BYJU'S Classes

Solid State

Effect of T and P on Crystal and Introduction to Crystal Defects

What you already know

- Radius ratio rule
- Radius ratio for tetrahedral void, octahedral void and cubical void
- Structure of ionic compounds

What you will learn

- Anti-Fluorite (Na_2O) structure: radius ratio and coordination number calculation
- Caesium chloride (CsCl) structure
- Effect of temperature and pressure on crystal structure
- Truncated polyhedron
- Defects in crystals
- Types of point defects

KCl crystallises in the same type of lattice as does NaCl. Given that

$$\frac{r_{Na^+}}{r_{Cl^-}} = 0.55 \qquad \frac{r_{K^+}}{r_{Cl^-}} = 0.74$$

Calculate the ratio of the side of the unit cell of KCl to that of NaCl:

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Solution

$$\frac{a_{KCl}}{a_{NaCl}} = \frac{2(r_{K^+} + r_{Cl^-})}{2(r_{Na^+} + r_{Cl^-})}$$

$$= \frac{0.74x + x}{0.55x + x}$$

$$= \frac{1.74}{1.55} = \frac{1.55 + 0.19}{1.55}$$

$$= 1 + \frac{0.19}{1.55} \approx \frac{0.2}{1.6}$$

.125

Hence, option (a) is the correct answer.

a	1.123
b	0.891
c	1.414
d	0.414

Ionic solid Na^+A^- crystallise in rock salt type structure. 2.592 g of ionic solid NaA dissolved in water to make 2 litre solution. The pH of this solution is 8. If distance between cation and anion is 300 pm, calculate density of ionic solid (in g/cm^3). (Given $pK_w = 13$, pK_a (HA) = 5, $N_A = 6 \times 10^{23}$)

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Solution

$$\rho = \frac{4 \times 129.6}{6\times10^{23}\,(6\times10^{-8})^3}$$

$$= \frac{4\times129.6}{6\times6^3\times10^{-1}}$$

$$= \frac{4\times1296}{6\times6\times6\times10^{-1}} = 4\,g/cm^3$$

$r_{Br^-} + r_{Na^+} = 300\,pm$; $a = 2(r_{Br^-} + r_{Na^+}) = 600\,pm$

$$\rho = \frac{4\,M_{NaBr}}{N_A \cdot a^3}$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$c - x \qquad x \qquad x$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-13}}{10^{-5}} = 10^{-8}$$

$[A^-]$

$[H^+] = 10^{-8}\,M \quad (\because pH = 8)$

$$\therefore [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-13}}{10^{-8}} = 10^{-5}\,M$$

$$= x$$

$$K_b = \frac{x \cdot x}{c - x}$$

$$\therefore 10^{-8} = \frac{10^{-10}}{c - 10^{-5}}$$

$$\therefore c = 10^{-5} + 10^{-2}$$

$$\approx 10^{-2}\,M$$

$$c = \frac{\left(\frac{2.592}{M}\right)}{2L} = 0.01 \quad \therefore M = \frac{2.592}{2}$$

$$= 1.30 - 0.4 = 129.6$$

Hence, the density of the ionic solid is 4 g/cm³.

A crystal is made of particles A and B. A forms FCC packing and B occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then, the formula of the crystal would be:

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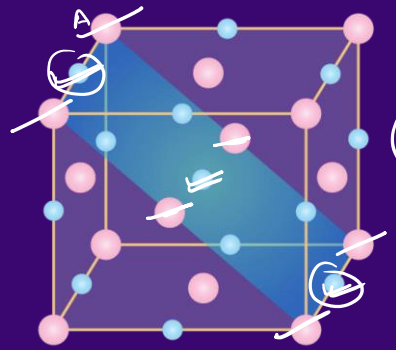


A fcc

B

A_4 B_4 | $A_{2.5}B_{2.5}$

Solution

$4 \times \frac{1}{8} + 2 \times \frac{1}{2} = \frac{3}{2}$ A missing

B missing : $\frac{1}{4} \times 2 + 1 = \frac{3}{2}$

a	AB
b	A_5B_7
c	A_7B_5
d	None of these

Hence, option (a) is the correct answer.

Given: A spinel where oxides ions are arranged in CCP layers, 1/8th of the tetrahedral holes occupied by one type of metal ion, one-half of the octahedral holes occupied by another type of metal ion. Zn^{2+}, Al^{3+} and O^{2-} with Zn^{2+} in the tetrahedral holes

To find: Formula of the compound as $Zn_xAl_yO_z$ and value of (x + y + z)

B

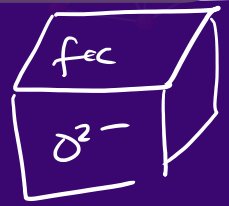
Solution

$\frac{1}{8}$ TV ; $\frac{1}{2}$ O.V. , O^{2-} fcc

Zn^{2+} Al^{3+}

$8 \times \frac{1}{8}$ $\frac{1}{2} \times 4$ $4\ O^{2-}$

$= 1\ Zn^{2+}$ $= 2\ Al^{3+}$



$ZnAl_2O_4$

$Zn(AlO_2)_2$

$x = 1$
$y = 2$
$z = 4$

Hence, value of x + y + z = 7

Anti-Fluorite Structure (Na_2O)

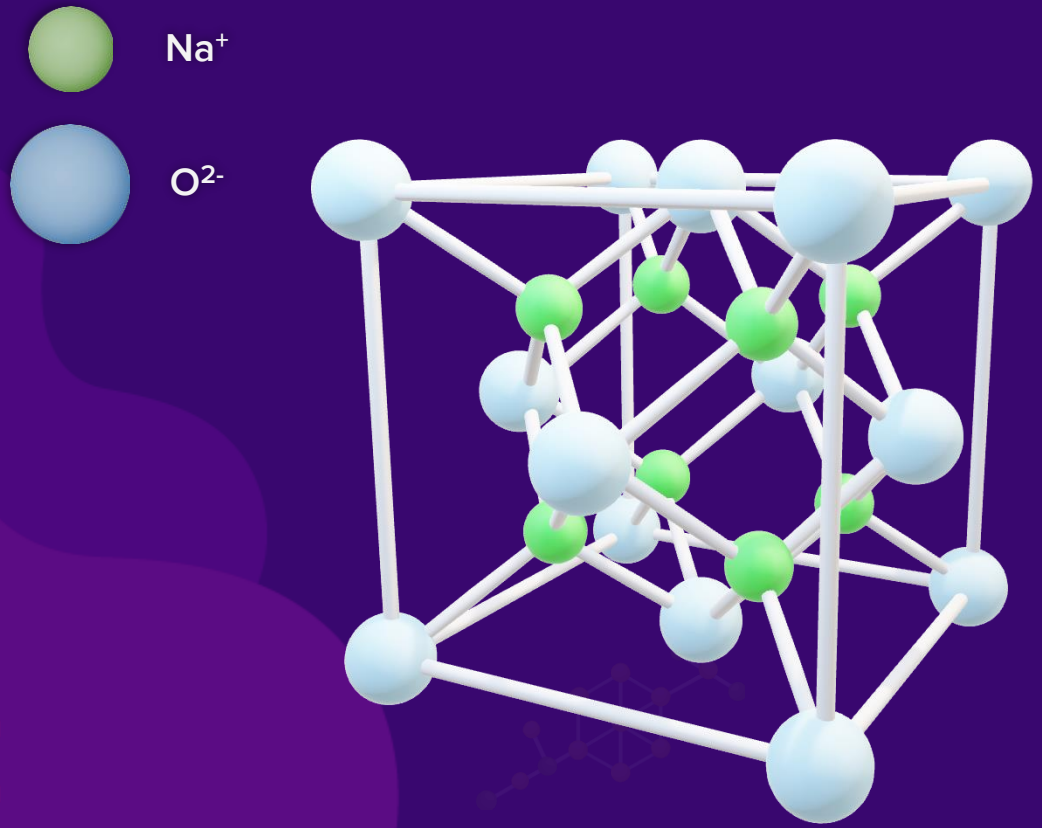
Experimental ratio,

$$0.225 \leq \frac{r_{Na^+}}{r_{O^{2-}}} < 0.414$$

O^{2-} ions form the CCP lattice

Na^+ ion occupies all tetrahedral voids

Anti-Fluorite Structure (Na_2O)



Note

$\sqrt{2}a > 4r_{O^{2-}}$

Anion–anion contact is **not** present

$r_{Na^+} + r_{O^{2-}} = \frac{\sqrt{3}}{4} a_{FCC}$

Anti-Fluorite Structure (Na_2O)

Effective number of **Na^+ ions** per unit cell	=	**8**
Effective number of **O^{2-} ions** per unit cell	=	**4**

Anti-Fluorite Structure (Na_2O)

Formula of unit cell: Na_8O_4

Formula of ionic compound	=	Na_2O
Effective number of formula units (Z)	=	4

Anti-Fluorite Structure (Na_2O)

Coordination number

4 : 8

4 → Coordination number of cations

8 → Coordination number of anions

Examples

Li_2O, Na_2O,
K_2O & Rb_2O

Caesium Chloride (CsCl)

Experimental ratio, $\frac{r_{Cs^+}}{r_{Cl^-}} \simeq 0.93$

$$0.732 \leq \frac{r_{Cs^+}}{r_{Cl^-}} < 1$$

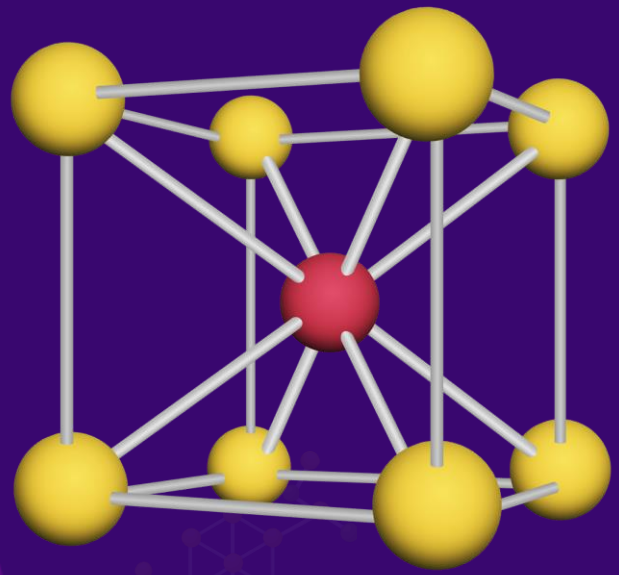
Cl^- ions form simple cubic lattice

Cs^+ ion occupies cubical void

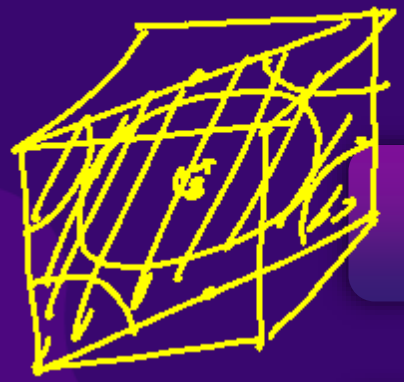
Caesium Chloride (CsCl)

Cs^+

Cl^-



Caesium Chloride (CsCl)



$a\sqrt{3} = 2(r_{Cs^+} + r_{Cl^-})$

$a > 2r_{Cl^-}$

Anion–anion contact is **not** present

$$\underbrace{r_{Cs^+} + r_{Cl^-}}_{} = \frac{\sqrt{3}}{2} a_{FCC}$$

$= a/2$

Caesium Chloride (CsCl)

Effective number of Cs^+ ions per unit cell = 1

Effective number of Cl^- ions per unit cell = 1

Caesium Chloride (CsCl)

Formula of unit cell: CsCl

Formula of ionic compound	=	CsCl
Effective number of formula unit (Z)	=	1

Caesium Chloride (CsCl)

Coordination number

8 : 8

Coordination number of **cations**

Coordination number of **anions**

Examples

CsBr, CsI

Summary

Crystal	Structural arrangement
NaCl	$Cl^- \rightarrow$ FCC $Na^+ \rightarrow$ All O.V.
ZnS (Zinc blende)	$S^{2-} \rightarrow$ FCC $Zn^{2+} \rightarrow$ Alternate T.V.
CaF_2 (Fluorite)	$Ca^{2+} \rightarrow$ FCC $F^- \rightarrow$ All T.V.
Na_2O (Anti fluorite)	$O^{2-} \rightarrow$ FCC $Na^+ \rightarrow$ All T.V.
CsCl	$Cl^- \rightarrow$ Simple cubic lattice $Cs^+ \rightarrow$ Body centred void (cubic void)

Effect of Temperature & Pressure on Crystal Structure

Effect of Temperature on Crystal Structure

Temperature ↑ ⟹ Coordination number ↓

8 : 8 $\xrightarrow{T\uparrow}$ 6 : 6

Effect of Pressure on Crystal Structure

Pressure ↑ » Coordination number ↑

4 : 4 —P↑→ 6 : 6

In which of the following compounds, the cations are present in alternate tetrahedral voids:

ZnS

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a. NaCl

b. ZnS

c. CaF_2

d. Na_2O

Given: Ionic solid MX with NaCl structure. Construct a new structure (Z), whose unit cell is constructed from unit cell of MX following the sequential instruction given below.

(i) Remove all the anions (X) except the central one.

(ii) Replace all the face centred cations (M) by anions (X).

(iii) Remove all the corner cations (M).

(iv) Replace the central anion (X) with cation (M).

To find: The value of $\frac{\text{number of anions}}{\text{number of cations}}$ in Z: $\frac{3}{1} = 3$

M_1X_3

anions | cations

bc (1) → replace (M) z

ec (3) → remove (0)

fc (3) → replace (3X)

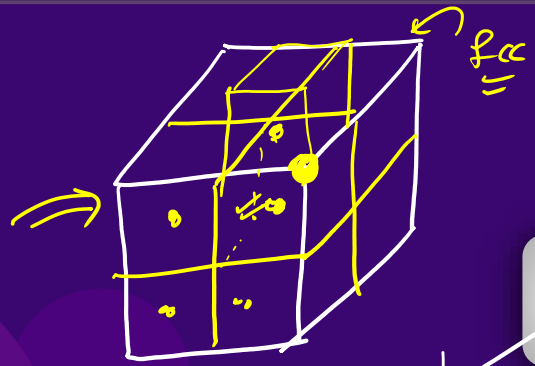
corner (1) → (0)

=

Solution

After following the sequential instructions, anions are present on all face centred position,and cations are present at the body centred octahedral void. The formula of the compound become M_1X_3.
Thus, the value of number of anion is 3 and cation is 1.

Which of the following statements are correct?



a The coordination number of each type of ion in CsCl crystal is 8.

Ca^{2+} Fcc

F^- all T.Vs

b Fluorite structures can also be imagined as simple cubic lattice of F^- with Ca^{2+} occupying alternate cubical void.

Which of the following statements are correct?

$r_{\oplus} = 95$

$r_{\ominus} = 181$

276

$\times 2$

552

c A unit cell of ionic crystal shares some of its ion with other unit cells.

d The length of the unit cell in NaCl is 552 pm. ($r_{(Na^+)}$ = 95 pm, $r_{(Cl^-)}$ = 181 pm)

Solution

Hence, all options are correct.

The radius of calcium ion is 94 pm and of oxide ion is 146 pm. Predict the crystal structure of calcium oxide.

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CaO 1:1

$\frac{r_{\oplus}}{r_{\ominus}} = \frac{94}{146} \simeq \frac{97}{150} = \frac{194}{300} = \frac{1.94}{3} \simeq 0.64$

0.414 < 0.64 < 0.732

Solution

a. CaF_2 type (1:2)

b. ZnS type (< .414)

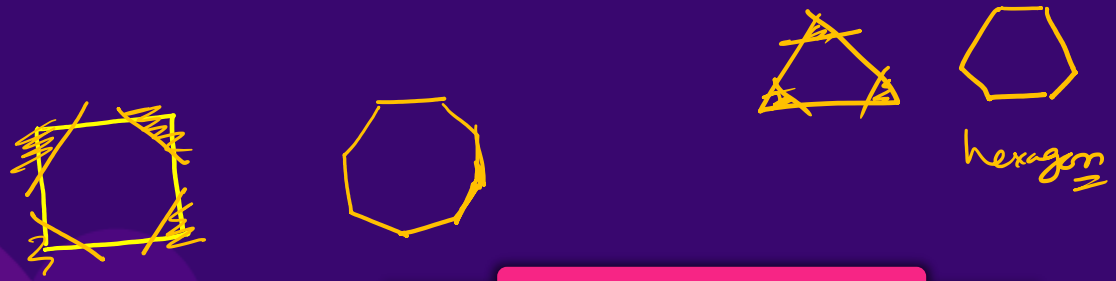
c. CsCl type (≈ 1)

d. NaCl type (1:1)

Hence, option (d) is the correct answer.

Truncated Polyhedron

Truncated Polyhedron



Truncated polyhedron is generated by **cutting the vertices** (**or corners**) of a polyhedron.

Truncated Cube

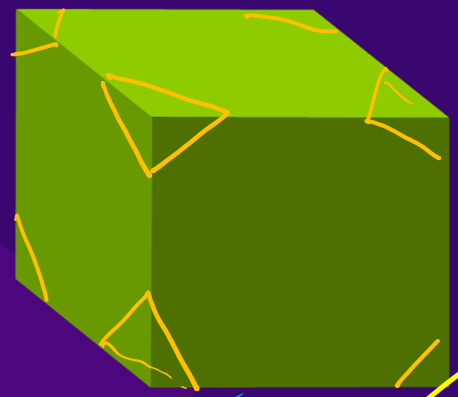
4+4+4+4+4+4

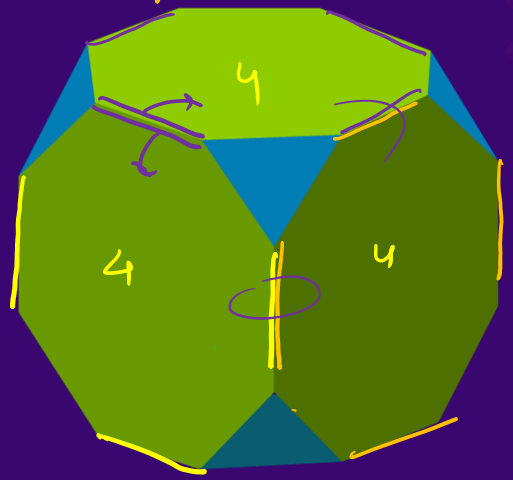
2+2+2+2+2+2

2×6 = 12

8 triangles

6 octagons





8×3 = 24 edges of △

12

+

36

Truncated Cube

- **Square** face (4 edges) is converted into **octagon** (8 edges)

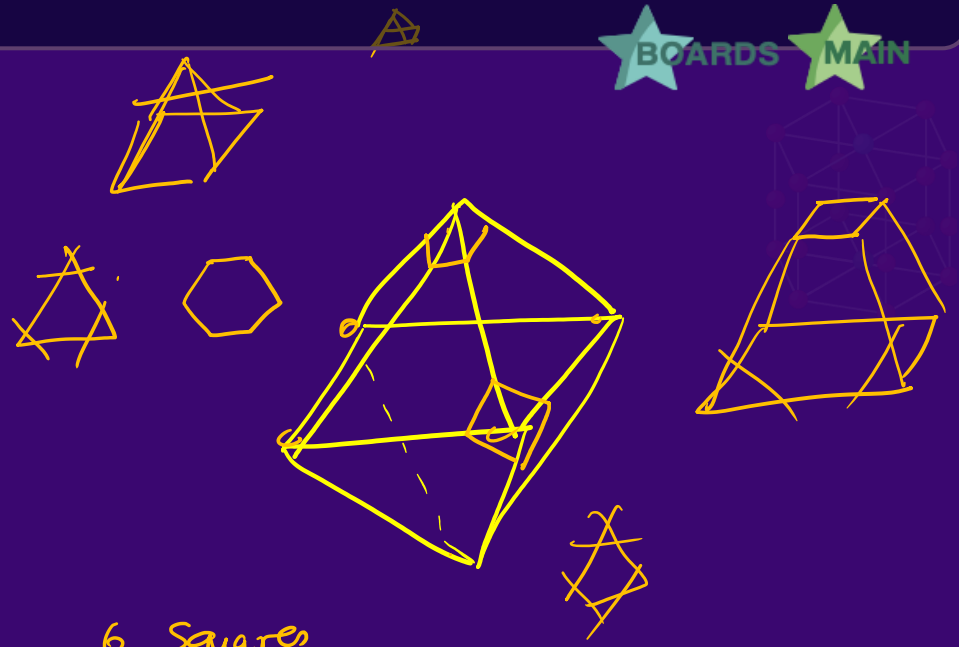
- In a truncated cube, **6 octagonal** faces and **8 triangular** faces are present.

Truncated Cube

8 triangles × 3 = 24

Number of **vertex** (corners)	=	24
Number of **edges**	=	36

The number of hexagonal faces that are present in a truncated octahedron is:



Since, we know that truncated triangle generates a hexagon and if we observe there are 8 triangular faces present in an octahedron.

6 Squares

8 hexagons

Defects in Crystals

In a **perfect crystal**, all atoms would be on their **correct lattice positions** in the structure.

This situation can only exist at the **absolute zero of temperature**, 0 K. **Above** 0 K, **defects** occur in the structure.

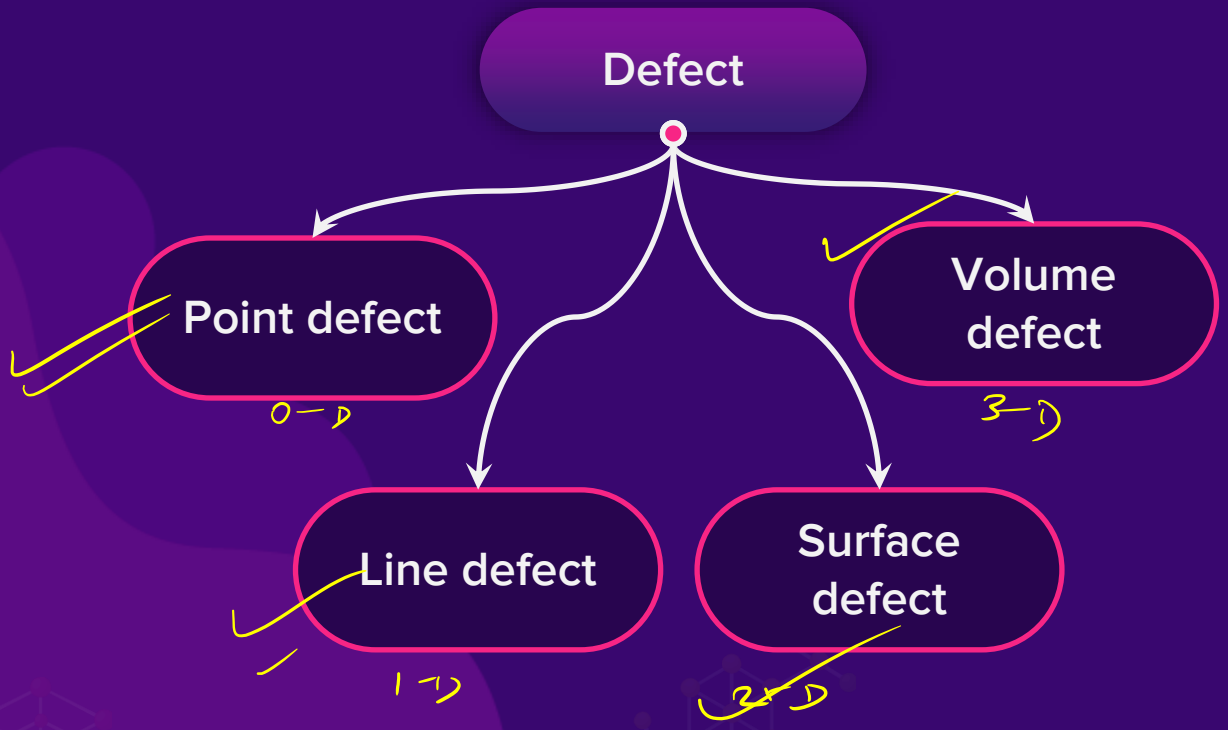
Defects in Crystals

Defects

Imperfections can be because of:

1. Conditions under which crystals have been developed.
2. Impurities
3. Temperature (because of thermal conductivity some atoms/ions can get displaced)

Defects in Crystals



Point Defects

Defects will only be at certain lattice positions.

Point defects in ionic solids

- Stoichiometric defects
- Non-stoichiometric defects
- Impurity defects

Stoichiometric Defects

The formula of compound remains the same even after the presence of these defects.

Also called thermodynamic or intrinsic defects.