

Crystal Defects in Ionic Solids

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- Defect:

Introduction: In actual practice it is difficult to grow a perfect crystal. Even single crystals grown with all care are found to maintain many internal irregularities. These irregularities are called crystal defects and can also be defined as **"any departure from perfectly ordered arrangement of atoms in a crystal even at 0K temp. is called imperfection or defect"**.

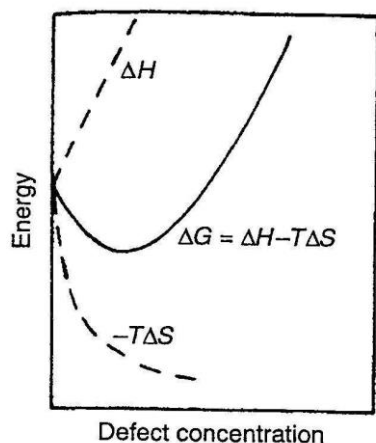
*Such defects can **cause** new properties like **colour, conductivity, magnetism** etc with in a system.*

Perfect ionic solid due to higher lattice energy factor, the migration of electrons is quite less for which electrical conductivity also low. But, Due in cases of defective ionic solid due to the vacancies, movement of electron become easy which allow crystal to show more electrical conductivity.

Q. **Why electrical conductivity of a defective solid is higher than perfect solid?**

✓ Physical concepts of defect:

At 0K temp. a crystal can show defect mainly due to the presence of **zero-point energy** within it. But however, with increasing temperature the possibilities of crystal defect increasing particularly due to the **favorable entropic factor** (randomness increasing; $\Delta S > 0$) rather than the ΔH factor. Higher temperature increases entropy of the system thereby $\Delta G = (-)ve$ following the equation $\Delta G = \Delta H - T \Delta S$.



- Creation of a defect normally costs energy.
- But it also increases the entropy of the crystal!
- Defects increase in concentration until the free energy is a minimum.

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➤ About Several Defects with Types:

The **Imperfections/Defects** are basically irregularities in the arrangement of constituent particles.

Broadly speaking, the defects are of two types;

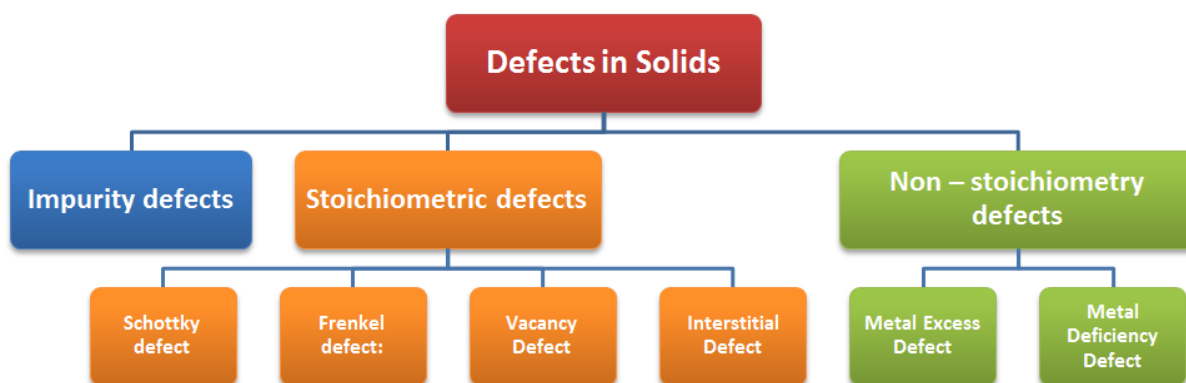
a. **Point defects (Intrinsic)**: The irregularities or deviations from ideal arrangement around a point or an **atom in a crystalline substance**.

b. **Line defects**: The irregularities or deviations from ideal arrangement in entire rows of lattice points.

These irregularities are collectively called ‘**Crystal Defects**’.

Point defects can be classified into three types :

- (i) Stoichiometric Defects (Eg: Vacancy Defect, Interstitial Defect)
- (ii) Impurity Defects
- (iii) Non-Stoichiometric Defects (Eg: Metal Excess Defect, Metal Deficiency Defect)



(i) Stoichiometric Defects

These are the point defects that do not disturb the stoichiometry of the solid. They are also called ***intrinsic or thermodynamic defects***. Basically, these are of two types, vacancy defects and interstitial defects.

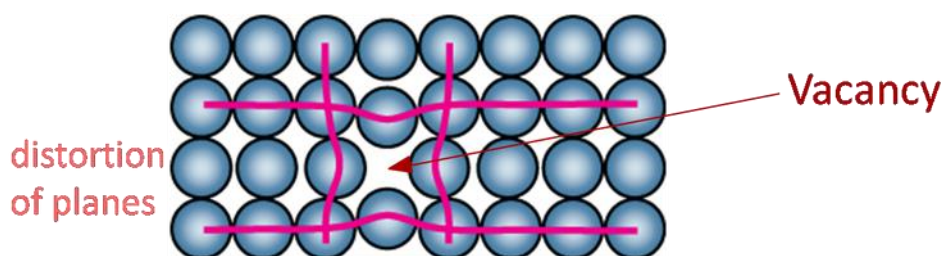
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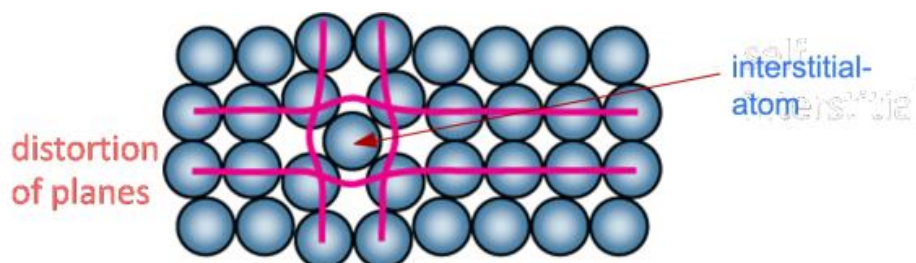
(a) **Vacancy Defect:** When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

(b) **Interstitial Defect:** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the substance.

Vacancy and interstitial defects as explained above can be shown by **non-ionic solids**.



Vacancy Defect



Interstitial Defect

Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as Frenkel and Schottky defects.

✓ **Extrinsic point defects**

If cationic impurities are introduced into a solid and the dopant does not have the same valence as the cation it is replacing extrinsic defects will be introduced

- Fe_{1-x}O (Wustite) and Ca^{2+} or Cd^{2+} in NaCl have cation vacancies

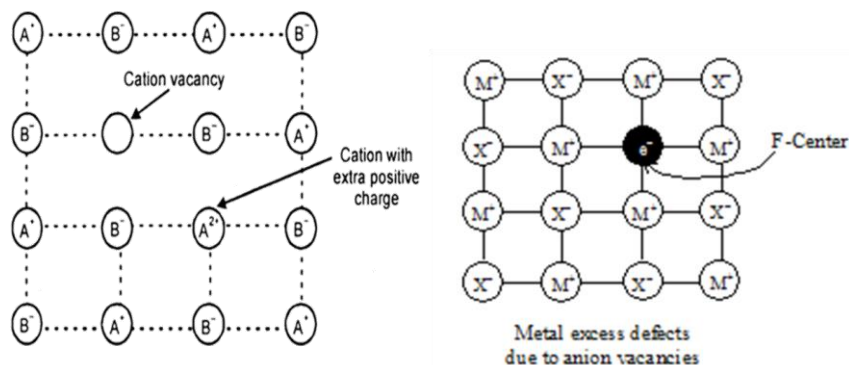
- Ca^{2+} in ZrO and Y^{3+} in ZrO have anion vacancies.

Real crystals contain both intrinsic and extrinsic defects – the dominant defect type depends upon temperature and doping/non-stoichiometry level.

Pictures of cation and anion vacancy:

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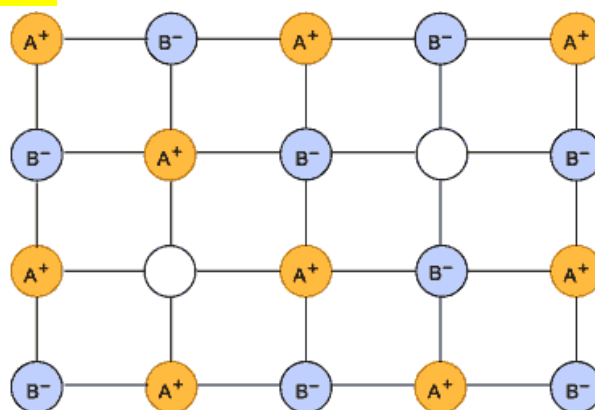
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▪ Detail of Stoichiometry defects:

If the imperfection in crystals is such that the ratio between the cations and the anions remains the same as described in its molecular formula, this defect is called Stoichiometry defect. These can be further categorized **into two ways** normally as:

- a) **Schottky defect:** *In an ionic crystal like of A^+B^- type, if equal number of cations and anions are missing from their lattice sites causing distinct holes or vacancies (without any interstitial cations or anions), the defect is called Schottky defect. In this defect electron neutrality principle is maintained due to the disappearance of similar number of cations and anions (lattice vacancy). Such defect decreases the density of solid in an ionic lattice.*



The Schottky defect is shown by the ionic compounds having: (condition):

- High co-ordination number
- Small difference in the size of cations and anions ($r_+ \approx r_-$)

e.g: NaCl (6 :6), KCl (6:6), CsCl (8:8) (mostly ionic type where pair of ions missing from surface) etc.

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Derivation of number of Schottky defect:

- Consider a 1:1 ionic crystal with N cation sites, N anion site, n_s Schottky cation vacancies and n_s anion vacancies.
- The vacancies will be able to take up many different possible positions in the crystal so there will be a *configurational entropy* associated with their distribution

$$\Delta S = k \ln W = k \ln W_c W_a$$

N boxes (lattice sites) with n_s identical objects (vacancies) to put in

$$W_c = \frac{N(N-1)(N-2)\dots(N-n_s-1)}{n_s!}$$

$$= \left(\frac{N!}{(N-n_s)!} \right) \times \frac{1}{n_s!}$$

$$\Delta S = k \ln W_c W_a = 2k \ln W_c$$

$$= 2k [N \ln N - (N-n_s) \ln (N-n_s) - n_s \ln n_s]$$

$$\Delta G = \Delta H - T \Delta S$$

$$= n_s \Delta H_s - 2kT [N \ln N - (N-n_s) \ln (N-n_s) - n_s \ln n_s]$$

$$\frac{dG}{dn_s} = 0 \text{ at equilibrium}$$

$$= \Delta H_s - 2kT [\ln (N-n_s) + 1 - \ln n_s - 1]$$

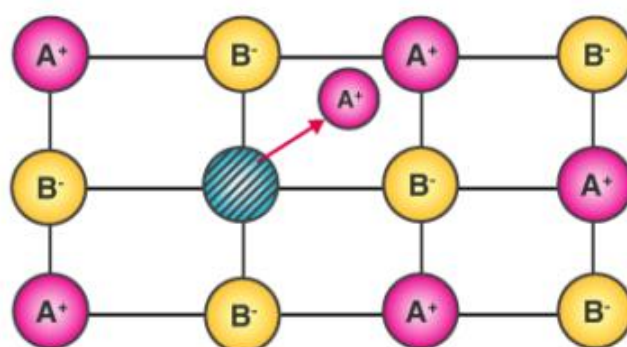
$$\Delta H_s = 2kT \ln \frac{N-n_s}{n_s}$$

$$n_s = N \exp\left(-\frac{\Delta H_s}{2kT}\right) \text{ (Schottky defects)}$$

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b) **Frenkel's defect:** In an ionic lattice when an ion is missing from its lattice sites causing a hole or vacancy there and occupies interstitial site, then the defect is called Frenkel's defect.



Frenkel Defect

In this defect the electrical neutrality and stoichiometry of the compound is maintained as ion does not leave the crystal completely. Due to this defect the density of the ionic solid remains unchanged.

Such Frenkel defect is shown by the ionic compounds having: (condition):

- i) Low co-ordination number
- ii) Difference in the size of cations and anions is very large
- iii) Highly polarizable anions are preferred

e.g: **AgBr (4:4), ZnS (4:4) (mostly covalent type).** Other : CaF_2 , SrF_2 , ZrO_2 , UO_2

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➤ *Derivation of number of Frenkel Defects:*

If N = number of possible normal lattice sites, N' = number of possible interstitial site. ($N=N'$ for most of the cases), and n = number of Frenkel defects.

$$\text{Number of ways to arrange the interstitial atoms} = {}^{N'}C_n = \frac{N'!}{(N'-n)!n!}$$

$$\text{Number of ways to arrange the vacancies} = {}^NC_n = \frac{N!}{(N-n)!n!}$$

$$\text{Total number of possible ways} = \frac{N'!}{(N'-n)!n!} \times \frac{N!}{(N-n)!n!}$$

$$\therefore S = k_B \ln \Omega = k_B \ln \frac{N'!}{(N'-n)!n!} \times \frac{N!}{(N-n)!n!}$$

Stirling's approximation : $\ln(x!) \approx x \ln x - x$

$$S \approx k_B [(N' \ln N' - N') + (N \ln N - N) - (N'-n) \ln(N'-n) - (N-n) \ln(N-n) - 2n \ln n]$$

If E_I = energy required to form one defect

$$\therefore F = U - ST = nE_I - k_B T [(N' \ln N' - N') + (N \ln N - N) - (N'-n) \ln(N'-n) - (N-n) \ln(N-n) - 2n \ln n]$$

n is determined by minimizing the free energy :

$$\frac{\partial F}{\partial n} = 0 \Rightarrow E_I - k_B T [(\ln(N'-n) + 1) + (\ln(N-n) + 1) - 2 - 2 \ln n] = 0$$

$$\Rightarrow E_I - k_B T \left[\ln \frac{N'-n}{n} + \ln \frac{N-n}{n} \right] = 0$$

$$\Rightarrow E_I = k_B T \left[\ln \frac{(N'-n)(N-n)}{n^2} \right]$$

For $n \ll N, N'$,

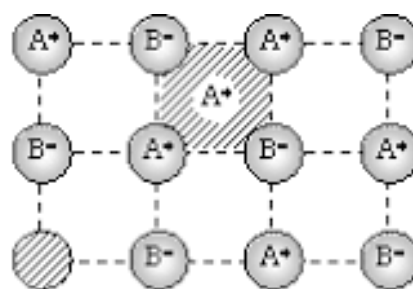
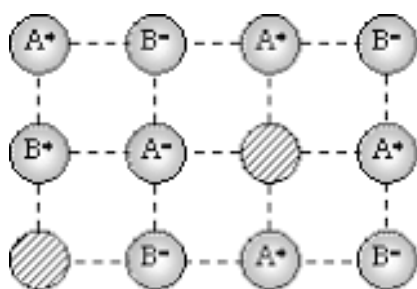
$$E_I \approx k_B T \left[\ln \frac{N'N}{n^2} \right] \Rightarrow n = \sqrt{N'N} e^{-E_I/2k_B T}$$

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➤ **Distinction of Schottky and Frenkel Defects:

Points	Schottky Defect	Frenkel Defect
Definition	It appears due to the missing of equal quantity of both cations and anions from their respective lattice sites maintaining the electro-neutrality principle.	It appears due to the missing of individual cations or anions (mainly cations) from lattice sites and appears in the interstitial position maintaining electro-neutrality principle.
Condition	Higher co-ordination number and Small difference in the size of cations and anions.	Lower co-ordination number and large difference in the size of cations and anions.
Change in charge density	Not so significantly decrease or increase.	Significantly change
Density Change	Density significantly reduced.	Density is not significantly affected.
Coloration and Conductivity	Due to mainly migration of holes.	Due to movement of both holes and interstitial ions.
Energy Require	Lower amount of energy need	More energy demanding process.
Example	NaCl, KCl	AgBr, ZnS



Q. 1. What is Schottky defect and what are the necessary conditions of such defect?

Q. 2. What is Frenkel defect and what are the necessary conditions of such defect?

*Q.3 .What are the distinction of Schottky and Frenkel defects?

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▪ Non-Stoichiometry defects:

If an imperfection causes the ratio of cations to anions to become different from that indicated by the ideal chemical formula, the defect is called non-stoichiometry. e.g: Fe_xO where $0.957 > x > 0.83$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($1 > x > 0$).

There are three types:

- Metal excess
- Metal deficiency
- Impurity defects.

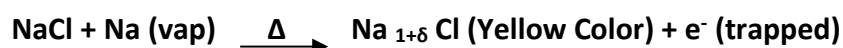
❖ *Metal excess

This may occur in either of the following two ways:

➤ Metal excess defect by anion vacancies ($\text{A}_{1+\delta}\text{B}$)

A negative ion may be missing from its lattice site, leaving a hole, which is occupied by an electron thereby maintaining an electrical balance. The trapped electrons are called F-centres or color centres (Farbe centre: *electron trapped in anion vacancy and the color center as trapped electron leads to absorption in visible*) because they are responsible for imparting color to the crystal (color arises due to transitions between electron in a box levels). This defect is found in crystals having Schottky defects. F-centre band depends on the lattice structure not on the source. Trapped electrons can be produced by – irradiation of the sample or treatment with an electron donor like sodium or potassium vapour.

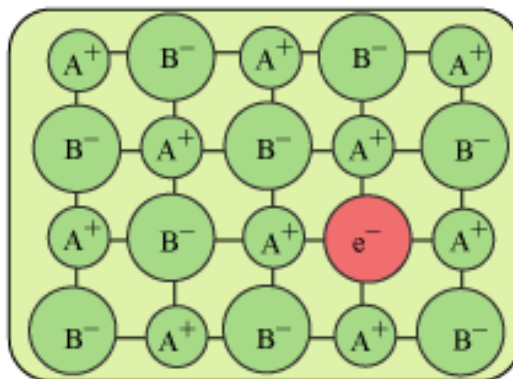
****Example:** NaCl when heated in Na vapour or molten Na, the excess Na deposits on the surface. Cl^- diffuses to the surface where they combine with the Na atoms, which lose the electrons.



The electrons diffuse into the vacant site created. The electrons absorb some energy from the white light and **re-emit the yellow color** particularly due to F-centre band arising out of this metal-excess defect by anion-vacancies.

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Metal excess defect due to anion vacancy forming F-centre.

[Excess of Li in LiCl gives a pink color. Excess of K in KCl makes it violet. All these are the example of metal excess defects by anion vacancies.]

****[N.B.- The trapped electrons in the lattice sites in metal excess defect by anion vacancy ($A_{1+\delta}B$) can carry electricity by the migration of the electrons by Hopping mechanism. Such phenomenon is called photo-conductivity of the crystals by irradiation of light. That is the reason of carrying electricity of molten state of NaCl than solid NaCl.]**

****Q. 1. Predict the observation of color change when NaCl is heated with Na (vap) or molten Na.**

***Q. 2. Predict the observation of color change when KCl is heated with K (vap) or molten K.**

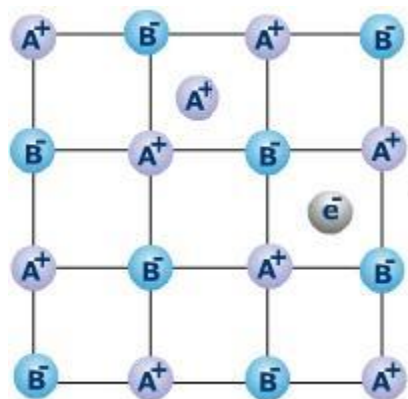
**** Why molten NaCl is a good conductor of electricity than solid NaCl?**

➤ **Metal excess defect by presence of extra cations in the interstitial sites**

Extra cations occupying interstitial sites with electrons present in another interstitial site to maintain electrical neutrality can cause metal excess. This defect is similar to Frenkel defect and is formed in crystals having Frenkel defects. Crystals with either type of metal excess act as semiconductors which can transport electricity.

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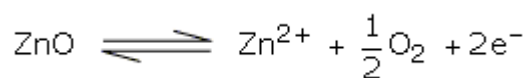
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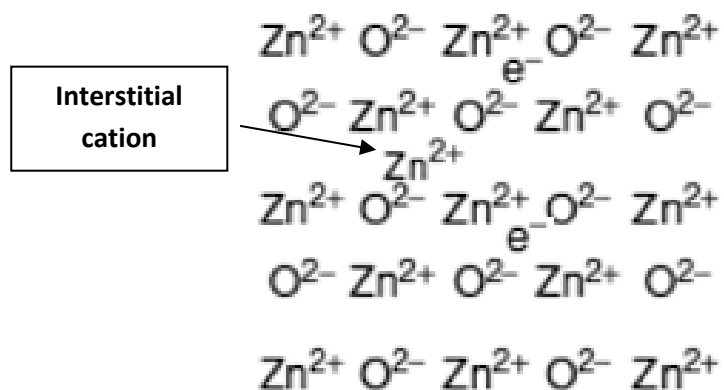
Metal excess defect caused by extra cation in interstitial position

****Example:**

If ZnO is heated, it loses oxygen and turns yellow when hot due to the formation of $\text{Zn}_{1+\delta}\text{O}$ as:



The excess Zn^{2+} ions thus formed get trapped into the vacant interstitial sites and the electrons in the neighboring interstitial sites as shown in the given figure:



It turns yellow when hot due to the migration of both cation and electrons in interstitial position to neighboring interstitial sites particularly for the formation metal **excess defect** caused by extra cation in *interstitial position* and It becomes white when cold as it return to the original state.

***Q.1 Predict the observation: **Why ZnO looks yellow when hot white when cold?**

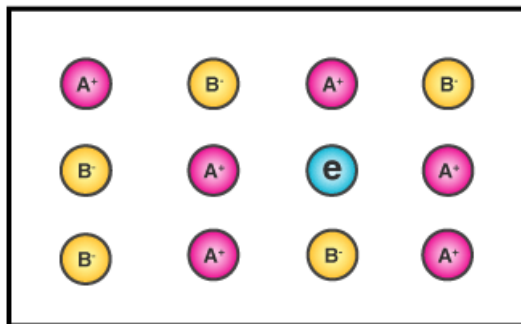
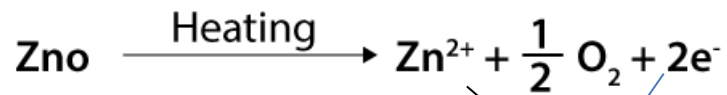
Q 2. Predict the observation: Why CdO looks yellow when hot and cold?

(Ans. is as same as ZnO.)

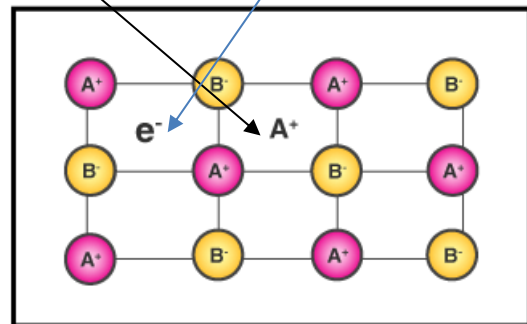
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Metal excess defect due to anionic vacancy



Metal excess defect due to the presence of interstitial cation:

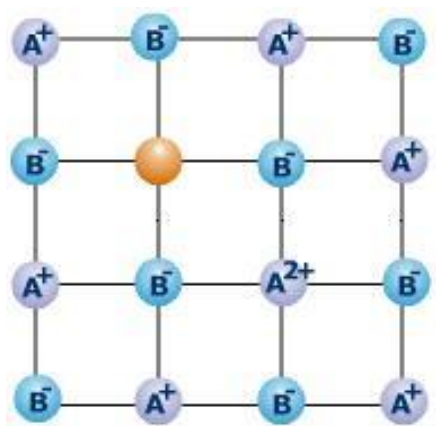
(Metal excess defects due to the presence of extra cation in the in the interstitial sites in ZnO upon heating.)

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❖ Metal deficiency: ($A_{1-x} B$)

Metal deficiency (non-stoichiometric) occurs when the metal shows variable valency i.e. transition metal.



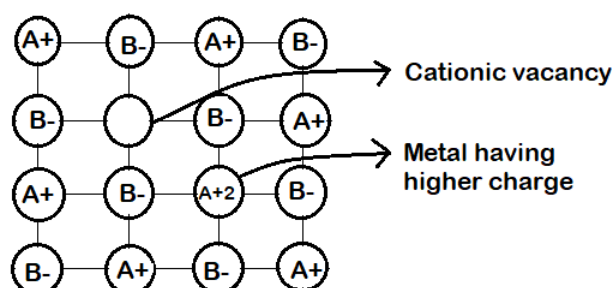
Metal Deficiency Defect

Metal deficiency defect due to missing of a cation of lower valency and presence of a cation of higher valency occurs when metals show variable valency.

Example:
FeO is mostly found with a composition of $Fe_{0.95}O$. In crystals of FeO, some Fe^{2+} ions are missing, and the loss of positive charge is made up by the presence of the required number of Fe^{3+} ions.

[Metal deficiency defect ($A_{1-x} B$) due to missing of a cation of lower valency and presence of a cation of higher valency occurs (for maintaining electro-neutrality) when metals show variable valency.]

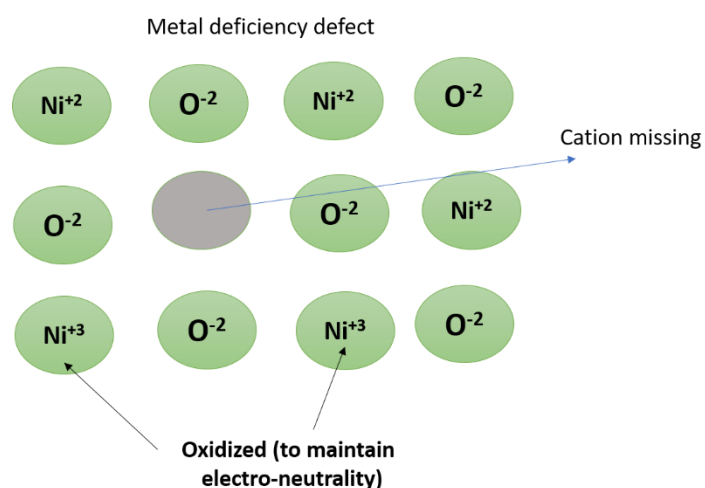
***Example:** Transition elements It occurs due to the missing of a cation from its lattice site creating a hole and presence of the cation with higher charge (e.g., +2 instead of +1) in the adjacent site.



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Examples: **FeO_{0.98}**, **FeS** and **NiO**:



These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. The formation of former depends upon the electronic structure of the impurity while that of the latter on the size of the impurity.

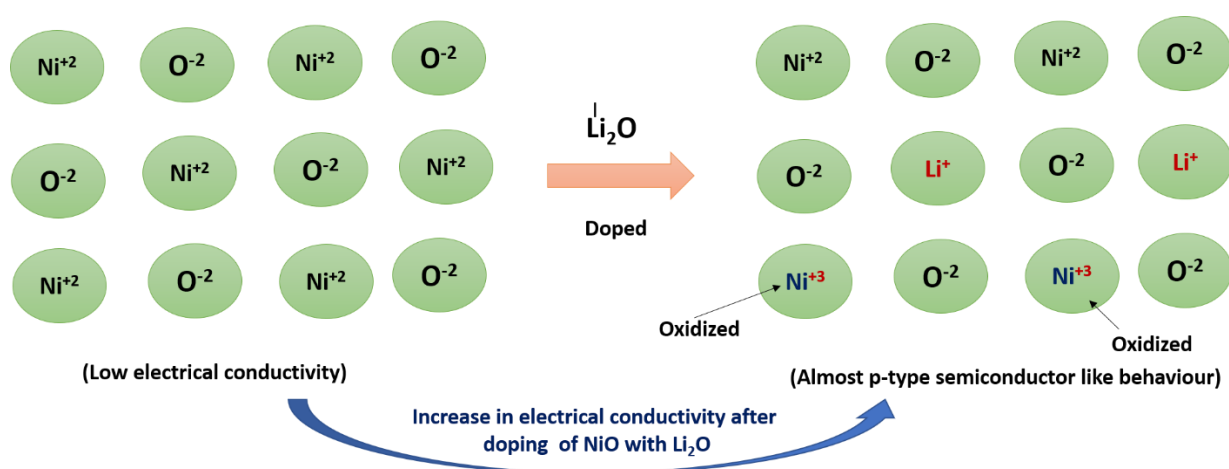
****Q. 1. Discuss the metal deficiency defects in FeO_{0.98} and NiO.**

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❖ ** Li₂O doped NiO crystals:

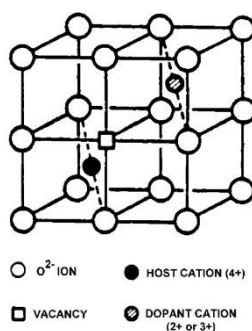
When NiO is doped with a small quantity of Li₂O, some Ni²⁺ can be expected to be replaced by Li⁺ ions. To maintain electro-neutrality principle equal number of neighboring Ni²⁺ (3d⁸) ions are oxidized into Ni³⁺ (3d⁷). A decrease in unpaired electrons would make NiO a **p-type semiconductor** (like creation of + holes i.e. **like acceptor impurity levels**; controlled valence semiconductor).



Besides the change in electrical conductor there is also a change in colour of the entire doped-system.

Q. When NiO is doped with very small amount of Li₂O, the system behaves like p-type semiconductor. Explain.

[N.B.; When Zr^{IV}O₂ is doped with small-quantity-of Ca^{II}O then few Zr(IV) ions are expected to be replaced by Ca(II) ions and to maintain electro-neutrality equal number of oxide ions (O²⁻) leaves the lattice side creating anion vacancy.]



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Few Math From JAM/NET/GATE:

MgO crystallizes as rock-salt structure with unit cell length $2.12 \text{ \AA}$. From electro-static model, the calculate lattice energy is kJ/mol is _____.

$N_A = 6.022 \times 10^{23}$
 $A = 1.748$
 $\epsilon_0 = 8.854 \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
 $e = 1.602 \times 10^{-19} \text{ C}$

$a = 2.12 \text{ \AA}$ (unit cell distance)
 $r_0 = (r_+ + r_-) = \frac{a}{2} = \frac{2.12 \text{ \AA}}{2}$
 $= 1.06 \text{ \AA}$
 $= 1.06 \times 10^{-8} \text{ cm}$
 $= 1.06 \times 10^{-10} \text{ m}$

$$U = \frac{-A |z^+ z^-| e^2 \cdot N_A \left(1 - \frac{1}{n}\right)}{r_0}$$

$N_A = \text{Avogadro no.}$
 $z^+ = \text{charge of cation}$
 $z^- = \text{charge of anion}$
 $r_0 = \text{Eqn. inter ionic distance} = r_+ + r_-$
 $n = \text{Born - exponential}$
 $K = 1 \text{ (in CGS)}$
 $= \frac{1}{4\pi\epsilon_0} \text{ (in SI)}$
 $\epsilon_0 = 8.854 \cdot \text{J}^{-1} \text{ C}^2 \text{ m}^{-1}$

$$U = \frac{-1.748 |2 \times 2| (1.602 \times 10^{-19})^2 \times 6.022 \times 10^{23}}{(1.06 \times 10^{-10}) \times 4 \times 3.14 \times 8.854} \left(1 - \frac{1}{7}\right)$$

$$= 7.85 \times 10^6 \text{ J/mol}$$

$$= 7.85 \times 10^3 \times 10^3 \text{ J/mol}$$

$$= 7850 \text{ kJ/mol}$$

Alternative

$$U = \frac{-1.748 \times |2 \times 2| (4.8 \times 10^{-10})^2 \times 6.022 \times 10^{23}}{1.06 \times 10^{-8}} \left(1 - \frac{1}{7}\right)$$

$$= 7.844 \times 10^{13} \text{ erg/mole}$$

$$= 7.844 \times 10^6 \text{ J/mole}$$

$$= 7.844 \times 10^3 \times 10^3 \text{ J/mole}$$

$$= 7.844 \times 10^3 \text{ kJ/mole}$$

$$= 7844 \text{ kJ/mole}$$

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Calcium crystallises in fcc lattice of unit cell length $5.56 \text{ \AA}$ and density 1.4848 g cm^{-3} . The Percentage of Schottky defects (rounded off to one decimal place) in the crystal is $\rightarrow$

(Given: Atomic mass of Ca is 40 g mol^{-1} ; $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$)

$$\rho = Z \times \left(\frac{m}{V} \right) \times \frac{1}{N_A} = Z \times \frac{m}{(a^3) \times N_A}$$
$$\therefore Z = \frac{\rho \times V \times N_A}{m} = \frac{\rho \times a^3 \times N_A}{m}$$
$$= \frac{1.4848 \times (5.56 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{40}$$
$$= 3.84$$

we know

Ca in fcc (Z) = 4 ≈ 3.96

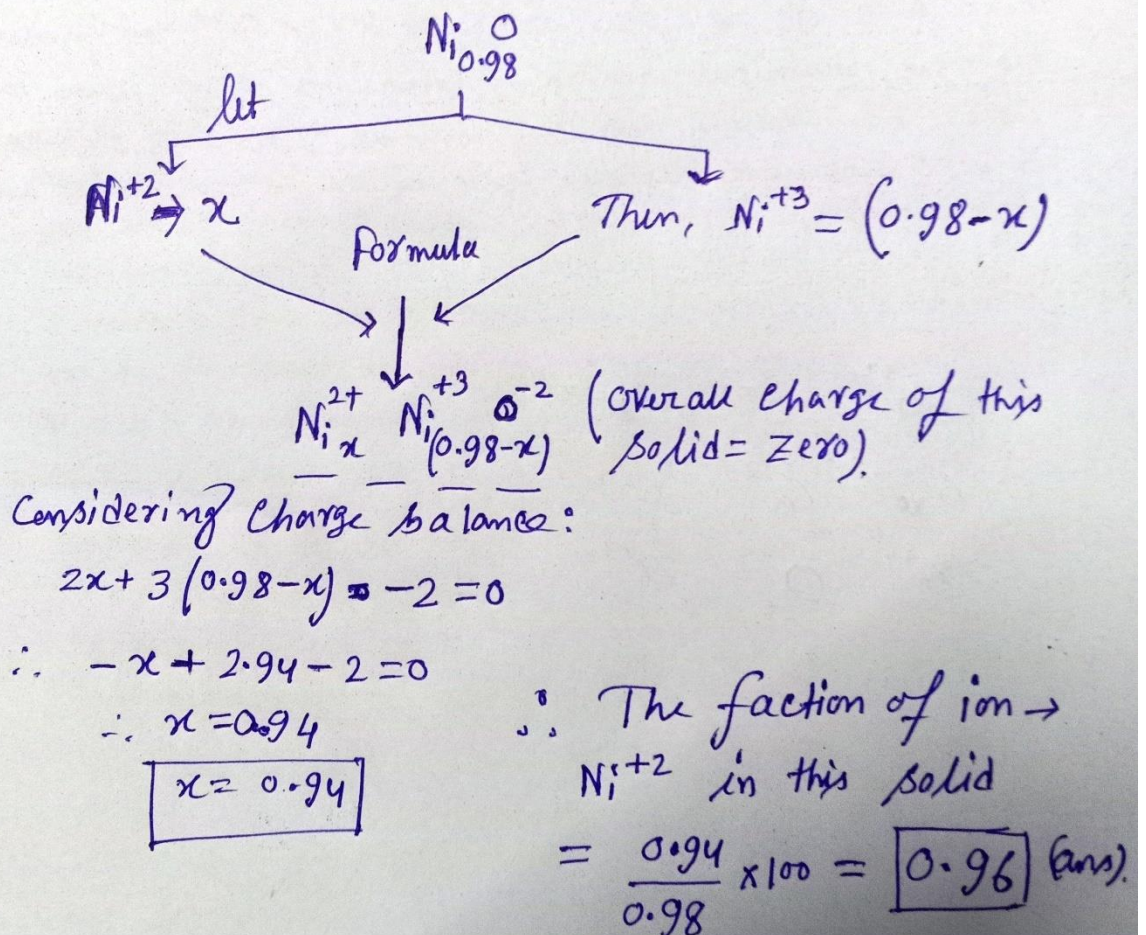
$\therefore$ Here deviation = $(4 - 3.84) = 0.16$

$\therefore$ % of defect = $\frac{0.16}{4} \times 100\% = 4\%$

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❑ Formula of Nickel oxide with metal deficiency defect in its crystal is $\boxed{\text{Ni}_{0.98}\text{O}}$. The solid contains Ni^{+2} and Ni^{+3} ions. The fraction of Ni-existing as Ni^{+2} ions in the crystal is —.

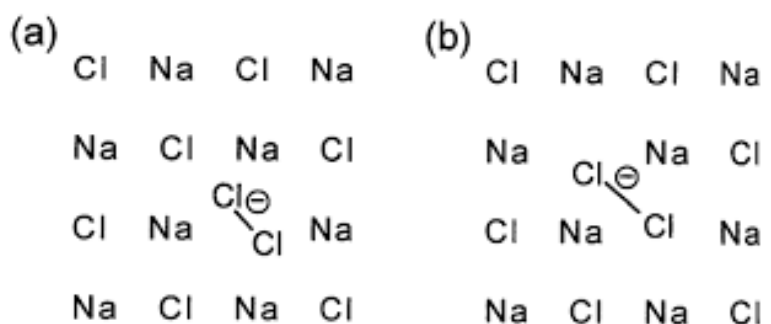


Crystal Defects in Ionic Solids

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✓ H Center and V Center:

H Center interstitial Cl atom bonds to lattice Cl whereas in V Center – electron removed from lattice anion site, resulting Cl atom pairs with neighboring Cl.



❖ **Introducing impurity defect (Extinct) in covalent solids**

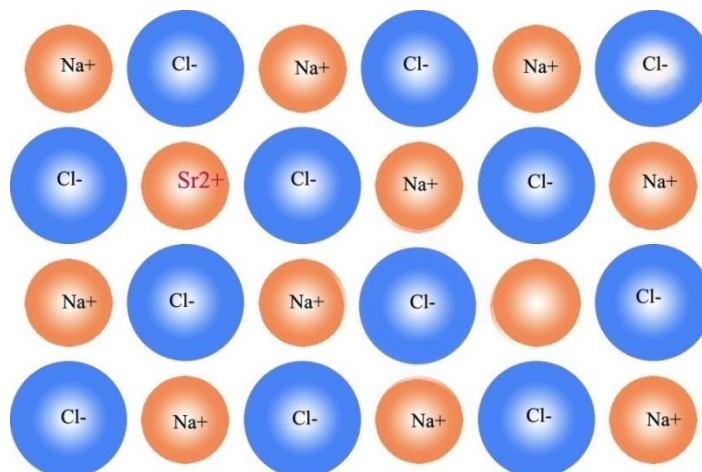
Group 13 elements such as Ga and Al and group 15 elements such as P and As can enter the crystal structure of group 14 elements Ge or Si substitutionally. Group 15 elements have one excess valence electron as compared to Group 14 elements (Si or Ge). Therefore after forming four covalent bonds, one electron remains excess which give rise to **electrical conduction**. Group 13 elements have one valence electron less compared to group 14 elements leading to electron deficient bond or a hole. Such holes can move across the crystal giving rise to electrical conductivity. Group 14 doped with group 15 elements are called n-type semiconductors - (**n**) - negative charge flow. Group 14 doped with group 13 elements are called p - type semiconductors - (**P**) - **Positive hole movement**.

❖ **Introducing impurity defect in ionic solids**

In case of ionic solids, the impurities are introduced by adding impurity of ions. If the impurity ions are in a different oxidation state from that of the host ions, vacancies are created. For e.g., If molten NaCl, containing a little of SrCl_2 as impurity is allowed to cool, in the crystals of NaCl formed, at some lattice sites Na^+ ions are substituted by Sr^{2+} ion.

Crystal Defects in Ionic Solids

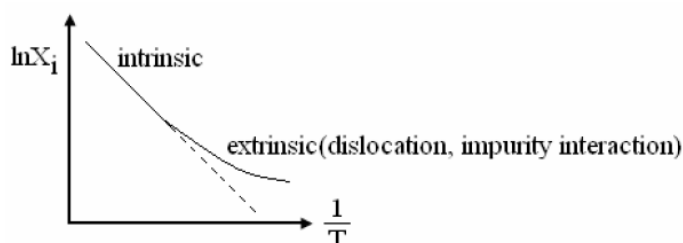
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Impurity defect in ionic solid

➤ Effect of Temperature:

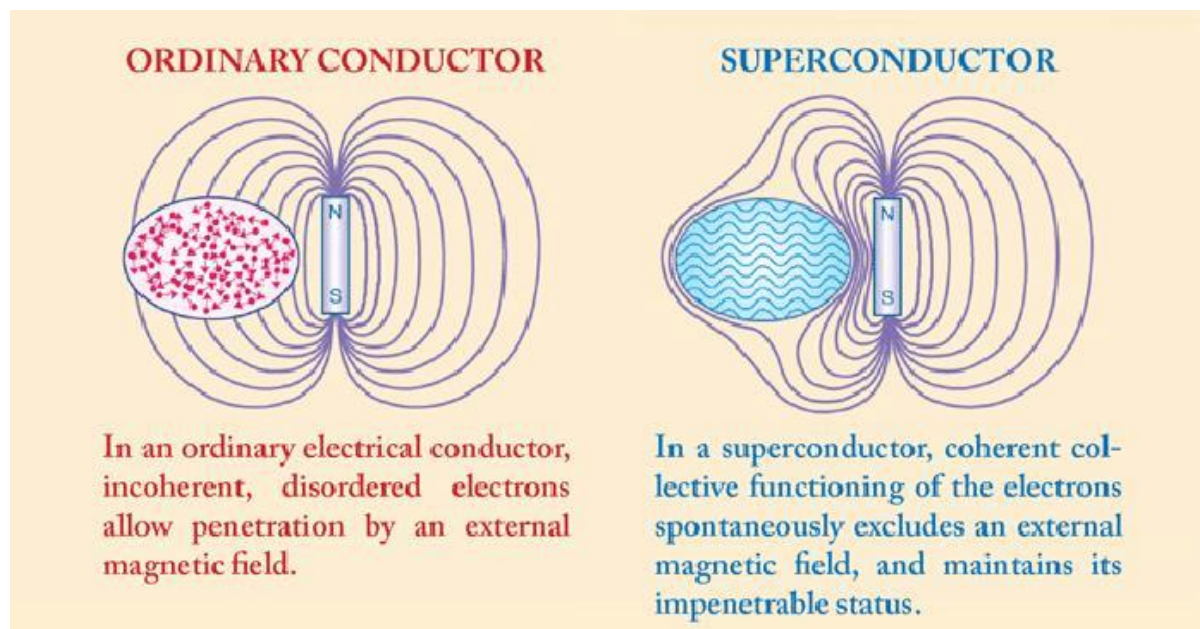
* If the formation of vacancies is influenced by factors other than temp., non-linearity will be observed in the $(\ln X_i)$ vs. $(\frac{1}{T})$ plot.



	Material	Conductivity / (S m ⁻¹)
Ionic Conductors	Ionic crystals	<10 ⁻¹⁶ – 10 ⁻²
	Solid electrolytes	10 ⁻¹ – 10 ³
	Strong (liquid) electrolytes	10 ⁻¹ – 10 ³
Electronic conductors	Metals	10 ³ – 10 ⁷
	Semiconductors	10 ⁻³ – 10 ⁴
	Insulators	<10 ⁻¹⁰

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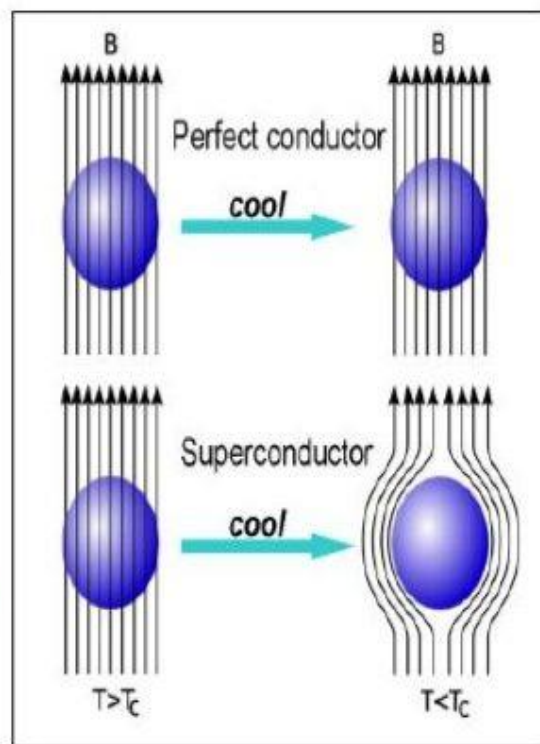
Meissner Effect:

Meissner and Ochsenfeld in 1933 observed—

When a superconducting material at temp. $T > T_c$ is placed in ext. magnetic field, lines of magnetic induction pass through its body, but when it is cooled below the critical temp. i.e., $T < T_c$, these lines of induction are pushed out of the superconducting body.

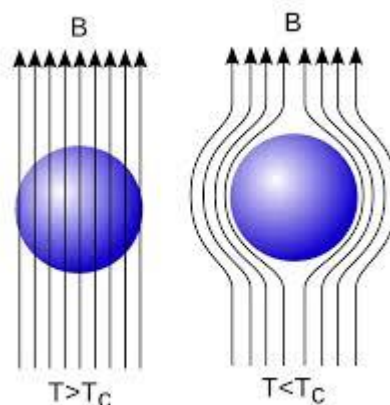
So, **inside the SC body $B = 0$**

This is known as **Meissner Effect**, which is the characteristic property of a superconductor



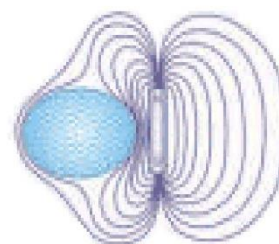
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MEISSNER EFFECT

- When the superconducting material is placed in a magnetic field under the condition when $T \leq T_c$ and $H \leq H_c$, the flux lines are excluded from the material.
- Material exhibits perfect diamagnetism or flux exclusion.
- Deciding property
- $\chi = I/H = -1$
- Reversible (flux lines penetrate when $T \uparrow$ from T_c)
- Conditions for a material to be a superconductor
 - i. Resistivity $\rho = 0$
 - ii. Magnetic Induction $B = 0$ when in an uniform magnetic field
- Simultaneous existence of conditions

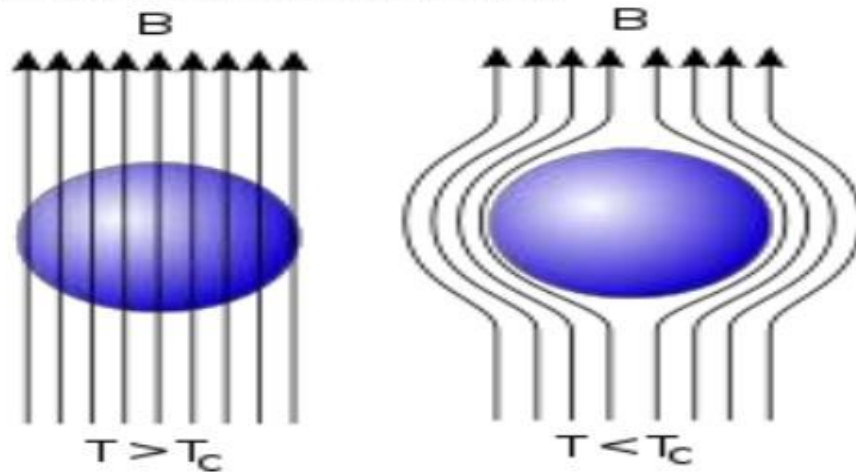


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MEISSNER EFFECT

- The phenomenon of exclusion of magnetic flux or ejection of lines of magnetic induction from the interior of bulk superconductors, when they are cooled below the transition temperature is called Meissner's effect.



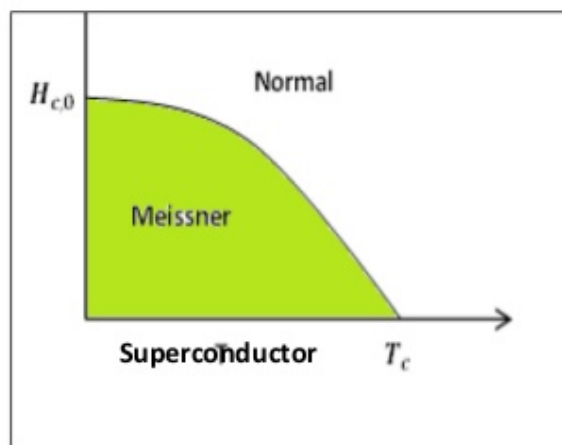
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Critical magnetic field :

- A superconductor when placed in ext. magnetic field, at a particular value loses its superconducting property.
- The magnetic field responsible for the destruction of superconducting property is called critical magnetic field (H_c)
- It is a function of temp. at T_c , H_c is zero, i.e., $H_c(T_c) = 0$
- SC state is stable for definite ranges of magnetic field and temp.
- Normal conducting state is more stable at high temp. and high magnetic field.

$$H_c = H_0 \left(1 - \frac{T^2}{T_c^2} \right)$$



$$H_c = H_0 \left[1 - \left(\frac{T}{T_c} \right)^2 \right]$$

H_0 is the magnetic field at 0K
 H_c is the magnetic field at TK
 T_c is critical temp.

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Hall Effect

Theory and Working Formula:

When a current carrying semiconductor is placed in a transverse magnetic field, a voltage is induced in the direction perpendicular to both current and magnetic field.

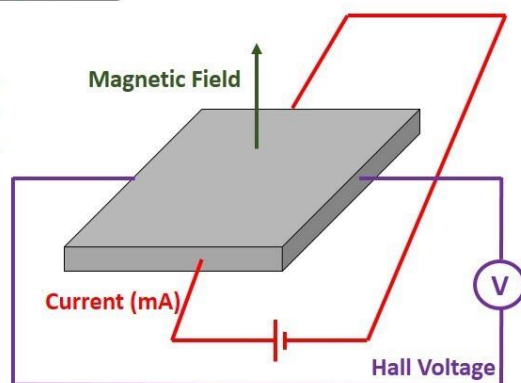
Hall Coefficient (R_H) and Density of Charge Carrier (n) is given by:

$$R_H = \frac{z \times V_H}{I \times B}$$

$$n = \frac{1}{R_H e}$$

Where

z = Thickness of Crystal, V_H = Hall Voltage
 I = Probe Current, B = Applied Magnetic Field,
 e = electric charge



Hall Effect Schematic Diagram

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$$eE_H = Bev \quad \text{----- (1)}$$

Where e is the magnitude of charge on electron or hole and v is the drift velocity.

Now electric field,

$$E_H = \frac{V_H}{d}$$

$$\text{Or } V_H = E_H d = Bvd \text{ because } E_H = Bv \quad \text{----- (2)}$$

Where d is the distance between surface 1 and surface 2.

$$\text{The Current density is given as } J = \frac{I}{A} = \frac{I}{wd} = \rho v$$

Where ρ is the charge density and w is the width of specimen.

$$v = \frac{I}{\rho wd} \quad \text{----- (3)}$$

from above equations i.e. (2) and (3), we have

$$V_H = \frac{BdI}{\rho wd} = \frac{BI}{\rho w}$$