stirling's formula

$$\ln x! = x \ln x - x.$$

$$\begin{aligned} \ln \frac{N!}{(N-n)!n!} + \ln \frac{N_i!}{(N_i-n)!n!} &\approx N \ln N + N_i \ln N_i \\ &- (N-n) \ln (N-n) - (N_i-n) \ln (N_i-n) - 2n \ln n. \end{aligned} \quad \dots (3)$$

Substituting (3) into (2), we get

$$F = nE_i - kT [N \ln N + N_i \ln N_i - (N-n) \ln (N-n) - (N_i-n) \ln (N_i-n) - 2n \ln n] \quad \dots (4)$$

Differentiating Eq. (3) with respect to  $n$ ,

$$\left( \frac{\partial F}{\partial n} \right)_T = E_i - kT \ln \frac{(N-n)(N_i-n)}{n^2} \quad \dots (5)$$

At equilibrium  $(\partial F / \partial n)_T = 0$ .

$$\therefore E_i = kT \ln \left[ \frac{(N-n)(N_i-n)}{n^2} \right]$$

Now,  $N \gg n$  and  $N_i \gg n$ .

$$\begin{aligned} \therefore \frac{E_i}{kT} &\approx \ln \frac{NN_i}{n^2} \\ &= \ln (NN_i) - 2 \ln n \end{aligned}$$

Rearranging the terms, we have

$$\ln n = \frac{1}{2} \ln (NN_i) - \frac{E_i}{2kT} \quad \dots (6)$$

$$\therefore n = (NN_i)^{\frac{1}{2}} e^{-E_i/2kT}$$

In silver halides, the most prevalent defects below 700 K are Frenkel defects.

### 77.16 To Derive an Expression for the Number of Vacancies at a Given Temperature

In all crystals vacancies are present. The main cause for these defects is thermal agitation. Suppose  $E_v$  is the energy required to take an atom from a lattice site inside the crystal to a lattice site on the surface. Suppose there are  $N$  atoms.

The amount of energy required to produce  $n$  number of isolated vacancies is

$$E = nE_v \quad \dots(1)$$

The total number of ways in which  $n$  number of atoms can be removed out of  $N$  number of atoms in a crystal on to the surface is

$$P = \frac{N!}{(N-n)!n!} \quad \dots(2)$$

The increase in entropy due to formation of  $n$  vacancies is

$$S = k \ln P = k \ln \left\{ \frac{N!}{(N-n)!n!} \right\}$$

The change in the Helmholtz free energy produced by the creation of  $n$  vacancies is

$$F = E - TS$$

$$\therefore F = nE_v - kT \ln \left\{ \frac{N!}{(N-n)!n!} \right\}$$

$$F = nE_v - kT [\ln N! - \ln (N-n)! - \ln n!]$$

The factorial terms are simplified by using Stirling approximation,

$$\ln x! = x \ln x - x.$$

$$F = nE_v - kT [N \ln N - N - (N-n) \ln (N-n) + (N-n) - n \ln n + n]$$

$$F = nE_v - kT [N \ln N - (N-n) \ln (N-n) - n \ln n] \quad \dots(3)$$

At thermal equilibrium, free energy is constant and minimum.

Differentiating Eq. (3) with respect to  $n$ ,

$$\left( \frac{\partial F}{\partial n} \right)_T = 0 = E_v - kT \left[ 0 - (N-n) \frac{-1}{(N-n)} - (-1) \ln (N-n) - n \frac{1}{n} - 1 \ln n \right]$$

$$E_v = kT [1 + \ln (N-n) - 1 + \ln n]$$

$$E_v = kT \ln \left[ \frac{(N-n)}{n} \right]$$

$$\frac{N-n}{n} = \exp \left( \frac{E_v}{kT} \right)$$

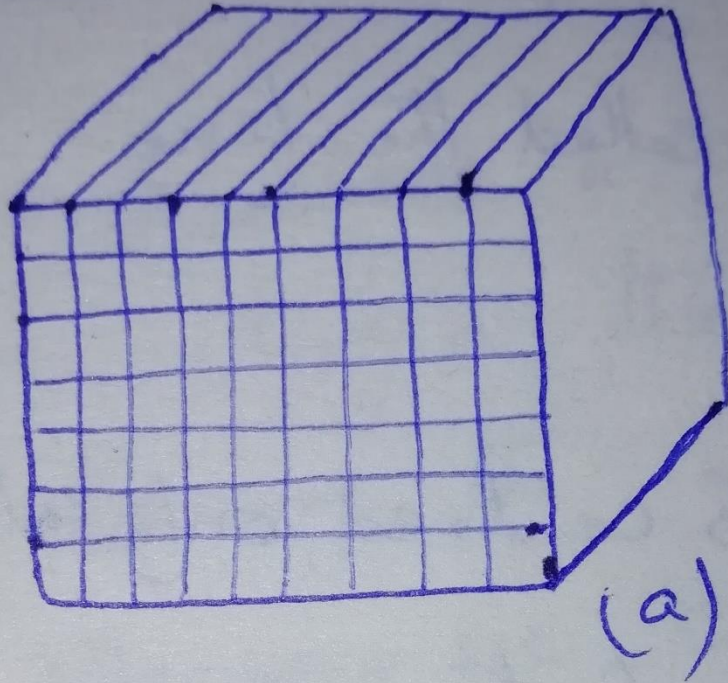
$$n \equiv (N-n) \exp \left[ \frac{-E_v}{kT} \right]$$

If  $n \ll N$ ,  $n$  can be neglected.

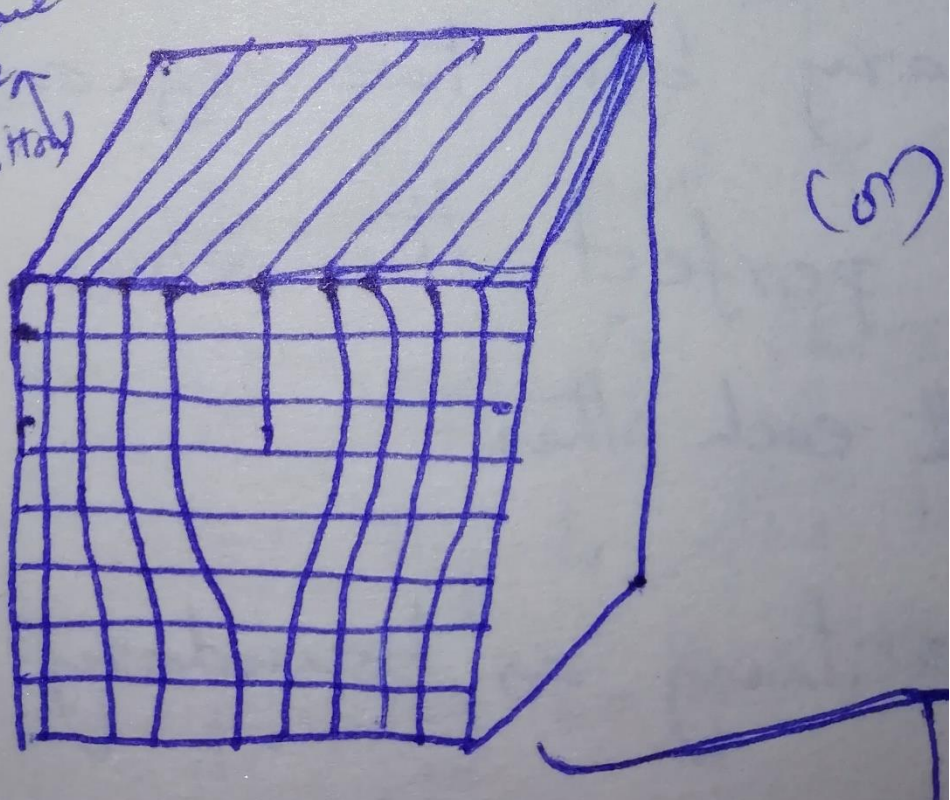
$$\therefore n \equiv N \exp \left[ \frac{-E_v}{kT} \right]$$

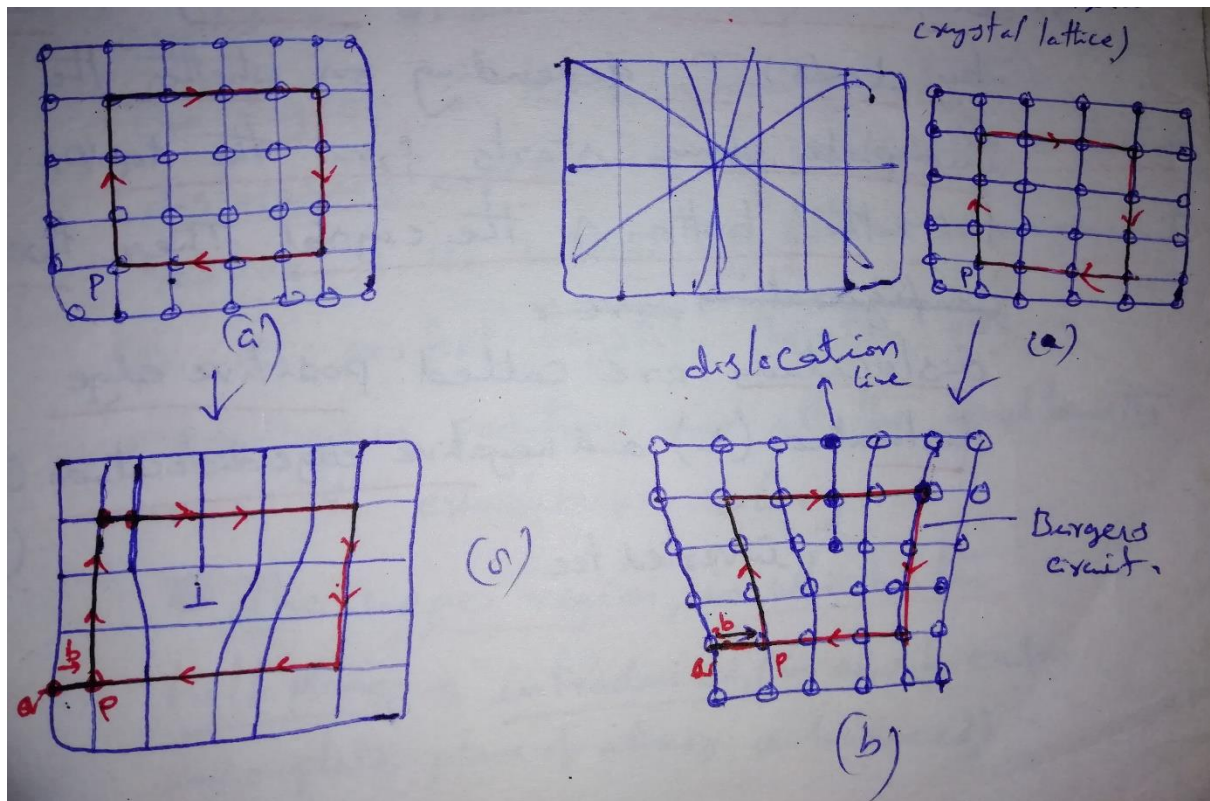


## (a) Edge dislocation:-



as same  
as above  
(except bottom)







second basic type of dislocation

cation.

