

Imperfections in crystals

Any deviation from perfect ideal crystal is known as imperfection or defect. There are generally two types of defects in crystal:-

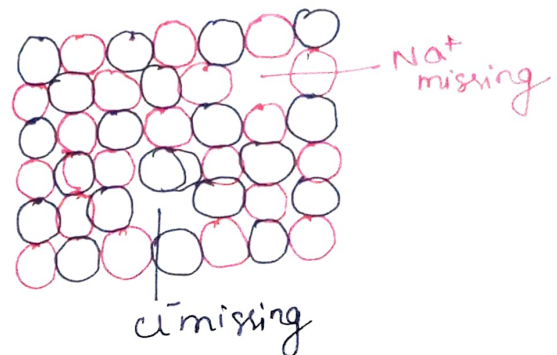
- 1) Point defect
- 2) Line defect

Point defects:-

- If the deviation occurs because of missing atoms, displaced atoms or extra atoms, the imperfection is named as point defect.
- Such defect can be the result of imperfect packing during the original crystallization or they may arise from thermal vibrations of atoms at elevated temperatures because with increase in thermal energy there is increased probability of individual atoms jumping out of their positions of lowest energy.
- The most common point defects are the Schottky defect and the Frenkel defect.

Schottky defects:-

These defects arise due to missing ions from the lattice points. The lattice points that are unoccupied are called lattice vacancies.



As shown in the diagram there is a missing pair of cation and anion from the lattice. The crystal is neutral overall as there are equal no. of cations and anions.

The size of cations and anions do not differ much in case of Schottky defects.

NaCl and CsCl are the lattice systems that show Schottky defects.

• Due to Schottky defect crystals show slight conductance of electricity by ionic mechanism. It happens by following mechanism:-

- a) As the electric field is applied, a nearby ion moves from its lattice site to occupy a vacancy.
- b) This results in creating a new vacancy and another ion moves into it and the process goes on.
- c) The process goes on till it reaches from one end to another by the migration of vacancy and ion.
- d) In this way electricity is conducted along the whole crystal.

* The existence of vacancies also enable ways for the easy movement of atoms or ions in the crystal changing places with one another. This accounts for the phenomenon for diffusion in solids.

Number of Schottky defects:-

1) Let us consider an ionic crystal containing N ions in which n Schottky defects are produced by the removal of n cations and n anions from the crystal lattice in the interior.

2) The different ways in which the ions can be removed be given by:-

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

3) The different ways Schottky defects can be produced by, is obtained by squaring the equation (1) because the cation and anion vacancies are equal.

$$W = \left(\frac{N!}{(N-n)!n!} \right)^2 \quad \text{--- (2)}$$

4) Creation of defect in crystal implies a disorder. Since entropy is measure of disorder of the system, with the creation of defects there is increase in the entropy of crystal system. The entropy S is related to the thermodynamic probability W by Boltzmann equation i.e.

$$S = k \ln W \quad \text{--- (3)}$$

where $k \rightarrow$ Boltzmann constant
 $W \rightarrow$ entropy.

5) Increase in entropy causes a change in Helmholtz free energy. If E is the energy required to create a Schottky defect, then nE would be the energy required to create n Schottky defects.

6) Let this energy be designated as E . The Helmholtz free energy is given by $A = E - TS$

$$\begin{aligned}\Delta A &= \Delta E - T\Delta S \\ &= \Delta E - T(S - S_0) \\ &= E - TS \quad (\text{at OK } W = \infty) \\ &= E - T(k \ln W) \\ &= E - kT \ln \left(\frac{N!}{(N-n)!n!} \right)^2 \quad \text{--- (4)}\end{aligned}$$

7) Using Stirling approximation, viz, $\ln x! = x \ln x - x$, for evaluating factorial terms, we find that

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

$$\text{Hence } \Delta A = E - 2kT [N \ln N - (N-n) \ln (N-n) - n \ln n] \quad \text{--- (6)}$$

At equilibrium, at a given temperature,

$$\left(\frac{\partial (\Delta A)}{\partial n} \right)_T = 0 \quad \text{--- (7)}$$

since N is constant,
hence $\left(\frac{\partial N}{\partial n}\right)_T = 0$.

Thus eqn (5) becomes

$$\left(\frac{\partial A}{\partial n}\right)_T = E - 2kT \ln \frac{N-n}{n} = 0 \quad \text{--- (7)}$$

$$E = 2kT \ln [(N-n)/n] \quad \text{--- (8)}$$

$$\text{or } \frac{(N-n)}{n} = \exp\left(\frac{E}{2kT}\right) \quad \text{--- (9)}$$

Since the number of Schottky defect n is much smaller than no. of ions N i.e. $n \ll N$

Thus $N-n = N$

Hence eq. (8) can be rewritten as

$$\boxed{n = N \exp\left(-\frac{E}{2kT}\right)} \quad \text{--- (10)}$$

Eq. (10) is the equation for the calculation Schottky defects in the system.

* For NaCl, $E \approx 2\text{eV}$, the Schottky defect comes out to be 10^6 per cm^3 . Since the number of Na^+ & Cl^- is approx. 10^{22} per cm^3 , it can be predicted that there is a Schottky defect per 10^{22} per cm^3 of ion.

Hence stirring approximation is quite justified.