

Stoichiometric - Crystal defect :

Imperfection defect : Any deviation of ideally perfect crystal from the periodic arrangements from the periodic arrangements of its constituents.

Point Defect :

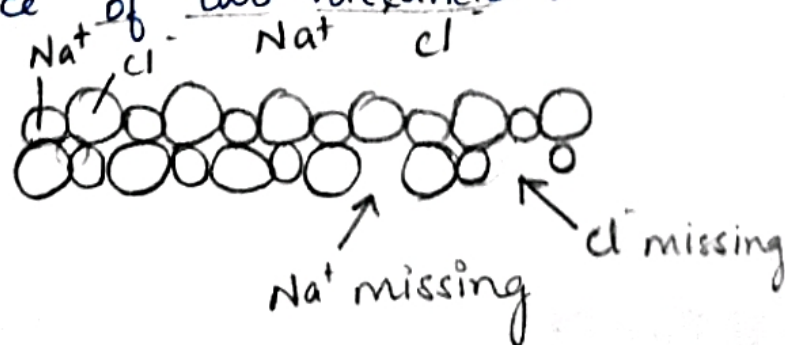
Occurs due to → missing atoms / displaced atoms / Extra atoms
→ imperfect packing during crystallization
→ Thermal vibrations of atoms at high temperature.

Common (point) defects $\begin{cases} \rightarrow \text{Schottky} \\ \rightarrow \text{Frenkel} \end{cases}$

Schottky :

It arises when some lattice points are unoccupied.
It is called lattice vacancies.

Existence of two vacancies :



As a whole;

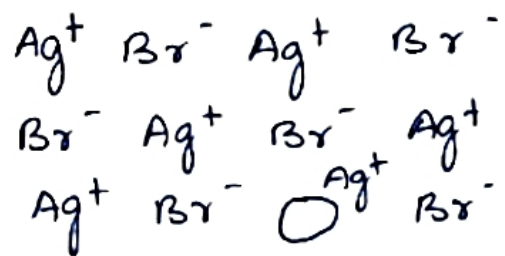
- The charge of the crystal is will remain neutral, as the number of missing Na^+ and Cl^- is same.
- Generally occurs in ionic crystal in which (+)ve and (-)ve ions do not differ much in size.
examples: NaCl , CsCl .
- It conducts electricity (a small extent) by an ionic mechanism.

Under Electric field;

- nearby ion moves to a vacancy and creates ~~a~~ a new vacancy and another nearby ion move into it and so on.
- This process continues resulting in the migration of the vacancy and intern ~~of~~ the ion from one end to other end of the crystal.
- This accounts for the phenomenon of diffusion in solids.

Frankel:

These defects arise when an ion occupies an interstitial position between the lattice points.



As seen, the Ag^+ occupies a position in the interstitial space rather than its own appropriate site in the crystal lattice.

A ~~vacca~~ vacancy is created and crystal remains neutral.

The presence of Ag^+ in interstitial site is responsible for the formation of photographic image on exposing to light. (photographic plate)

Another example : $\text{ZnS} \Rightarrow \text{Zn}^{2+}$ entrapped in interstitial.

The defects appear in crystal in which the (-)ve ions are much larger than the (+)ve ions.

It is responsible for the conduction of electricity and for the phenomenon of diffusion in solids.

Non-stoichiometric Defect :

→ less common defect.

Metal excess

NaCl - Heated in Na - vapor
 \downarrow
 acquires yellow ~~color~~
 colour

→ It is due to non-stoichiometric compound of NaCl in which there is a slight excess of Na^+ .

Na → metal gets doped → in NaCl crystal

Na → ionises as $\text{Na}^+ + e^-$.
due to crystal energy.

↓
(crystal stability - more energy less stable)

→ Herein the e^- occupies a site that would otherwise be filled by Cl^- ion.

→ There are 6 Na^+ ions adjacent to the central e^- .

→ The extra e^- is thus shared between the six Na^+ ions which implies that e^- delocalises.

→ Light energy absorbed, when this e^- makes easy transition from ground state to an excited state.

→ Thus, non-stoichiometric form of NaCl appears coloured.

→ The sites, occupied by the extra e^- are known as colour centres, also called as F. centres.

→ Non stoichiometric NaCl is represented as $\text{Na}(1+\delta)\text{Cl}$, where δ is excess sodium metal doped.

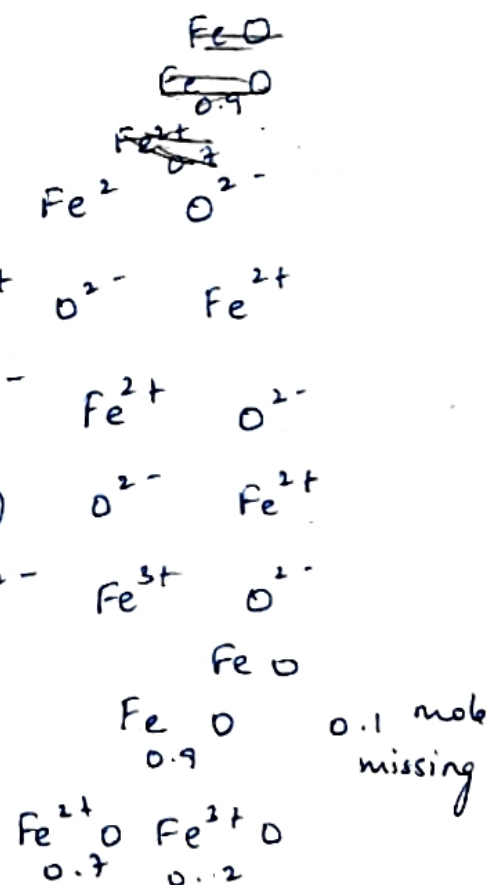
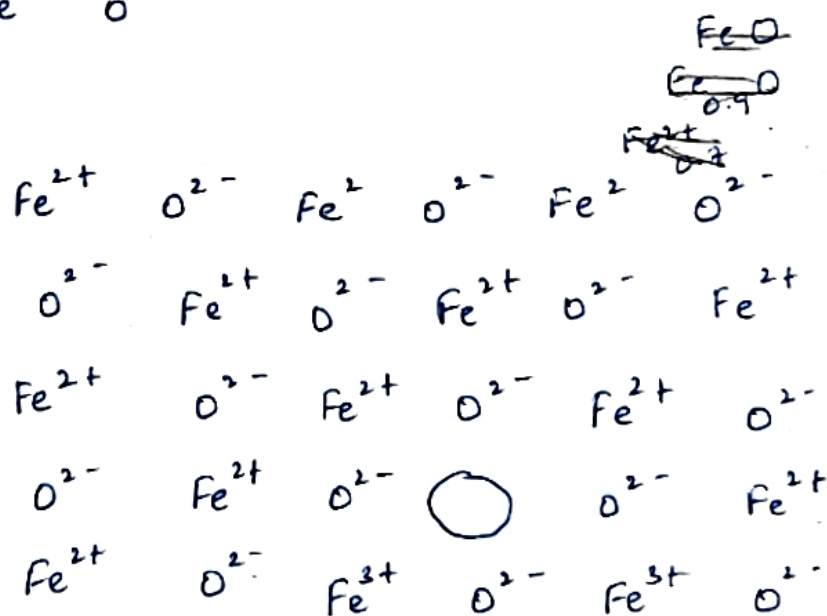
parallelly, the KCl crystal gets doped with extra K atom, by exposing the KCl to K metal vapor. The non-stoichiometric crystal exhibit magenta colour.

Metal Deficiency:

In certain cases, one of the positive ions is missing from its ~~the~~ lattice site and the extra (-)ve charge is balanced by some nearby metal ion by acquiring higher (addition) charges.

Example: $\text{Fe}^{2+} \text{O}^{2-}$

crystal



Creation of vacancies / Holes lowers the density as well as crystal ~~energy~~ lattice energy (Energy released during crystallization)
(o) stability of the crystal.

more energy released \rightarrow more stability.

less energy release \rightarrow less stability.