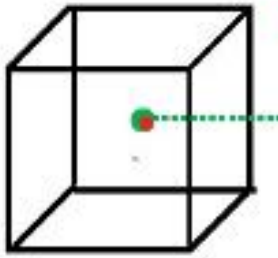
Centre of Symmetry

An imaginary point within the crystal such that any line drawn through it intersects surface of crystal at equal distances in both directions

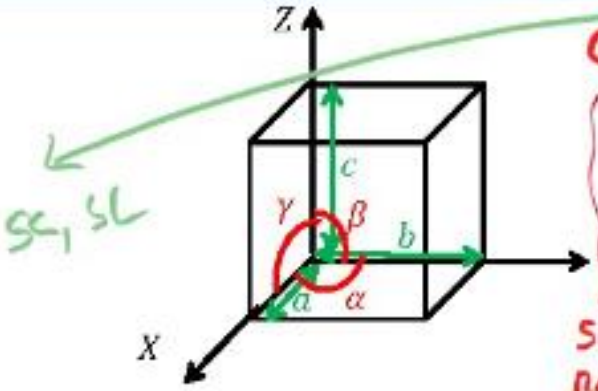
1) E → 12
2) F → 6
3) C → 8
4) BC → 1
5) FC → 6
6) FD → 12
7) BD → 4

For a cubic crystal



Note that There is only one Centre of symmetry in a cubic crystal

Crystal System: 7 Types

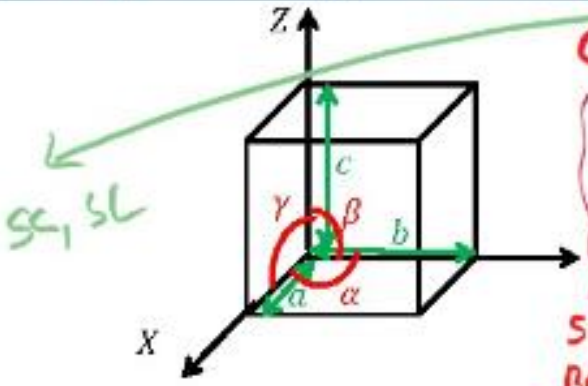


3 2 4 1 2 1 1

SC
SC, BC
SC, SL
C T O T M R H
Rhombohedral
Hexagonal
Monoclinic
Tetragonal
Triclinic
SC
BC
FC
SC BC
SC
BC
FC, BC

Crystal system	Edge Length	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$

Crystal System: 7 Types



3 2 4 1 2 1 1

C T O T M R H

SC

SC, BC

Rhombohedral

Hexagonal

Monoclinic

Tetragonal

Triclinic

SC, SL

SC
BC
FC

SC BC

SC
BC

FC, EC

Crystal system	Edge Length	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
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Theoretical Density of Cubic Crystal (ρ)

$$\rho = \frac{Z.M}{N.V}$$

Z = number of atoms in unit cell ✓

M = molar mass of substance ✓

V = Volume of unit Cell ✓

N = Avogadro constant ✓

Unit cell Content

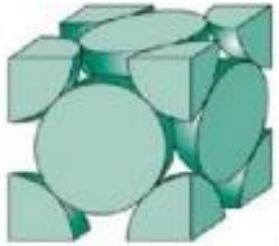
NOTE: The calculation of ρ is based on assumption that each lattice point is occupied by the species

Percentage Occupancy of a Crystal

Practically, some lattice points remain vacant

Note that $\rho_{obs} < \rho_{theoretical}$

$\rho_{observed}$ is different from $\rho_{theoretical}$

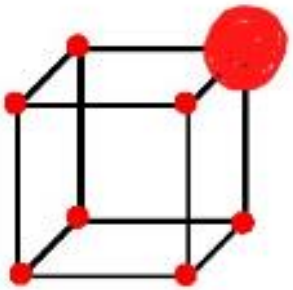


$$\% \ occupancy = \frac{\rho_{observed}}{\rho_{theoretical}} \times 100$$

void percentage

Bravais Lattices

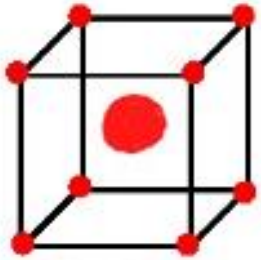
Crystals belonging to cubic system have 3 kinds of Bravais lattices



Simple/ Primitive cubic lattice

$8\ atoms\ at\ 8\ corners$

$8 \times \frac{1}{8} = 1\ (z)$

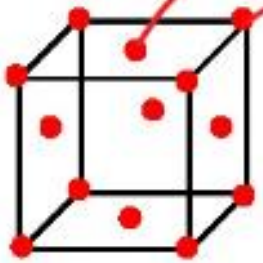


Body-centered cubic lattice $(B.C.C)$

$8\ atoms\ at\ 8\ corners$

1 atom at Centre, touching all 8

$8 \times \frac{1}{8} + 1 = 2\ (z)$



face- centered cubic lattice $(F.C.C)$

$8\ atoms\ at\ 8\ corners$

1 atom at each of 6 faces

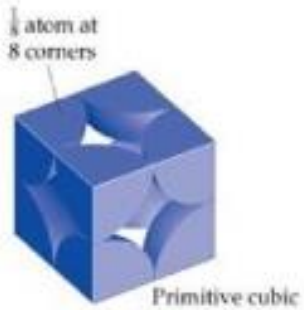
$6 \times \frac{1}{2} = 3$

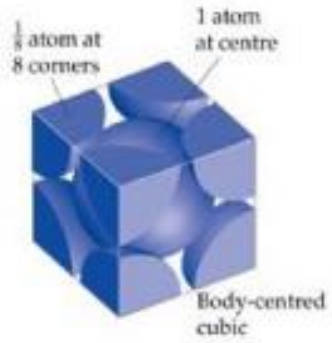
$4\ (z)$

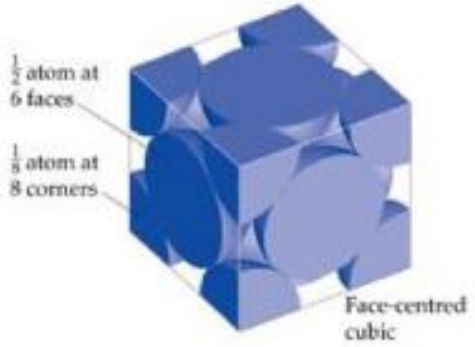
Lattice Points

There are 4 ***kinds*** of Lattice points

- At the corners → Shared among 8 unit cells
- At the face Centre → Shared among 2 unit cells
- Within the unit cell → It contributes one complete point to a cell
- At the edge Centre → Shared among 4 unit cells







Unit Cell Content (Z)

Total number of atoms contained within the unit cell = Z

For simple cubic unit cell

Z = no. of corner atom × contribution to 1 unit cell

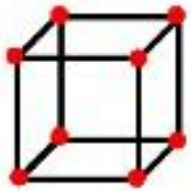
$= 8 \times \frac{1}{8}$

$= 1$

AB → Corners
Faces

AB_3 ✓ A_7B_{24} ✓

$A_{6/8}$ $B_{3/2}$ = AB_2



For B.C.C

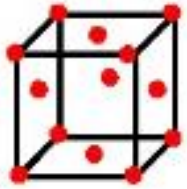
$Z = 8 \times \frac{1}{8} + 1$ (one atom at body Centre, not shared by other cells)

$= 2$

For F.C.C

$Z = 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$ (6 atoms at each face shared by 2 cells)

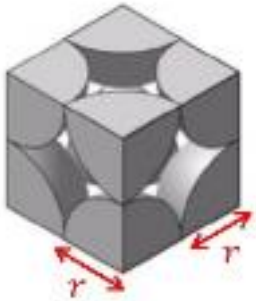
$= 4$



Atomic Radius (r) of atoms in Bravais Lattices

Note that touching of atoms depends upon type of cubic lattice.
And atoms are assumed as spheres

Simple cubic cell

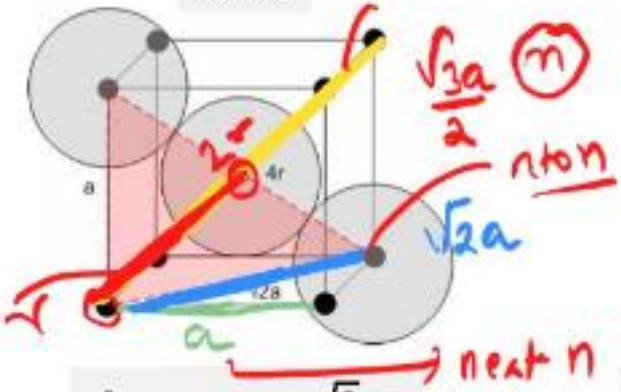


$$2r = a$$

$$r = \frac{a}{2}$$

2 adjacent corner atoms touch each other

B.C.C.

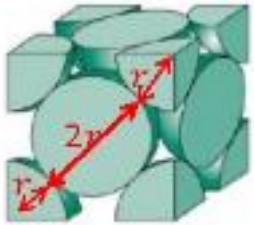


$$2r + r + r = \sqrt{3}.a$$

$$r = \frac{\sqrt{3}.a}{4}$$

Atoms at Centre of cube touch all corner atoms

F.C.C.



$$2r + r + r = \sqrt{2}.a$$

$$r = \frac{\sqrt{2}.a}{4}$$

Atoms at face Centre touches its adjacent corner atoms

Packing Fraction in Closest Packing

Fraction of total volume of unit cell occupied by atom(s) is called packing fraction

$$= \frac{Z \times (\text{volume of 1 atom})}{\text{volume of 1 unit cell}}$$

→ Z is the unit cell content

$$= \frac{Z \times \left(\frac{4}{3} . \pi . r^3\right)}{V}$$

SCC	BCC	FCC
$\pi/6$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\sqrt{2}\pi}{6}$

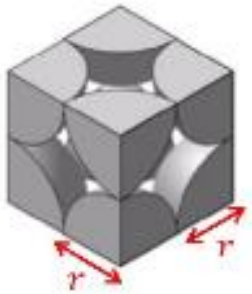
Note that in closest packing, spherical balls must have vacant space in the crystal

Atomic Radius (r) of atoms in Bravais Lattices

Note that touching of atoms depends upon type of cubic lattice.
And atoms are assumed as spheres

a = 2r

Simple cubic cell

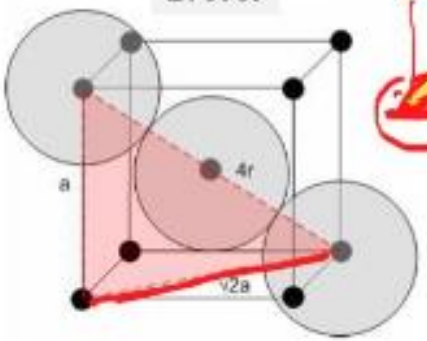


$$2r = a$$

$$r = \frac{a}{2}$$

2 adjacent corner atoms touch each other

B.C.C.

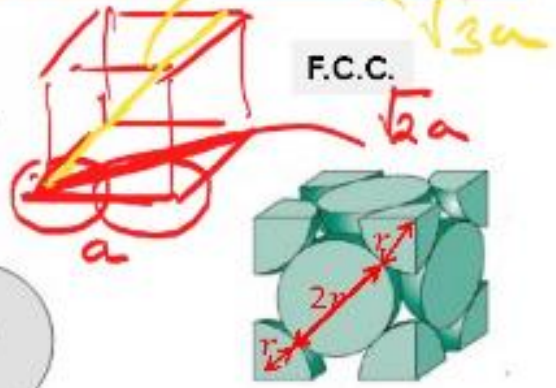


$$2r + r + r = \sqrt{3}.a$$

$$r = \frac{\sqrt{3}.a}{4}$$

Atoms at Centre of cube touch all corner atoms

F.C.C.



$$2r + r + r = \sqrt{2}.a$$

$$r = \frac{\sqrt{2}.a}{4}$$

Atoms at face Centre touches its adjacent corner atoms

Co-ordination Number (CN)

CN = number of nearest neighbours that a particle has in a crystal

Example:

For a simple cubic unit cell → **CN** = 6 ✓

For a $B.C.C$ unit cell → $CN = 8$ ✓

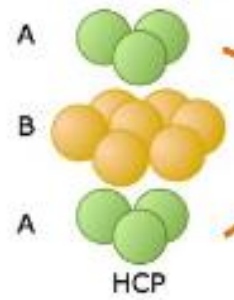
fcc → CN = 12

NOTE: All atoms in a Bravais lattice have same co-ordination number

Hexagonal Closed-Packed Structure(H.C.P)

ABABAB ABAB

Arrangement is of type ABABAB ....

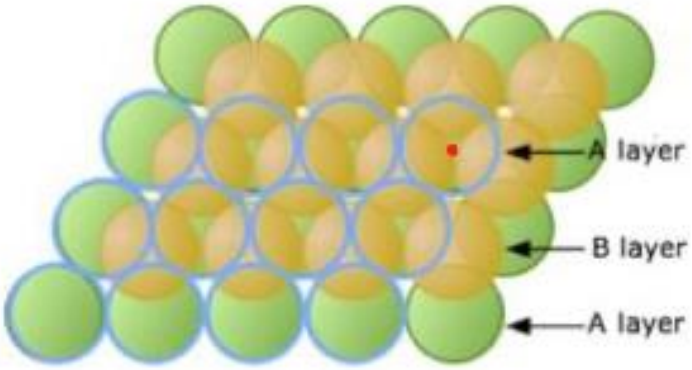


HCP

NOTE: The triangular layers are oriented in the same direction

ABCABC ABC

2TV → 1OV



ABA hexagonal close packed

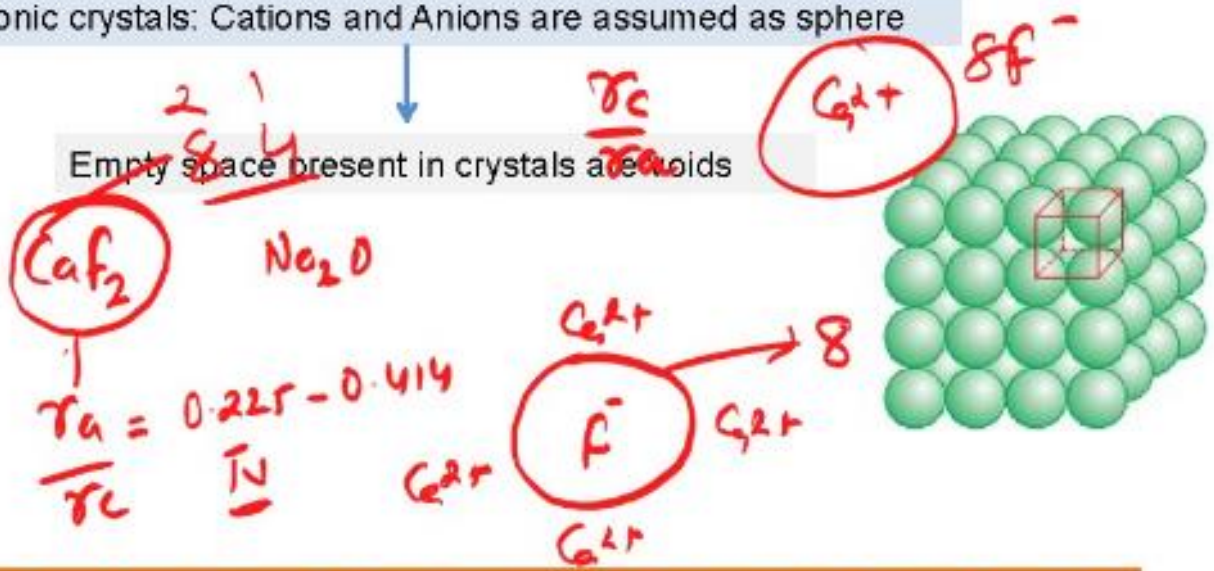
$Z = 2$

$\mathbf{CN} = 12$ → Note that it results in crystal of comparatively high density

Voids in Closest-Packed Structures

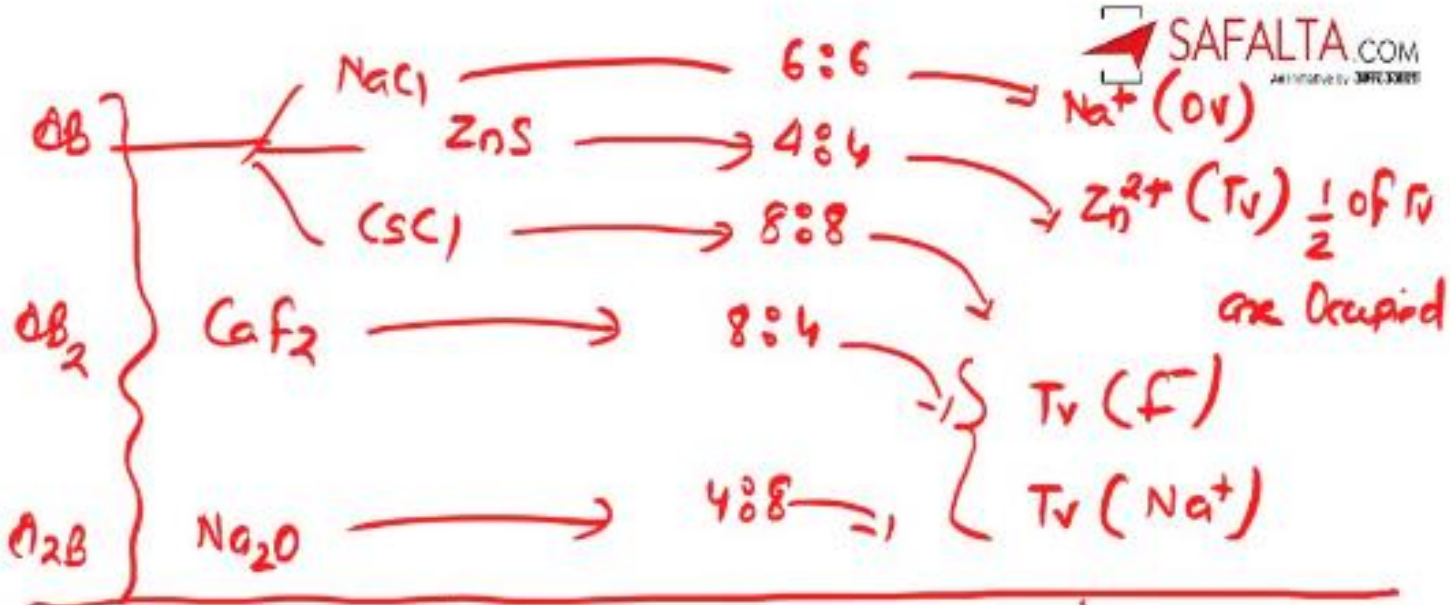
In ionic crystals: Cations and Anions are assumed as sphere

Empty space present in crystals are voids



Please Note that anions are normally larger than cations in closed packed structures and hence cations occupy the voids/ holes

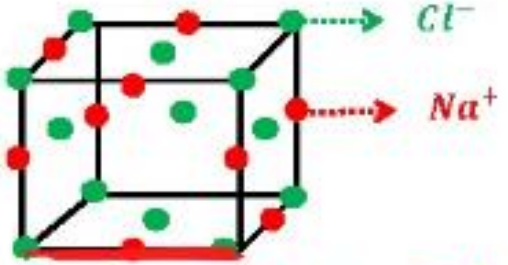
For reverse case anions will occupy voids


SAFALTA.COM
AB
NaCl
ZnS
CsCl
6:6
4:4
8:8
Na^+ (Ov)
Zn^{2+} (Tv) $\frac{1}{2}$ of Tv are Occupied
AB_2
CaF_2
8:4
Tv (F^-)
Tv (Na^+)
A_{2B}
Na_2O
4:8
2 Tv → 1 Ov
no of sphere = n
no of Ov = n
no of Tv = 2n

NaCl Cubic Crystal

Both Na^+ ions as well as Cl^- ions form F.C.C structure

F.C.C



$a = 2(r^+ + r^-)$

$\frac{r^+}{r^-} = 0.525$

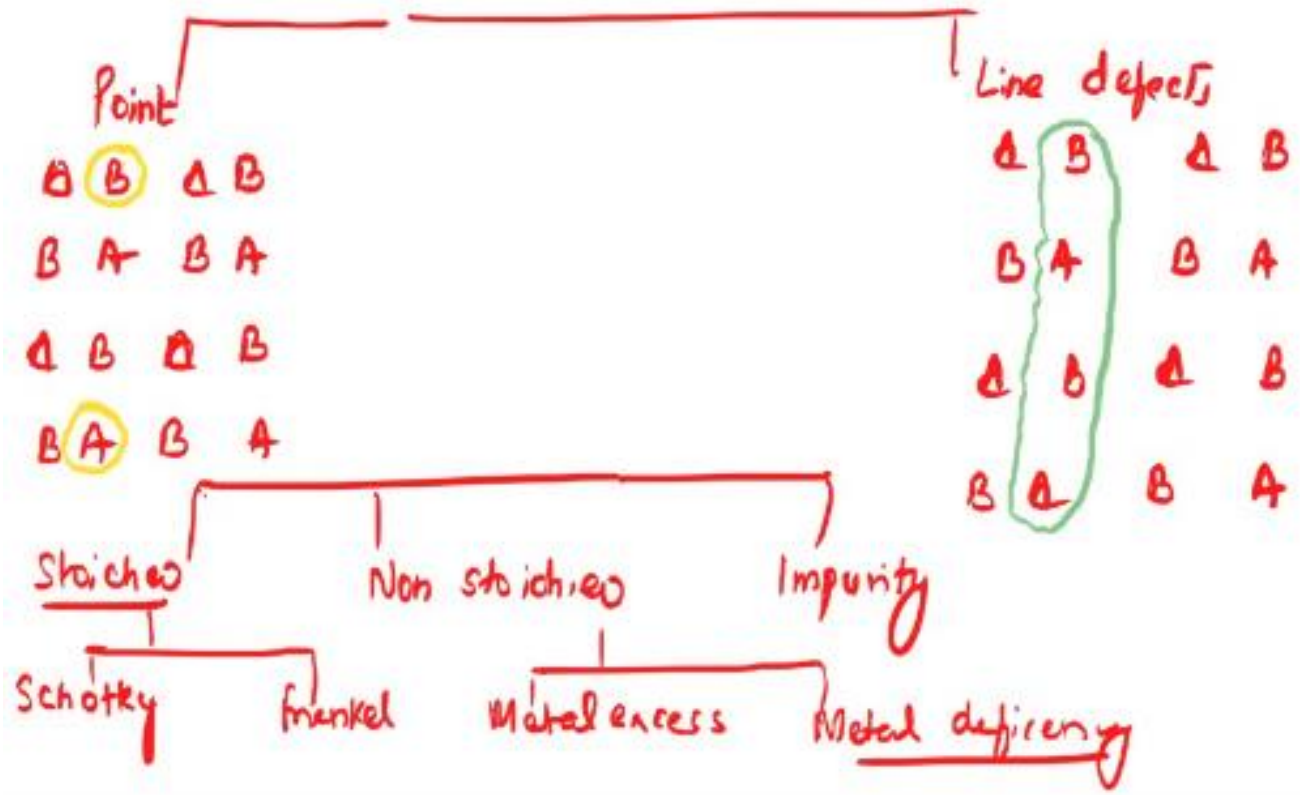
$Z = 4$

0.414 — 0.732

Each Na^+ ion is octahedral surrounded by 6 Cl^- ions and vice-versa → C.N. of both **Cl⁻** and **Na⁺** is equal to 6

Defects → Entropy (disorder) from 3rd law of TD

T = 0K , S = 0



Schottky defect:

- high CON
- Small diff in Size of cation & anion
- decreases density of crystal
- Lattice energy decreases

Ex NaCl, CsCl, KBr, KCl, AgBr

Frenkel defect:

- low CON
- large diff in size of cation & anion

ZnS, AgBr, AgI, AgCl

Defects → Entropy (disorder) from 3rd law of TD

T = 0K , S = 0