

IMPORTANT PROPERTY OF SOLID STATE REACTION

- 1- Solid state reaction are diffusion controlled process(migration of ion)
- 2-In solid state reaction mixing does not occurs at the molecular level.
- 3-In all type solid state reaction at least one of the reactant must diffuse towards the other reactant.
- 4-The solid state reaction generally depend on the biography of the solid ie method of the preperation storage condition and primary treatment.
- 5-Defect dislocation generally controlled the process diffusion

CLASSIFICATION OF SOLID STATE REACTION

- 1- Decomposition reaction-

- It is possible when a solid is heated below its melting point.

- FOR EXAMPLE-



- 2-Addition reaction-



Exchange reaction-

The exchange reaction are generly possible in following three types-



FOR EXAMPLE-



- This type of reaction are also common in solid state reaction because both of the reactants are generally solid this types of reaction need more temp i.e more than 1000 c.
- 4- Gas solid reaction-:
- Tarnishing reaction are very common example gas solid reaction this terms (tarnishing) is used for a process in which a solid reaction with the gas and to form a solid compound and which build up a thick layer of the product between the two reactants.

- **EXAMPLE-:**
- Oxidation of metals are very common example these type of reaction
- Generally depends on the compactness of the product layer which is formed in b/w the reactant this type of reaction is a very good example of diffusion controlled process.

- **5-:SOLID LIQUID REACTION-:**



- The corrosion of anodic dissociation and electro decomposition of metals are common example of this type of reaction.
- The hydration of a cement is also example of this class.

THE IMPORTANT PRINCIPLE OF INVOLVED IS SOLID STATE REACTION

- The solids do not usually react together at room temperature and it is necessary to heat them reactants at much more higher temp 1000-1500c
- This show that thermodynamics and the kinetic factor are very important is in solid state reaction.
- The thermodynamics process shows the reaction occurs at which temp by considering the exchange in the free energy and the kinetics factor its determined the rate of reaction at which the solid state reaction takes place.
- For example
- $\text{Mgo(s)} + \text{Al}_2\text{O}_3(\text{s}) \longrightarrow \text{MgAl}_2\text{O}_4(\text{s})$

FACTORS

- **1:-REACTION CONDITION:-**

The above reaction is extrimally slow at the room temp but over $>1000-1200^{\circ}\text{C}$

The reaction begins to occurs and the completion of the reaction takes place at 1500°C

- **2-STRUCTURAL CONSIDRATION:-**

The final compound MgAl_2O_4 has a crystal structure which show similarity and differences to that of reactants.

The MgO and final compound MgAl_2O_4 have a cubic structure of the oxide ions on the other hand Al_2O_3 have a distorted hexagonal closed packed structure of the oxide ions. THE ALUMINIUM ION



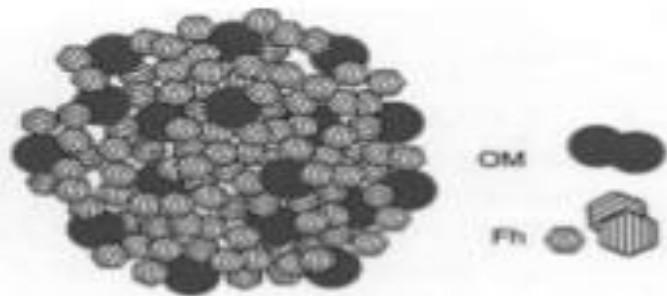
- The aluminium ions occupies octahedral sites in aluminium oxide or well as in the products.
- Where as the Mg^{2+} ions Occupies tetrahedral in final product but octahedral in mg oxide this is the similarlly and dissimilarly of the Mg ion as well as in final product.
- After the a perticular heat treatment the crytal form in the shape of MgAl_2O_4 at the interface and it is suppose tobe formed is between two reactants.



CO-PRECIPITATION TECHNIQUES IN SOLID STATE REACTION

Introduction :

In chemistry, coprecipitation (CPT) or co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed. Analogously, in medicine, coprecipitation is specifically the precipitation of an unbound "antigen along with an antigen-antibody complex".



Coprecipitation is an important issue in chemical analysis, where it is often undesirable, but in some cases it can be exploited. In gravimetric analysis, which consists on precipitating the analyte and measuring its mass to determine its concentration or purity, coprecipitation is a problem because undesired impurities often coprecipitate with the analyte, resulting in excess mass. This problem can often be mitigated by "digestion" (waiting for the precipitate to equilibrate and form larger, purer particles) or by redissolving the sample and precipitating it again



Types of coprecipitation

There are four types of coprecipitation:

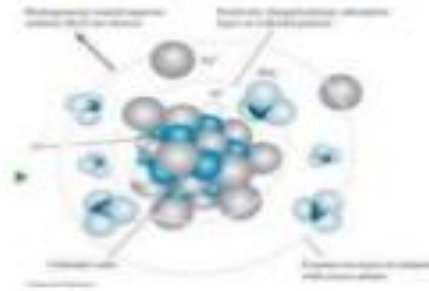
- (1) surface adsorption,
- (2) mixed-crystal formation,
- (3) occlusion, and
- (4) mechanical entrapment.

(1) & (2) are equilibrium processes, while (3) & (4) arise from kinetics of crystal growth.



Surface Adsorption

- Adsorption is a common source of coprecipitation that is likely to cause significant contamination of precipitates with large specific surface areas (coagulated colloids).
- Coagulation of a colloid does not significantly decrease the amount of adsorption.
- The net effect of surface adsorption is therefore the carrying down of an otherwise soluble compound as a surface contaminant.
- Ex. Coagulated silver chloride is contaminated with primarily adsorbed Ag^+ along with nitrate or other anions.

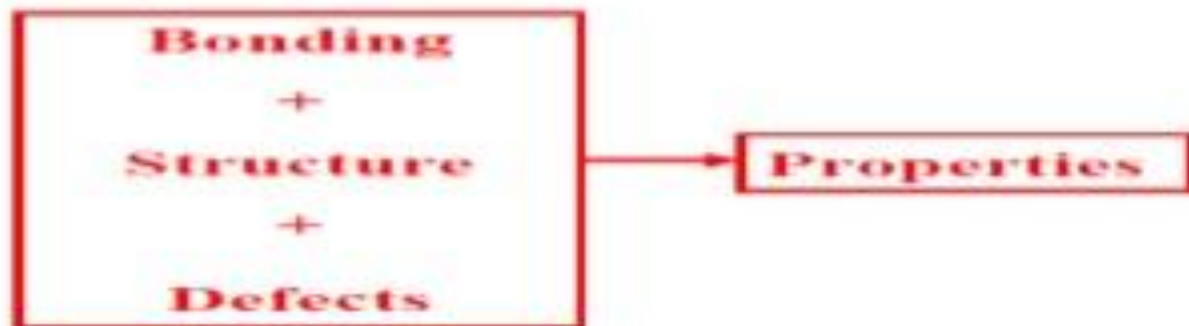


What is Defect?

An ideally perfect crystal is one which has the same unit cell and contains the same lattice points throughout the crystal.

The term **imperfection** or **defect** is generally used to describe any deviation of the ideally perfect crystal from the periodic arrangement of its constituents.

Defects have a profound impact on the macroscopic properties of materials

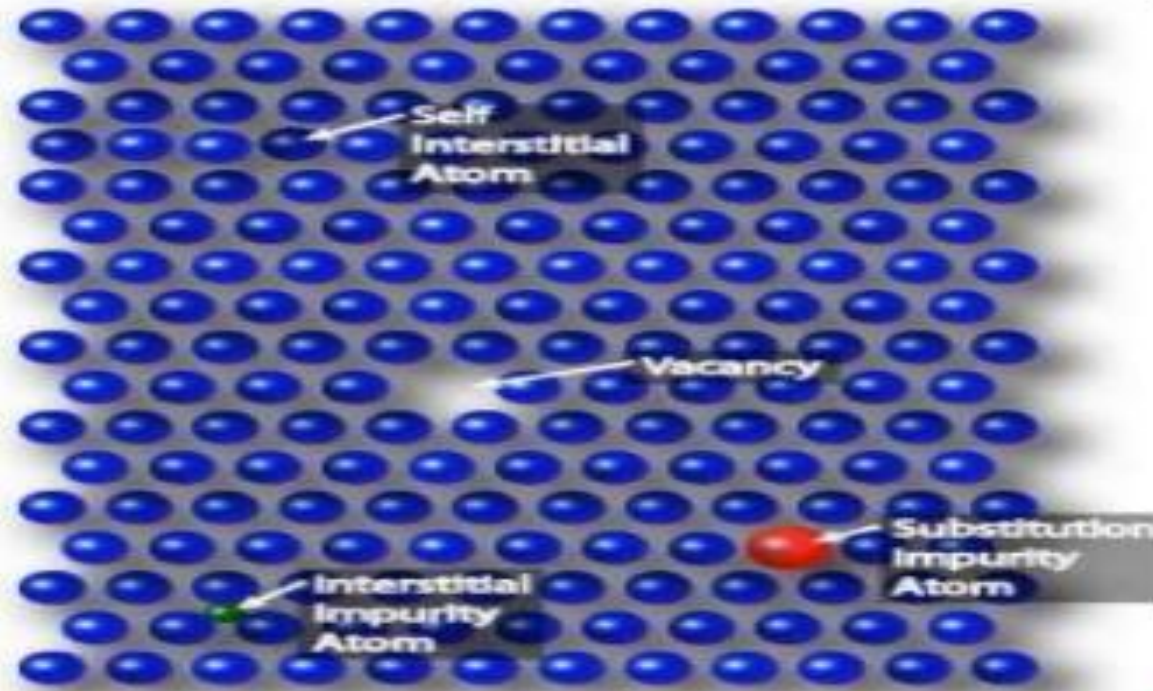


Types of defects in solids

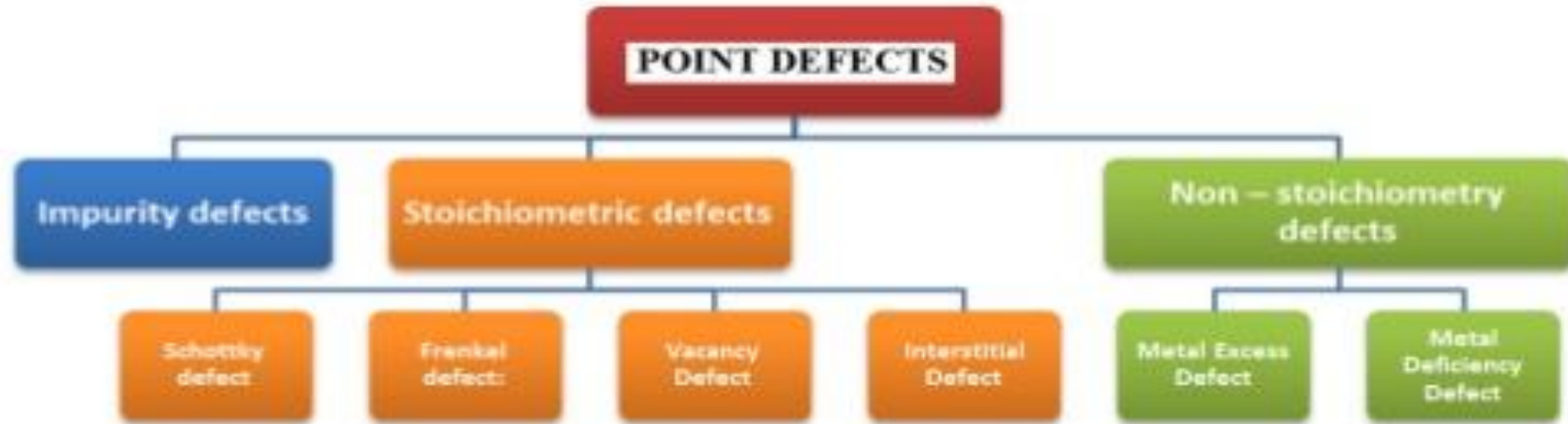
It is broadly categorised into following :

- 1) Point defect
- 2) Line defect
- 3) Surface defect
- 4) Volume defect

EXAMPLE



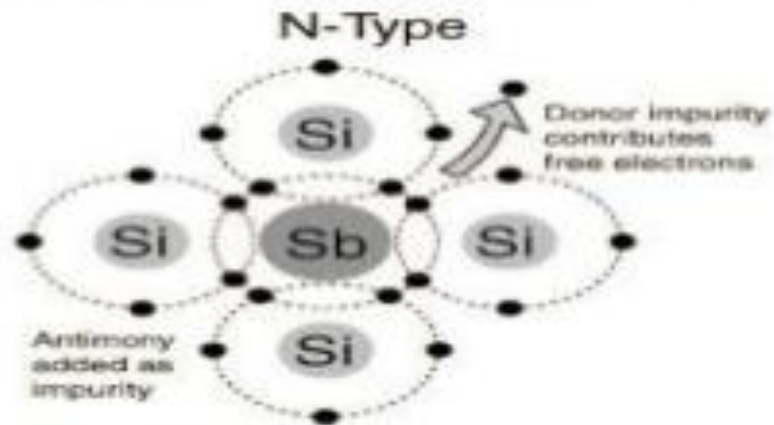
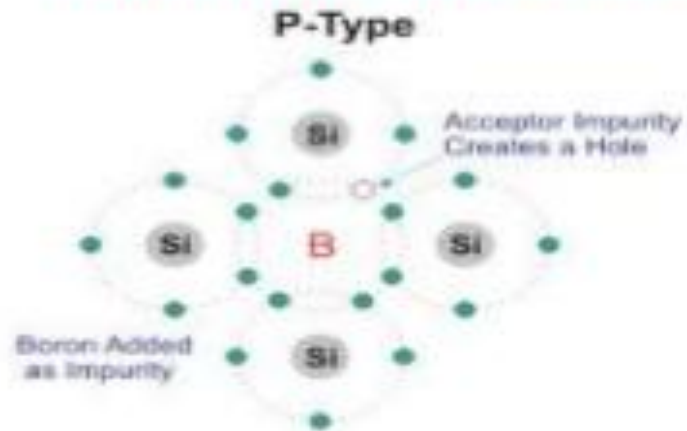
POINT DEFECT TYPES



IMPURITY DEFECTS

These defects arise when foreign atoms are present at the lattice site in place of the host atom. Or it is present at the vacant interstitial site example n – type semi conductor, p – type semi conductor.

The process of adding impurities to the crystalline is called as doping.



STOICHIOMETRIC DEFECTS

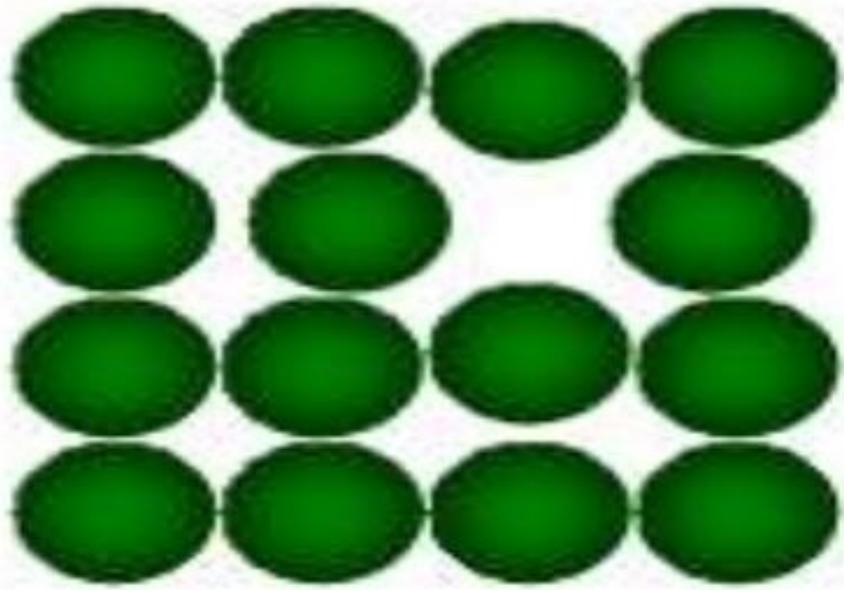
The compounds in which the number of cation and anions are exactly in the same ratio as represented by their chemical formula are called stoichiometric compounds. The defects that do not disturb the ratio of cations and anions are called stoichiometric defect.

Types of stoichiometric defects

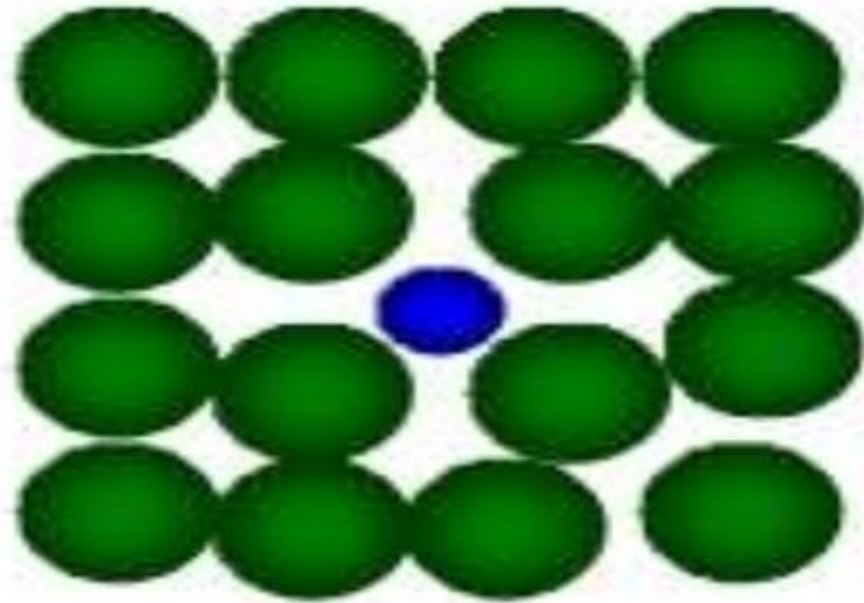
- 1) Frenkel Defect
- 2) Schottky defect
- 3) Vacancy Defect
- 4) Interstitial Defect



Example



Vacancy



Interstitial impurity



FRENKEL DEFECT

If an ion is missing from its correct lattice sites (causing a vacancy or a hole) and occupies an interstitial site, electrical neutrality as well as stoichiometry of the compounds are maintained

This type of defect is called **Frenkel defect**.

Since cations are usually smaller, it is more common to find the cations occupying interstitial sites.

This type of defect is present in ionic compounds which have:

- i) Low co ordinations number
- ii) Larger difference in size of cation and anions
- iii) Compounds having highly polarising cation and easily polarisable anion. A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS etc.



SCHOTTKY DEFECT

If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice. It is called **Schottky defect**.

This type of defect is shown by highly ionic compounds which have:

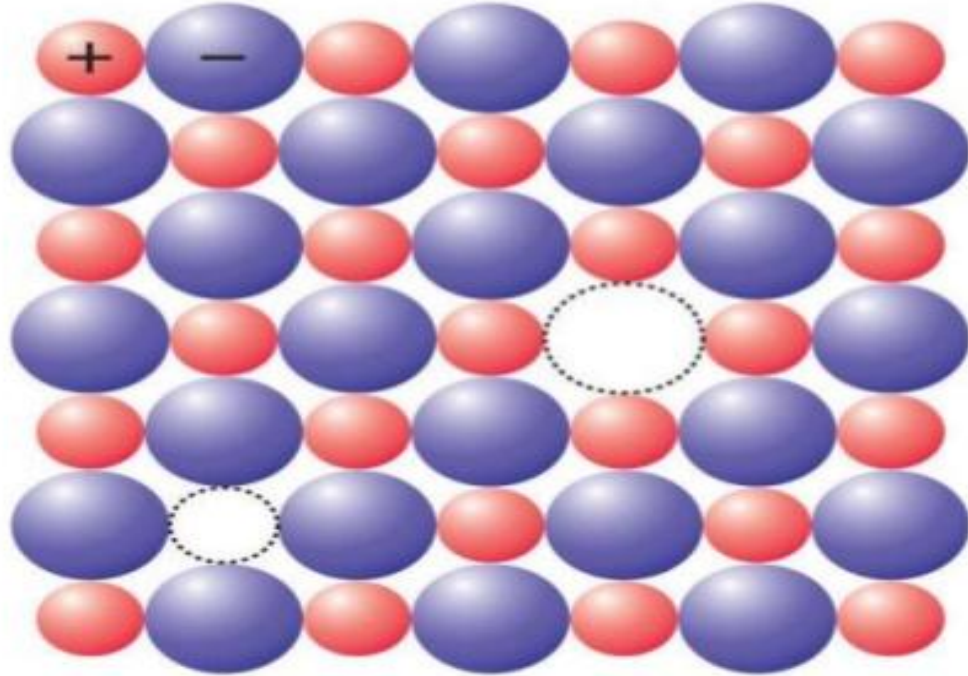
- i) High Co – ordination number and
- ii) Small difference in the sizes of cations and anions

A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr and CsCl.

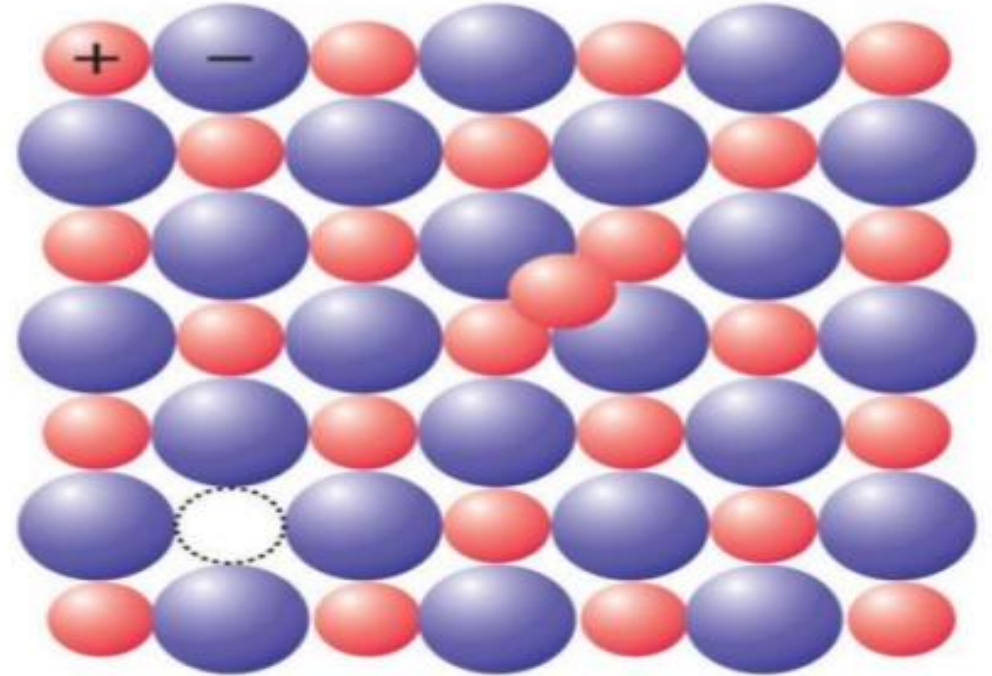
AgBr **shows both type of defect**.



Example of Frenkel and Schottky Defects



(a) Schottky defect



(b) Frenkel defect



NON – STOICHIOMETRIC DEFECTS

If as a result of imperfection, the ratio of number of cation to anion becomes different from that indicated by the ideal chemical formula, the defects are called **non – stoichiometric defects**.

These defects arise either due to excess of metal atoms or non metal atom or presence of impurities / foreign particle.



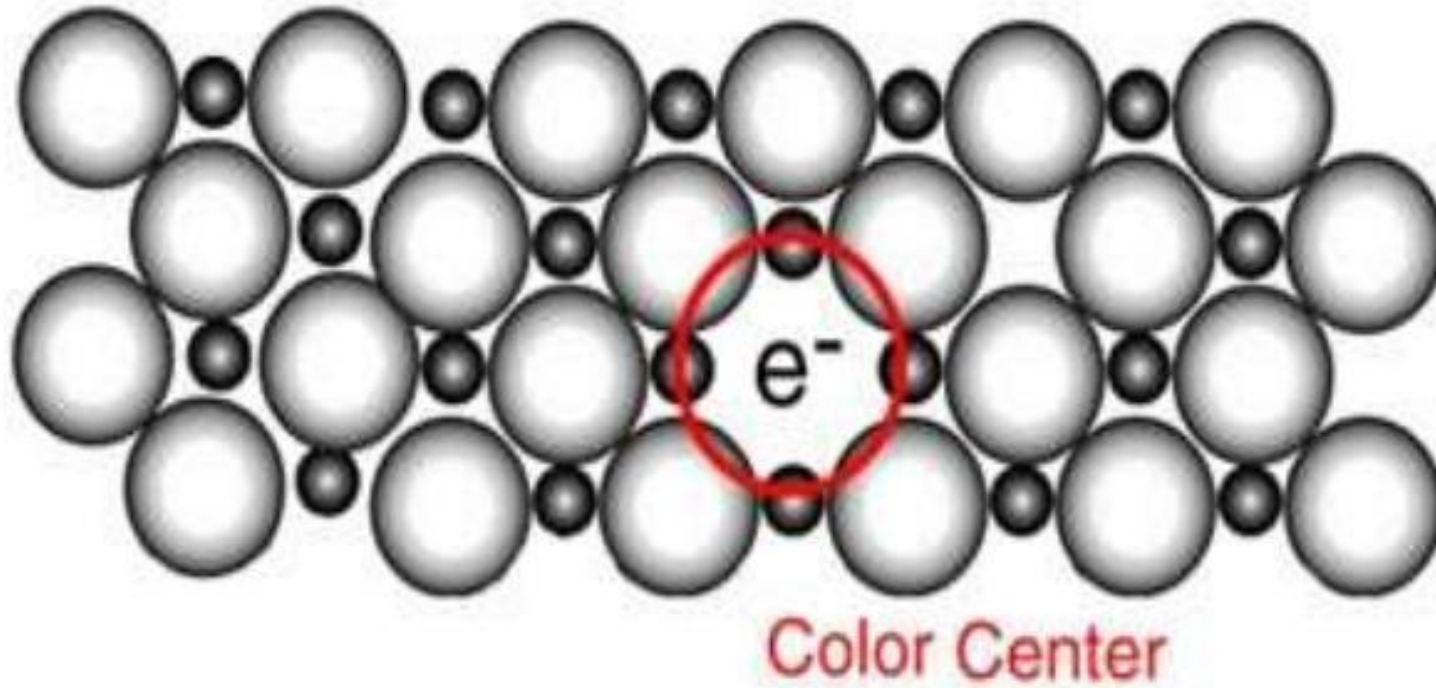
Types

i) Metal Excess Defects (**The Colour Centres**)

ii) Metal Deficiency defects



Example



*Thank
you*

