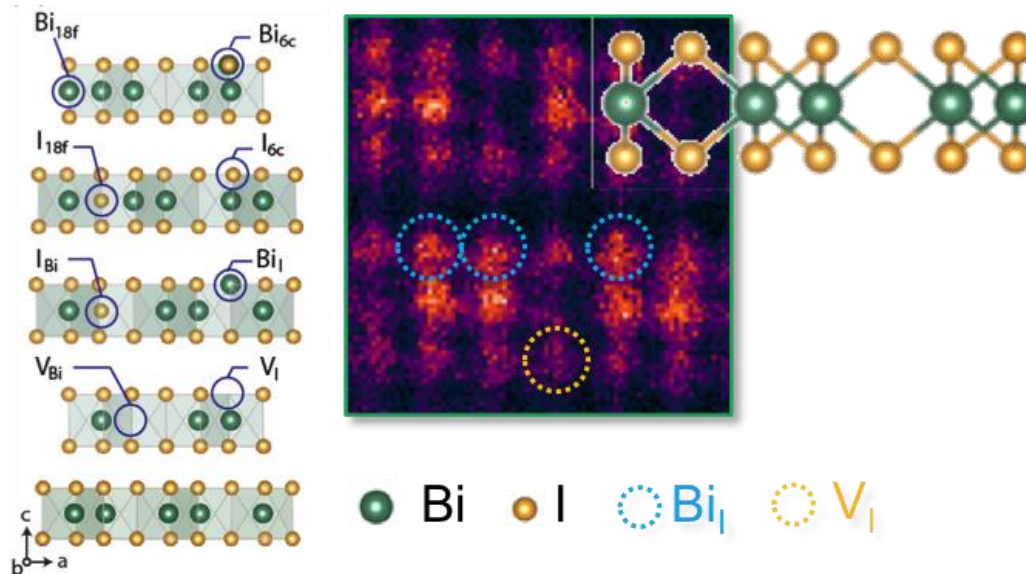


Lecture 2

Types of Defect: 0D – Point Defects



Point defects are divided into three types based on stoichiometry:

- ✓ Stoichiometric Defects
- ✓ Impurities Defects
- ✓ Non-stoichiometric Defects

Stoichiometric Defects:

- ✓ the ratio of positive and negative ions (stoichiometry) and electrical neutrality of a solid is not disturbed.
- ✓ This is also known as **intrinsic or thermodynamic defects**.

Types of stoichiometric defects:

- ✓ Vacancy Defects
- ✓ Interstitial defects
- ✓ Frenkel Defects
- ✓ Schottky Defects

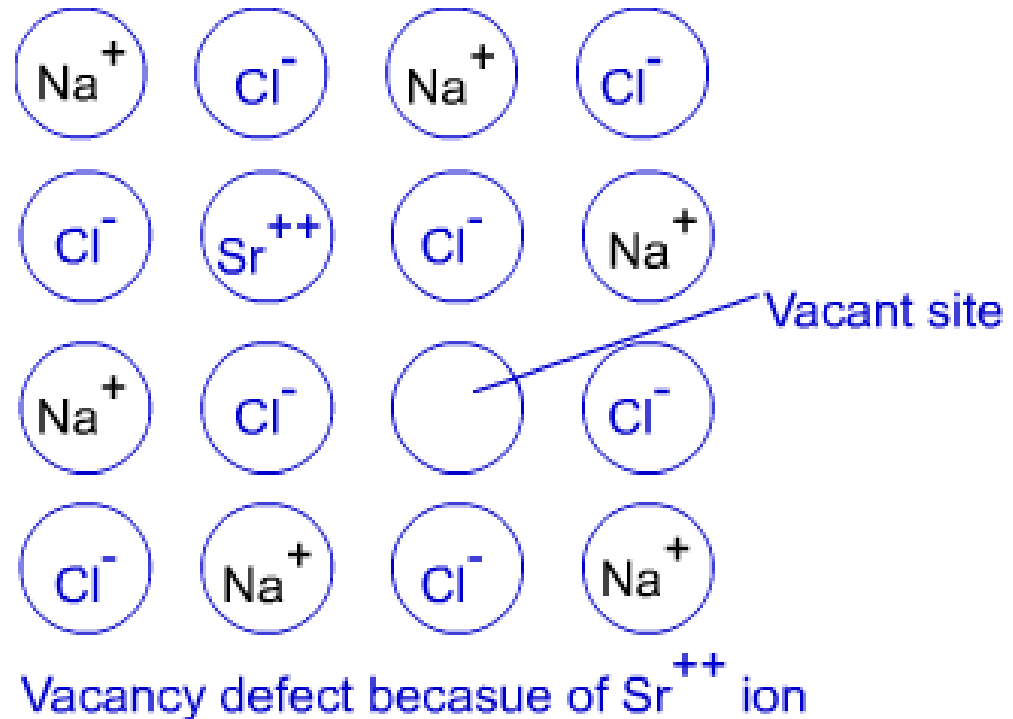
A non-ionic compound mainly shows vacancy and interstitial defects.

An ionic compound shows the same in Frenkel and Schottky defect.

(ii) Impurities Defects:

Defects in ionic compounds because of replacement of ions by the ions of other compound is called **impurities defects**.

- ✓ In NaCl, during crystallization, a little amount of SrCl_2 is also crystallized.
- ✓ In this process, Sr^{2+} ions get the place of Na^+ ions and create impurities defects in the crystal of NaCl.
- ✓ In this defect, each of the Sr^{2+} ion replaces two Na^+ ions.
- ✓ Sr^{2+} ion occupies one site of Na^+ ion, leaving other site vacant.
- ✓ Hence it creates cationic vacancies equal number of Sr^{2+} ions.
- ✓ CaCl_2 , AgCl , etc. also shows impurities defects.



(iii) **Non-stoichiometric Defects:**

There are large numbers of inorganic solids found which contain the constituent particles in non-stoichiometric ratio because of defects in their crystal structure. Thus, defects because of presence of constituent particles in non-stoichiometric ratio in the crystal structure are called **Non-stoichiometric Defects**.

Non-stoichiometric Defects is mainly of two types:

- ✓ **Metal Excess Defects**
- ✓ **Metal Deficiency Defects.**

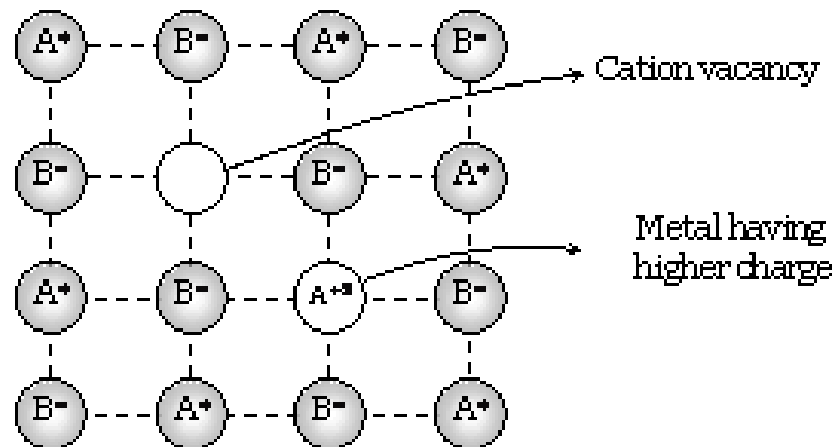


Fig. 5.22

Non-stoichiometric defects

- overall stoichiometry of material changes
- substitution $A \rightarrow A_{1-x}B_x$
interstitial $AB \rightarrow A_{1+x}B$
vacancy $AB \rightarrow A_{1-x}B$
- i.e. atom ratios change and foreign atoms may be present - extrinsic defects
- Introduction of aliovalent foreign ions requires creation of vacancies or interstitials to maintain charge balance

(iii) Non-stoichiometric Defects:

The composition of a non-stoichiometric compound usually varies in a continuous manner over a narrow range.

Thus, the formula for wüstite is written as Fe_{1-x}O , where x is a small number (0.05 in the previous example) representing the deviation from the "ideal" formula.

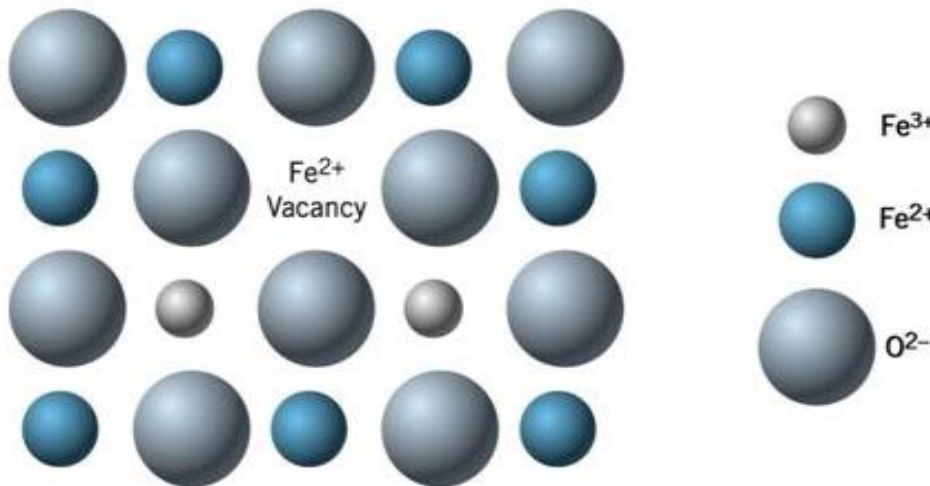
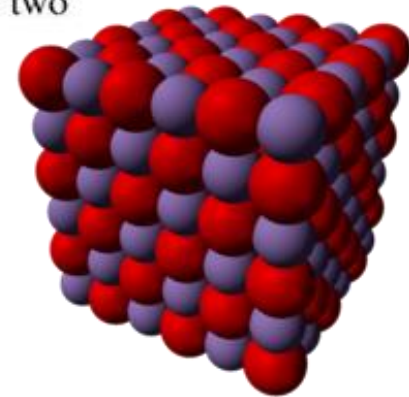
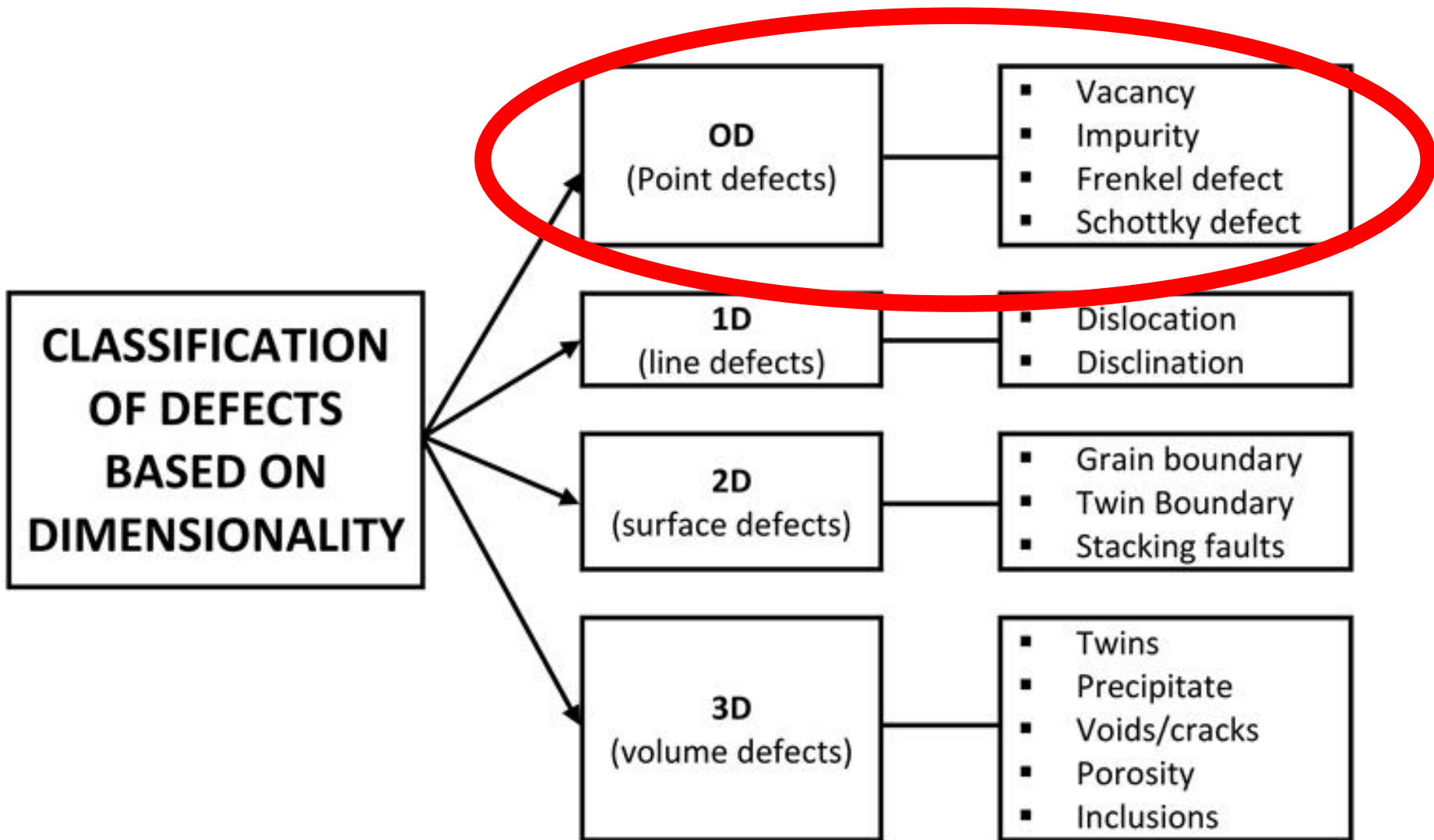


FIGURE 12.22 Schematic representation of an Fe^{2+} vacancy in FeO that results from the formation of two Fe^{3+} ions.

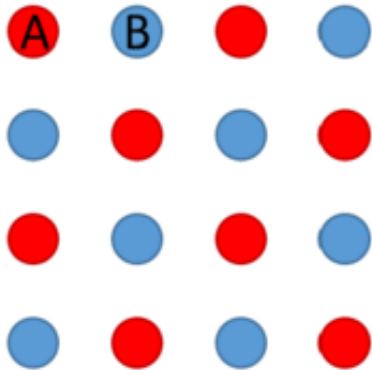


Thus, the difference between stoichiometric and nonstoichiometric defects is that the stoichiometric defects do not disturb the stoichiometry of the compound whereas nonstoichiometric defects disturb the stoichiometry of the compound.

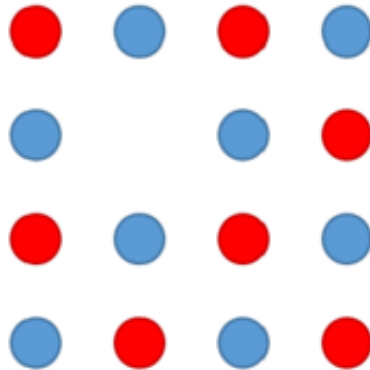


Point Defects:

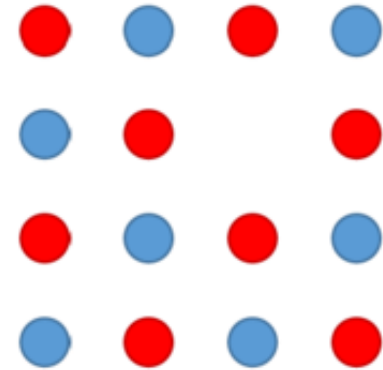
Perfect lattice



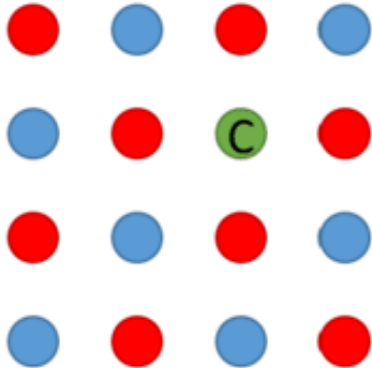
Vacancy of A (V_A)



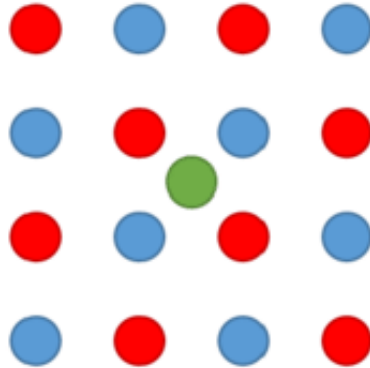
Vacancy of B (V_B)



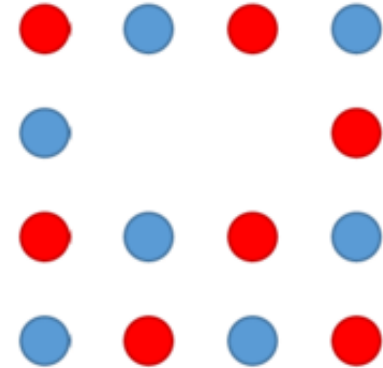
C on A antisite (C_A)



Interstitial C (C_i)



Di-vacancy of A and B (V_A-V_B)



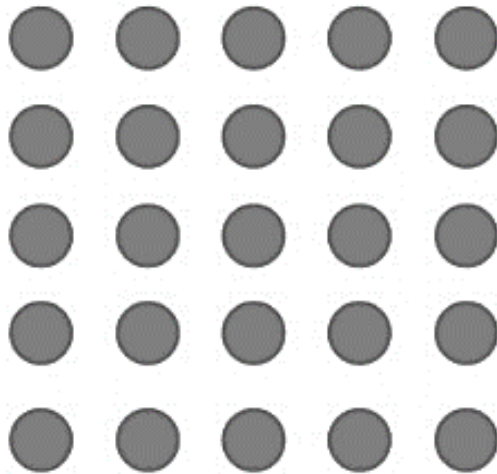
Frenkel defect

Schottky defect

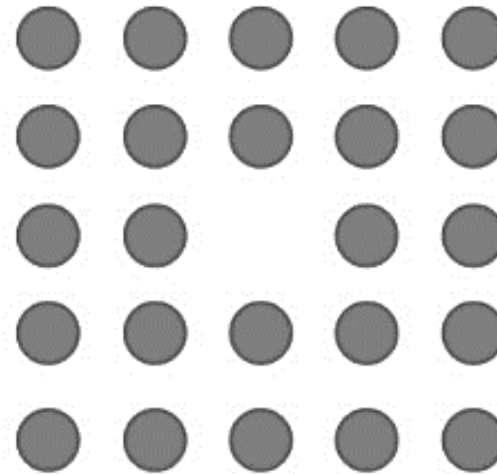
Vacancy defect

Where vacancy defects can be found?

- ✓ Vacancy defect can occur in any crystalline solid, in fact, it is inherent.
- ✓ Any material whose temperature is above absolute zero temperature (0K), can contain vacancies.
- ✓ With increase in temperature, number of vacancy defects increases exponentially.



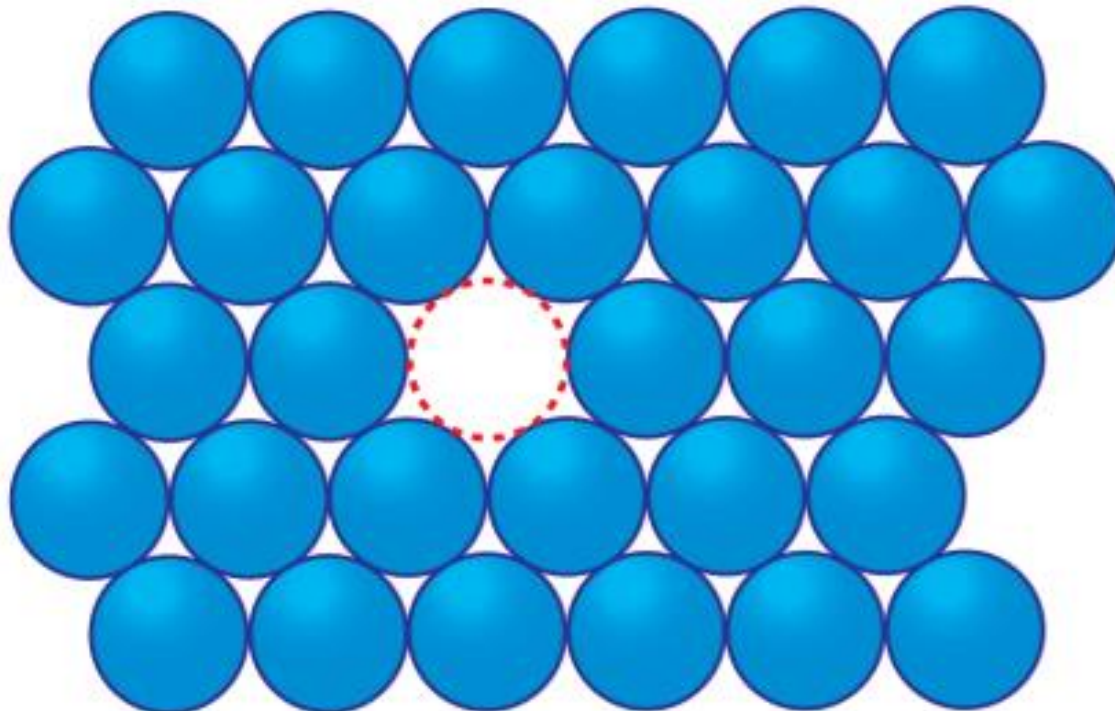
Perfect Crystal



Vacancy - Point Defect

This figure illustrates the difference between a perfect crystal and crystal structure with a vacancy defect. Vacancy defect is caused by loss of one atom from its lattice site.

- ✓ At 1 quadrillion (10^{15}) atoms comes at room temperature about one vacancy.
- ✓ Immediately below the melting temperature already one vacancy comes at 10,000 atoms (10^4).

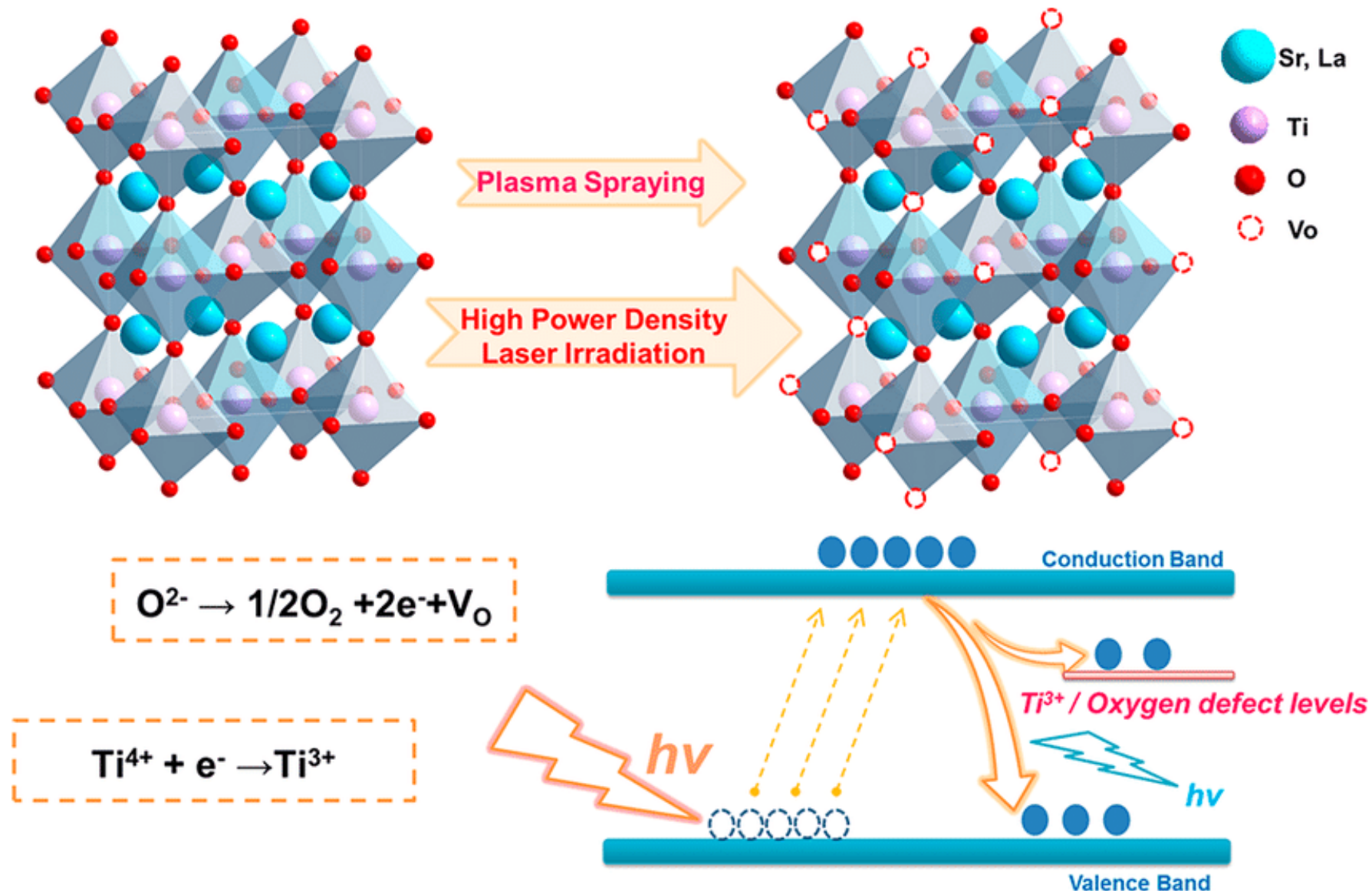


vacancy (missing atom)

Causes of vacancy defects in solids:

Vacancy, a point defect, may occur due to various reasons, as enlisted below:

- ✓ For not allowing directional solidification, usually during casting.
- ✓ Due to increase in temperature of the solid for various processing like heat treatment, coating, etc. Number of vacancies in a specific amount of solid increases exponentially.
- ✓ Due to irradiation or sputtering effect.
- ✓ Due to presence of residual tensile stress within the solid.

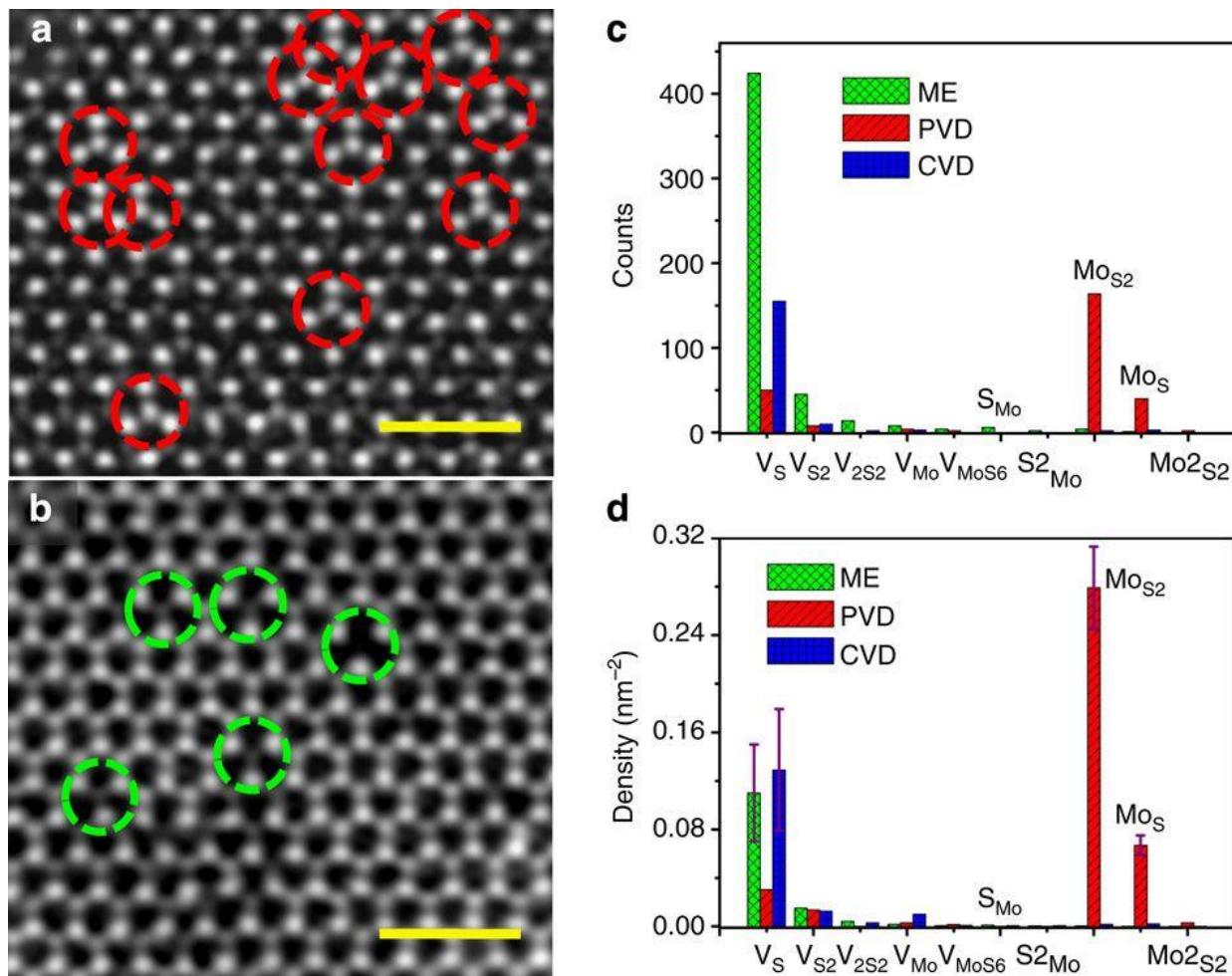


Schematic diagram of oxygen vacancy/Ti 3+ formation and the corresponding energy level in the La_{1-x}Sr_xTiO_{3+δ} coating.

Effects of vacancies in solid:

- ✓ Although depends on material and its crystal structure, in general, vacancies can decrease the bulk modulus and can increase the Young's modulus.
- ✓ Large vacancy concentration can reduce the ductility of the crystalline solid; however, can increase the hardness.
- ✓ It can alter the thermal and electrical resistivity of the solid.
- ✓ Common physical properties, like melting point, color, etc. can also vary due to presence of vacancies.





(a) Antisite defects in PVD MoS₂ monolayers. Scale bar, 1 nm. **(b)** Vacancies including V_S and V_{S2} observed in ME monolayers, similar to that observed for CVD sample. Scale bar, 1 nm. **(c,d)** Histograms of various point defects in PVD, CVD and ME monolayers. Error estimates are given for the dominant defects (more details on the statistics can be found in [Supplementary Fig. 6](#)). ME data are in green, PVD data in red and CVD in blue.

Hong, J., Hu, Z., Probert, M. *et al.* Exploring atomic defects in molybdenum disulphide monolayers. *Nat Commun* **6**, 6293 (2015). <https://doi.org/10.1038/ncomms7293>

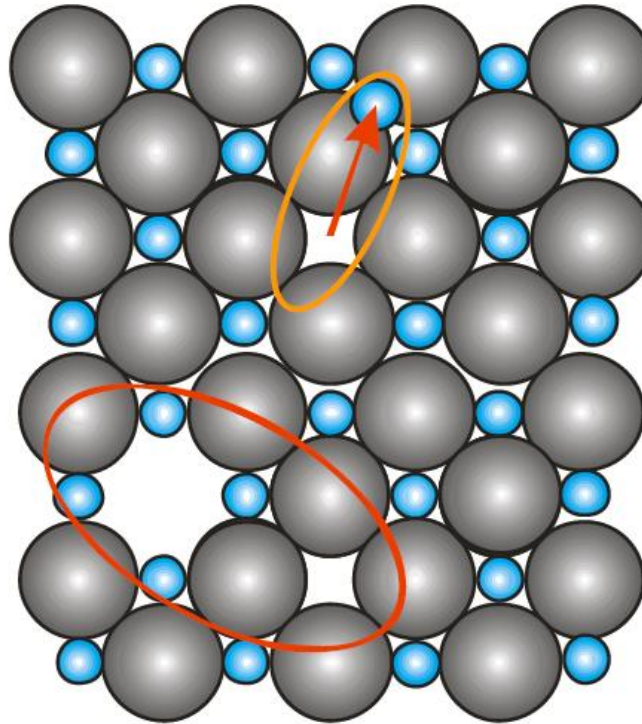
Point defects in ionic compounds

◆ Schottky defect

- A pair of oppositely charge ion vacancies

◆ Frenkel defect

- A vacancy-interstitialcy combination



Frenkel
defect

Cation vacancy
+
cation interstitial

Schottky
defect

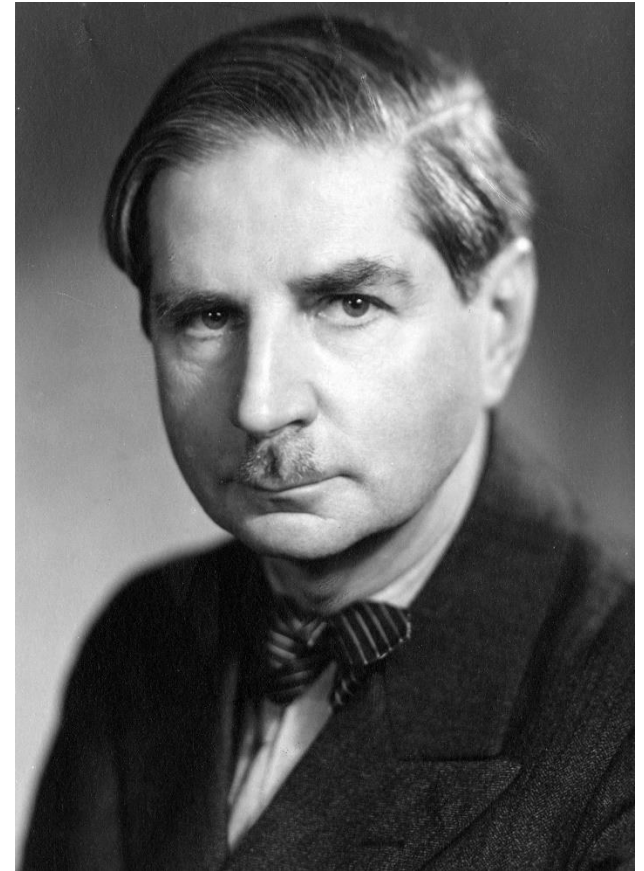
Cation vacancy
+
anion vacancy

Schottky defect

Walter Hans Schottky

(23 July 1886 – 4 March 1976)

- a German physicist who played a major early role in developing the theory of electron and ion emission phenomena, invented the screen-grid vacuum tube in 1915 while working at Siemens, co-invented the ribbon microphone and ribbon loudspeaker along with Dr. Erwin Gerlach in 1924 and later made many significant contributions in the areas of semiconductor devices, technical physics and technology.

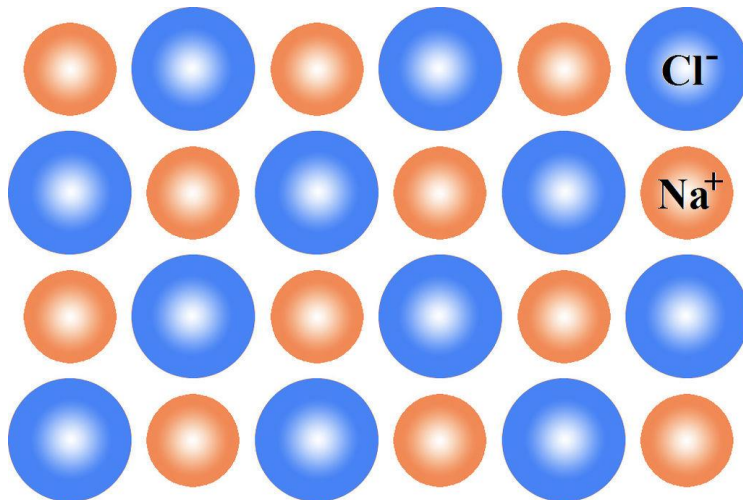


Schottky defect

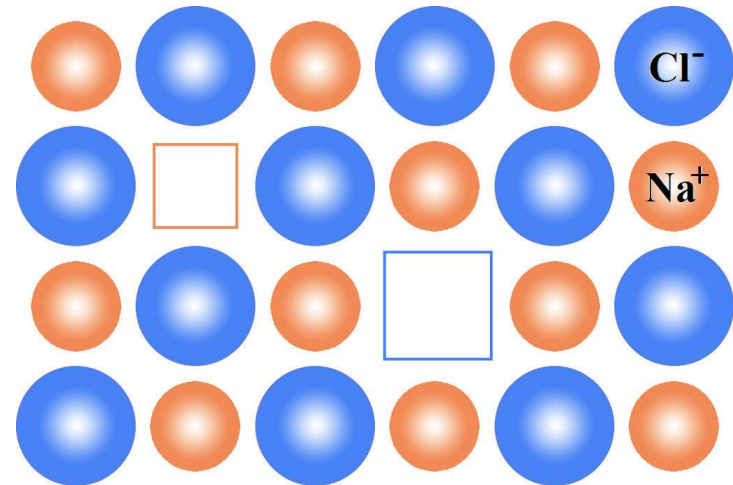
In ionic crystals, this type of point defect forms when oppositely charged ions leave their lattice sites, creating vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid.

The surrounding atoms then move to fill these vacancies, causing new vacancies to form. Normally these defects will lead to a decrease in the density of the crystal or metal.

This can be illustrated schematically with a two-dimensional diagram of a [sodium chloride](#) crystal lattice:



The defect-free NaCl structure

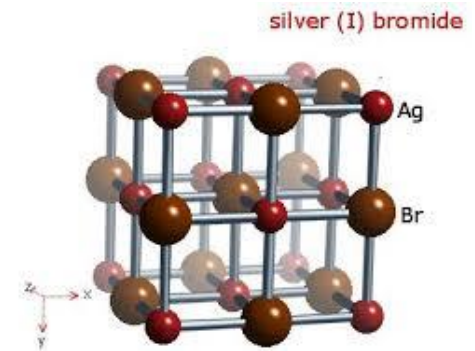
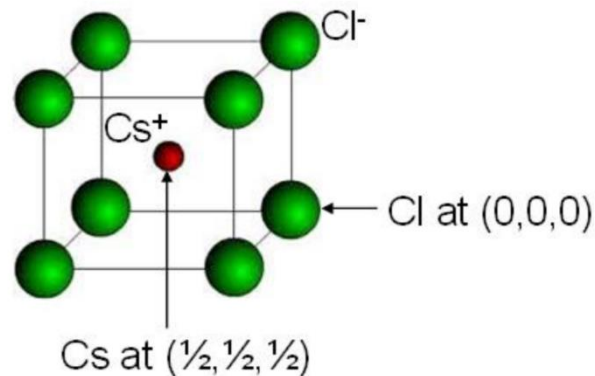
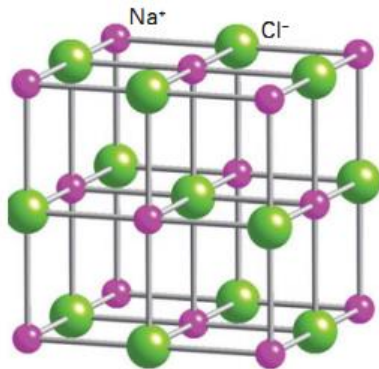


Schottky defects within the NaCl structure

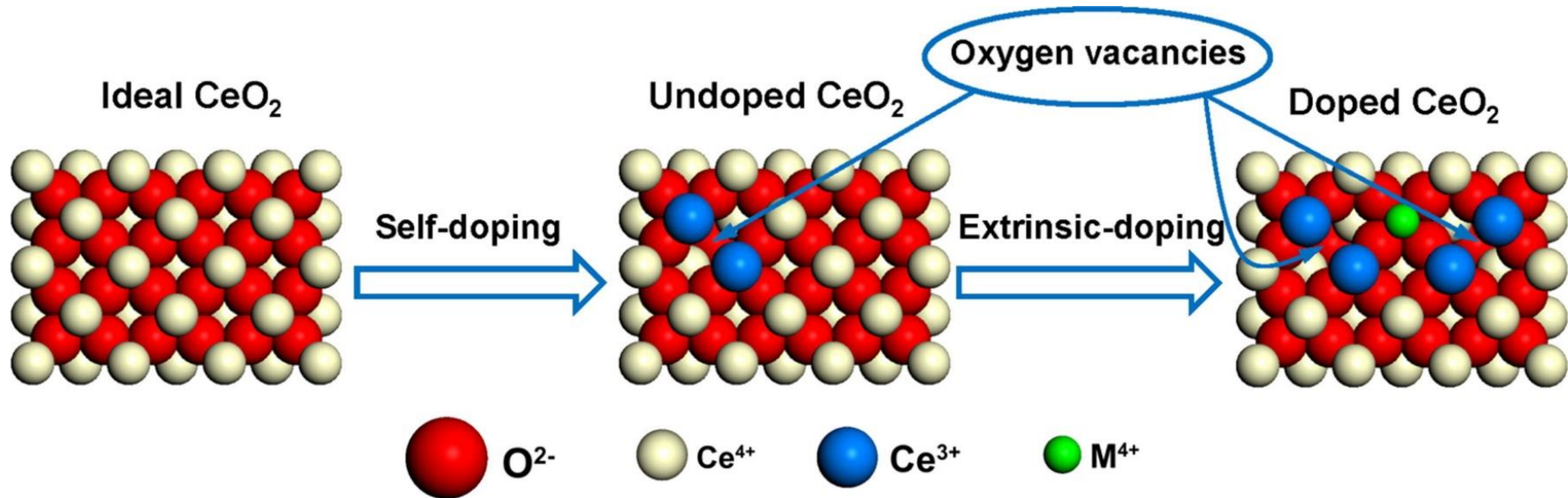
Examples

This type of defect is typically observed in highly ionic compounds, highly coordinated compounds, and where there is only a small difference in sizes of cations and anions of which the compound lattice is composed.

Typical salts where Schottky disorder is observed are NaCl, KCl, KBr, CsCl and AgBr.

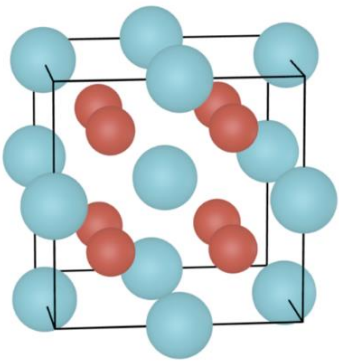


(a) stoichiometric oxide CeO_2 in a perfect fluorite structure, this structure is unstable and transforms into (b) a nonstoichiometric oxide $\text{CeO}_{2-x/2}$ through the formation of Ce^{3+} and oxygen vacancies; and (c) doping of smaller cations ($\text{M}^{4+}=\text{Hf}, \text{Zr}$) into CeO_2 decreases recombination and produces Ce^{3+} together with more oxygen vacancies, finally forming $\text{Ce}_{1-m}\text{M}_m\text{O}_{2-x/2-y}$.



Doping CeO_2 with certain metallic ions has been shown to be an effective route to improving its oxygen storage capacity (OSC).

This systematic study provides a new strategy for the design of three-way catalysts.

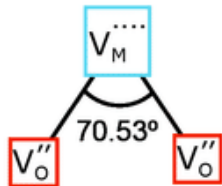
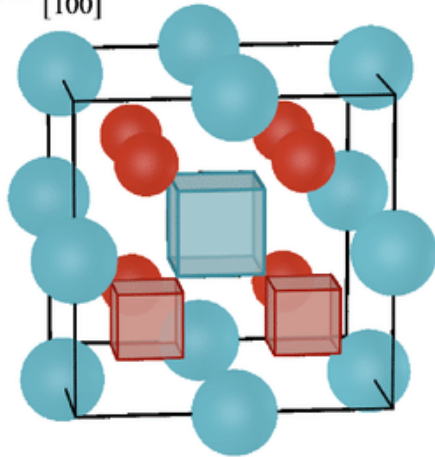


Bound and dilute defects

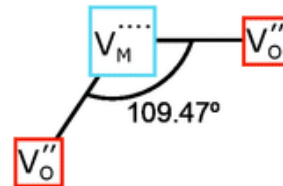
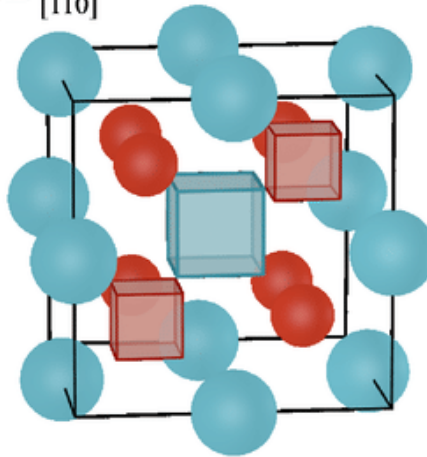
- ✓ Three bound configurations of Schottky defects in an oxide with Fluorite structure.
- ✓ Spheres represent atoms, cubes represent vacancies.

fluorite structure

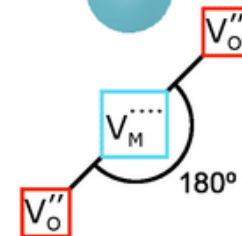
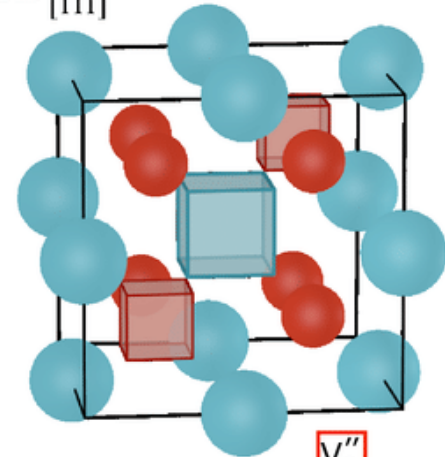
$SD_{[100]}$



$SD_{[110]}$



$SD_{[111]}$



Bound Schottky defects in CeO_2 , or any other compound with fluorite structure

Frenkel Defect

A Frenkel defect or dislocation defect is a type of point defect in crystalline solids named after its discoverer Yakov Frenkel.

The defect forms when an atom or smaller ion (usually cation) leaves its place in the lattice, creating a vacancy, and becomes an interstitial by lodging in a nearby location.

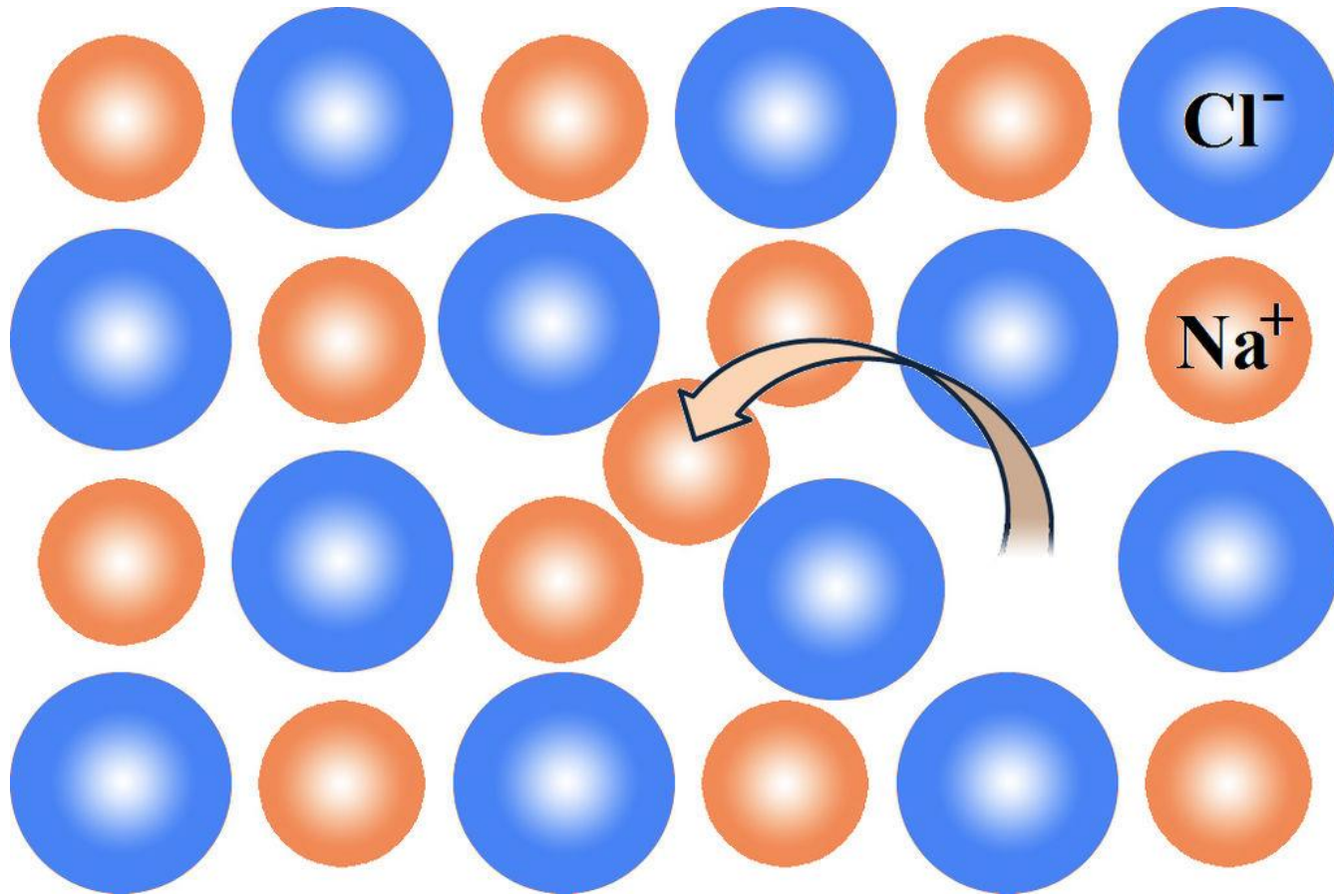
Their primary mechanism of generation is by particle irradiation, as their equilibrium concentration according to the Boltzmann distribution is much smaller than the pure interstitial atoms.

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.



Yakov Il'ich Frenkel

(Russian: Яков Ильич Френкель)
(10 February 1894 – 23 January 1952)
- a Soviet physicist renowned for his works in the field of condensed matter physics.



The Frenkel defect within the NaCl structure

Examples

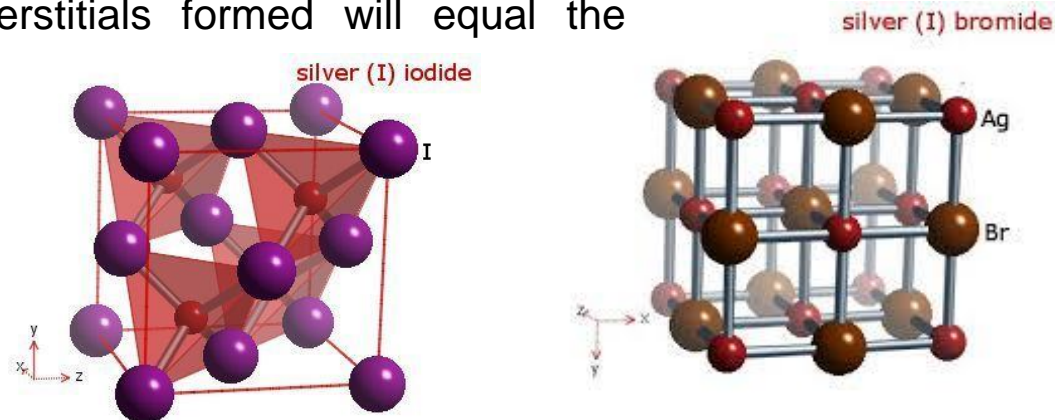
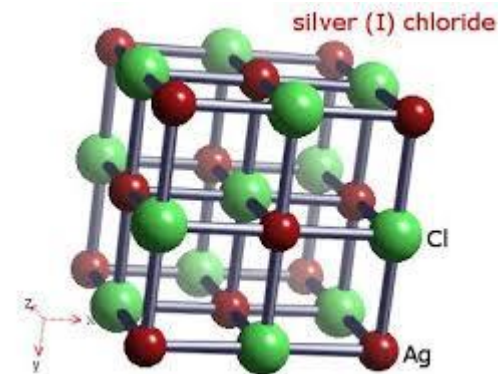
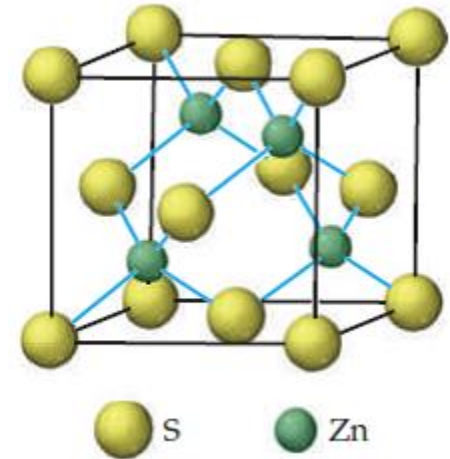
Frenkel defects are exhibited in ionic solids with a large size difference between the anion and cation (with the cation usually smaller due to an increased effective nuclear charge).

Some examples of solids which exhibit Frenkel defects:

zinc sulfide,
silver(I) chloride,
silver(I) bromide (also shows Schottky defects),
silver(I) iodide.

These are due to the comparatively smaller size of Zn^{2+} (0.88) and Ag^+ (1.29) ions.

For example, consider a lattice formed by X^{n-} and M^{n+} ions. Suppose an M ion leaves the M sublattice, leaving the X sublattice unchanged. The number of interstitials formed will equal the number of vacancies formed.



Traditional and Kröger-Vink notations of defects in TiO₂ and N-doped TiO₂ systems.

Traditional Notation	Description	Kröger-Vink Notation
$\text{Ti}_{\text{Ti}}^{+4}$	Ti ⁺⁴ ion in titanium lattice site	Ti_{Ti}^x
$\text{Ti}_{\text{Ti}}^{+3}$	Ti ⁺³ ion in titanium lattice site	e'
V_{Ti}	Titanium vacancy	V_{Ti}'''
Ti_i^{+3}	Ti ⁺³ in an interstitial site	Ti_i'''
Ti_i^{+4}	Ti ⁺⁴ in an interstitial site	Ti_i''''
O_o^{-2}	O ⁻² ion in an oxygen lattice site	O_o^x
V_o	Oxygen vacancy	V_o''
O_o^{-}	O ⁻ ion in an oxygen lattice site	h^*
N_o^{-3}	N ⁻³ ion in an oxygen lattice site	N_o'''
N_i^{-3}	N ⁻³ ion in an interstitial site	N_i'''

- Published in Scientific Reports 2017
- DOI:[10.1038/s41598-017-02124-1](https://doi.org/10.1038/s41598-017-02124-1)

Kröger-Vink Notation X_Y^Z

Examples:

interstitial Ag ion in AgCl: Ag_i^\bullet

vacancy on a Ag site in AgCl: V_{Ag}'

Ca^{2+} ion on a Na site in NaCl: $Ca_{Na}^{\bullet\bullet}$

vacancy on an O site in Al_2O_3 : $V_O^{\bullet\bullet}$

Cu^+ on a Cu^{2+} site CuO: Cu_{Cu}'

In a generic discussion of defect reactions, M and X are often used:
 M - atom of electropositive element
 X - atom of electronegative element

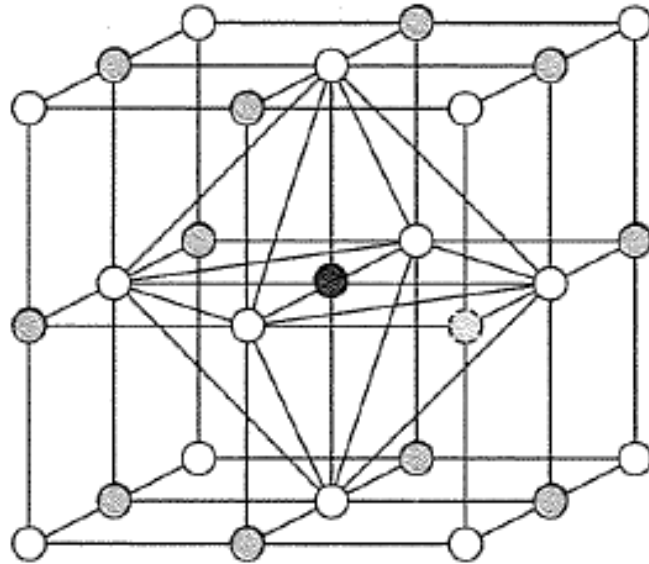
Intrinsic point defects and Pu impurity in UO_2 crystal



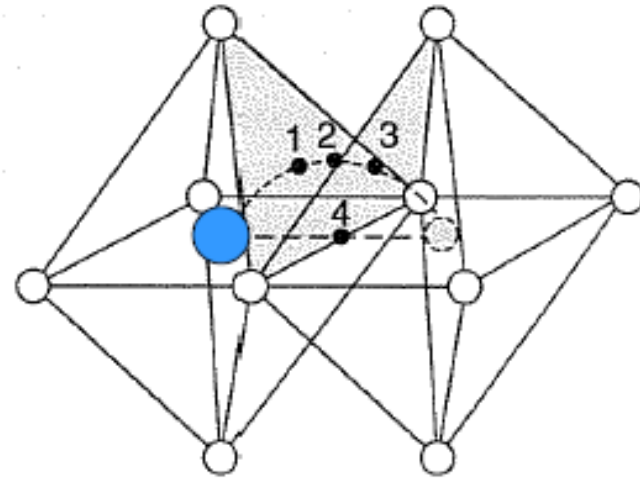
Y \ X	U^{4+} ion	O^{2-} ion	Vacancy	Pu^{4+} ion
U site	U_U^x	$O_U^{\bullet\bullet}$	$V_U^{\bullet\bullet}$	Pu_U^x
O site	$U_O^{\bullet\bullet\bullet\bullet}$	O_O^x	$V_O^{\bullet\bullet}$	$Pu_O^{\bullet\bullet\bullet\bullet}$
<i>i</i> site	$U_i^{\bullet\bullet\bullet\bullet}$	O_i^{\bullet}	V_i^x	$Pu_i^{\bullet\bullet\bullet\bullet}$

Ion Migration (Schottky defects)

Na^+ ions move, but meet resistance in the crystal structure



(a)

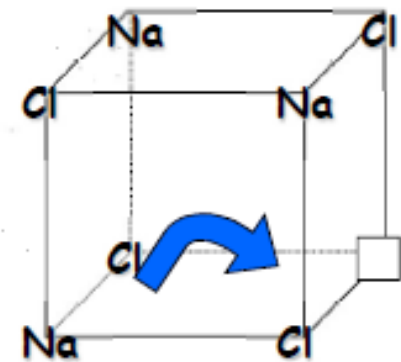
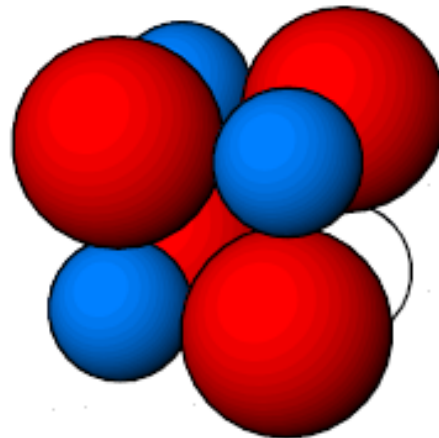


(b)

○ X^-

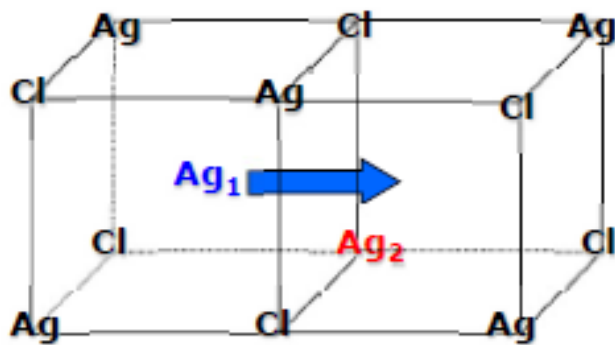
● M^+

⊙ M^+ vacancy

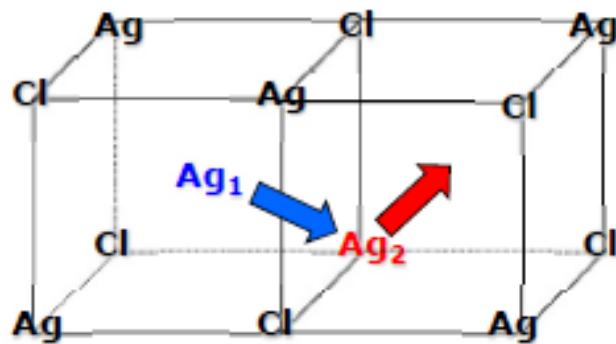
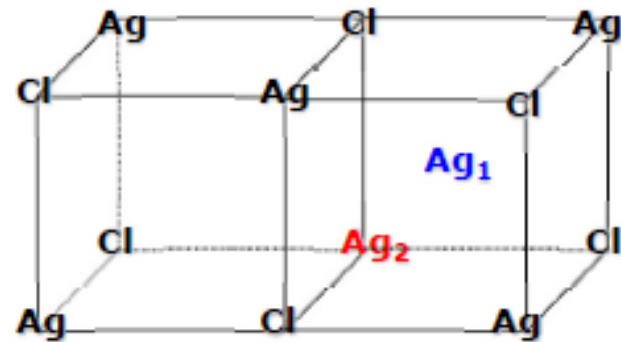


Ion Migration (Frenkel Defects)

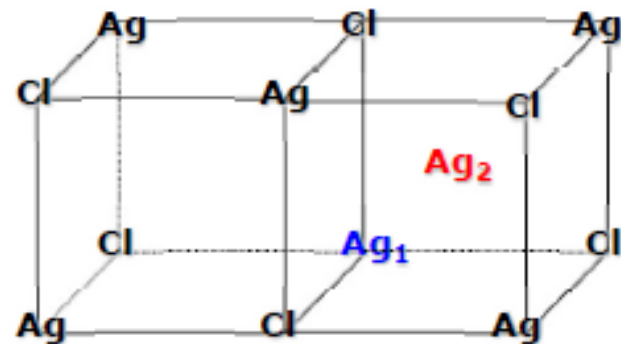
The Frenkel defects in AgCl can migrate via two mechanisms.



Direct Interstitial Jump



Interstitialcy Mechanism



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

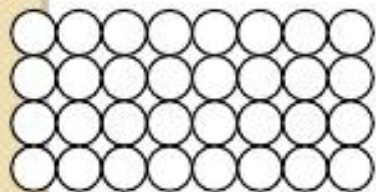
No. of potential defect sites.

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

Activation energy

Boltzmann's constant

Temperature



Each lattice site
is a potential
vacancy site

$$(1.38 \times 10^{-23} \text{ J/atom-K})$$
$$(8.62 \times 10^{-5} \text{ eV/atom-K})$$