CHAPTER-2

METALLIC BONDING

Imperfections in Solids

- Constituent particles in crystalline solids are arranged in a short range as well as long range order yet crystals are not perfect.
- They possess small crystals have defects that are irregularities in the arrangement of constituent particles in them when crystallization process occurs at fast or moderate rate.
- These defects are of two types- point defects and line defects.
- The irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.

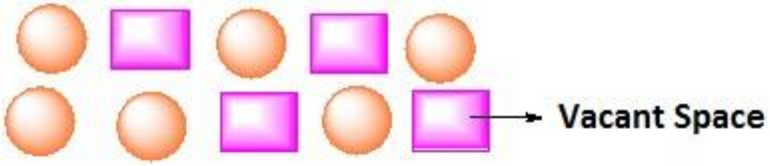
- The irregularities or deviations from ideal arrangement in entire rows of lattice points are known as line defects.
- These irregularities are called *crystal defects*.
- Point defects can be classified into three types: (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects

Stoichiometric Defects

- These ranges of point defects do not disturb the stoichiometry of the solid.
- They are also called *intrinsic* or **thermodynamic defects.**
- Non-ionic solids exhibit their defects as vacancy defects and interstitial defects.

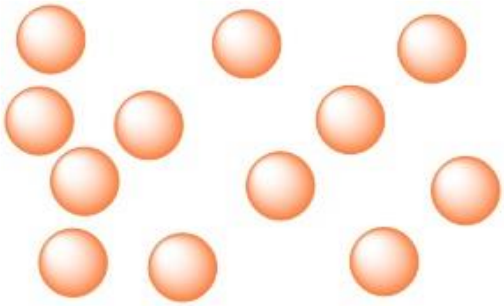
Vacancy Defect:

A crystal containing vacant lattice sites is said to have **vacancy defect.** This defect can also develop due to heating up of a substance.



Interstitial Defect:

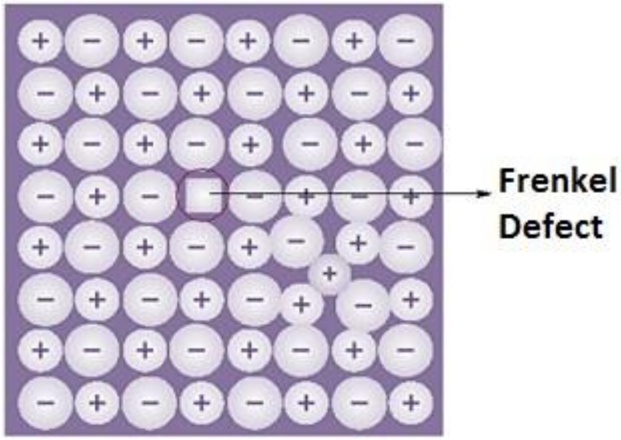
A crystal in which some constituent particles occupy an **interstitial** site,
are said to have **interstitial defect** which increases the density of the substance.



Ionic solids exhibit their defects as **Frenkel and Schottky defects.**

Frenkel Defect:

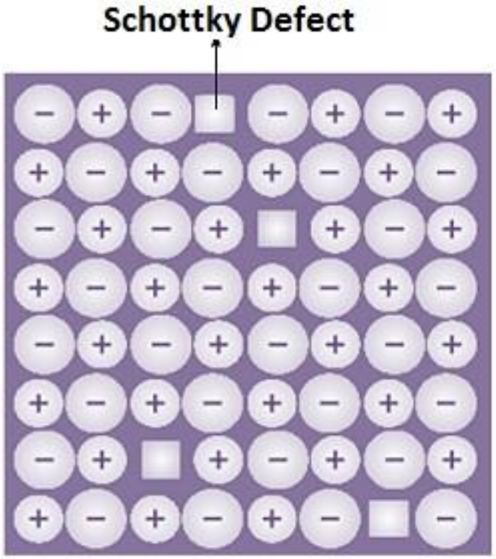
- This defect is exhibited by the ionic substances due to the large difference in size of ions.
- The smaller ion (cation) is displaced from its normal site to an interstitial site which creates a vacancy defect at its original site and an interstitial defect at the new location.
- It is also called dislocation defect.
- It does not alter the density of the solid.
- For example, ZnS, AgCl, AgBr and AgI due to small size of Zn2+ and Ag+ ions.



Schottky Defect:

- This defect in ionic solids is equivalent to the vacancy defect in non-ionic solids.
- In order to maintain electrical neutrality, the number of missing cations and anions are equal
- Schottky defect also decreases the density of the substance.

- This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.
- In NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} Thus, there is one Schottky defect per 10^{16} ions.
- For example, NaCl, KCl, CsCl and AgBr.
- Out of these AgBr shows both, Frenkel as well as Schottky defects.



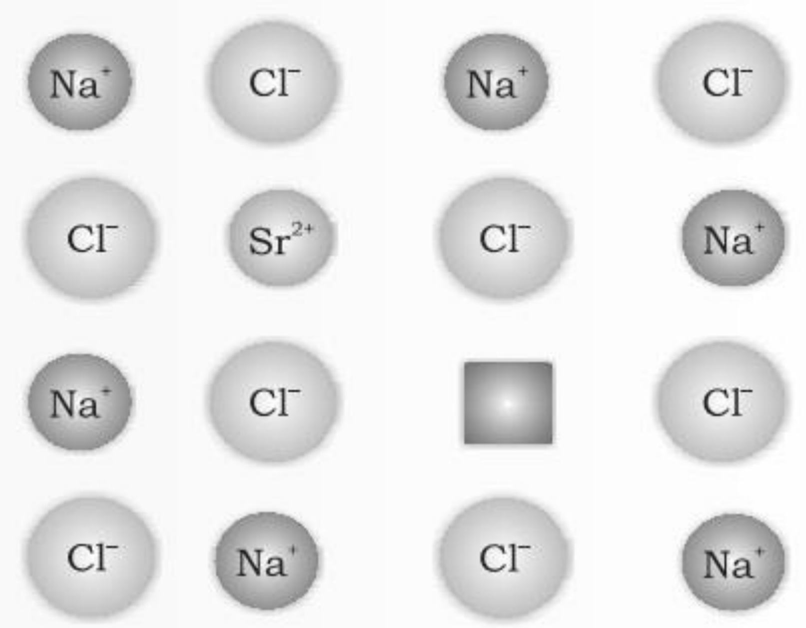
Difference between Schottky Defect and Frenkel Defect

Schottky Defect	Frenkel Defect
Schottky defect occurs in those ionic crystals where difference in size between cation and anion is small.	Frenkel defect usually occurs in those ionic crystals where size of anion is quite large as compared to that of the cation.
In Schottky defect, both cation and anion leave the solid crystal.	In Frenkel defect, only the smaller ion (cation) leaves its original lattice site; whereas, the anion remains in original lattice sites.
The atoms permanently leave the crystal.	Here, atoms leave the original lattice site and occupy interstitial position. So atoms reside within the solid crystal.
One Schottky defect leads to the formation of two vacancies.	One Frenkel defect creates one vacancy and one self-interstitial defect.

Two atoms reduce from the crystal for each Schottky defect.	The number of atoms present in the crystal before and after Frenkel defect remains same.
Due to vacancy formation, Schottky defect reduces density of the solid.	Density of the solid crystal before and after Frenkel defect remains same as no atom leaves the solid.
Common materials where Schottky defect can be found are: • Sodium Chloride (NaCl) • Potassium Chloride (KCl) • Potassium Bromide (KBr) • Silver Bromide (AgBr) • Cerium Dioxide (CeO_2) • Thorium Dioxide (ThO_2)	Common materials where Frenkel defect can be found are: • Zinc Sulfide (ZnS) • Silver Chloride (AgCl) • Silver Bromide (AgBr)

Impurity defect

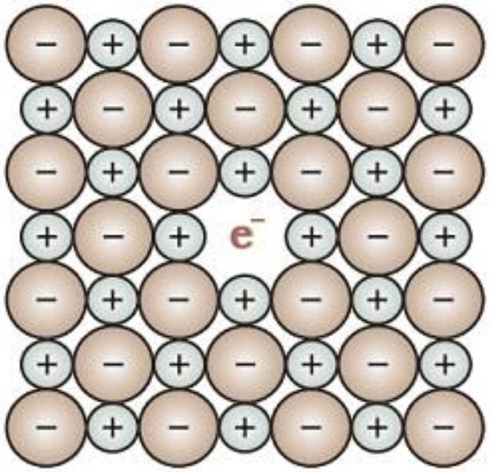
- Crystallization of molten NaCl with little amount of $SrCl_2$ results in Sr^{2+} occupying some of the sites of Na^+
- Each Sr^{2+} replaces two Na+ ions.
- It occupies the site of one ion and the other site remains vacant.
- The cationic vacancies thereby produced are equal in number to that of Sr^{2+}
- Solid solution of $CdCl_2$ and AgCl.



Non-Stoichiometric Defects

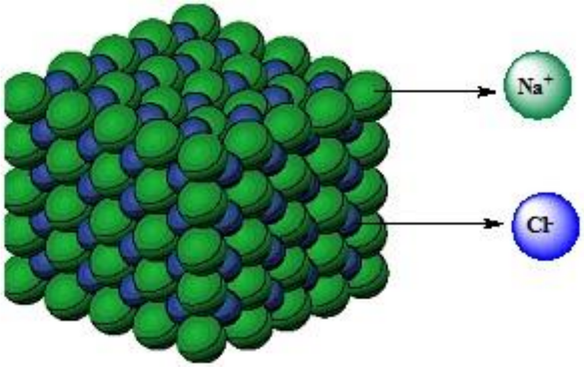
- Nonstoichiometric inorganic solids contain the constituent elements in a non-stoichiometric ratio due to defects in their crystal structures.
- These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect.



- Metal excess defect due to anionic vacancies:
- This type of defect is exhibited by alkali halides like NaCl and KCl.
- Application of heat to NaCl in an atmosphere of sodium vapour results in deposition of the sodium atoms on the surface of the crystal.
- The sodium atoms lose electron to form Na^+

- The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl.



- The released electrons diffuse into the crystal and occupy anionic sites.
- The anionic sites occupied by unpaired electrons are called F-centres that imparts yellow colour to the crystals of NaCl due to the excitation of the electrons on absorption of energy from the visible light falling on the crystals.
- Excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet.

- Metal excess defect due to the presence of extra cations at interstitial sites:
- Heating Zinc oxide that exists in white colour at room temperature loses oxygen and turns yellow.

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

- This results in excess of zinc in the crystal and its formula becomes Zn1+xO.
- The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

Metal Deficiency Defect:

- Many solids possess less amount of the metal as compared to the stoichiometric proportion.
- For example, FeO is mostly found with a composition ranging from $Fe_{93}O$ to $Fe_{0.96}O$.

- In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+}

Electrical Properties of soilds

Solids exhibit electrical conductivities that extend from 27 orders of magnitude ranging from 10^{-20} to 10^{7} ohm^{-1} m^{-1}.

Conductors:

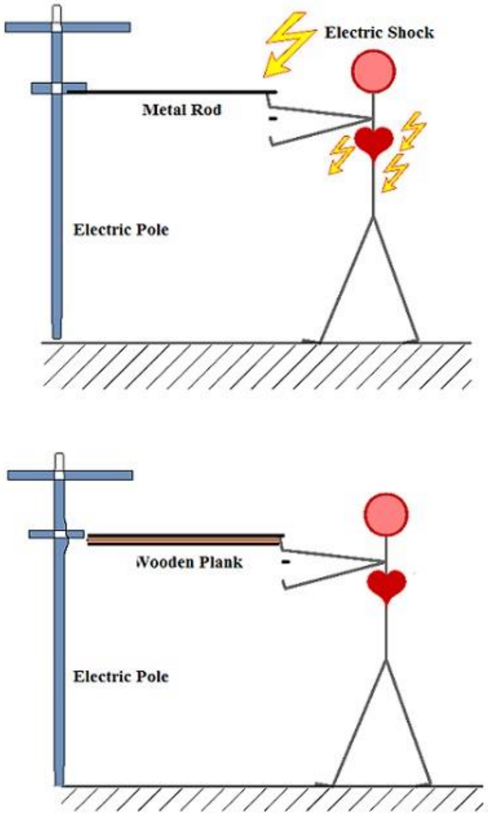
- Solids with conductivities ranging between 10^{4} to 10^{7} $ohm^{-1}m^{-1}$ are conductors.
- Metals have conductivities in the order of 10^{7} $ohm^{-1}m^{-1}$ are good conductors.
- For example, Iron, Copper, Aluminum.

Fig. Metal is used at the tip of the plug that is inserted into the socket.

Insulators:

- Solids with very low conductivities ranging between 10^{-20} to 10^{-10} $\text{ohm}^{-1}\text{m}^{-1}$.
- For example, Wood, plastic, cloth, glass.

Fig. Wood and plastics are also solids but are insulators

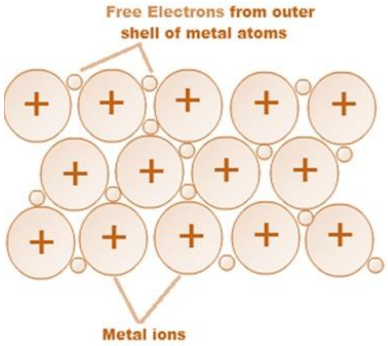


A man touching the electric pole with a metal rod will get an electric shock because metal rod is a conductor whereas a man touching the same with a wooden plank will be safe because wood is an insulator.

- Semiconductors:
- Solids with conductivities in the intermediate range from 10–6 to 104 ohm^{-1} m^{-1}.
- For example, Gallium, Germanium, Silicon

Conduction of Electricity in Metals

- A conductor conducts electricity due to the movement of electrons or ions.



- Metals conduct electricity both in solid state as well as molten state.
- The conductivity of metals depends upon the number of valence electrons available per atom.
- The atomic orbitals of metal atoms form molecular orbitals that are close in energy to each other as to form a band.
- Partial filling or overlapping with a higher energy unoccupied conduction band enables the electrons to flow easily under an applied electric field.
- This results in conductivity of metals.

If the gap between valence band and the conduction band is large, electrons cannot jump to it and such a substance has very low conductivity that makes it behave like an insulator

Conduction of Electricity in Semiconductors

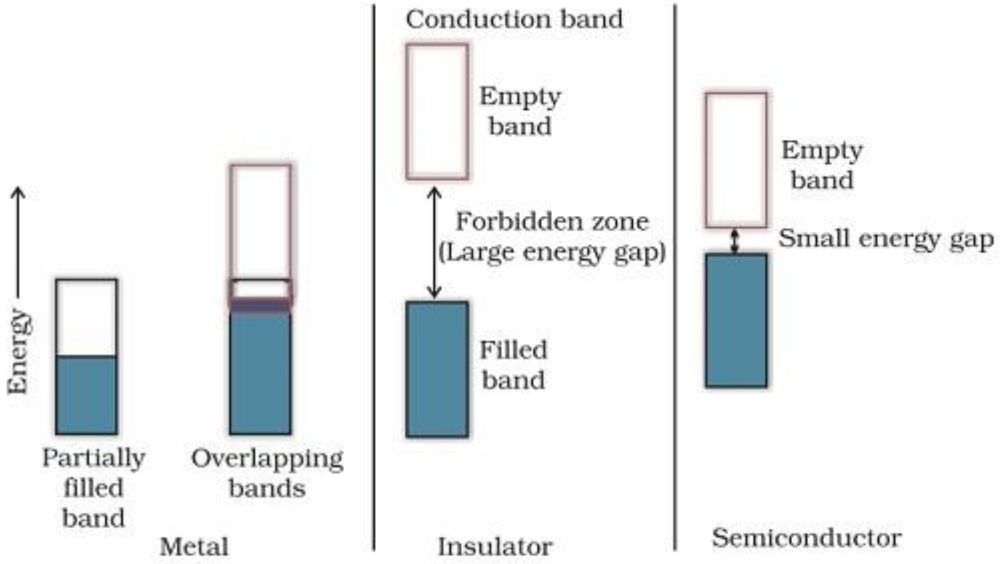
In semiconductors, the gap between the valence band and conduction band is small.

This enables some electrons to jump to conduction band and exhibit their conductivity.

Electrical conductivity of semiconductors increases with increase in temperature, since more electrons can jump to the conduction band due to small gap between the valence band and conduction band.

Silicon and germanium exhibit this behavior and are called intrinsic semiconductors.

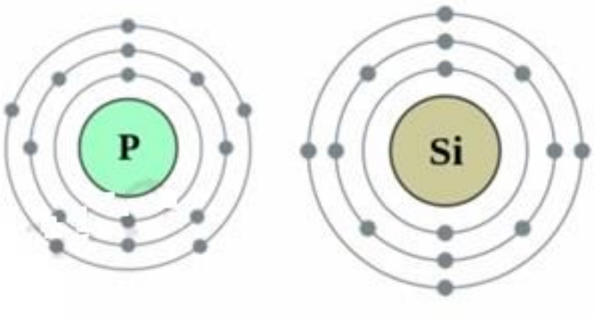
The conductivity of these intrinsic semiconductors is too low to be practically used.



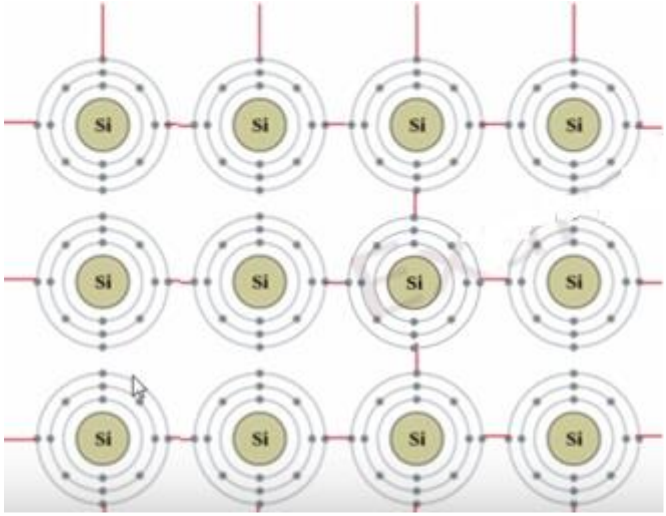
Electron – rich impurities

In a periodic table Silicon and germanium belongs to group 14 with four valence electrons each. In their crystals each atom forms four covalent bonds with surrounding atom.

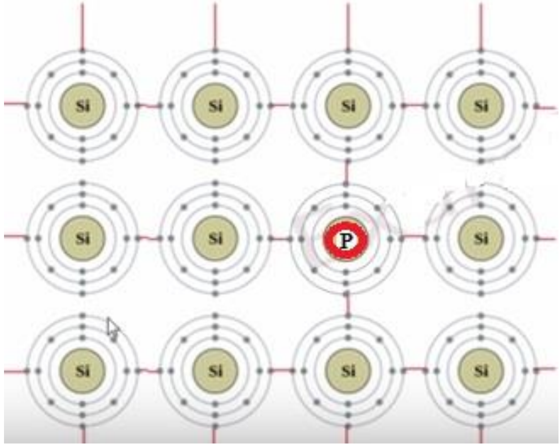
When doped with a group 15 element like P or As, which contains five valence electrons,



They occupy some of the lattice sites in silicon or germanium crystal.



Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron in P is extra and becomes delocalized.

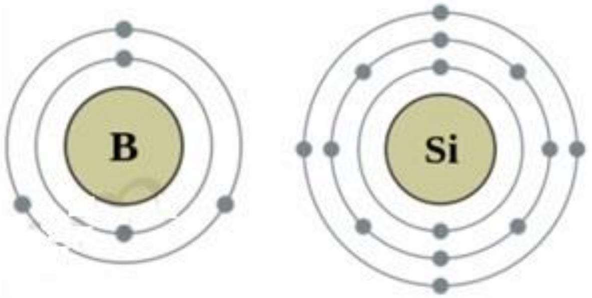


These delocalized electrons increase the conductivity of doped silicon (or germanium).

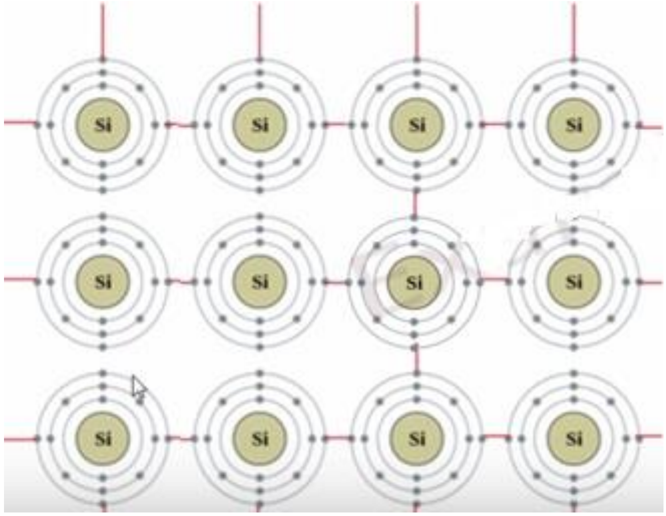
This type of semiconductor is known as n-type semiconductor because the increase in conductivity is due to the negatively charged electron.

Electron – deficit impurities

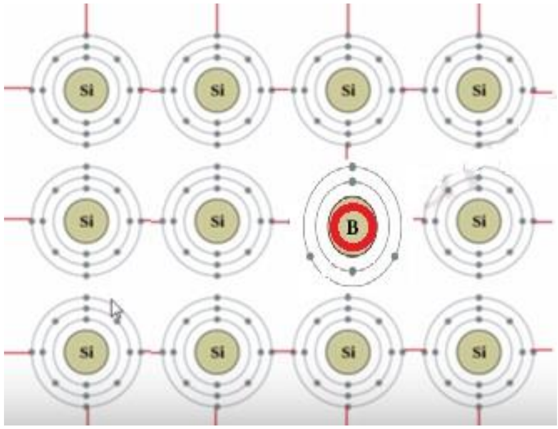
Silicon or germanium of group 14 can also be doped with elements of group 13 element like B, Al or Ga which contains only three valence electrons.



Three electrons of B form covalent bonds with three electrons of Si.



The fourth electron in Si is extra that remains isolated and creates an electron hole or electron vacancy.



An electron from a neighbouring atom can come and fill the electron hole, but leave an electron hole at its original position resulting in displacement of the electron hole in the direction opposite to that of the electron that filled it.

Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate.

These types of semiconductors are called p-type semiconductors.

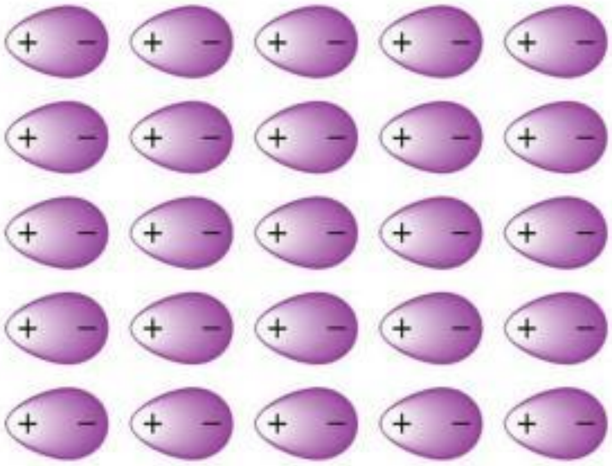
Applications of n-type and p-type semiconductors

- n-type and p-type semiconductors finds a great use in manufacturing electronic components.
- Diode is a combination of n-type and p-type semiconductors extensively used as a rectifier.

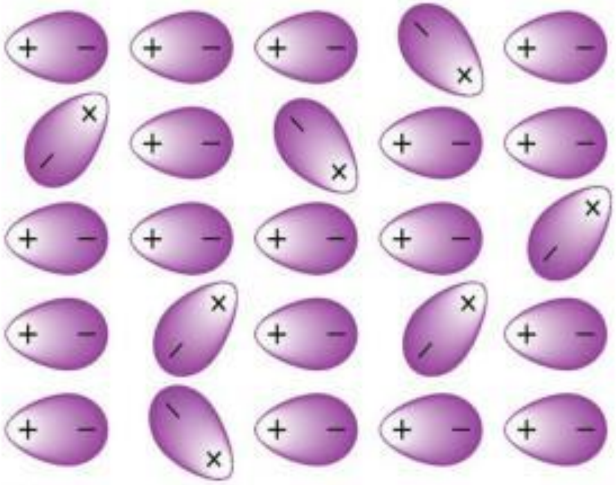
- Transistors are manufactured by keeping a layer of one type of semiconductor between two layers of another type of semiconductor.
- npn and pnp type of transistors are used to detect or amplify radio or audio signals.
- The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.
- Gallium arsenide (GaAs) semiconductors have very fast response and have transformed the design of semiconductor devices.
- Transition metal oxides show marked differences in electrical properties.
- TiO, CrO_2 and ReO_3 behave like metals.

  Rhenium oxide, ReO_3 resembles metallic copper in terms of its conductivity and appearance.Certain other oxides like VO, VO_2, VO_3 and TiO_3 exhibit metallic or insulating properties depending on temperature.

What is a Perfect Crystal?



(a)



(b)

Perfect crystal at 0 K,
so S =0

Crystal deforms for T > 0 K,
slight random motions
(wiggling in place), S>0

CRYSTAL IMPERFECTIONS

Crystal Imperfections are the defects in the regular geometrical arrangement of the atoms in a Crystalline solid.

A Perfect Crystal is an idealization; there is no such thing in nature.

The defects may be the results of the crystal deformation or rapid cooling from high temperature or high energy radiation striking the solid.

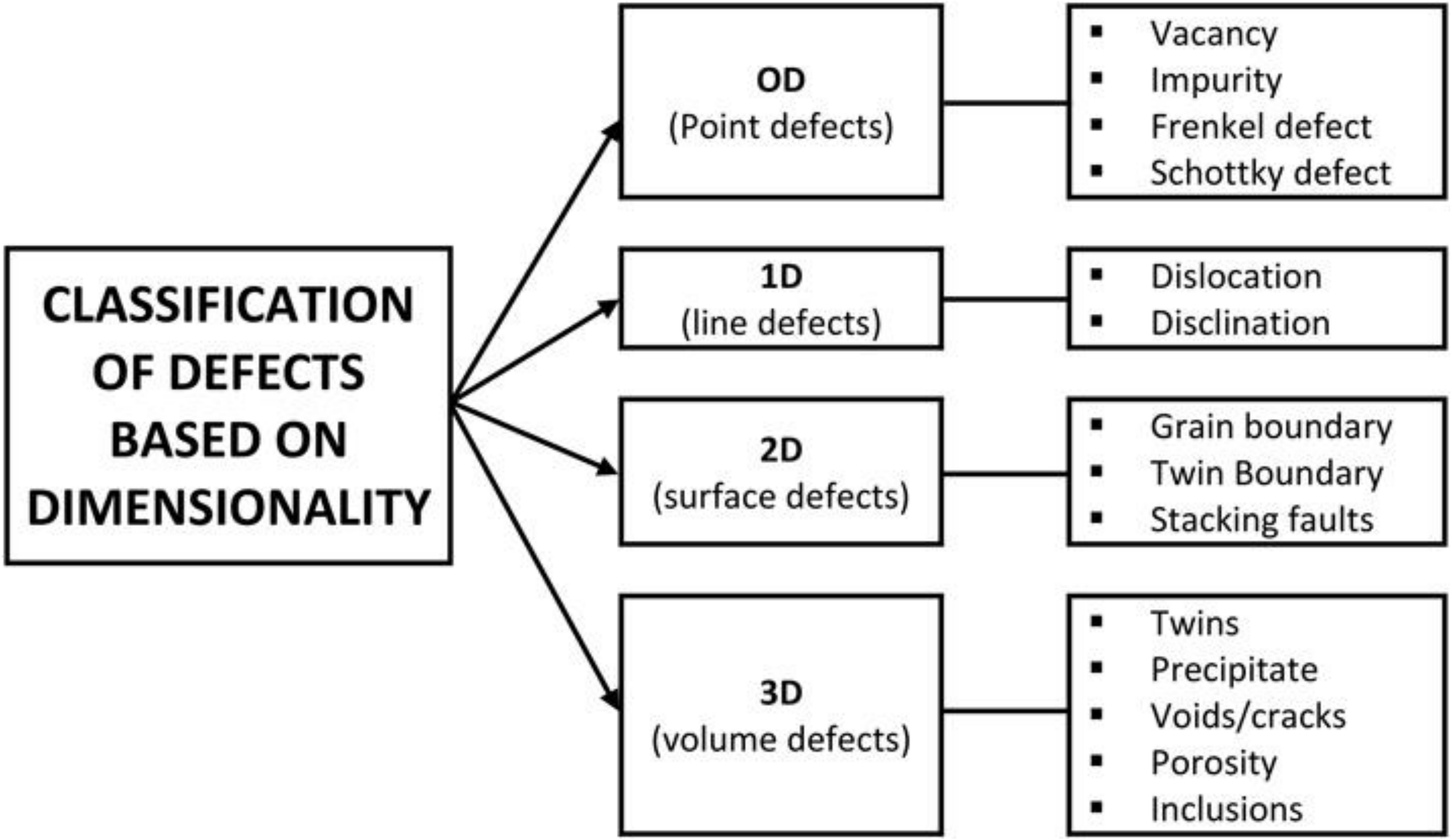
The defects influence the mechanical, electrical, and optical behavior of the crystal.

Defects in crystalline materials

- Crystalline materials are not perfect above 0K, since at finite temperatures atoms can move from their lattice positions.
- Also, impurities are nearly always introduced during crystal growth (intentionally or not!)
- We will be concentrating on point defects, which affect isolated atom sites, and have a significant effect on the chemistry of the crystal.

The imperfections may be classified widely as:

- Point Defects
- Line Defects
- Surface Defects
- Volume Defects



CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

OD
(Point defects)

- Vacancy
- Impurity
- Frenkel defect
- Schottky defect

1D
(line defects)

- Dislocation
- Disclination

2D
(surface defects)

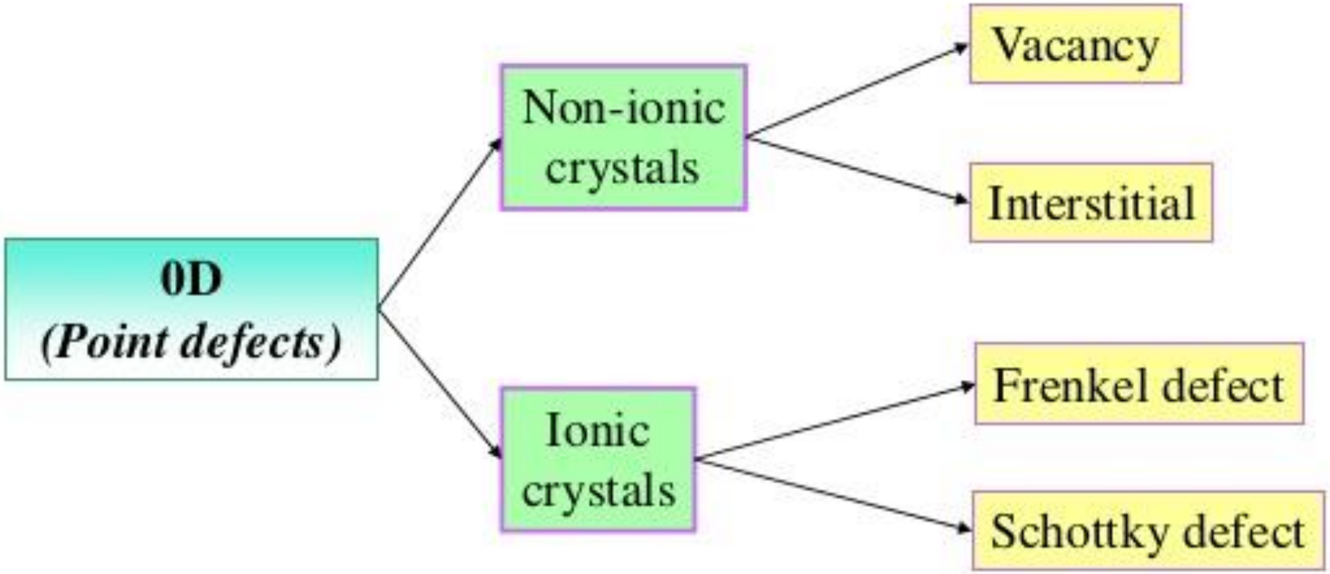
- Grain boundary
- Twin Boundary
- Stacking faults

3D
(volume defects)

- Twins
- Precipitate
- Voids/cracks
- Porosity
- Inclusions

POINT DEFECTS

Point Defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.



0D
(Point defects)

Non-ionic crystals

Vacancy

Interstitial

Ionic crystals

Frenkel defect

Schottky defect

POINT DEFECT-DEFINITION

Point defects are where an atom is missing or at an irregular place in the lattice structure.

The **stoichiometric defects** in the **ionic crystal** are the **defects** in which the equal no. of cations and anions from the **crystal** lattice are removed but the ratio of the cations and anions remains the same as the preceding ratio.....these **defects** results in the maintenance of electrical neutrality of **crystal**

Non-stoichiometric defects: The **defects** which disturb the **stoichiometry** of the compounds are called **non-stoichiometry defects**. These **defects** are either due to the presence of excess metal ions or deficiency of metal ions.

Classification of point defects

- First, distinguish between **intrinsic** and **extrinsic** defects.
- **Intrinsic defects** do not affect the chemical composition of the crystal, and include:
  - **vacancies** – atoms missing from the lattice
  - **interstitials** – atoms at non-lattice positions

Classification of intrinsic defects

- **Frenkel defects** occur when an atom moves from a lattice site to an interstitial site.

  (this will be illustrated)

- **Schottky defects** occur when a formula unit of vacancies is created. Note that this is still a neutral defect since both cation and anion vacancies are created (e.g. Na^+ and Cl^- vacancies in NaCl).

  (this will be illustrated)

Extrinsic defects

- Impurity atoms present in crystals are called **extrinsic defects**.
- They may be there deliberately, or as a consequence of the preparation process.
  - Examples are K^+ ions in NaCl
- Charge must always be **balanced** – e.g. if Ca^{2+} substitutes for Na^+ in NaCl, a Na^+ vacancy or Cl^- interstitial must be formed.

VACANCY DEFECT

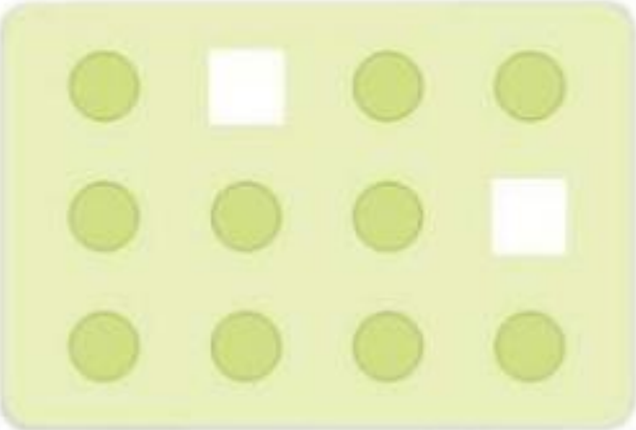
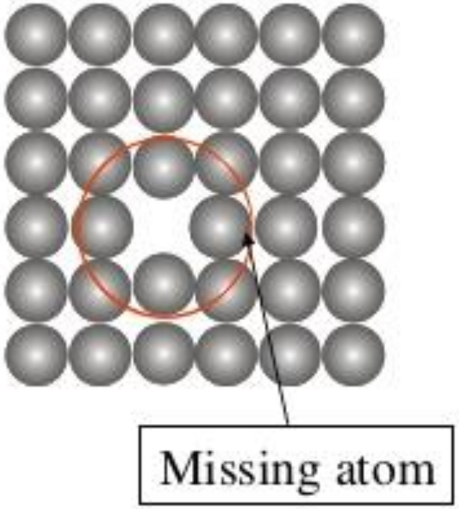
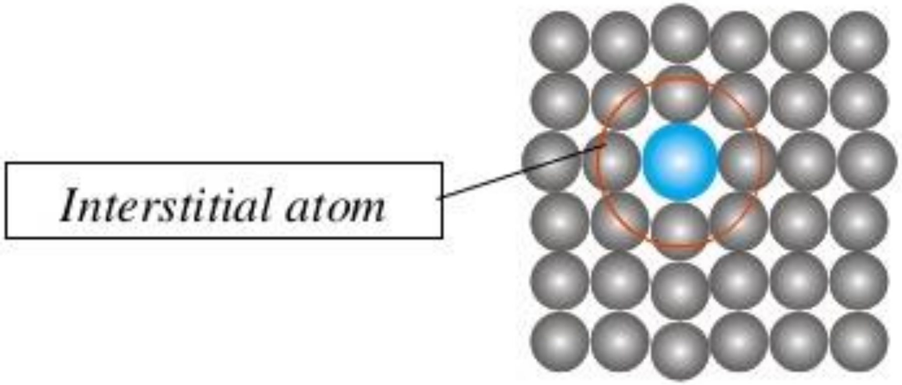


Fig. 1.23: Vacancy defects



- Atom missing from an atomic site
- Occur due to imperfect packing during crystallisation
- This results in decrease in density of the substance
- Number of vacancy defects depend on temperature

INTERSTITIALS DEFECT



- Addition of an extra atom within a crystal structure
- This defect increases the density of the substance
- Causes atomic distortion
- Vacancy and interstitials are inverse phenomena

SCHOTTKY DEFECT

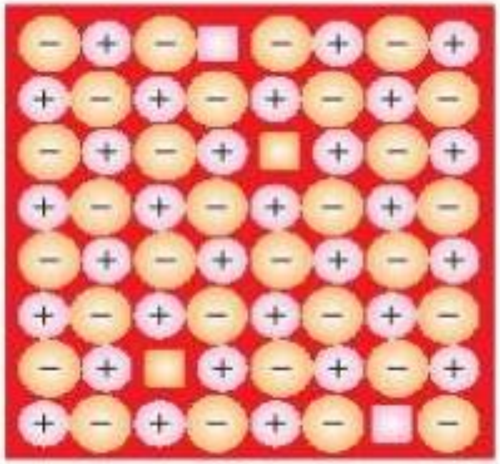
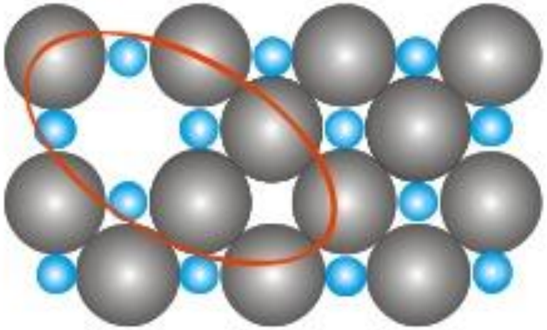


Fig. 1.26: Schottky defects



- Pair of anion and cation vacancies
- In order to maintain electrical neutrality, the number of missing cations and anions are equal
- It also decreases the density of crystal
- E.g. Alkali halides such as NaCl, KF, etc.

FRENKEL DEFECTS

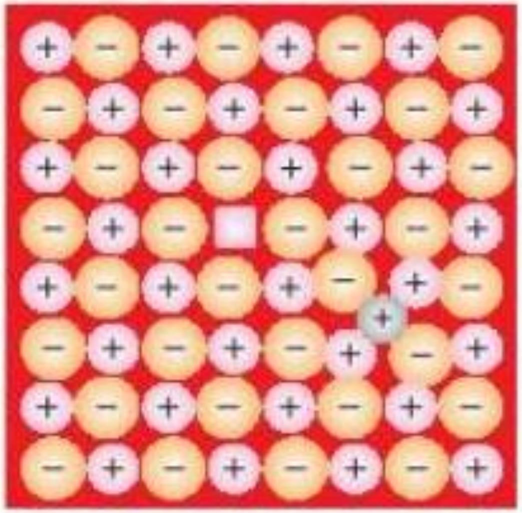
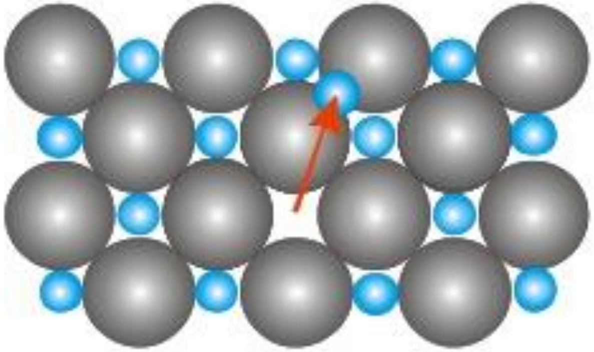


Fig. 1.25: Frenkel defects

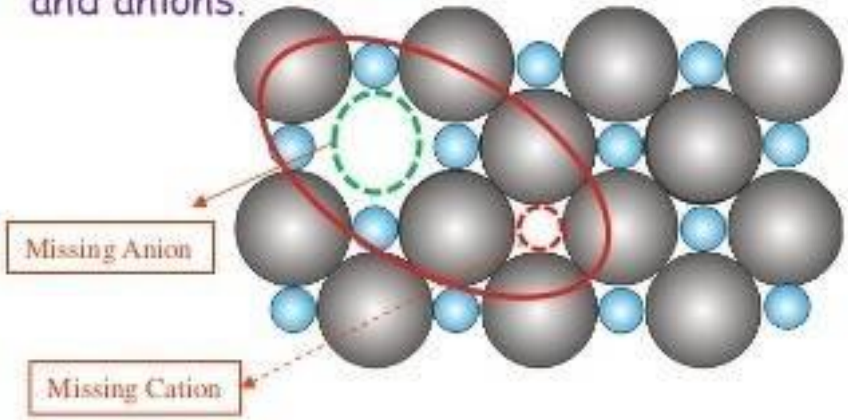


- Cation (being smaller get displaced to interstitial voids
- Combination of vacancy and interstitial atom
- No change in the density
- E.g. AgI, CaF_2

Schottky defect and Frenkel defect

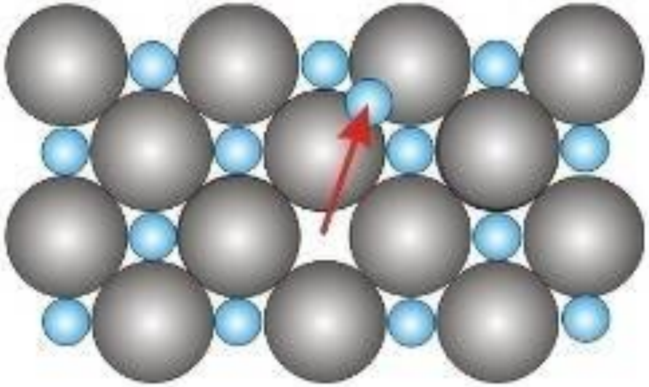
Schottky Defect:

- Forms when oppositely charged ions leave their lattice sites, creating vacancies.
- These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid.
- Density of the solid crystal is less than normal
- Occurs only when there is small difference in size between cations and anions.



Frenkel Defect:

- Smaller ion (usually the cation) is displaced from its lattice position to an interstitial site.
- Creates a **vacancy defect** at its original site and an **interstitial defect** at its new location.
- Does not change the density of the solid.
- Shown in ionic solids with large size difference between the anion and cation.



S.No.	Schottky defect	Frenkel defect
1.	It is due to equal number of cations and anions missing from the lattice sites.	It is due to the missing of ions (usually cations) from the lattice sites and they occupy the interstitial sites.
2.	This results in the decrease in density of crystal.	It has no effect on the density of crystal.
3.	This type of defect is found in highly ionic compounds with high coordination number, e.g. NaCl, CsCl, AgBr, etc.	This type of defect is found in crystals, where the difference in the size of cations and anions is very large, e.g. AgCl, AgBr, ZnS, etc.

F-centres- Metal excess defect

When the anionic sites of a crystal are occupied by unpaired electrons, the ionic sites are called **F-centres**. These unpaired electrons impart colour to the crystals. For **example**, when crystals of NaClare heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal.

The **F-centers** are point defects and can be readily **formed** in alkaline halides with the aid of a source of ionizing radiation, such as an X-ray source. Apparently, the ionizing radiation causes the loss of electrons from halide ions. An electron then becomes trapped in the halide ion vacancy.

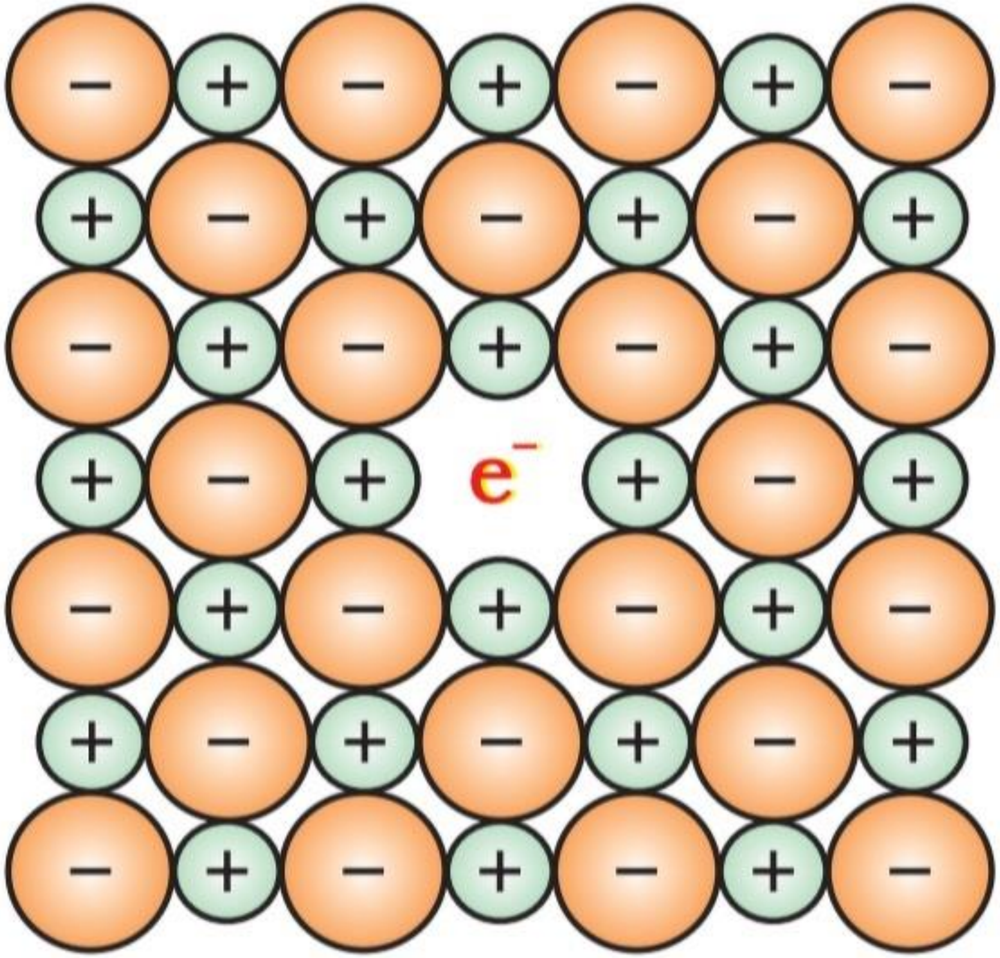
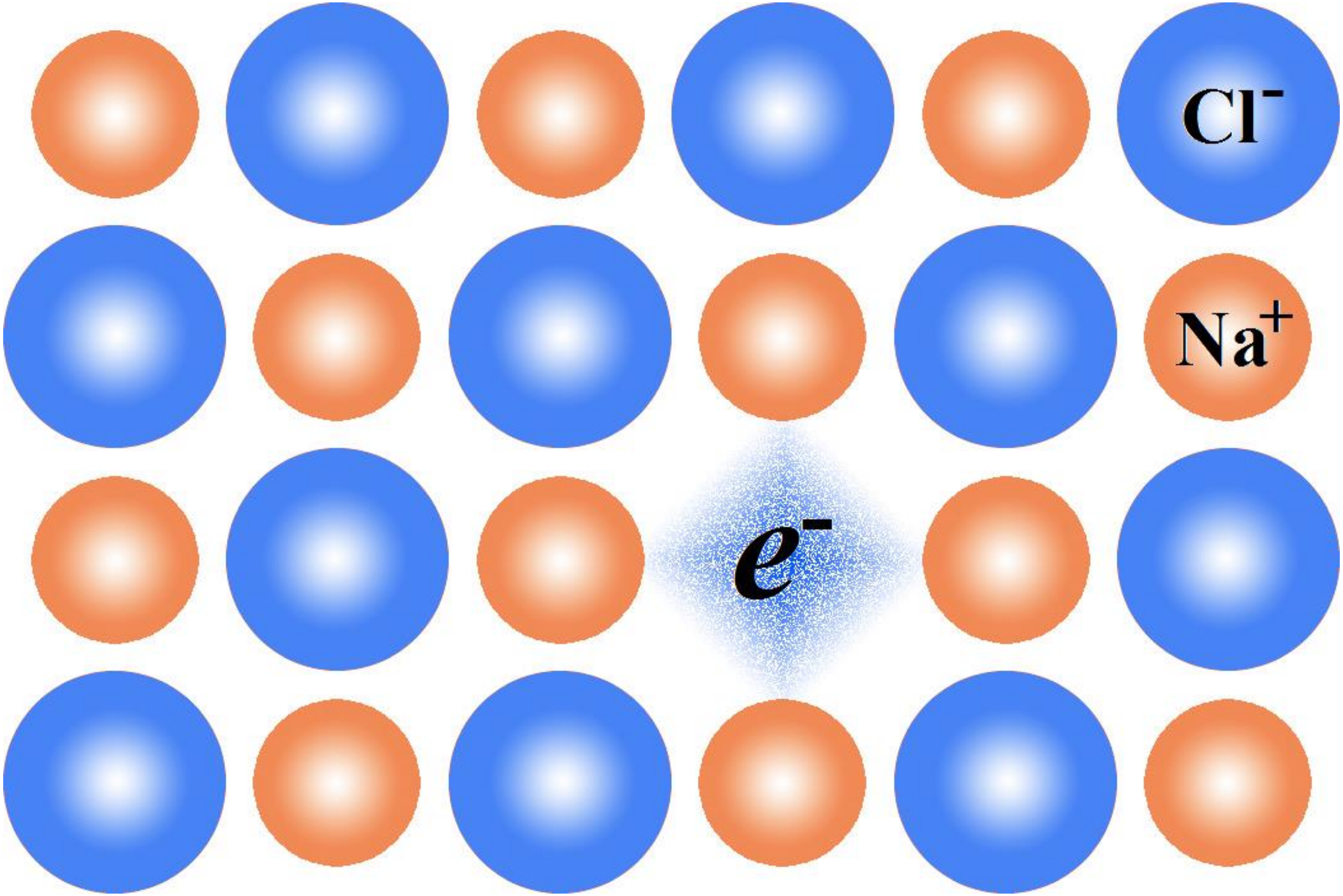
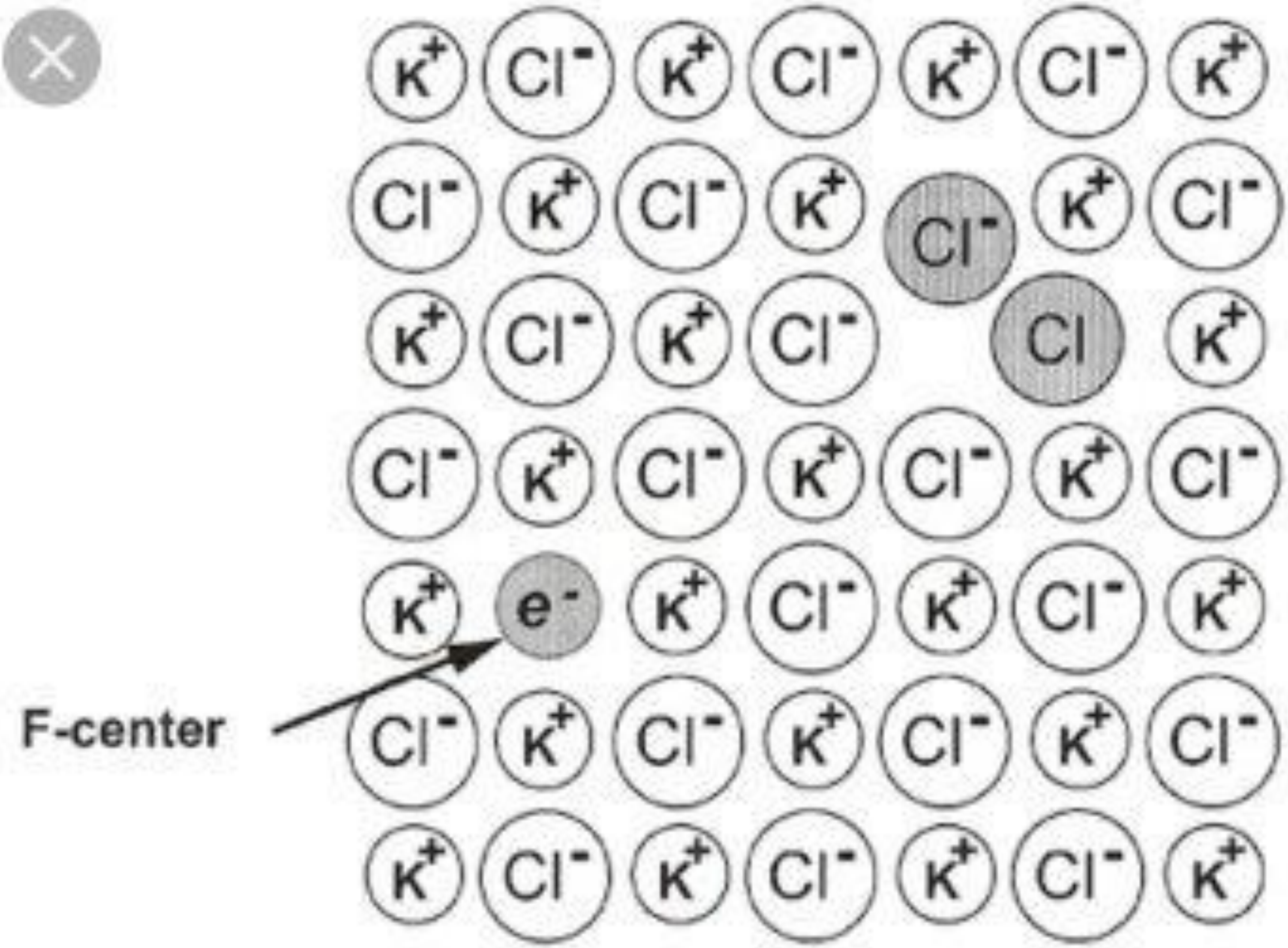
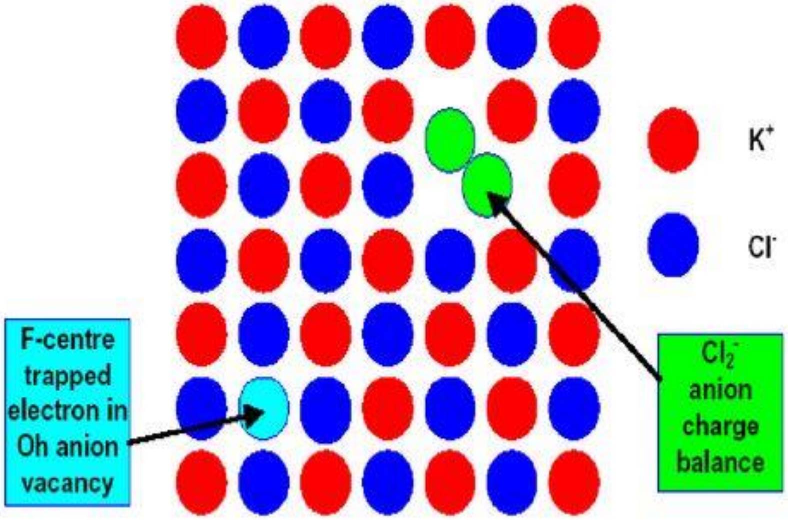


Fig. 1.28: *An F-centre in a crystal*


Cl-
Na+
e-


K^+ Cl^- K^+ Cl^- K^+ Cl^- K^+
Cl^- K^+ Cl^- K^+ Cl^- K^+ Cl^-
K^+ Cl^- K^+ Cl^- Cl K^+
Cl^- K^+ Cl^- K^+ Cl^- K^+ Cl^-
K^+ e^- K^+ Cl^- K^+ Cl^- K^+
F-center
Cl^- K^+ Cl^- K^+ Cl^- K^+ Cl^-
K^+ Cl^- K^+ Cl^- K^+ Cl^- K^+

COLOR CENTRES



Looks like an electron in an Oh halide box problem
Basis of the F-center laser

- **F-centre looks like an electron in an Oh cation box problem**
- **Defect formation alkali vapor: produces cation sites, equivalent number of anion vacancies, electron trapped at anion vacancy.**
- **Defect formation UV, X-ray, electrical excitation: anion ionized, electron trapped in anion vacancy, halogen neutral trapped at halide site to give H-centre Cl_2^-**
- **Basis of the F-center laser**