Defects in crystals

formation of defect is endothermic which increase entropy

$$\Delta G = \underbrace{\Delta H}_{+ve} - \underbrace{T.\Delta S}_{-ve} = -ve \Rightarrow \text{Spontaneous}$$

$$T\uparrow \Rightarrow \text{defect}\uparrow$$

If defect is present on a position/point in crystal then it is called point defect.

Types of Point Defects :

Point defect can be classified into three types:

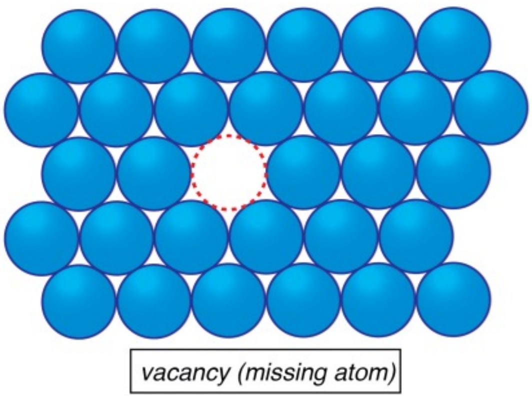
(i) Stoichiometric defects

(ii) Non-stoichiometric defects

(iii) Impurity added defect

Stoichiometric Defect :- If due to defect stoichiometry of crystal is not affected then it is called Stoichiometric defect.

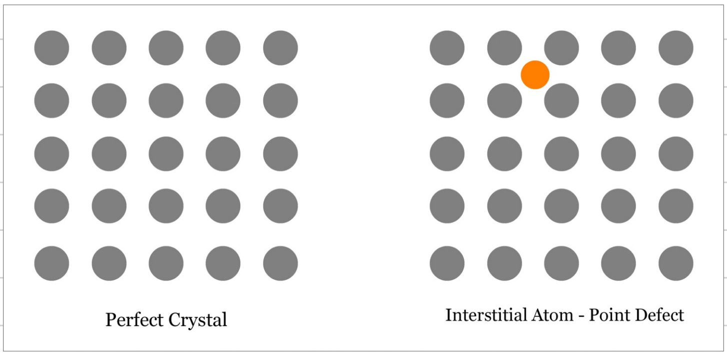
(a) Vacancy Defect :



density ↓

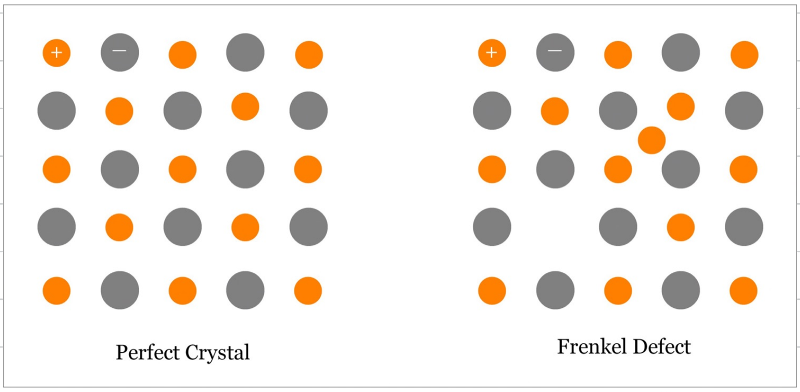
(b) Interstitial Defect :

density ↑



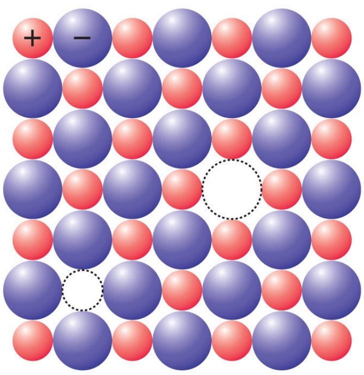
(c) Frenkel Defect :

⇒ density = Const
⇒ Dislocation defect.
⇒ Conduction ↑
⇒ Low coordination No compound. where diff in size of cation and anion is large
Dielectric constant



example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^{+} ions.

(d) Schottky Defect :



A^+B^-

density ↓
Conduction ↑
Diff in size of cation and anion is not very large.
High coordination No compound

10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16}

For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

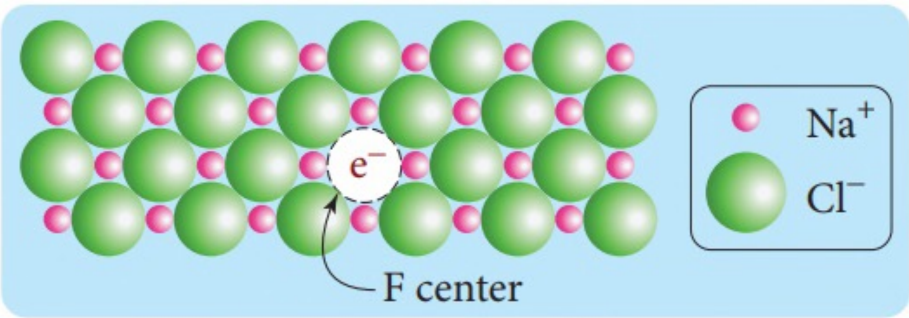
(ii) Non-Stoichiometric Defects :

(a) Metal excess defect.

(b) Metal deficiency defect.

(a) Metal Excess Defect

(I) Metal excess defect due to anionic vacancies :



Metal Excess Defect

→ density ↓

→ Conduction ↑

→ F-Centre are responsible for colour impurities

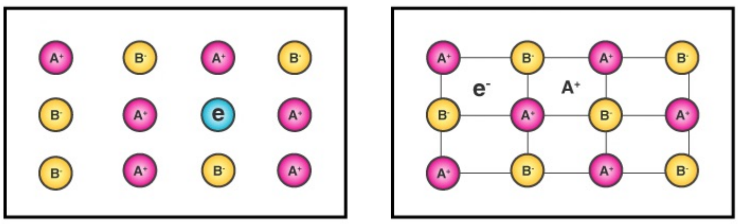
→ Schottkey defect.

⇒ $NaCl_{(1-x)}$

They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

(II) *Metal excess defect due to the presence of extra cations at interstitial sites :*

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + \frac{1}{2} O_2 + 2e^-$$



Metal excess defect due to anionic vacancy

Metal excess defect due to the presence of interstitial cation:

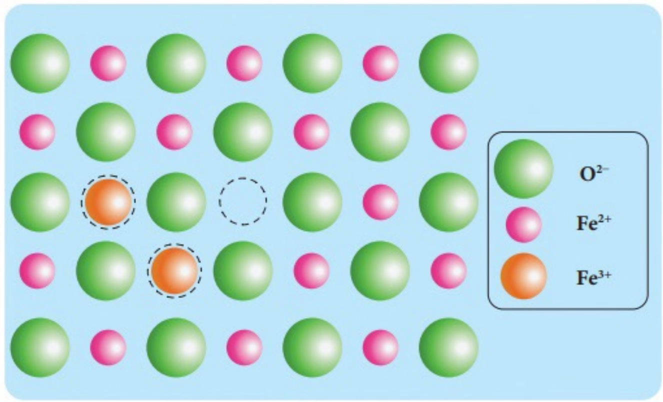
→ Frenkel defect

→ density ↑

⇒ Conduction ↑

⇒ $Zn_{(1+x)}O$

(b) Metal Deficiency Defect



Metal Deficiency Defect

$FeO \longrightarrow Fe_{0.92}O$

$FeO \downarrow Fe^{+2}$

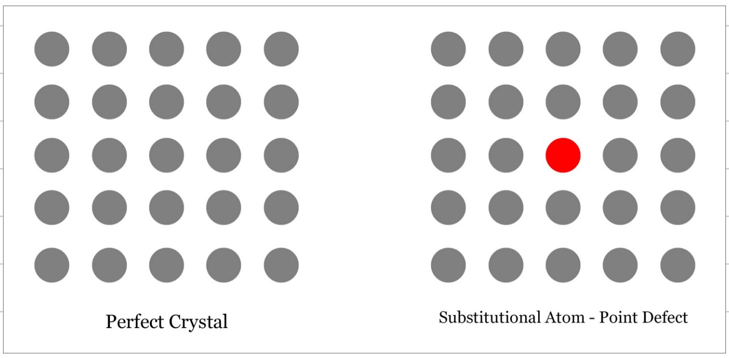
$Fe_{0.92}O \downarrow Fe^{+2}, Fe^{+3}$

→ density ↓

→ Conduction ↑

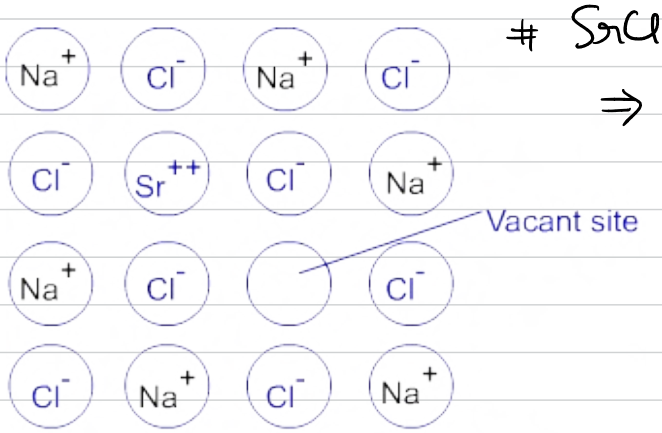
→ $Fe_{(1-x)}O$

(iii) Impurity Defects



density ↑ or ↓

eg:



Vacancy defect becasue of Sr^{++} ion

$SrCl_2$ in NaCl

⇒ $x\ SrCl_2$ ⇒ x Cationic Vacancy

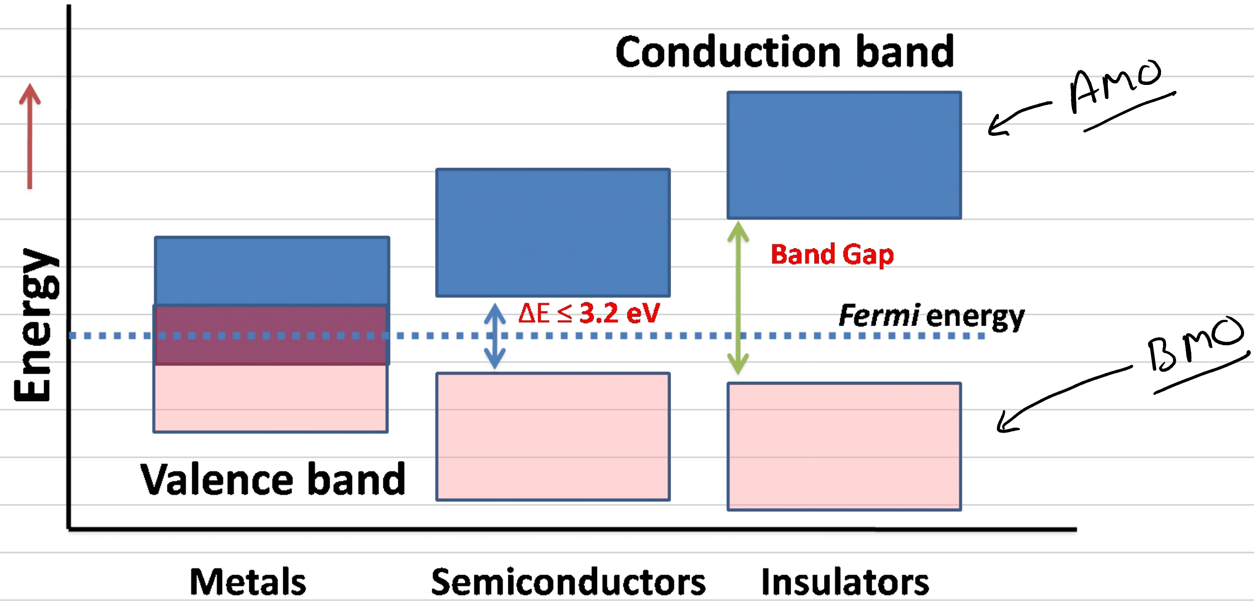
⇒ Conduction ↑

Electrical properties of solid:-

(i) **Conductors :** The solids with conductivities ranging between 10^4 to 10^7 $ohm^{-1}m^{-1}$ are called conductors. Metals having conductivities in the order of 10^7 $ohm^{-1}m^{-1}$ are good conductors.

(ii) **Insulators :** These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} $ohm^{-1}m^{-1}$.

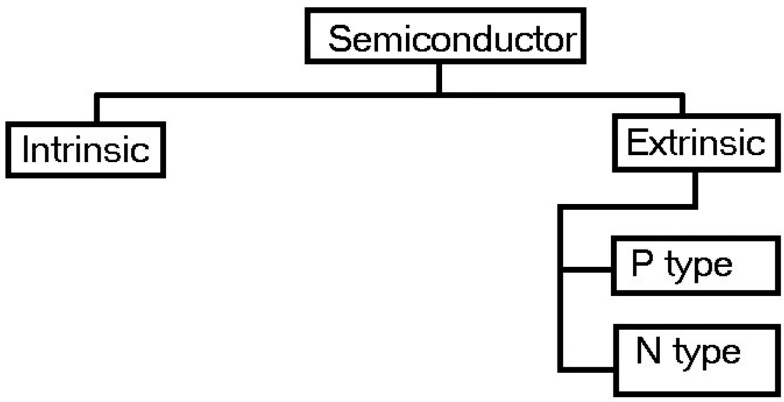
(iii) **Semiconductors :** These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 $Ohm^{-1}m^{-1}$.



Difference between conductor, insulator and semiconductor

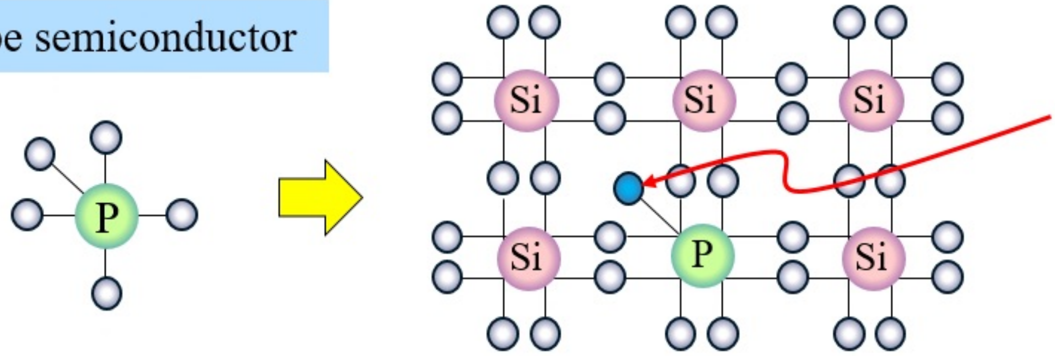
Conductor	Insulator	Semiconductor
The conductivity of conductor is very high.	The conductivity of insulator is very low.	The conductivity of semiconductor is moderate.
It has very low resistivity.	It has very high resistivity.	It has moderate resistivity.
It has no forbidden gap.	It has large forbidden gap.	It has small forbidden gap.
Conductor has positive temperature coefficient of resistance.	Insulator has negative temperature coefficient of resistance.	Semiconductor has negative temperature coefficient of resistance
In conductor, both the effect of resistance and temperature are increases	In insulator, effect of resistance is decreases and effect of temperature is increases.	In semiconductor, effect of resistance is decreases and effect of temperature is increases.
There is large number of electrons available for conduction.	There is small number of electrons available for conduction.	There is moderate number of electrons available for conduction.
Examples: Metals, aluminium, copper.	Paper, Mica glass.	Silicon, Germanium.

Semiconductors:-

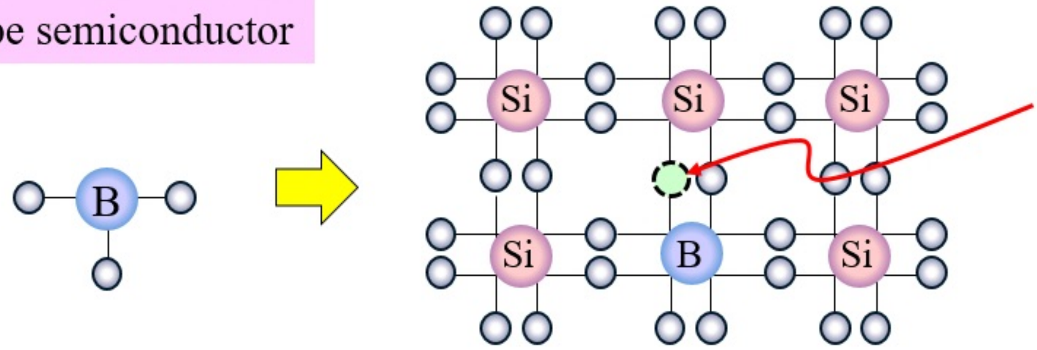


S.No	Intrinsic Semiconductor	Extrinsic Semiconductor
1.	Semiconductor in a pure form is called intrinsic semiconductor.	Semiconductor which are doped with impurity is called extrinsic semiconductor
2.	Here the change carriers are produced only due to thermal agitation.	Here the change carriers are produced due to impurities and may also be produced due to thermal agitation.
3.	They have low electrical conductivity.	They have high electrical conductivity.
4.	They have low operating temperature.	They have high operating temperature.
5.	At 0K, Fermi level exactly lies between conduction band and valence band.	At 0K, Fermi level exactly lies closer to conduction band in "n" type semiconductor and lies near valence band in "p" type semiconductor.
	Examples: Si,Ge,etc.	**Examples:** Si and Ge doped with Al, In,P,As etc

n-type semiconductor



p-type semiconductor



Difference between the P and N type semiconductors

Sl No	P-type Semi conductor	N-type semi conductor
1	P-type semiconductor is formed due to the dopping of III group elements i.e. Boron, Aluminium, Thallium.	N-type semi conductor is formed due to dopping of Nitrogen, Phosporus, Arsenic, Antimony, Bismoth.
2	These are also known as Trivalent semi conductors.	These are also known pentavalent semiconductor.
3	P-type semiconductors is positive type semiconductor it means it deficiency of 1 electron is required.	N-type semiconductor is negative type semi-conductor it means excess of 1 electron is required.
4	In P-type semiconductor majority charge carries are holes and minority charge carries are electrons.	In N-type semiconductor majority charge carries are electrons and minority charge carries are hole.
5	A hole indicates a missing electron. In this no. of holes is more than the no. of electrons.	In N-type semiconductor the no. of holes is less than the no. of free electron.

Germinium and Silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of group 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13-15 are InSb, AIP and GaAs. Gallium arsenide (GaAs) semiconductor have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12-16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO_2 and ReO_3 behave like metals. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

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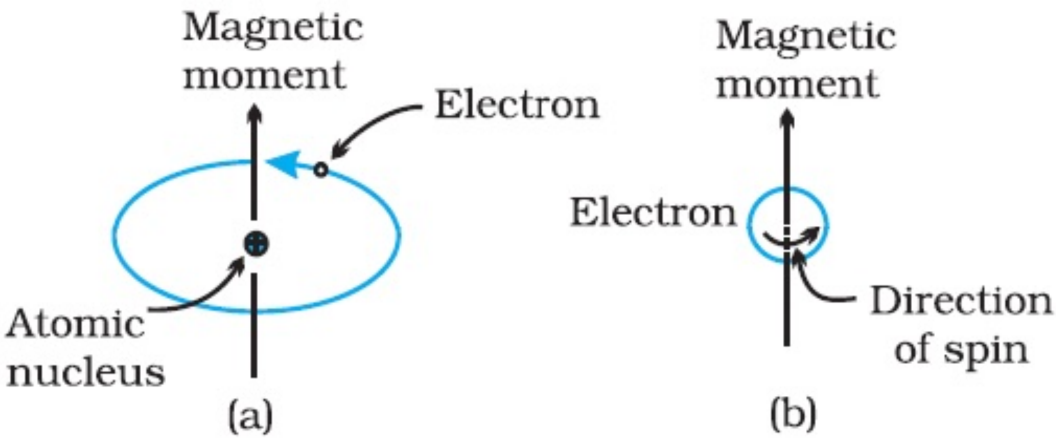
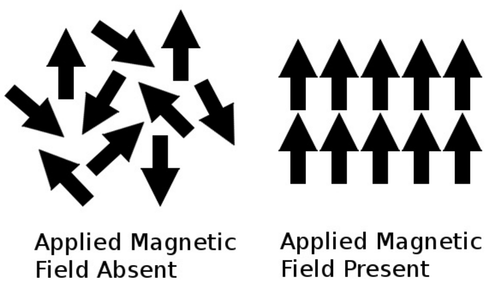
Magnetic properties:-



Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis . Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton, μ_B. It is equal to 9.27×10^{-24}A m^2.

Paramagnetism :

O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

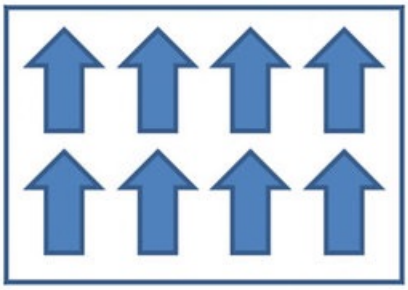


Diamagnetism :

H_2O, NaCl and C_6H_6

Ferromagnetism :

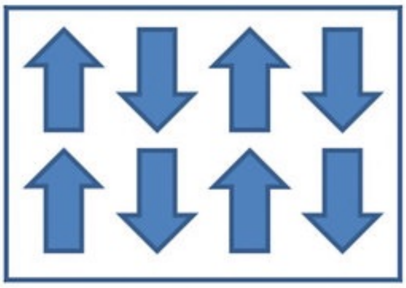
iron, cobalt, nickel, gadolinium and CrO_2



Ferromagnetism

Antiferromagnetism :

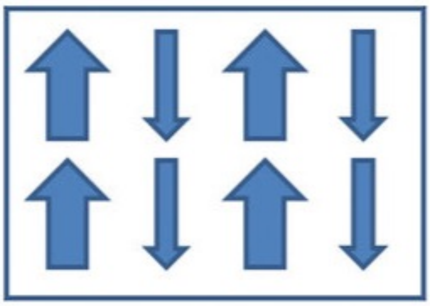
Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment



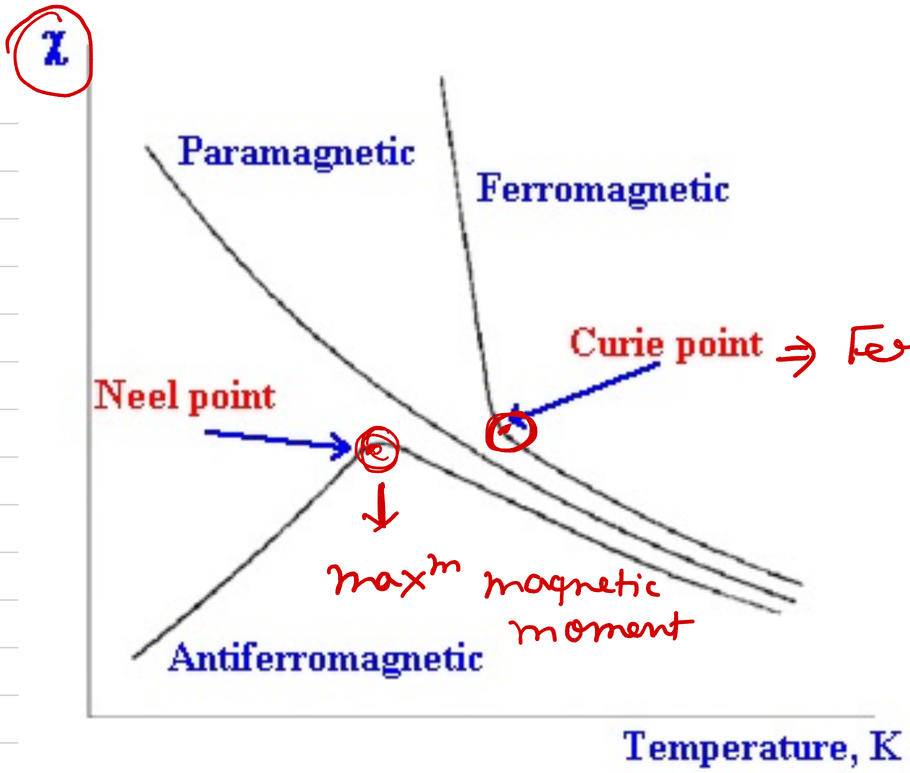
Anti-ferromagnetism

Ferrimagnetism :

Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances.



Ferrimagnetism



⇒ Ferro convert into para