

CRYSTAL DEFECTS

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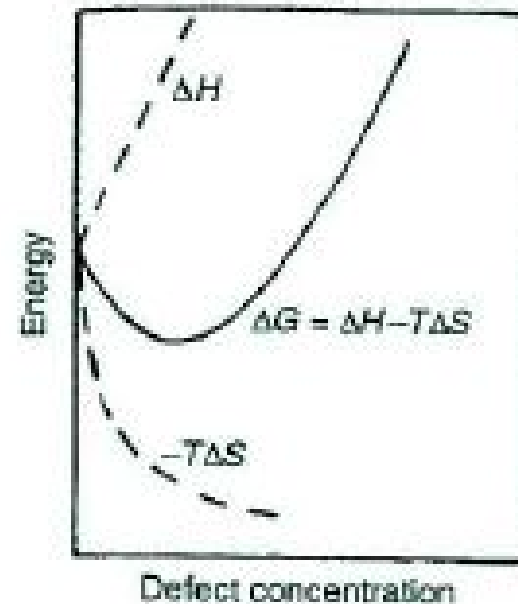
PALAYAMKOTTAI

CRYSTAL DEFECT

Crystalline solids exhibit a periodic crystal structure. The positions of atoms or molecules occur on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atoms or molecules in most crystalline materials is not perfect. The regular patterns are interrupted by crystal defects. The equilibrium structure at any temperature other than 0K will have some disorder or imperfection. The presence of defects in a crystal is a thermodynamic requirement for stability.

Why do they exist at equilibrium?

- 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.



➤ **STRUCTURAL PROPERTIES**

➤ **ELECTRONIC PROPERTIES**

➤ **CHEMICAL PROPERTIES**

➤ **SCATTERING PROPERTIES**

➤ **THERMODYNAMIC PROPERTIES**

CLASSIFICATION OF DEFECTS

0 -DIMENSIONAL DEFECTS

POINT DEFECTS

- ❖ VACANCY
- ❖ INTERSTITIAL
- ❖ SUBSTITUTION

1-DIMENSIONAL DEFECT

LINE DEFECTS

- ❖ EDGE DISLOCATION
- ❖ SCREW DISLOCATION

2-DIMENSIONAL DEFECTS

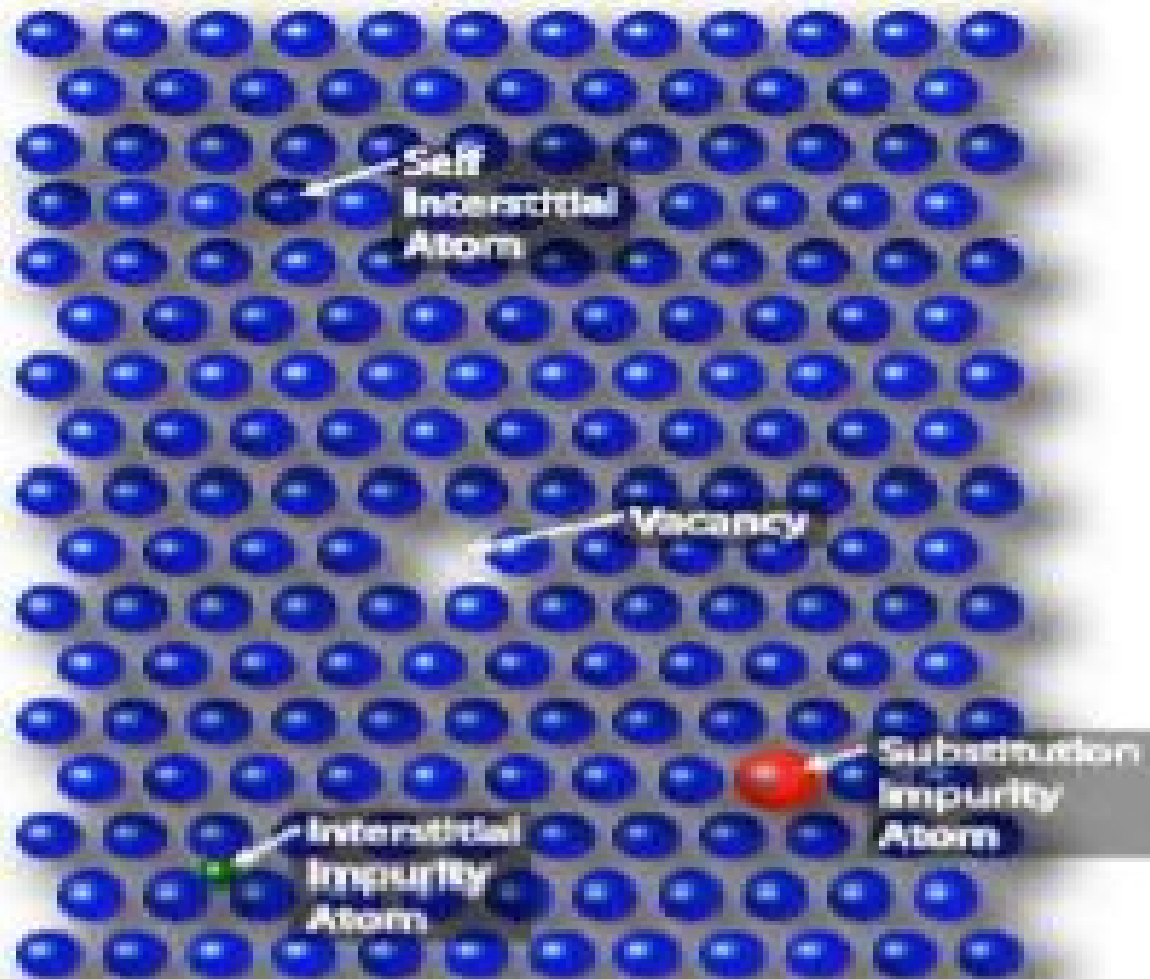
PLANE DEFECTS

- ❖ GRAIN BOUNDARY
- ❖ STACKING FAULTS

POINT DEFECT

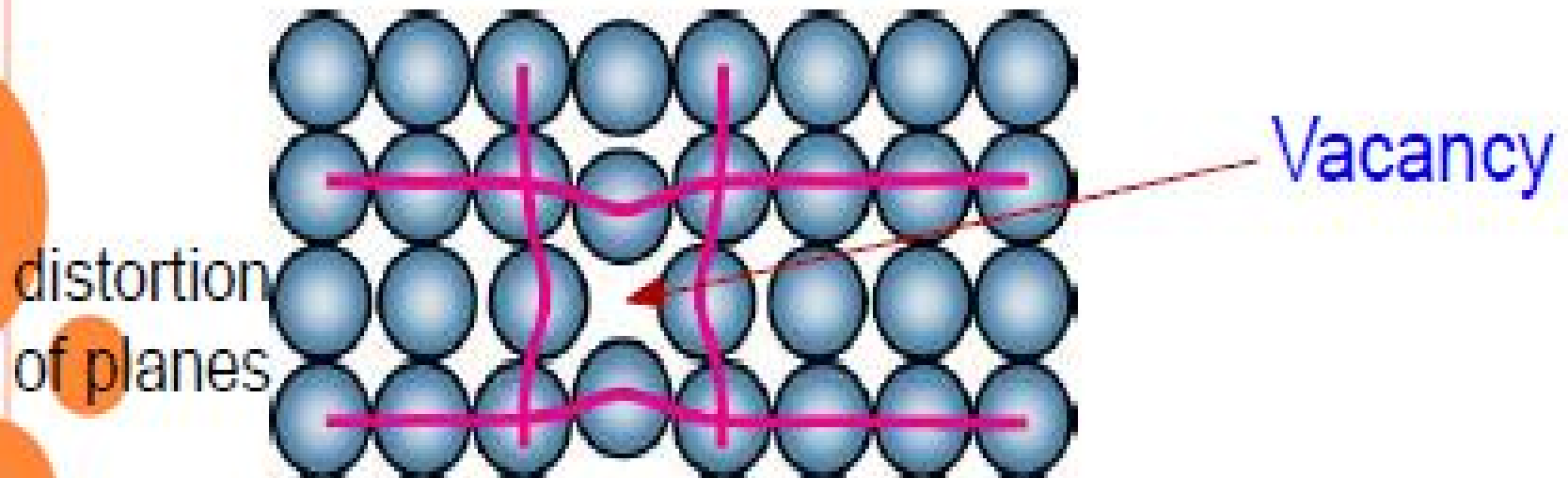
Point defects are defects that occur only at or around a single lattice point. Atoms in solid possess vibrational energy, some atoms have sufficient energy to break the bonds which hold them in equilibrium position. Hence, once the atoms are free they give rise to point defects.

POINT DEFECTS



VACANCY

- Missing atom from an atomic site.
- Atoms around the vacancy displaced.
- Tensile stress field produced in the vicinity.



VACANCY DEFECT

At any finite temperature, some of the lattice points normally occupied by metals ions are vacant giving rise to vacancy defects.

□ The no. of vacancies is determined by :-

- Temperature
- The total no. of metals atoms
- The average energy required to create a vacancy

Then,

$$n = f (N, E_v, T)$$

□ The concentration of vacancies increases with :-

- Increasing temperature
 - Decreasing activation energy
- The creation of a defect requires energy, i.e., the process is endothermic.
- In most cases Diffusion (mass transport by atomic motion can only occur because of vacancies.
- This defect results in decrease in density of the substance.

Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

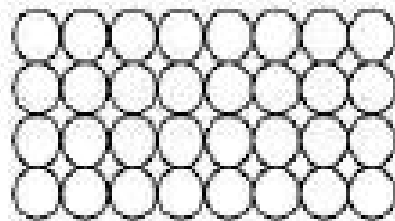
No. of potential defect sites.

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

Activation energy

Boltzmann's constant

Temperature



Each lattice site

is a potential
vacancy site

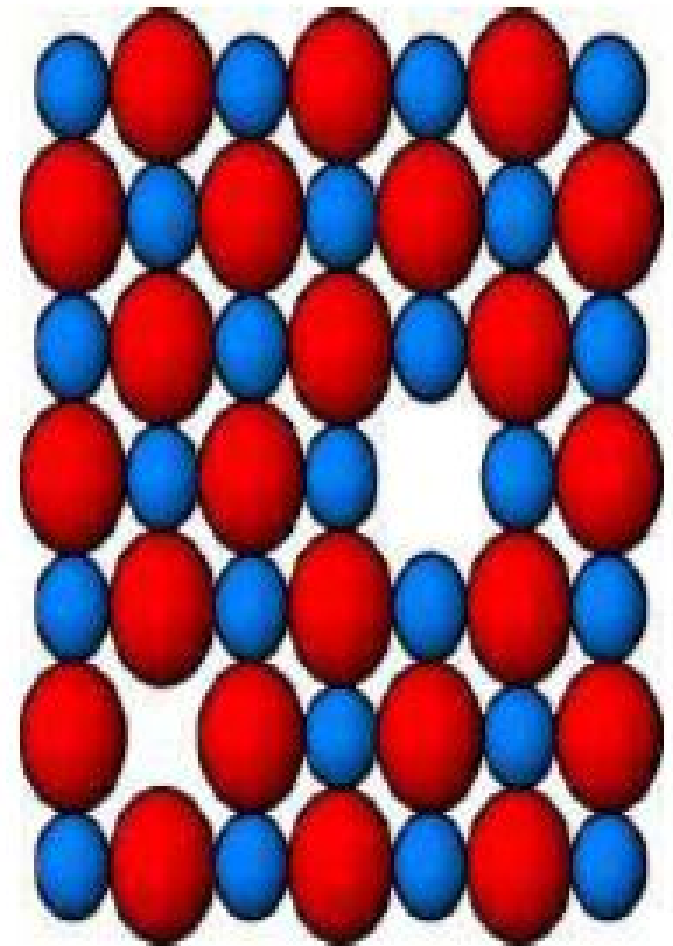
$$(1.38 \times 10^{-23} \text{ J/atom-K})$$

$$(8.62 \times 10^{-5} \text{ eV/atom-K})$$

SCHOTTKY DEFECT

A vacancy is created in a metal by the migration of a metal atom/ion to the surface; similarly, in a binary ionic crystal represented by A^+B^- , a cation anion pair (A^+B^-) will be missing from the respective lattice position, the energy absorbed during the creation of SCHOTTKY DEFECT is more than compensated by the resultant disorder in the lattice/structure.

Schottky defect are dominant in closest-packed structures such as ROCK SALT ($NaCl$) structure .



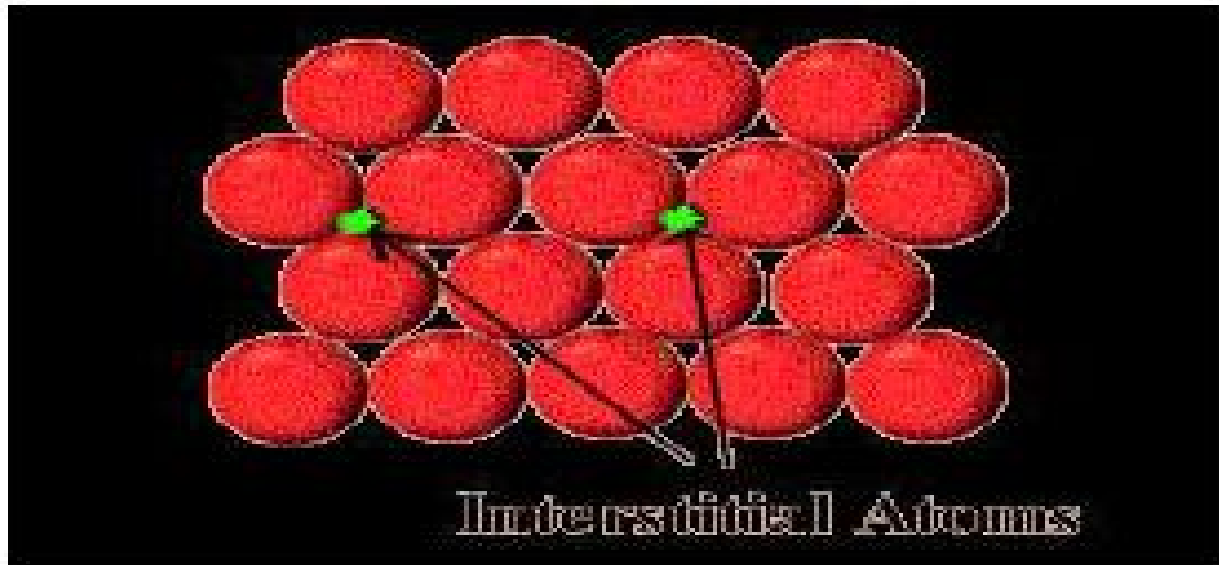
The no. of Schottky defects depends on :

- The total no. of ion-pairs, i.e., mass of the ionic crystal.
- The average energy required to produce a schottky defect.
- Temperature .

The fraction of Schottky defects increases exponentially with increasing temperature

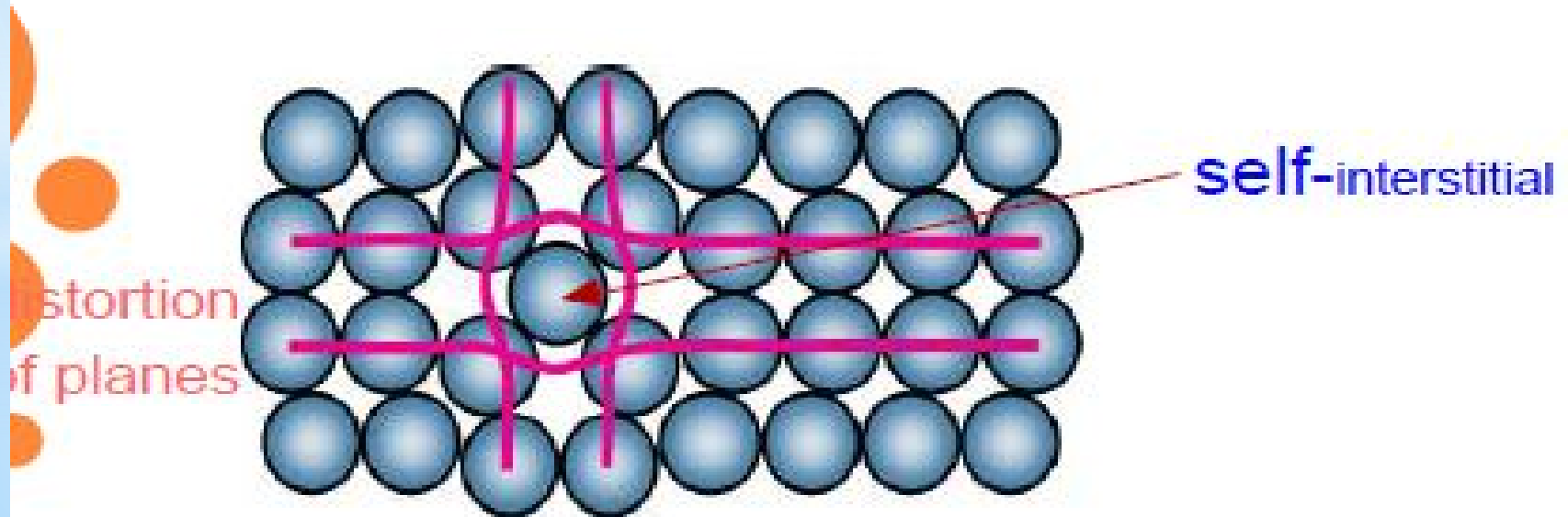
INTERSTITIAL DEFECT

- If an atom or ion is removed from its normal position in the lattice and is placed at an interstitial site, the point defect is known as an INTERSTITIAL .
- An example of interstitial impurity atoms is the carbon atoms that are added to iron to make steel.
- Carbon atoms, with a radius of 0.071nm, fit nicely in the open spaces between the larger (0.124nm) iron atoms.

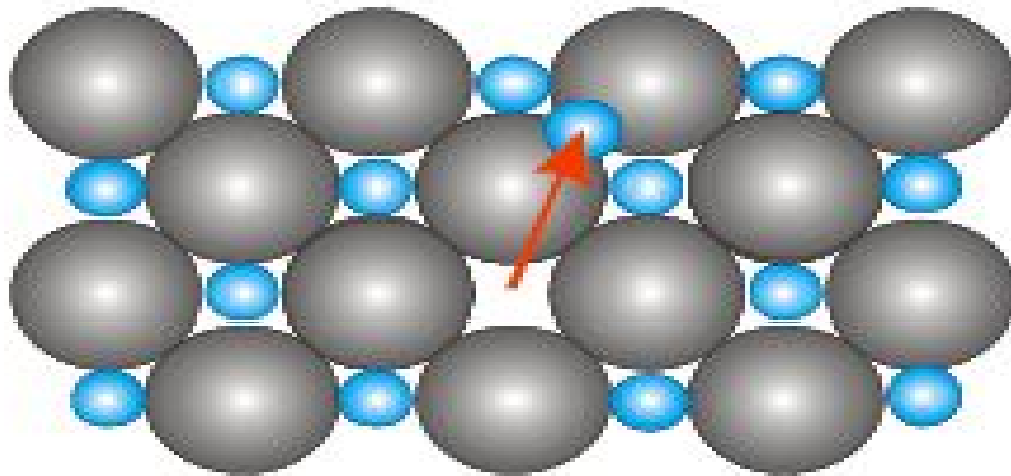


SELF – INTERSTITIAL

- If the matrix atom occupies its own interstitial site, the defect is called self interstitial.
- Self-interstitials in metals introduce large distortions in the surrounding lattice.



FRENKEL DEFECT



- When an atom leaves its regular site and occupy nearby interstitial site it give rise to FRENKEL DEFECT.
- A crystal with FRENKEL DEFECT will have equal no. of vacancies and interstitials.
- These defects are prevalent in open structures such as those of silver halides .
- For eg. \rightarrow AgI , CaF_2

SUBSTITUTIONAL DEFECTS

Impurities occur because materials are never 100% pure. In the case of an impurity, the atom is often incorporated at a regular atomic site in a crystal structure. This is neither a vacant site nor is the atom on an interstitial site and it is called a SUBSTITUTIONAL defect.

Substitution of a lattice ion by an impurity ion of different charge will disturb the charge balance.

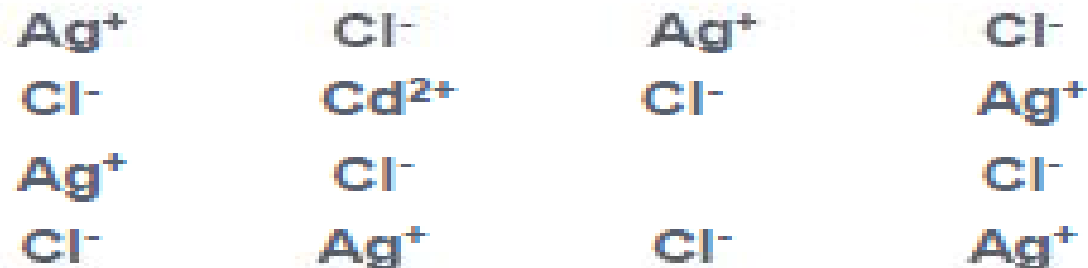
In order to maintain the charge neutrality of the lattice, such substitution may be accompanied either by the creation of a lattice vacancy or by the change of the oxidation state of an ion in the lattice.

Substitution of Ag^+ by Cd^{2+} in AgCl leads to the creation of a lattice vacancy.

Substitution of Ni^{2+} by Li^+ in NiO lattice gives rise to the change of the oxidation state of an ion in the lattice

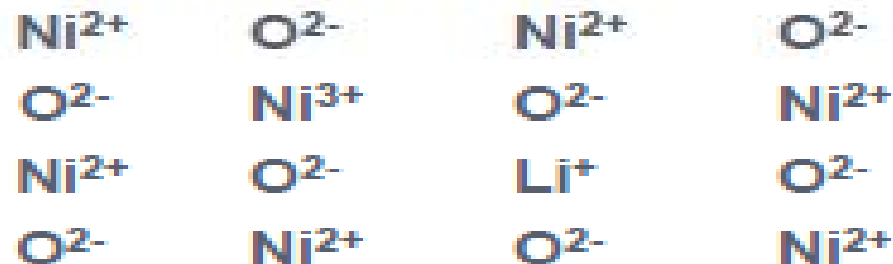
SUBSTITUTIONAL DEFECT

Substitution of Ag^+ by Cd^{2+} in AgCl leads to the creation of a lattice vacancy.



**vacancy produced by
 Cd^{2+} substitution**

Substitution of Ni^{2+} by Li^+ in NiO lattice gives rise to the change of the oxidation state of an ion in the lattice .



**valence defect produced
by Li^+ substitution**

NON-STOICHIOMETRIC DEFECT

Any deviation from stoichiometry in a predominantly ionic solid implies that one of the two elements present in it should be an excess of what is needed for stoichiometry.

For eg., in the oxide MO_{1-x} , the excess M may be due to the presence of extra metal atoms in the interstitial positions.

It may be also due to the presence of oxygen vacancy in greater no. than metal vacancy.

This would also require that the metal is present in more than one oxidation state as the charge neutrality of the solid cannot be maintained otherwise .

Charge neutrality may also be maintained by electronic defects (electrons or holes trapped at the defects).

Non-stoichiometric defects depend upon whether the positive ions are in excess or negative ions are in excess.

Metal Excess Defects

In these defects, the positive ions are in excess.

These may arise due to:

- i) Anionic vacancies
- ii) Presence of extra cations in interstitial sites.

Metal Deficient Defects

These contain less no. of positive ions than negative ions.

These arise due to:

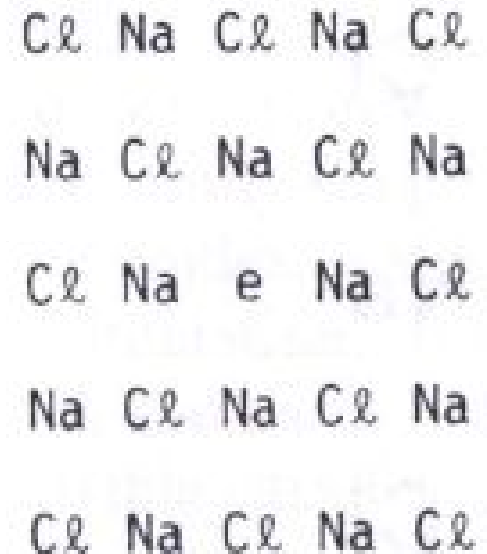
- i) Cation vacancies
- ii) Extra anions occupying interstitial sites.

ANION VACANCIES

- ❖ In this case, negative ions may be missing from their lattice sites leaving holes in which the electrons remain entrapped to maintain the electrical neutrality.
- ❖ There is an excess of positive ion although, the crystal as whole is electrically neutral.
- ❖ In alkali metal halides, anion vacancies are produced when alkali metal halide crystals are heated in the atmosphere of the alkali metal vapours.

COLOUR CENTRES

- The defect that very much influences the electronic properties of the solids.
- These are the electronic defects.
- Solid has an anion vacancy. Hence this site has a strong positive potential and can trap electrons. It will need some energy to free the trapped electron.
- When sodium chloride is heated in sodium vapour, it acquires a yellow colour. The heating in excess sodium creates new lattice sites for sodium.
- To maintain the structure, an equal no. of chloride sites are also created, but the latter are vacant.
- The electron of the sodium atom that is ionized in the NaCl matrix is trapped by the chloride ion vacancy. This trapped electron can be freed into the crystal by absorbing visible light and hence the colour .
- A trapped electron at an anion vacancy is an electronic defect and it is known as F-centre(from German farbe meaning colour).
- Many of the point defects may have a charge different from the normal charge of the original site due to trapped electrons or holes. These electrons and holes can be released to the conduction band or to the valence band of the solid and this will modify its electronic properties.



EXCESS CATIONS OCCUPYING INTERSTITIAL SITES

·In this case, there are extra positive ions occupying interstitial sites and the electrons in another interstitial sites to maintain the electrical neutrality.

·For eg., Zinc Oxide

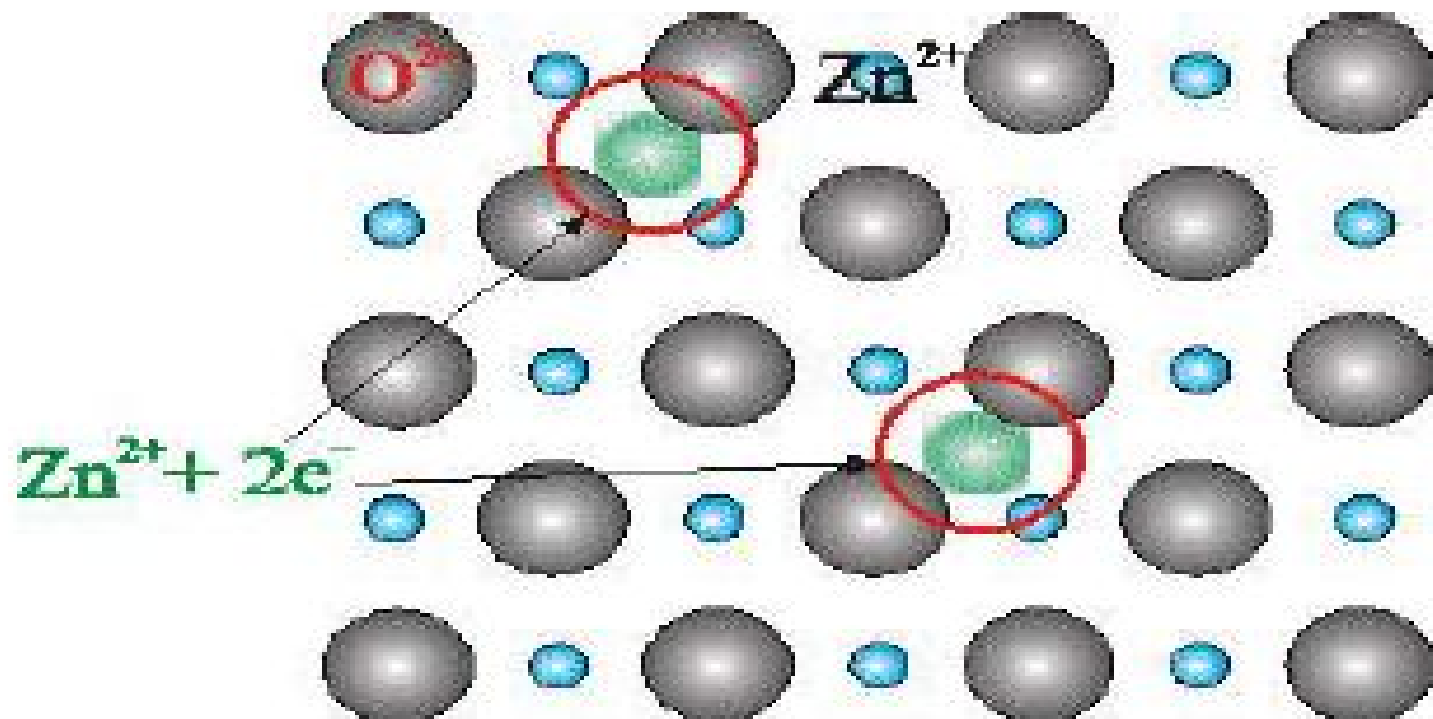
·Zinc Oxide (ZnO) is white in colour at room temperature . On heating it loses oxygen at high temperatures and turns yellow in colour.



·~~The excess of Zn²⁺~~ ions are trapped in interstitial sites and equal no. of electrons are trapped in the neighbourhood to balance the electrical charge .

·These electrons give rise to enhanced electrical conductivity.

- **Zno heated in Zn vapour Zn_yO ($y>1$)**
- **The excess cations occupy interstitial voids.**
- **The e^- s ($2e^-$) released stay associated to the interstitial cation.**



COSEQUENCE OF METAL EXCESS DEFECTS

- The crystals with metal excess defects conduct electricity due to free electrons.
- However, the conductivity is low because of the no. of defects and therefore, the no. of free electrons is very small.
- Because of low conductivity as compared to conductivity of the metals, these are called semi-conductors.
- These compounds are also called n-type semi conductors. Since the current is carried by the electrons in the normal way.
- The crystal with metal defects are generally coloured. For eg., non-stoichiometric sodium chloride is yellow, potassium chloride is violet and lithium chloride is pink.

CATION VACANCIES

In some cases, the positive ions may be missing from their lattice sites.

The extra negative charge may be balanced by some nearby metal ion acquiring two positive charges instead of one.

This type of defect is possible in metals which show variable oxidation state.

For eg., ferrous oxide, ferrous sulphide, nickel oxide etc.

In case of iron pyrites (FeS), two out of three ferrous ions in a lattice may be converted into Fe^{3+} state and the third Fe^{2+} ion may be missing from its lattice site.

Therefore, the crystal contains Fe^{2+} and Fe^{3+} ions.

This gives rise to exchange of electrons from one Fe^{2+} ion to Fe^{3+} ion in which Fe^{2+} changes to Fe^{3+} and Fe^{3+} changes to Fe^{2+} ion.

As a result crystal has metallic lustre .

Because of the natural colour of iron pyrites and metallic lustre some samples of minerals shine like gold.

Similarly, FeO is mostly found with a composition of $\text{Fe}_{0.95}\text{O}$ it may actually range from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$.

In crystal of FeO , some Fe^{2+} ions are missing and the loss of positive charge is made up by presence of required no. of Fe^{3+} ions. Moreover, since there is exchange of electrons, the substances become conductors.

FeO heated in oxygen atmosphere Fe_xO ($x < 1$)

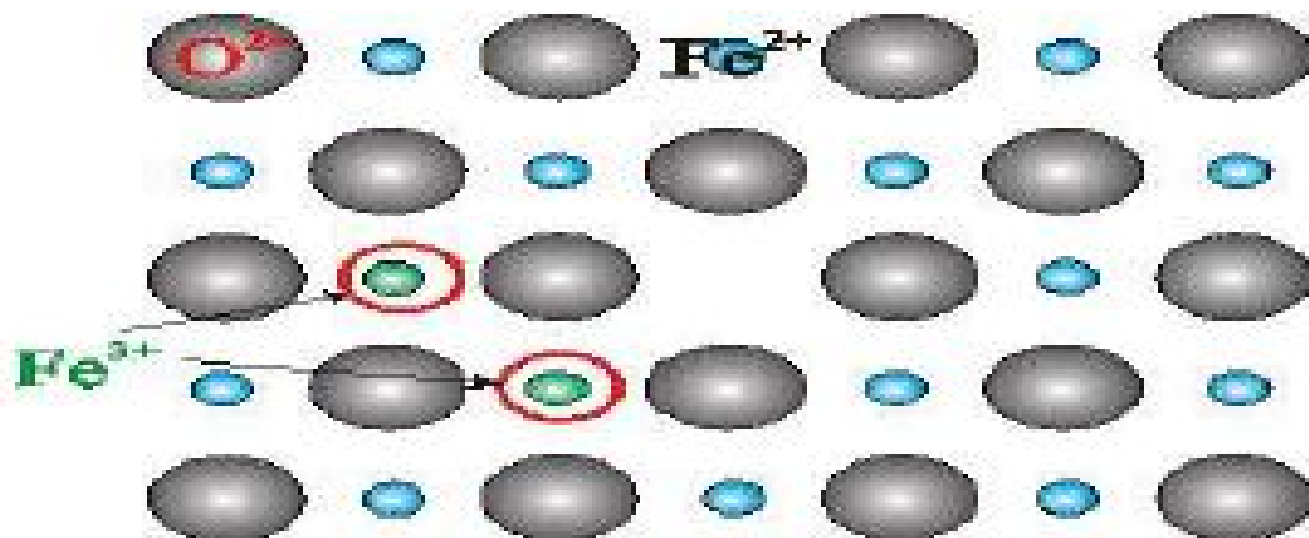
Vacant cation sites are permanent.

Charge is compensated by conversion of ferrous to ferric ion.

Fe^{2+}

$\text{Fe}^{3+} + e^-$

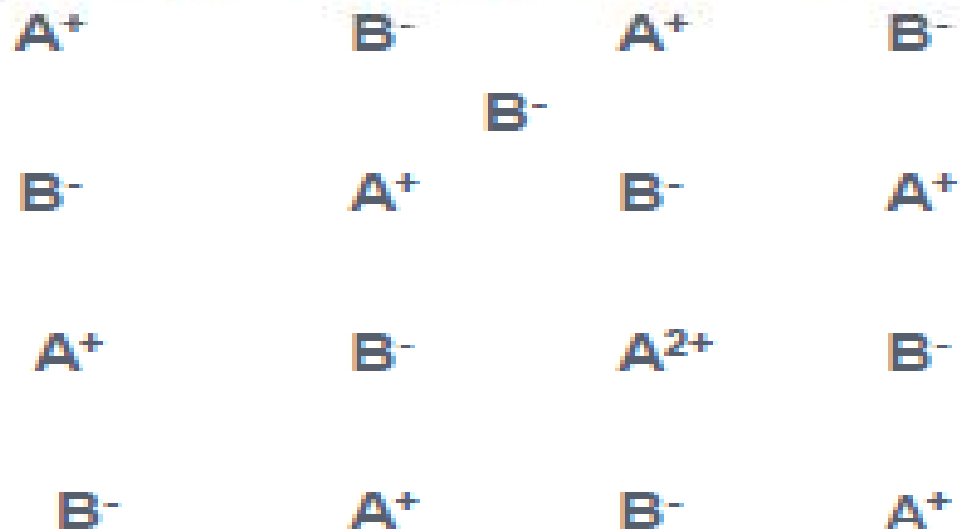
For every vacancy (of Fe cation) two ferrous ions are converted to ferric ions provide the $2e^-$ s required by excess oxygen.



EXTRA ANIONS OCCUPYING INTERSTITIAL SITES

In this case, the extra anion may be occupying interstitial positions. The extra negative charge is balanced by the extra charges (oxidation of equal no. of cations to higher oxidation states) on the adjacent metal ions.

Such type of defect is not common because the negative ions are usually very large and they cannot easily fit into the interstitial sites.



CONSEQUENCE OF METAL DEFICIENT DEFECT

Crystals with metal deficient defects are semi-conductors.

The conductivity is due to the movement of electrons from one ion to another.

For eg., When an electron moves from ion A^+ , it changes to A^{2+} . It is also called movement of positive hole and the substances are called p-type semi-conductors.

2. Line Defects (One dimensional)

- A dislocation is a line discontinuity in the regular crystal structure.
- A part of the line will be missing from its regular site and this missing row is dislocation. The dislocation is centered along a line and hence the line defect is called dislocation.

The dislocation is a boundary between the slipped and unslipped region and lies in the slip plane

- The structure and behaviour of dislocations affect many of the properties of engineering materials.

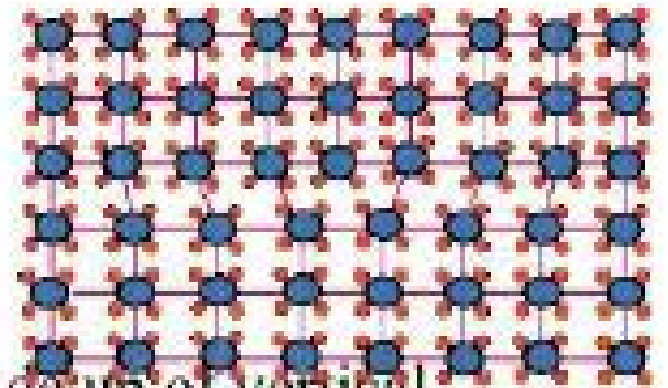
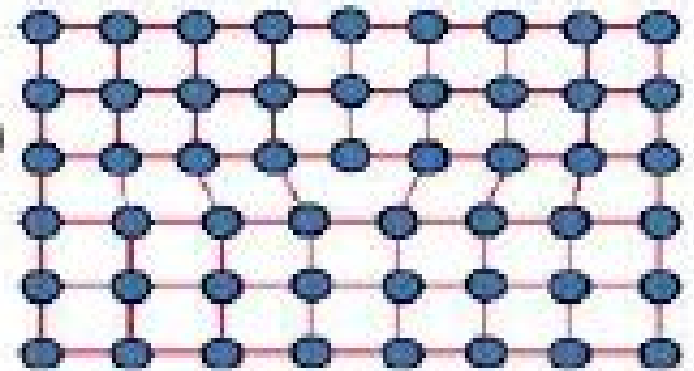
- There are two basic types:

- s Edge dislocations*

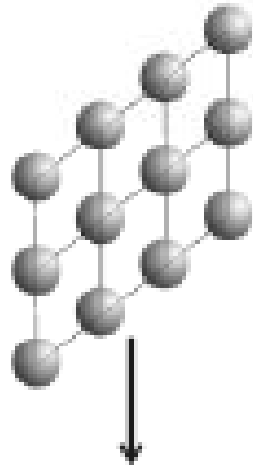
- s Screw dislocations.*

1) Edge dislocation

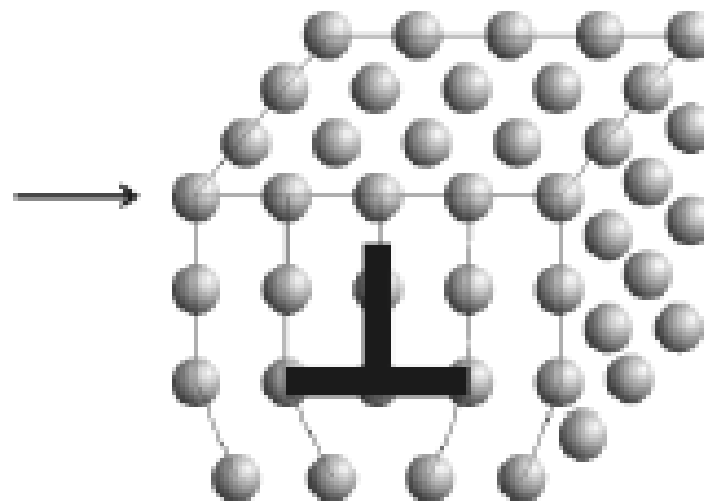
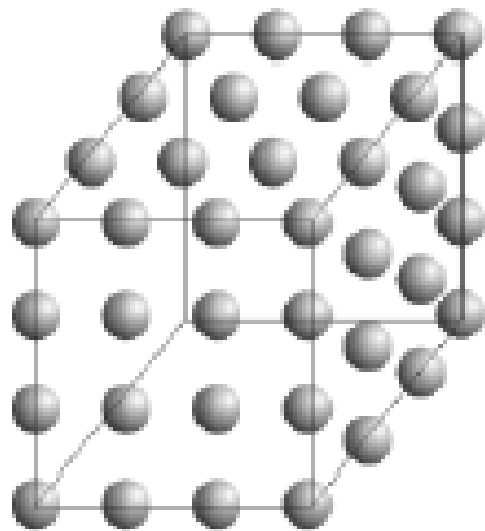
- An *Edge dislocation* in a metal may be regarded as the insertion (or removal) of an extra half plane of atoms in the crystal structure.
- In Ionic and Covalent solids edge dislocations involve extra half planes of *unit cells*.
- If we consider a perfect crystal to be made up of vertical planes parallel to one another and to the side faces. If one of these vertical planes does not extend from the top to the bottom of crystals but ends part way within crystal, it is called as edge dislocation.



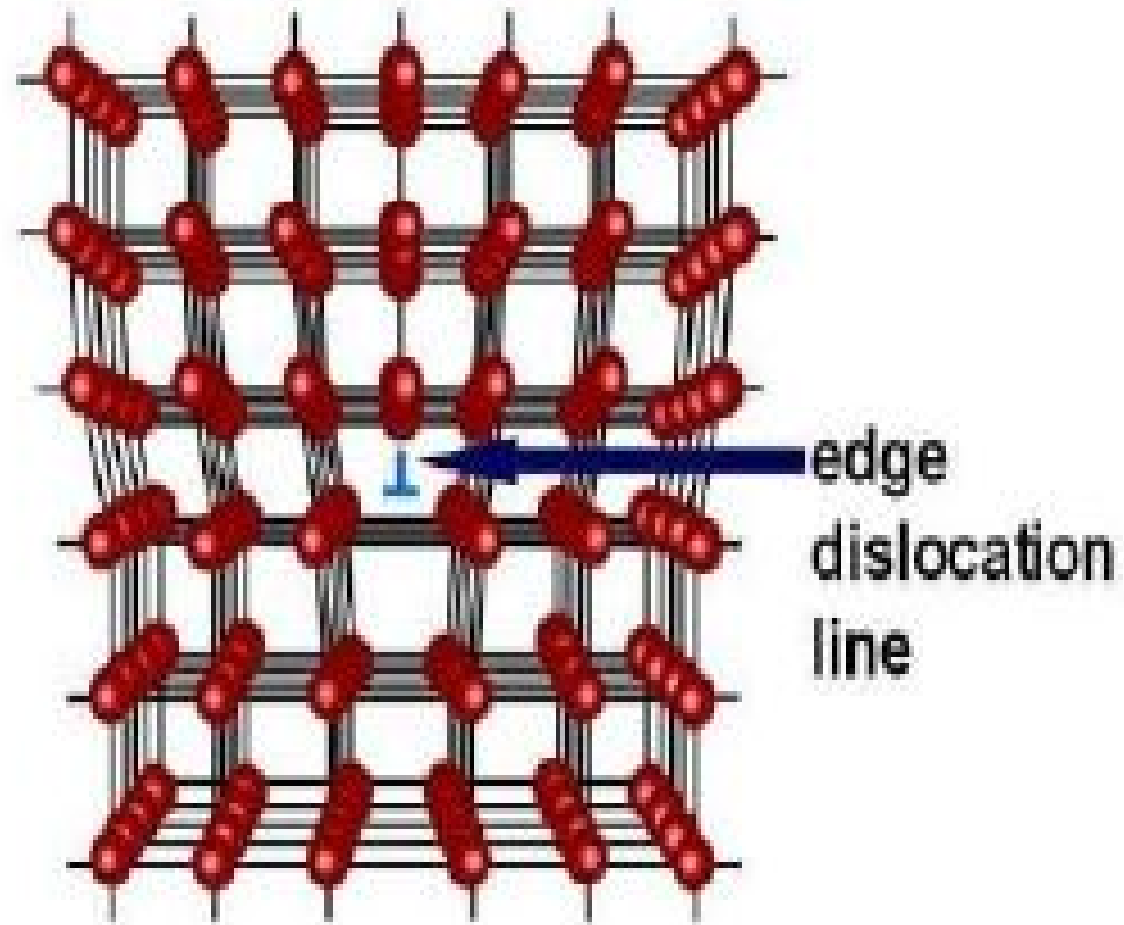
Dislocation geometry



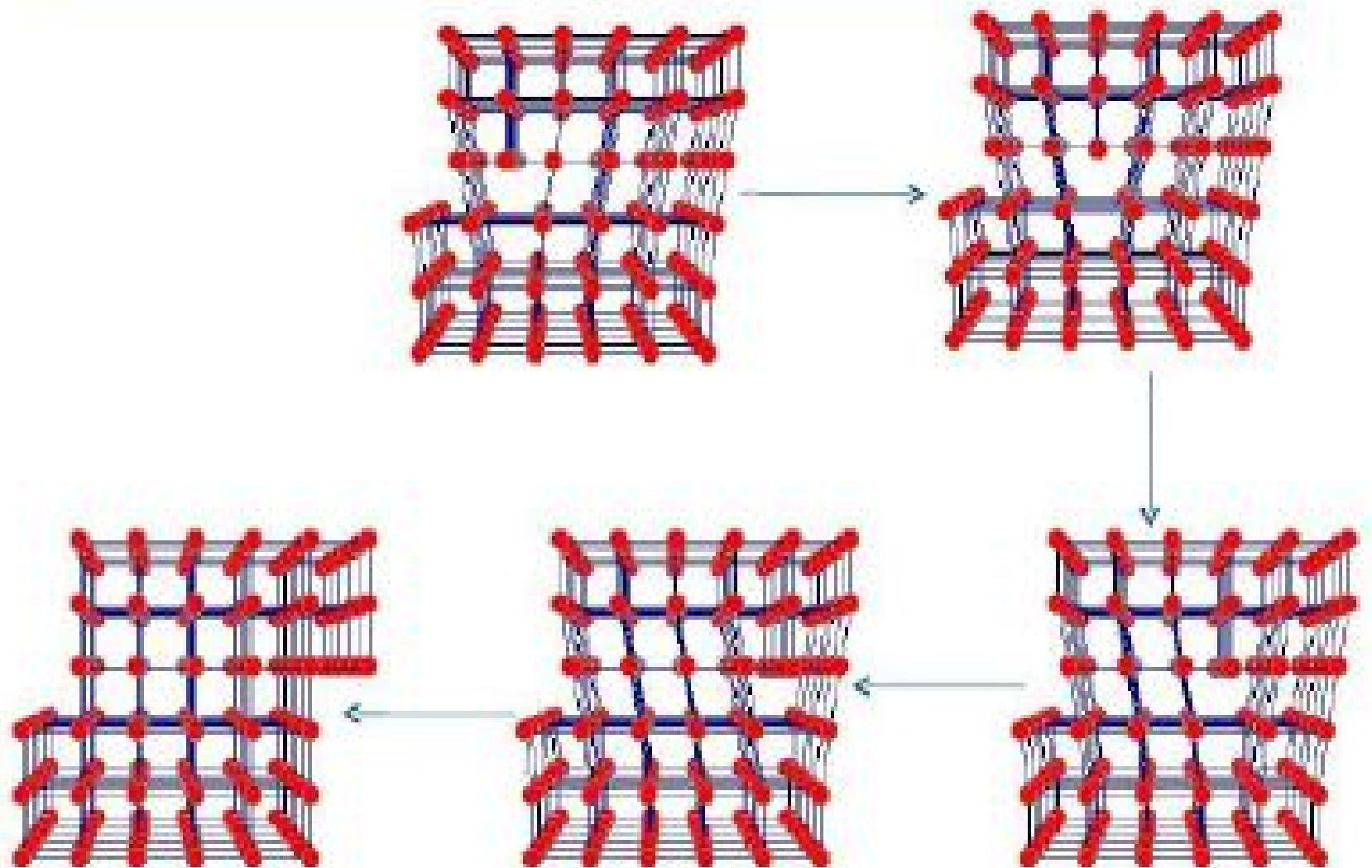
An edge dislocation can also be visualized as an extra half plane (or missing half plane):



- Berger vector is perpendicular to dislocation line.



Movement of an Edge Dislocation

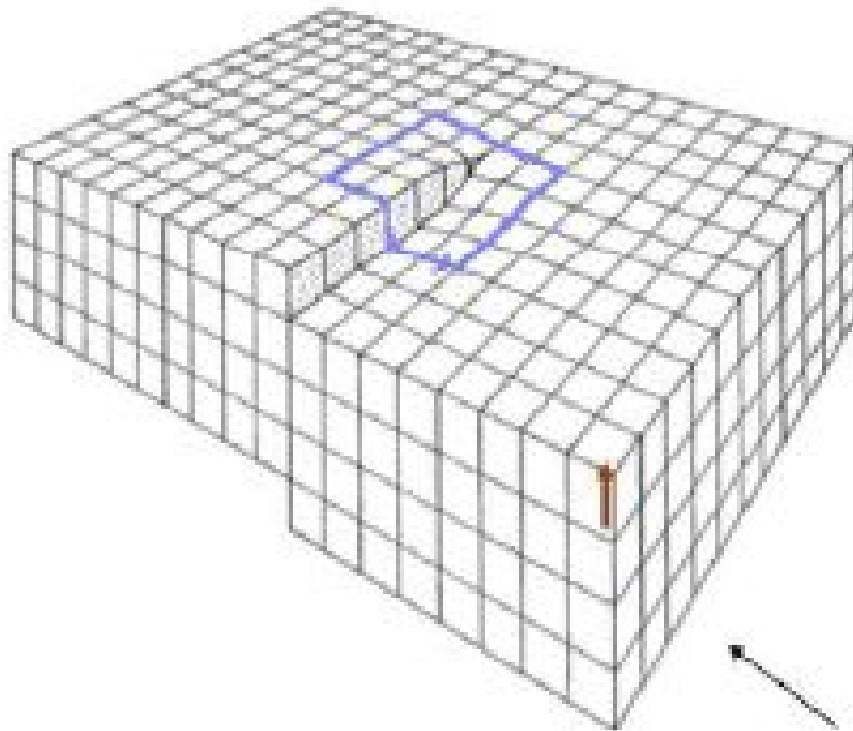


2) Screw dislocation

- In screw dislocation, there is transformation of successive atomic planes into the surface of helix around dislocation line due to shear stress i.e. it follows helical or screw path.
- A screw dislocation can be imagined as being produced by cutting the crystal partway through with a knife and then shearing one part of the crystal with respect to the other parallel to the cut.

Dislocation geometry

Second elementary dislocation type: screw dislocations



Looks like a parking ramp

Edge dislocation:

Burgers vector perpendicular to dislocation line.

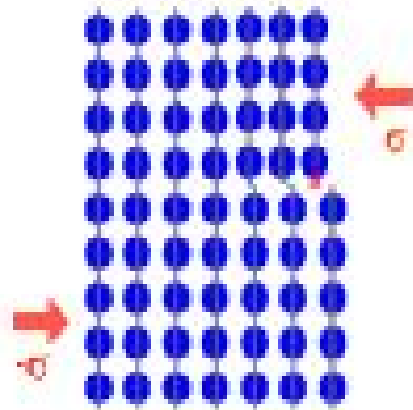
Screw dislocation:

Burgers vector parallel to dislocation line.

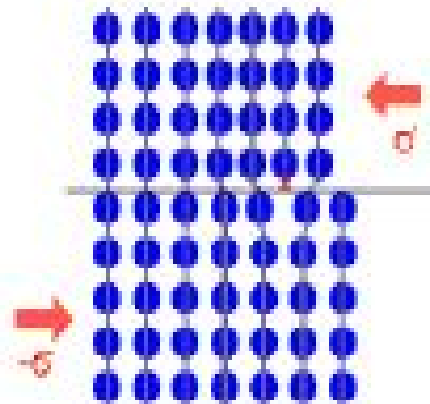


Dislocations: general features

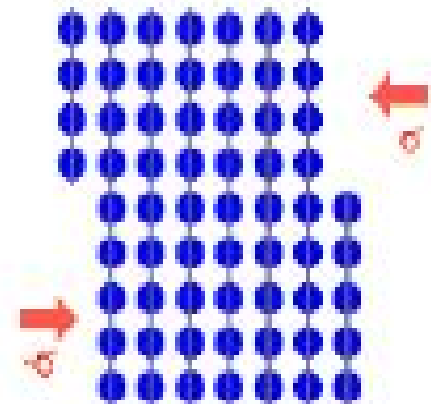
Dislocations are basic elements of plastic deformation:



As soon as critical shear stress is reached, dislocation starts moving: transition from elastic to plastic deformation



Dislocation moves on glide plane.

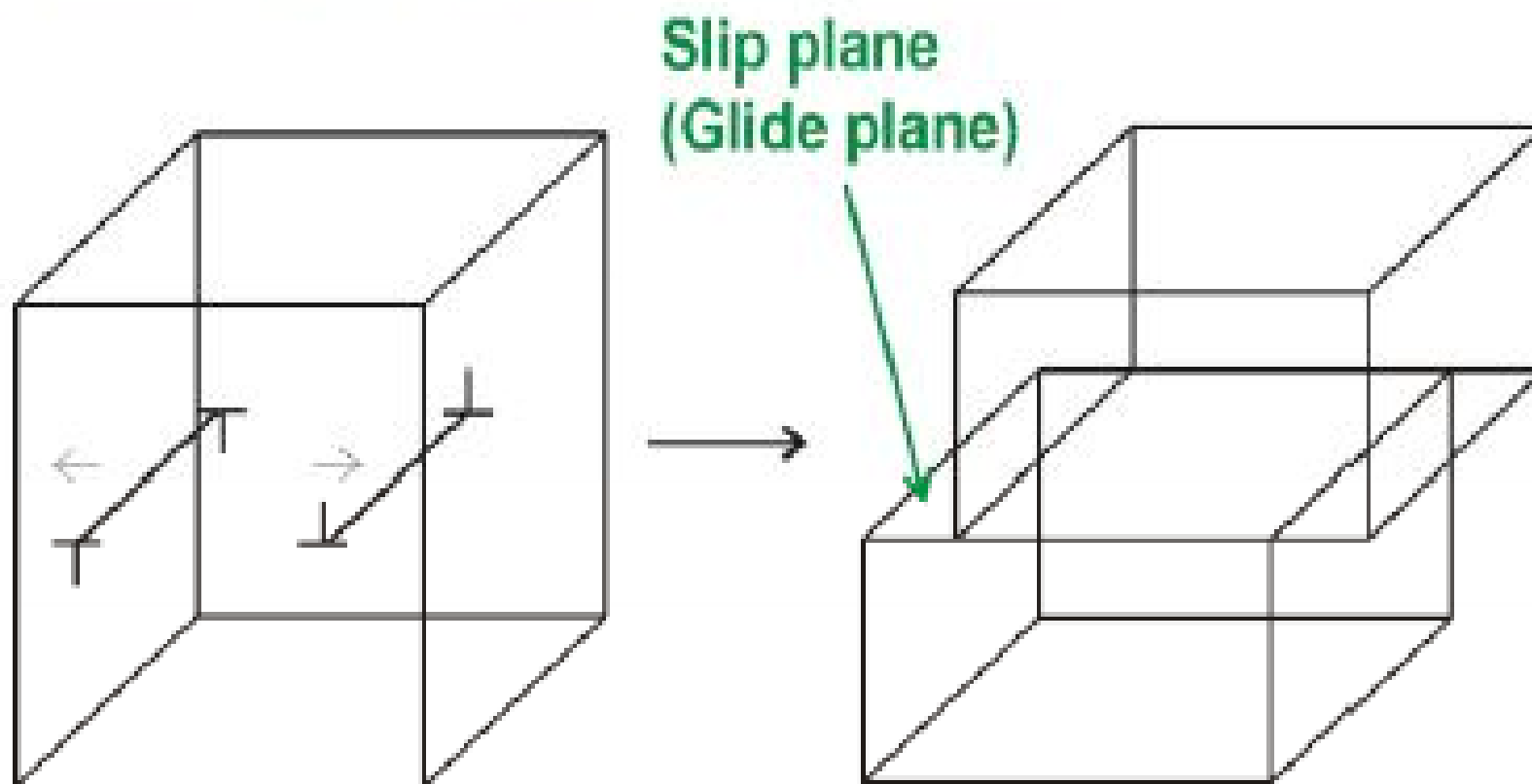


After dislocation has left the crystal, crystal is stress free.

Many dislocations are necessary to cause macroscopic deformation.

Dislocations: general features

Dislocations are basic elements of plastic deformation:



Slip produced by motion of two edge dislocations

PLANAR OR SURFACE DEFECTS

It is a two dimensional defect. Planar defects arise due to atomic planes during mechanical and thermal treatments. The change may be of the orientation or of the stacking sequence of the planes.

Planar defects are of the following types:

Grain boundaries

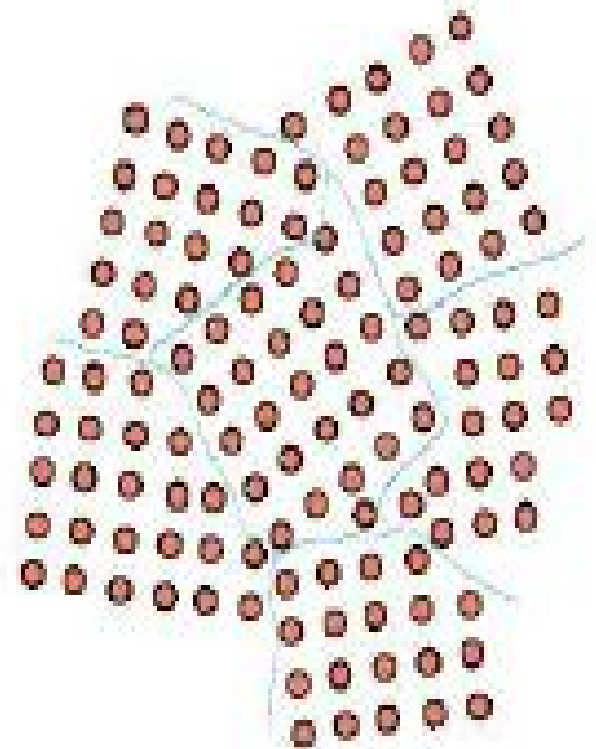
Tilt boundaries

Twin boundaries

Stacking faults

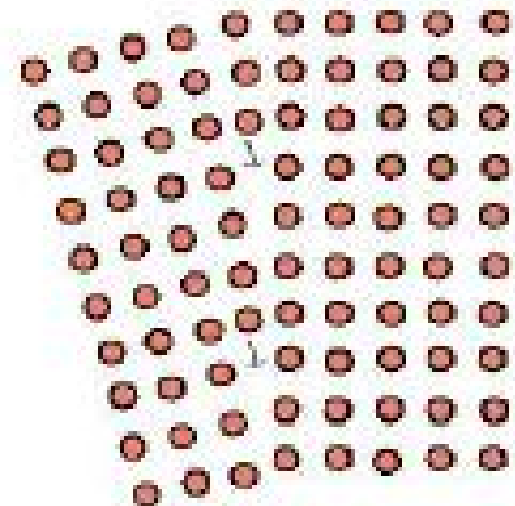
A) Grain Boundaries

- ▶ A Grain Boundary is a general planar defect that separates regions of different crystalline orientation (i.e. *grains*) within a polycrystalline solid . Grain boundaries are usually the result of uneven growth when the solid is crystallizing.



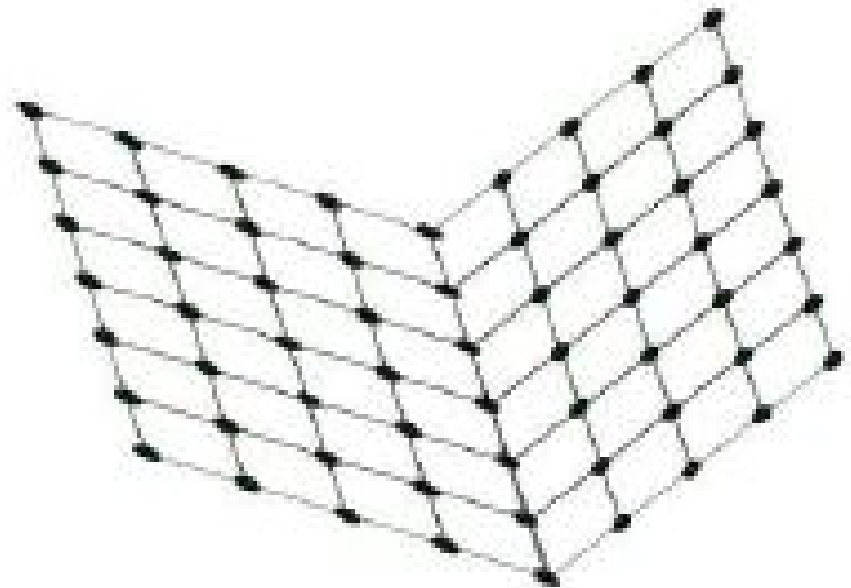
B) Tilt Boundaries

- When the angle between two crystals is less than 10° , the distortion is not so drastic as to be compared with a non crystalline material. They are also called low angle boundaries.
- It can be described as set of parallel, equally spaced edge dislocation of same sign located one above other.
- A Tilt Boundary, between two slightly mis-aligned grains appears as an array of edge dislocations.



C) Twin Boundaries

- These are the boundaries in the grains at which the atomic arrangement on one side of the boundary is the mirror image of the atoms on the other side. The volume of material which has an orientation similar to the mirror image of the matrix orientation is called a twin.
- The plane is called twinning plane.



STACKING FAULTS

Stacking faults occur in a number of crystals structures, but the common example is in close-packed structures. Face-centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in stacking order.

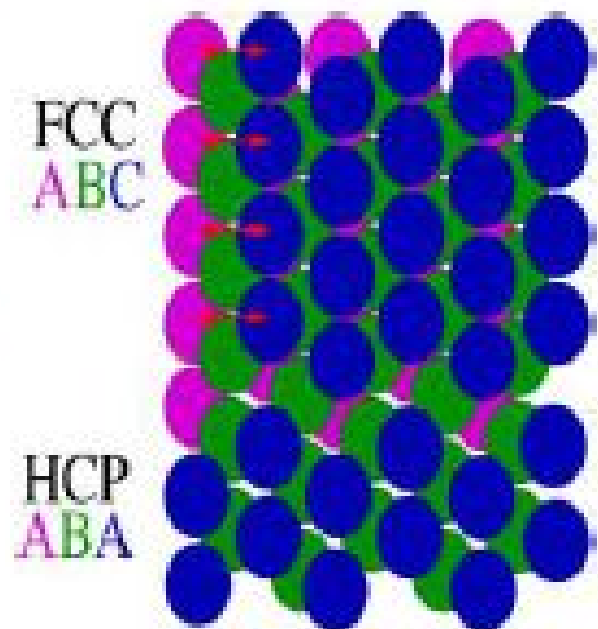
FCC and HCP packings are represented by ABCABCABC..... and ABABAB.....arrangements, respectively.

A deviation from the sequence in either of the stacking gives rise to a stacking faults,

e.g., ABCABABCAB.... in FCC and ABABBABA..... in HCP .

Stacking faults occur either due to dissociation of a dislocation or during the process of crystal growth.

However, the orientations on both sides of the stacking fault are the same except for translation with respect to one another by a fraction of a lattice vector.



DEFECTS DOES NOT NECESSARILY IMPLY A BAD THING :-

- Addition of C to Fe to make Steel.
- Addition of Cu to Ni to make thermocouple wires.
- Addition of Ge to Si to make thermoelectrical materials.
- Addition of Cr to Fe for corrosion resistance.
- Introduction of grain boundaries to strengthen materials.

REFERENCE

Principles of the Solid State by H.V. KEER

Solid State Chemistry by D.K. Chakrabarty

THANK YOU