BYJU'S Classes

Solid State

Radius Ratio Rule and Some Common Structures

What you already know

- Tetrahedral Voids and Octahedral Voids in FCC Unit Cell
- Distance between Voids in FCC
- Voids in HCP Unit Cell
- Types and Size of Voids
- Practice Questions

Radius Ratio Rule and Some Common Structures

What you will learn

- Radius Ratio Rule
- Radius Ratio for Tetrahedral Void, Octahedral Void and Cubical Void
- Structure of Ionic Compounds - (a) Rock Salt (NaCl) Structure (b) Zinc Blende (ZnS) Structure (c) Diamond Structure (d) Fluorite (CaF_2) Structure

Ionic Compounds

one type of ions → all
(+) or (−)

✓sc
fcc
hcp
} locations

Larger ions
(Generally anion)

Form the lattice.

Smaller ions
(Generally cation)

Occupy the voids such as T.V., O.V. etc.

Radius-Ratio Rule

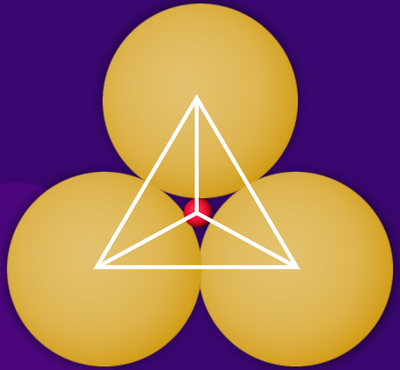
Type of void **occupied** by the **smaller ion** is decided by **radius ratio**.

The **ratio** of radius of **smaller ion** (generally cation) to the radius of **larger ion** (generally anion) is known as radius ratio of the **ionic solid**.

Generally,

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{r_+}{r_-}$$

Triangular Void



C.N. of ion in triangular void = 3

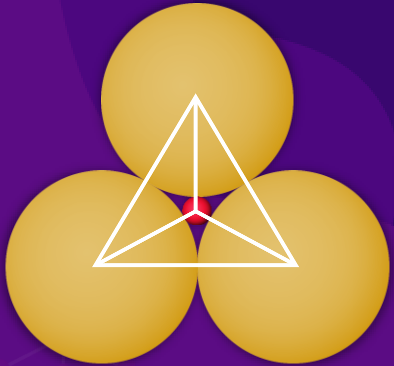
$$\frac{r}{R} = 0.155$$

Corresponds to **ideal crystal**

Note

Ideal crystal is **not desirable** as potential energy will be very high (hence less stability) if anions touch each other.

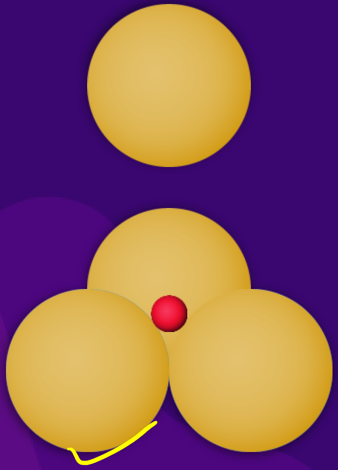
Anion-anion and **cation–cation** contact should be avoided.



$$0.155 \leq \frac{r}{R} < 0.225$$

E.g.: Boron oxide

Tetrahedral Void



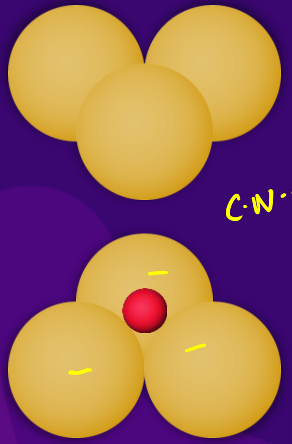
$0.155 < 0.225 < \frac{r}{R} = 0.3$

C.N. of ion in tetrahedral void = **4**

$0.225 \le \frac{r}{R} < 0.414$

E.g.: Zinc sulphide

Octahedral Void



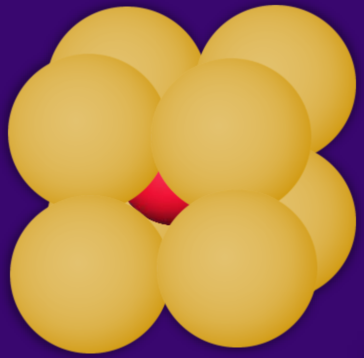
C.N. of ion in octahedral void = **6**

$$0.414 \leq \frac{r}{R} \leq 0.732$$

E.g.: Sodium chloride

Cubical Void

CN = 8



C.N. of ion in cubical void = **8**

$0.732 \leq \frac{r}{R} < 1$

E.g.: Caesium chloride

Summary

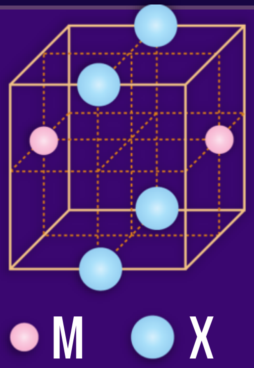
Radius ratio	Type of void occupied	C.N. of ion in void	Example
$0.155 \leqslant \frac{r}{R} \leqslant 0.225$	Triangular void	3	Boron oxide
$0.225 \leqslant \frac{r}{R} \leqslant 0.414$	Tetrahedral void	4	Zinc sulphide

Summary

Radius ratio	Type of void occupied	C.N. of ion in void	Example
$0.414 \leq \frac{r}{R} < 0.732$	Octahedral void	6	Sodium chloride
$0.732 \leq \frac{r}{R} < 1$	Cubical void	8	Caesium chloride

The **cubic unit cell** structure of a compound containing **cation M** and **anion X** is shown below. When compared to the anion, the **cation has smaller ionic radius**. Choose the **correct** statement(s).

MAIN BOARDS



a The empirical formula of the compound is MX.

b The cation M and anion X have different coordination geometries.

The **cubic unit cell** structure of a compound containing **cation M** and **anion X** is shown below. When compared to the anion, the **cation has smaller ionic radius**. Choose the **correct** statement(s).

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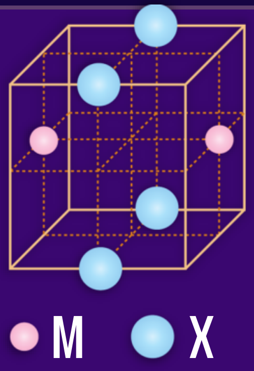

$\frac{r_+ + r_-}{a} = \frac{1}{2} = 0.5$

X

c The ratio of M-X bond length to the cubic unit cell edge length is 0.866.

$\frac{r_+}{r_-} = 0.414$

d The ratio of the ionic radii of cation M to anion X is 0.414.

Ionic Compounds

In ionic compounds
for **maximum stability**

(a) A **cation** must be **surrounded by** maximum number of **anions** and vice versa.

(b) **Anion-anion** and **cation-cation** contact should be **avoided**.

C.N. of **cation** = Number of anions surrounding any cation

C.N. of **anion** = Number of cations surrounding any anion

Consider an ionic compound in which **anions form CCP** and the **cations occupy all the tetrahedral holes**. Find the **relation** between edge length of unit cell (a_{FCC}), radius of cation (r_+), and radius of anion (r_-).

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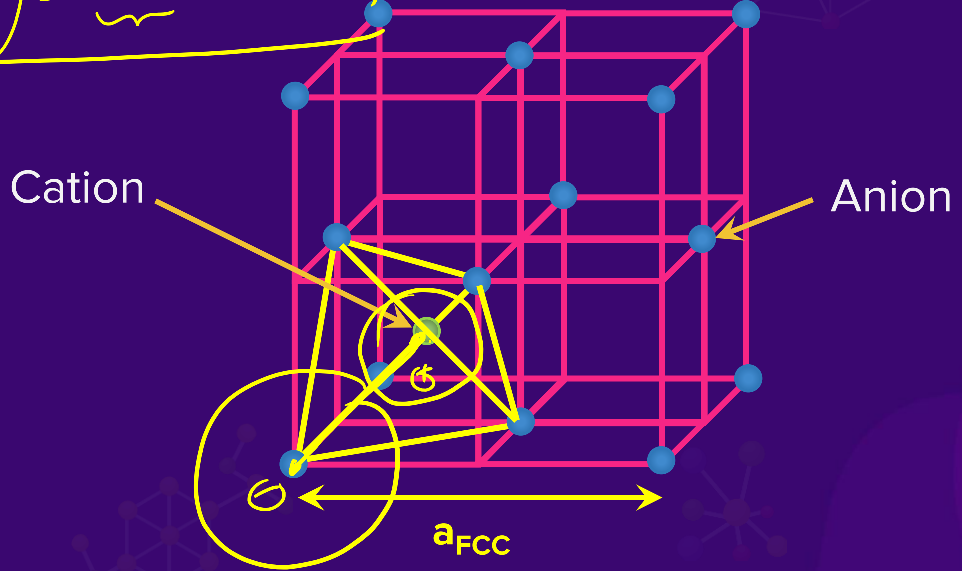
$$\frac{a\sqrt{3}}{4} = r_+ + r_-$$

$$a = \frac{4}{\sqrt{3}}(r_+ + r_-)$$



Cation will lie at the centre of the minicube of side $a_{FCC}/2$.

$$r_+ + r_- = \frac{1}{2} \times \text{Body diagonal of minicube}$$

$$r_+ + r_- = \frac{1}{2} \times \frac{a_{FCC}}{2}\sqrt{3}$$

$$a_{FCC} = \frac{4}{\sqrt{3}}(r_+ + r_-)$$

Rock Salt (NaCl)

Experimental ratio, $\frac{r_{Na^+}}{r_{Cl^-}} = 0.51$

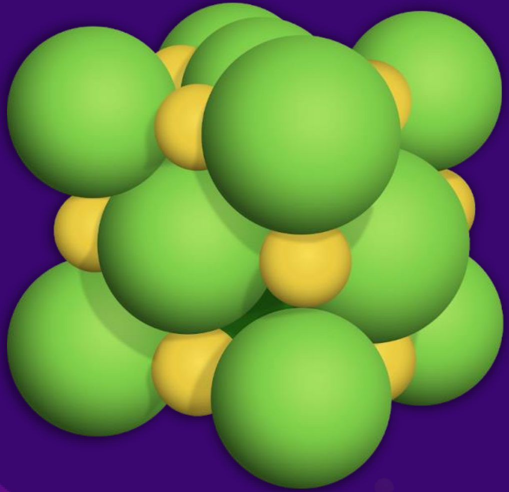
$$0.414 \leq \frac{r_{Na^+}}{r_{Cl^-}} < 0.732$$

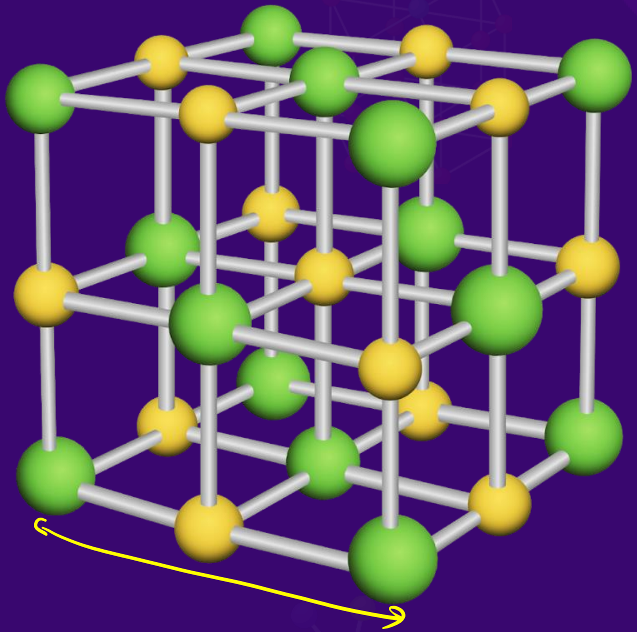
Cl^- forms a cubical closed-packing (**CCP**).

Na^+ ions occupy all the **octahedral voids**.

Na^+

Cl^-





$a = 2(r_{\oplus} + r_{\ominus})$

Note

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

↓

As anion–anion are **not in contact.**

$r_{Cl^-} + r_{Na^+} = \frac{a}{2}$

Rock Salt (NaCl)

$4 Cl^-$ 4 O.V.

$4 Na^+$

Formula of unit cell : Na_4Cl_4

4 (NaCl)

Effective number of Cl^- ions per unit cell = 4 = Z

Effective number of Na^+ ions per unit cell = 4

Formula of ionic compound = **NaCl**

Effective number of **formula units (Z)** = **4**

Remember

If for a salt, Ratio of coordination number of A and B, respectively is y : x

Then, General formula = A_xB_y

Coordination number 6 : 6

Coordination number of **cations**

Coordination number of **anions**

Rock Salt (NaCl)

Ratio of coordination number of Na^+ and Cl^-, respectively is

1 : 1

Formula = NaCl

For anion Cl^-,

Type of neighbour	Distance	Number of neighbours
Nearest	Na^+, $\frac{a}{2}$	6
Next nearest	Cl^-, $\frac{a}{\sqrt{2}}$	12

Rock Salt (NaCl)

For cation **Na^+**,

Type of neighbour	Distance	Number of neighbours
Nearest	Cl^-, $\frac{a}{2}$	6
Next nearest	Na^+, $\frac{a}{\sqrt{2}}$	12

Examples

MgO, CaO, SrO, BaO and all alkali halides **except** CsCl, CsBr and CsI.

Note

Lattice of **NaCl**

FCC arrangement of Cl^- in which all **octahedral voids** are occupied by **Na^+** ions.

or

FCC arrangement of Na^+ in which **octahedral voids** are occupied by **Cl^-** ions.

In a solid 'AB' having the NaCl structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is:

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

$B = 4$

A_4B_4

A_3B_4

a) AB_2

b) A_2B

c) A_4B_3

d) A_3B_4

ZnS Structure

ZnS

- Zinc Blende → **FCC**
- Wurtzite → **HCP**

Experimental ratio,

$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.3$$

$$0.225 \leq \frac{r_{Zn^{2+}}}{r_{S^{2-}}} < 0.414$$

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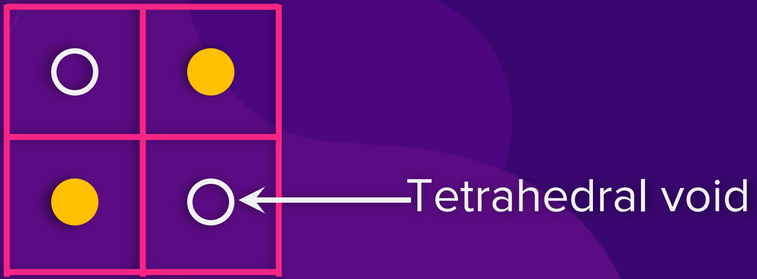
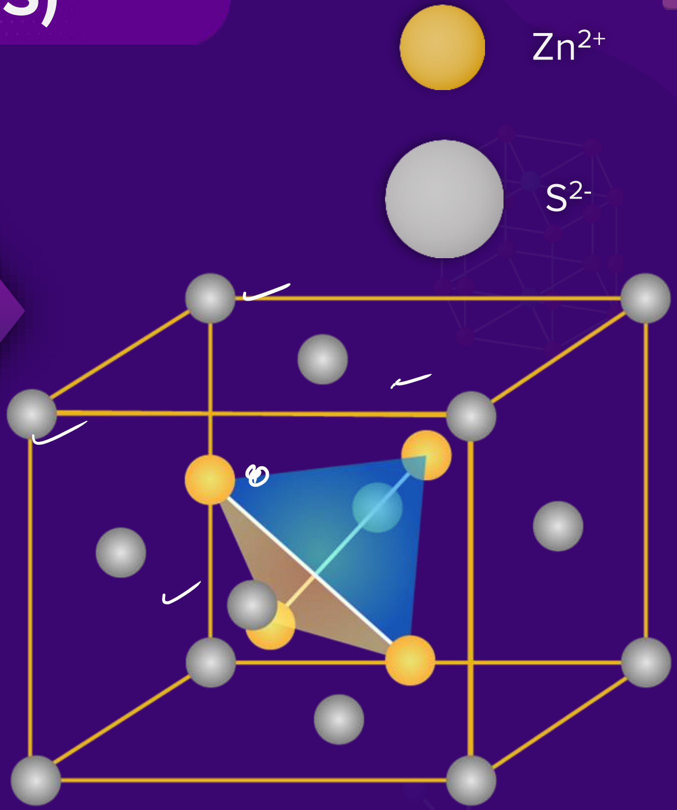
Zinc Blende (ZnS)

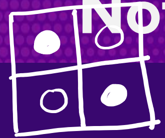
S^{2-} ions occupy **CCP** lattice

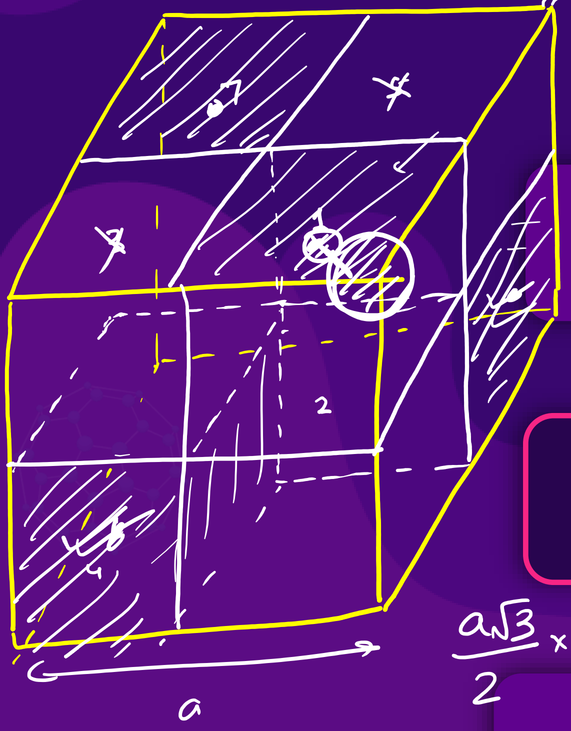
Zn^{2+} ion occupy alternate (non adjacent) four **tetrahedral voids**.





Note





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

Anion–anion contact is **not** present

Effective number of **S^{2-} ions** per unit cell = **4**

Effective number of **Zn^{2+} ions** per unit cell = **4**

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

Zinc Blende (ZnS)

Formula of unit cell: Zn_4S_4

Formula of ionic compound = **ZnS**

Effective number of **formula units (Z)** = **4**

For anion S^{2-},

Type of neighbour	Distance	Number of neighbours
Nearest	Zn^{2+}, $\frac{\sqrt{3}a}{4}$	4
Next nearest	S^{2-}, $\frac{a}{\sqrt{2}}$	12

Zinc Blende (ZnS)

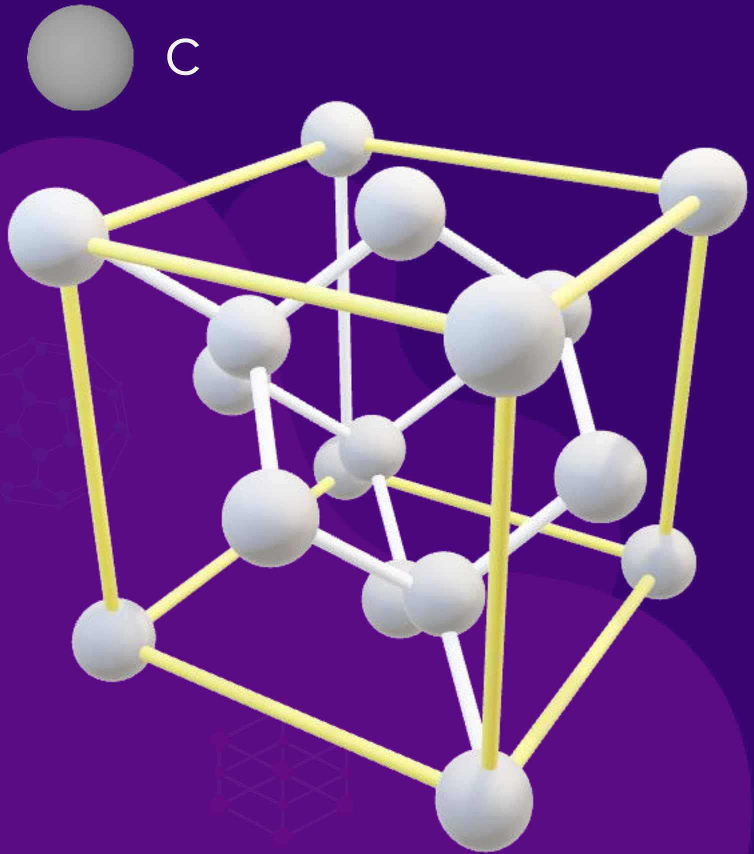
For cation **Zn^{2+}**,

Type of neighbour	Distance	Number of neighbours
Nearest	S^{2-}, $\frac{\sqrt{3}a}{4}$	4
Next nearest	Zn^{2+}, $\frac{a}{\sqrt{2}}$	12

Examples

ZnS, CuCl, CuBr, CuI, AgI.

Diamond Structure



All fcc → C

$\frac{1}{2}$ the TVs → C

Diamond has **ZnS type structure** in which all S^{2-} location and all Zn^{2+} location are **occupied by C atoms**.

Z = 8 atom per unit cell

Diamond Structure

$r_{\oplus} + r_{\ominus} = r_c + r_c = d_{c-c}$

$d_{c\text{-}c} = \frac{\sqrt{3}}{4} a_{FCC}$

$d_{c\text{-}c} = 2r_c$

$d_{c\text{-}c}$	Nearest distance between two C-atoms
r_c	Radius of C-atom

Packing efficiency = **34%**

In crystal lattice of diamond, **carbon** atoms adopt **FCC** arrangement with occupancy of **50% tetrahedral voids**.

	Cations	anions	
Rock Salt Structure (NaCl)	all O.Vs. (⇌)	fcc	$r_{+} + r_{-} = \frac{a}{2}$
Zinc Blende " (ZnS)	$\frac{1}{2}$ TVs (⇌)	fcc	$r_{+} + r_{-} = \frac{a\sqrt{3}}{4}$
Diamond Str. $\eta \simeq 34\%$	C atoms (at fcc + $\frac{1}{2}$ TVs)		$r = \frac{a\sqrt{3}}{8}$

Fluorite Structure (CaF_2)

Fluorite Structure (CaF_2)

Cations : FCC

Anions : all TVs

Experimental ratio,

$$0.225 \leq \frac{r_{F^-}}{r_{Ca^{2+}}} < 0.414$$

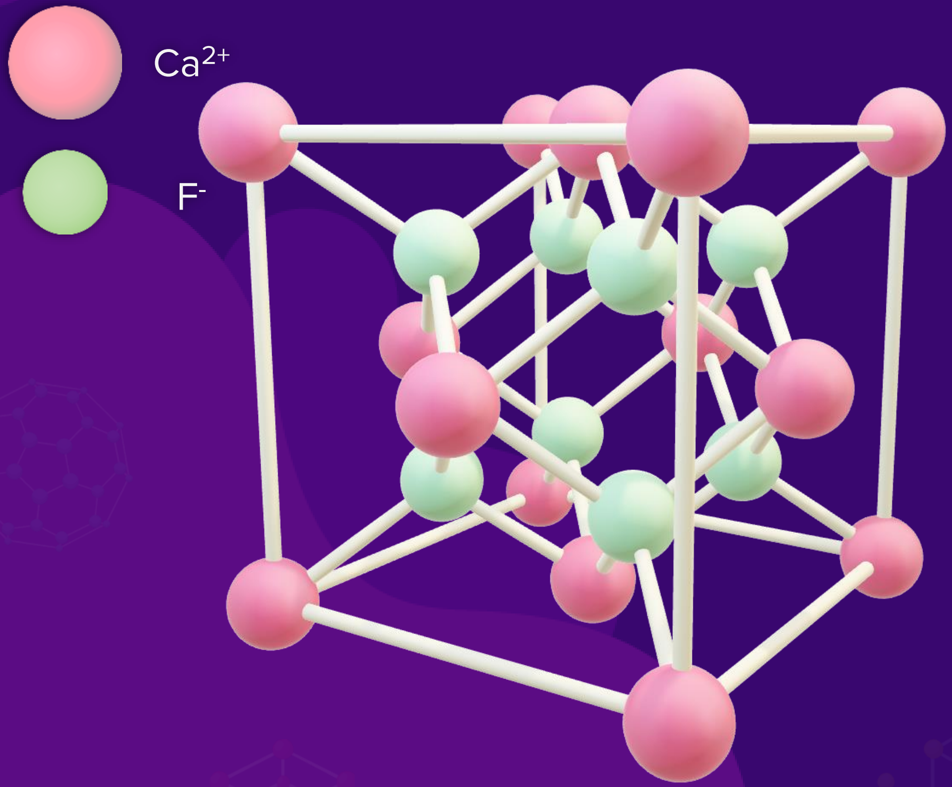
TVs

Ca^{2+} ions form the **CCP** lattice

F^- ion occupies all **tetrahedral voids**

$Ca_4(F^-)_8$ CaF_2

Fluorite Structure (CaF_2)



$\sqrt{2}a > 4r_{Ca^{2+}}$

Cation–cation contact is **not** present

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

Fluorite Structure (CaF_2)

Formula of unit cell: Ca_4F_8

Effective number of **Ca^{2+} ions** per unit cell = **4**

Effective number of **F^- ions** per unit cell = **8**

Formula of ionic compound = **CaF_2**

Effective number of **formula units (Z)** = **4**

Fluorite Structure (CaF_2)

For anion F^-,

Type of neighbour	Distance	Number of neighbours
Nearest	Ca^{2+}, $\frac{\sqrt{3}a}{4}$	4
Next nearest	F^-, $\frac{a}{2}$	6

For cation Ca^{2+},

Type of neighbour	Distance	Number of neighbours
Nearest	F^-, $\frac{\sqrt{3}a}{4}$	8
Next nearest	Ca^{2+}, $\frac{a}{\sqrt{2}}$	12

Examples

CaF_2	$CaCl_2$
SrF_2	$SrCl_2$
BaF_2	$BaCl_2$

BaF_2, $BaCl_2$, SrF_2, CaF_2 etc.

The coordination number of cation and anion in Fluorite CaF_2 and Zinc blende ZnS are x : y and a : b respectively. Find (x + y + a + b).

2 : 1   1 : 1

	CN.
Ca^{2+}	8
F^-	4
Zn	4
S	4

$2 + 1 + 1 + 1 = 5$

Percentage of void space in AB solid having rock salt structure if $\frac{r_+}{r_-} = \frac{1}{2}$ having cation anion contact. Given $\pi = 3.15$.

= 30%

$2r_{\oplus} = r_{\ominus}$

$\frac{6\cancel{3}0}{9} = 70\%$

$\rightarrow \frac{r_{\oplus}}{r_{\ominus}} = \frac{1}{2}$

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4NaCl

$4Na^+$ $4Cl^-$

$$\%\eta = \frac{4 \times \frac{4}{3}\pi\left[r_{\oplus}^3 + r_{\ominus}^3\right]}{\left[2(r_{\oplus} + r_{\ominus})\right]^3} \times 100$$

$$= \frac{16}{3}\pi\left[\frac{r^3 + 8r^3}{[2(3r)]^3}\right] \times 100$$

$$= \frac{16}{3} \times \frac{3.15}{6 \times 6 \times 6} \times \frac{9}{1} \times 100 = \frac{2 \times 3.15}{9} \times 100$$