

SOLID STATE

$$a = 4r$$

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

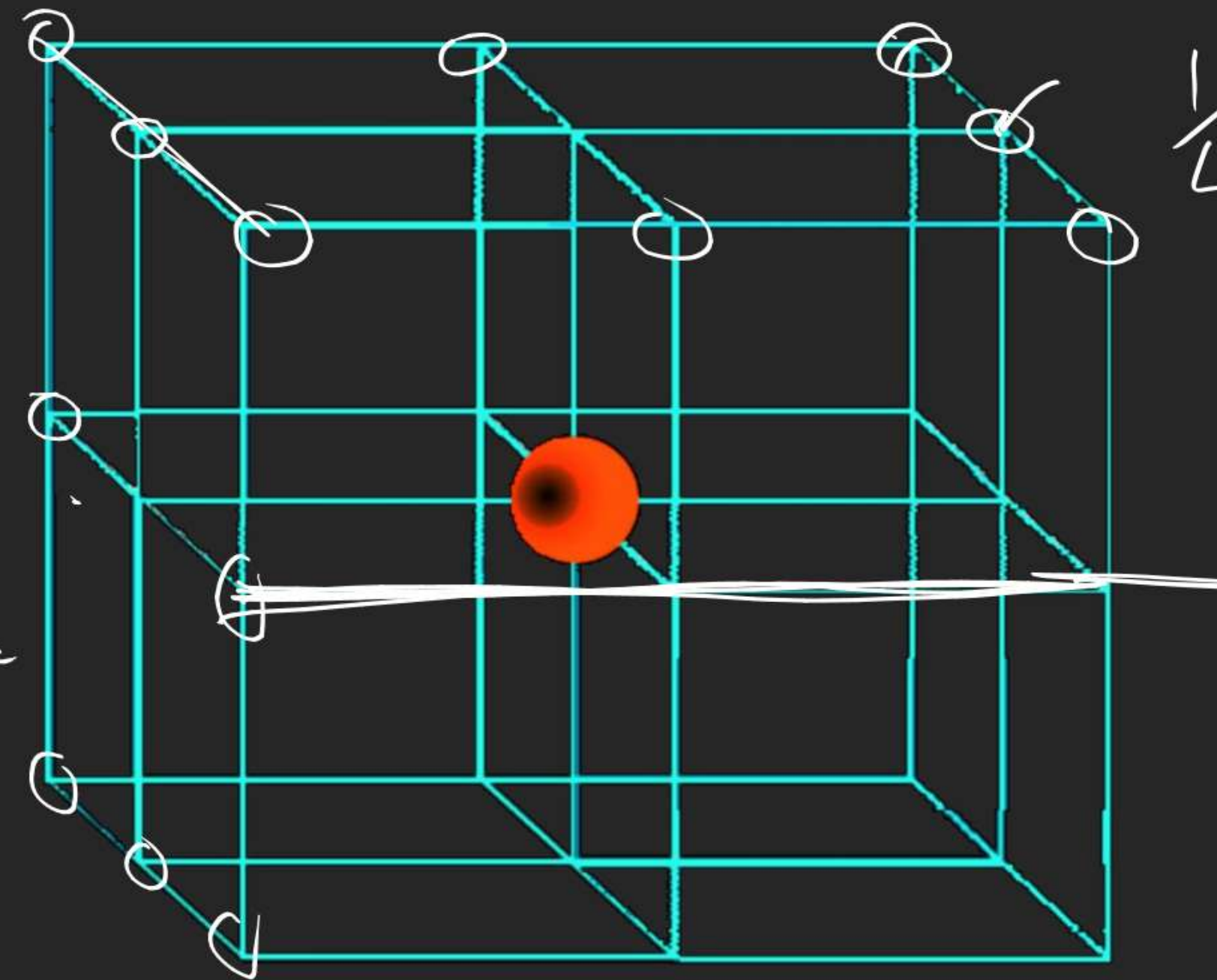
$$\frac{1}{4} \times 12 = 3$$

$$\frac{1}{4}$$

- 1 — 1
- 8 — 2^3
- 27 — 3^3
- 64 — 4^3

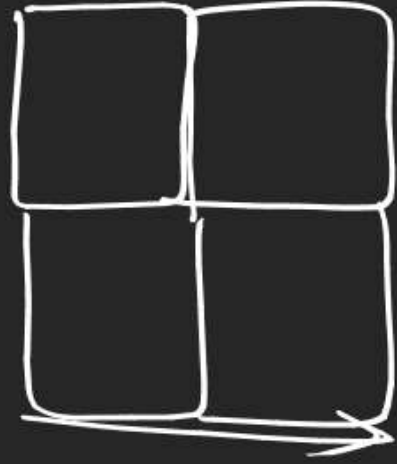
FCC
HCP

$$x^3$$

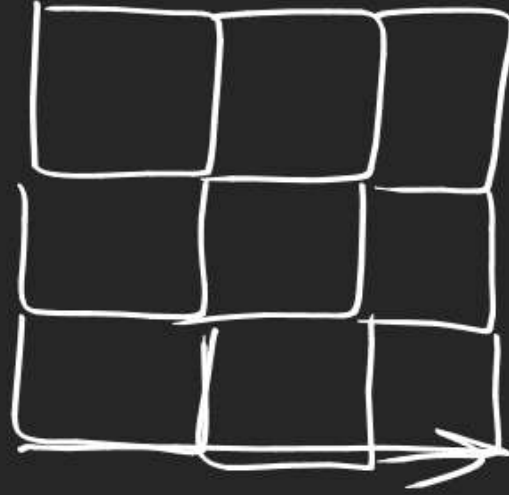




$$1$$



$$2^2$$

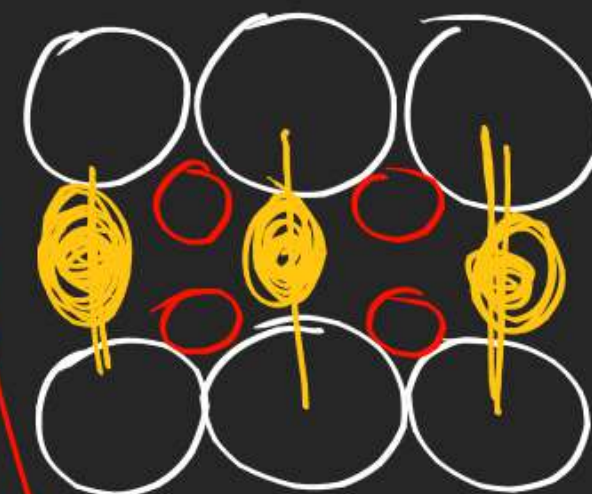
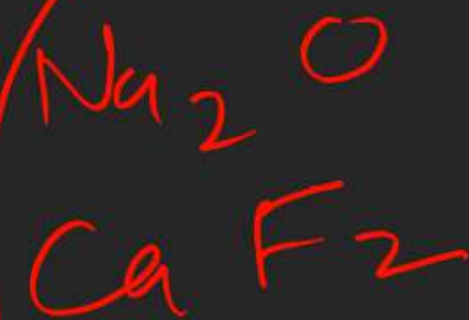
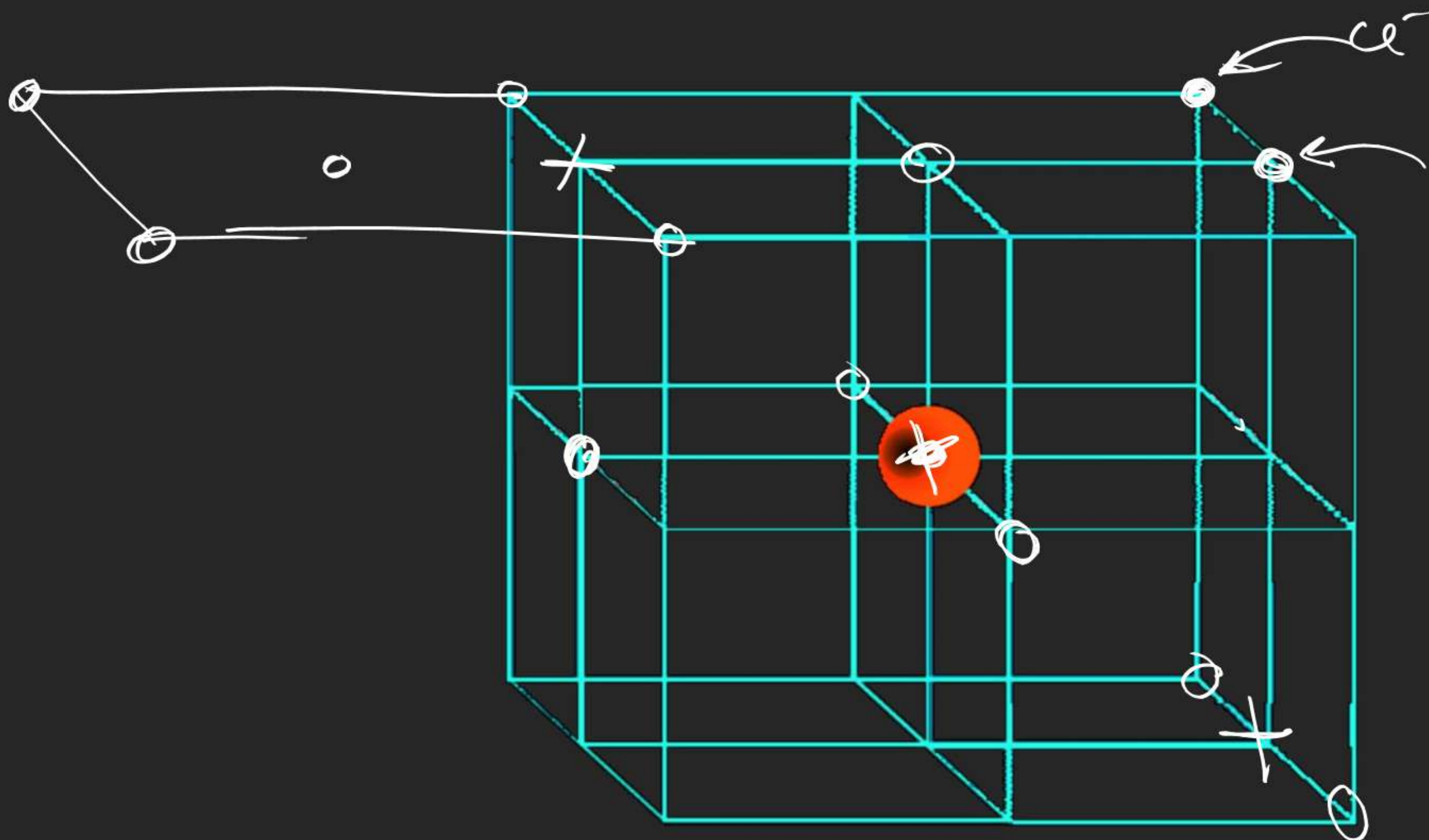


$$3^2$$

$$4^2$$

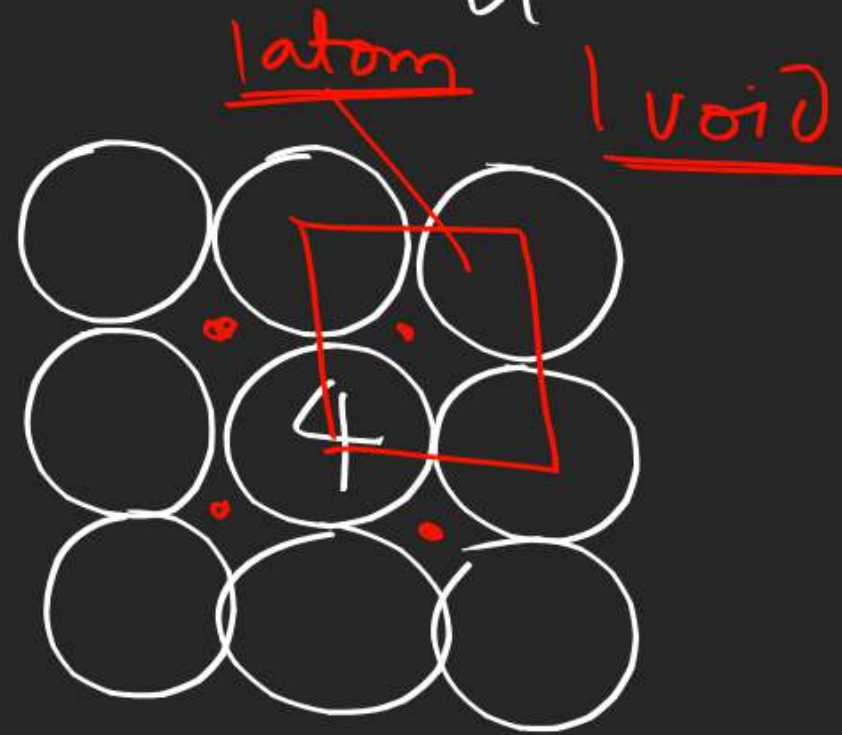
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SOLID STATE

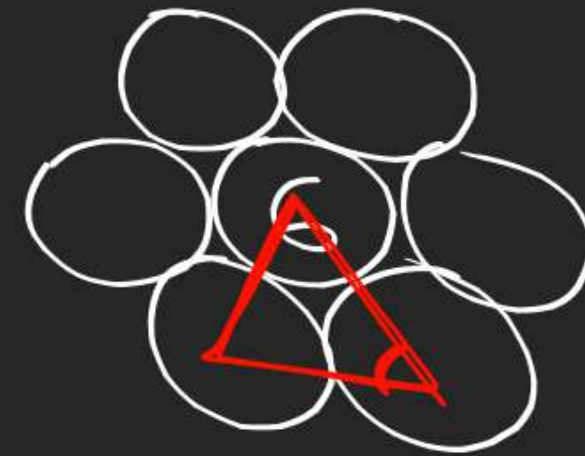


$$d = \frac{Z \times M_{\text{CaF}_2} / N_A}{a^3}$$

(5)

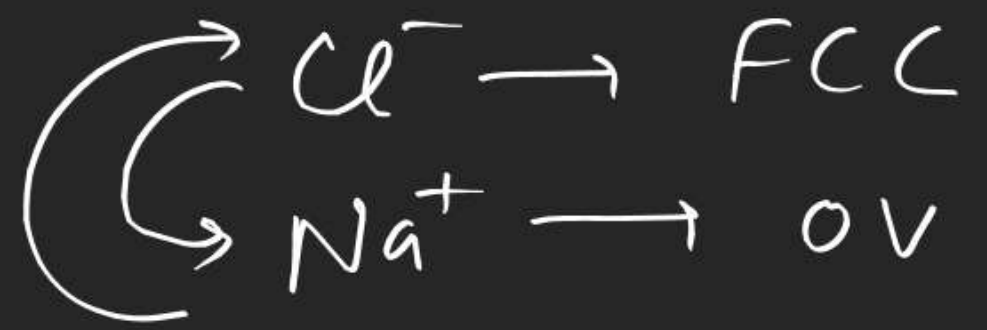


per atom 2 voids



$$= \frac{1}{6} \times 3 \quad \underline{\text{1 void}}$$

$$= \underline{\frac{1}{2} \text{ atom}}$$



②

A
FCC

④

B
O.V

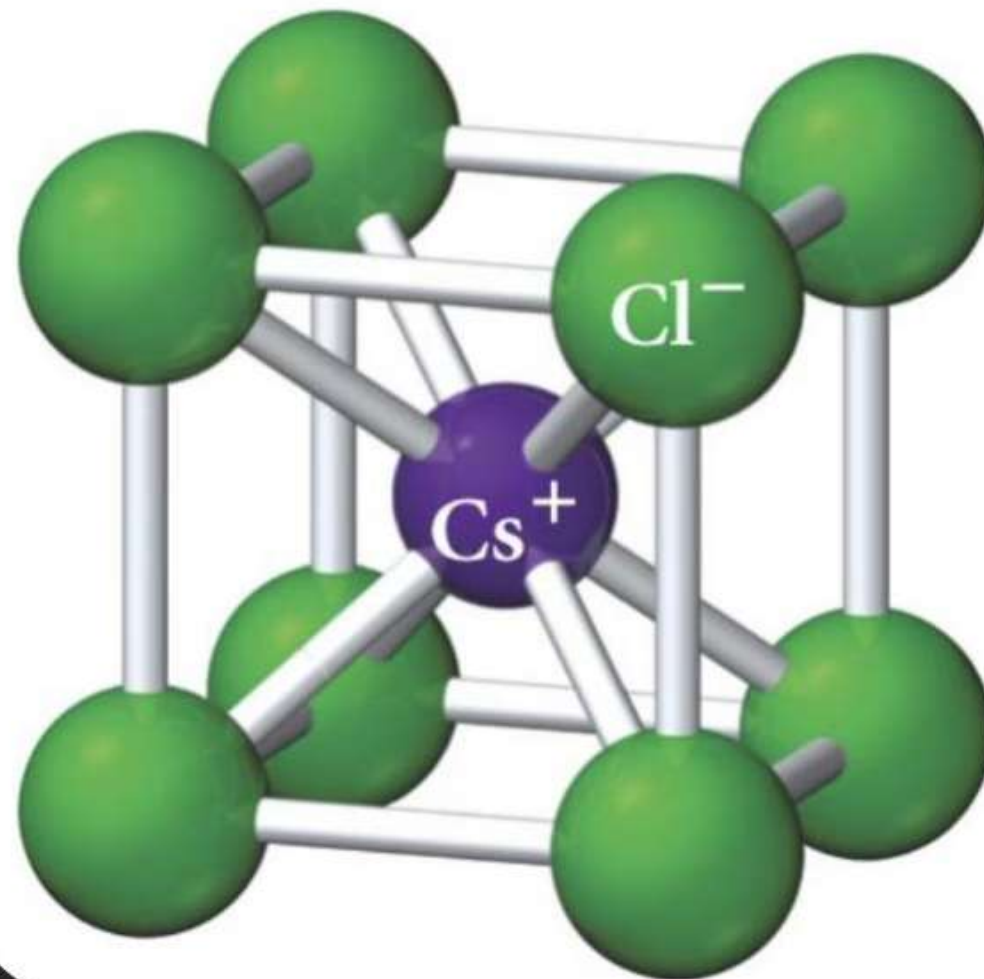
④

$$\begin{aligned} & \left[\begin{array}{l} 4 \text{ Corner} \\ 2 \text{ Face centres} \end{array} \right] \\ & \rightarrow 4 \times \frac{1}{8} + 2 \times \frac{1}{2} \\ & = \frac{1}{2} + 1 \\ & = \underline{\underline{1.5}} \end{aligned}$$

$$\begin{aligned} B - \text{Cube centre} &= 1 \\ 2 \text{ edge cent} \\ 2 \times \frac{1}{4} &= \frac{1}{2} \\ &= \underline{\underline{1.5}} \end{aligned}$$

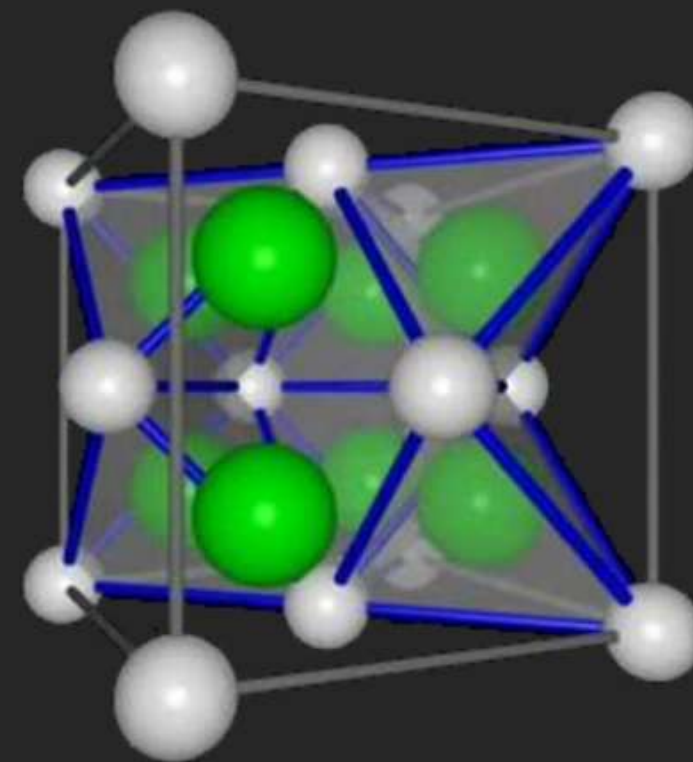
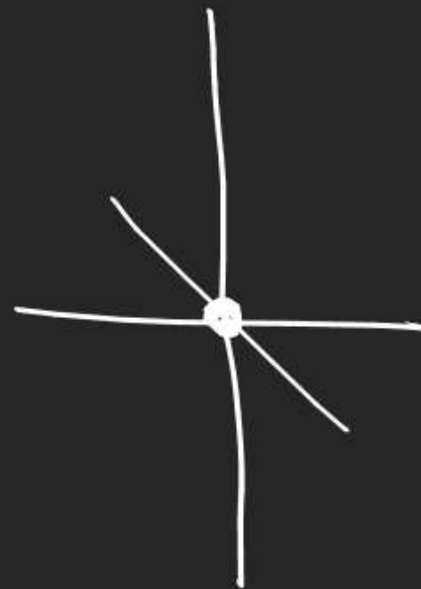
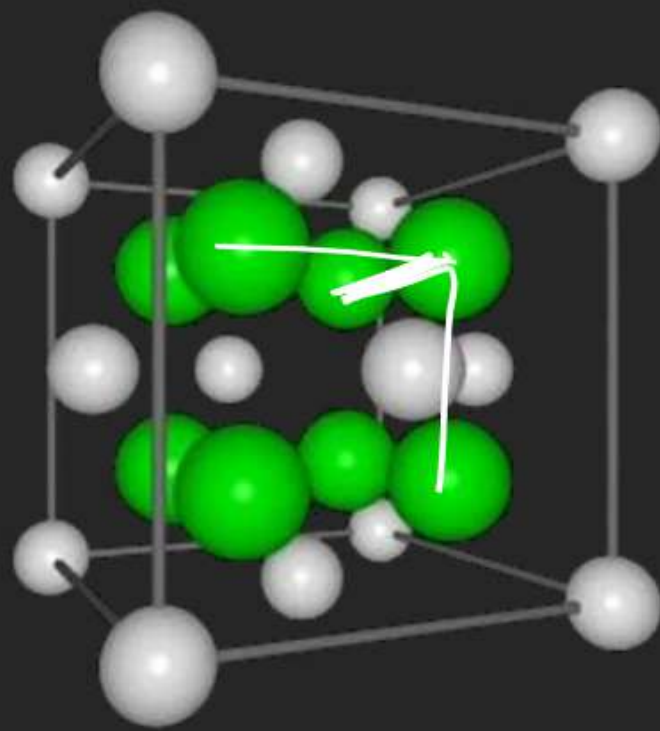
SOLID STATE

Cesium chloride (CsCl)



SOLID STATE

Fluoride Ions Occupy Tetrahedral Holes



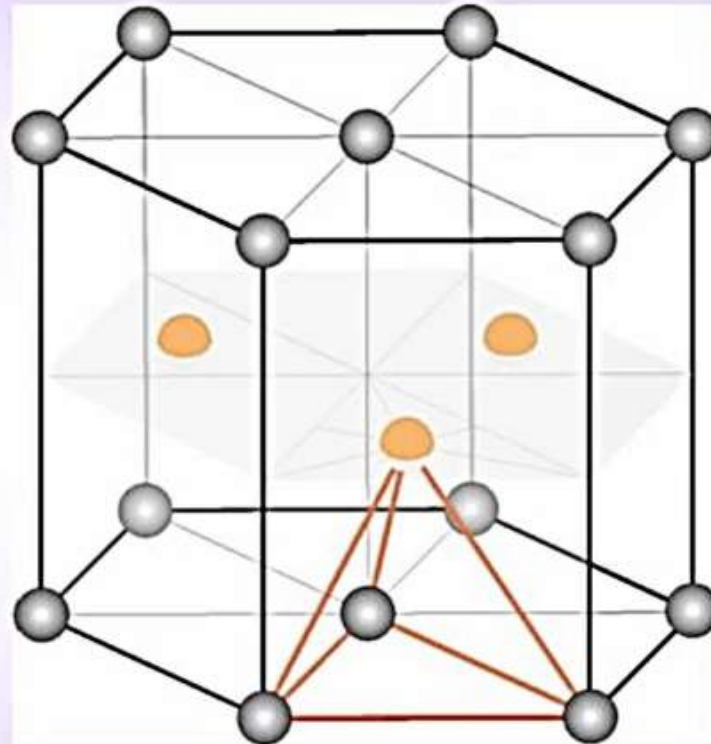
SOLID STATE

HCP

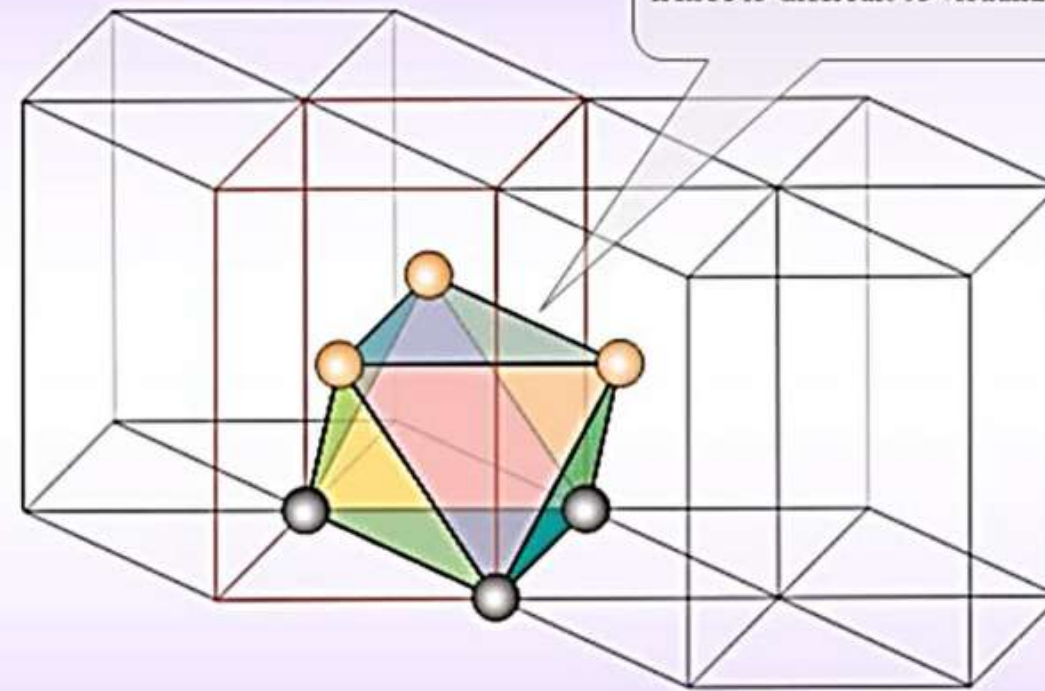
VOIDS

TETRAHEDRAL

OCTAHEDRAL



Coordinates: $(0,0,\frac{3}{8}), (0,0,\frac{5}{8}), (\frac{2}{3},\frac{1}{3},\frac{1}{8}), (\frac{2}{3},\frac{1}{3},\frac{7}{8})$



This void extends across 3 conventional unit cells and hence is difficult to visualize

Coordinates: $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4}), (\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$

- These voids are identical to the ones found in FCC (for ideal c/a ratio).
- When the c/a ratio is non-ideal then the octahedra and tetrahedra are distorted (non-regular).

Important Note: often in these discussions an ideal c/a ratio will be assumed (without stating the same explicitly).
If c/a ratio is not the ideal one—then the voids will not be 'regular' (i.e. regular octahedron and regular tetrahedron).

0-I

(35)

8:8

CsCl type.

$$\frac{\sqrt{3}a}{2} = r_+ + r_-$$

(38)

$$\frac{r_+}{r_-} = 0.225$$

NaCl

6:6

ZnS

4:4

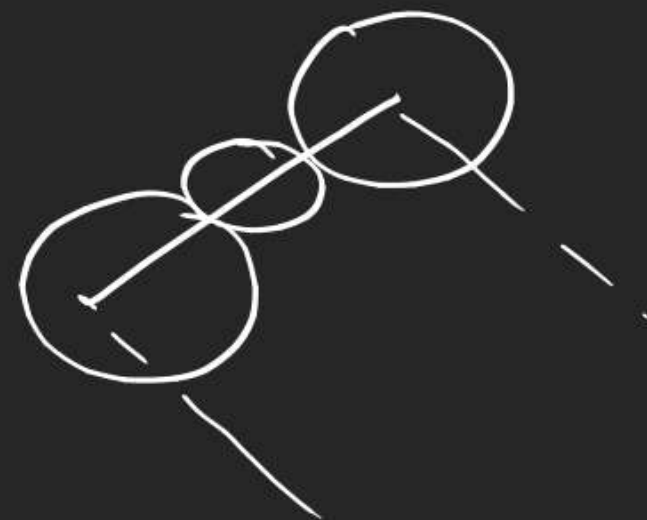
S-I (28)

$$a = 2\lambda_-$$

$$a = 2 \times 2.17 \text{ \AA}$$

(27)

$$\begin{aligned}\sqrt{3}a &= 2\lambda_+ + 2\lambda_- \\ &= 7 \text{ \AA}\end{aligned}$$



(26)

$$\frac{\sqrt{3}a}{2} = \lambda_+ + \lambda_- = \underline{\underline{200\sqrt{3} \text{ \AA}}}$$

$$\text{height} = 2r$$

$$\text{length} = 4r$$



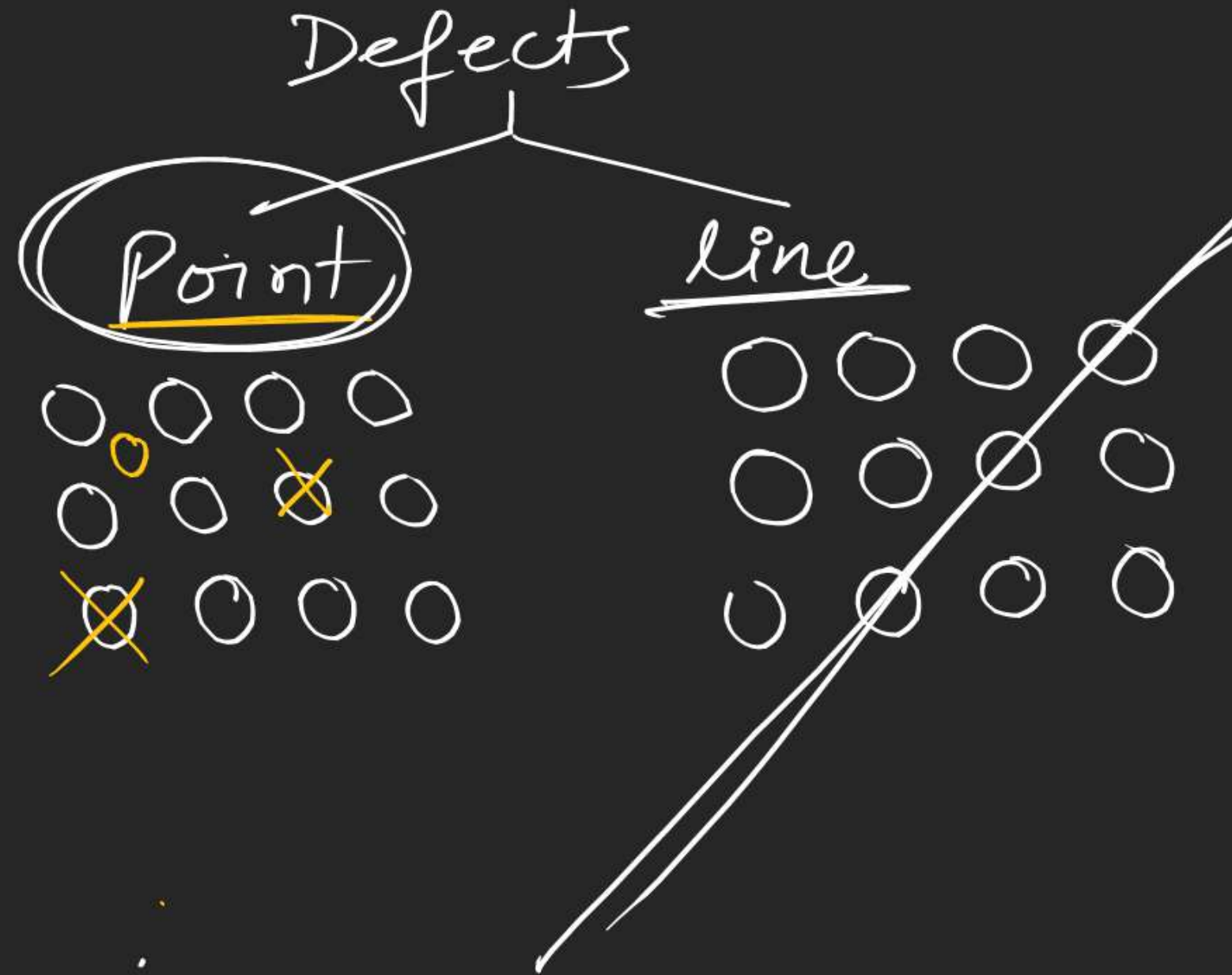
$$\text{Area} = (4r)^2$$

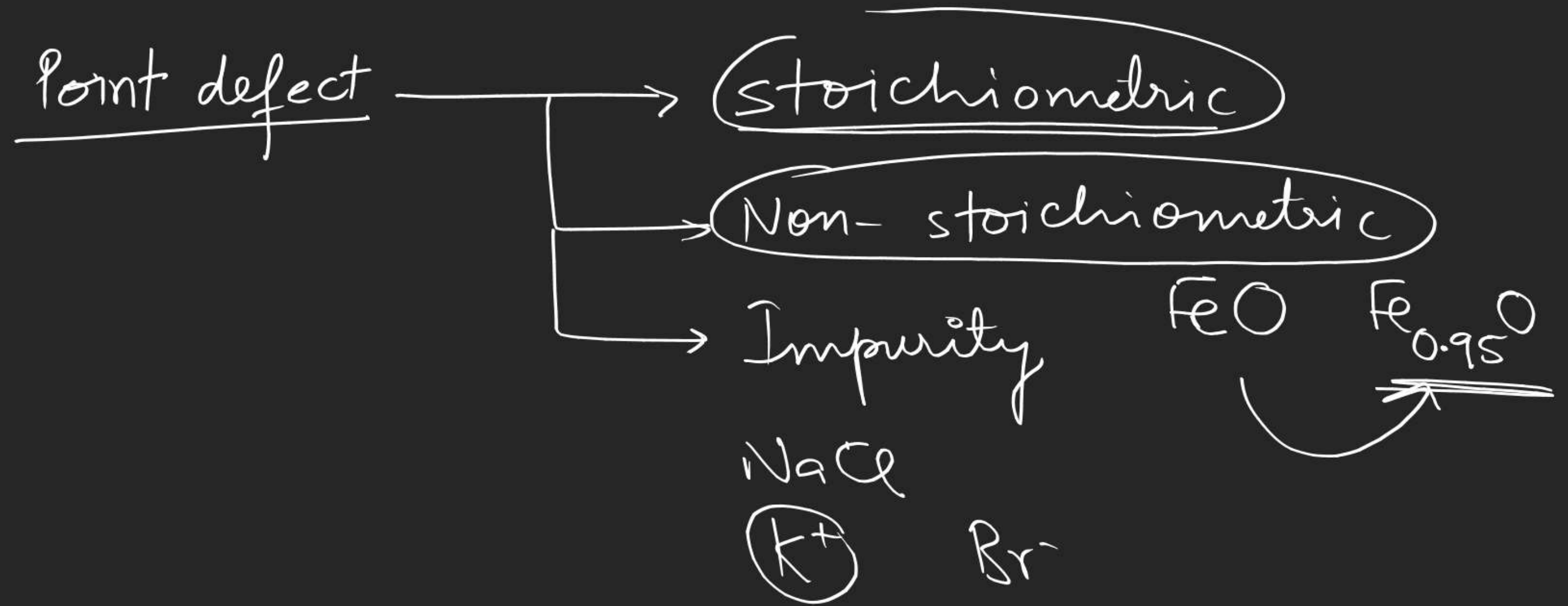
$$\text{Volume} = 32r^3$$

$$PF = \frac{4 \times \frac{4}{3} \pi r^3}{32 r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 100 - \frac{\pi}{6} \times 100$$

Defects \rightarrow Deviation from ideal arrangement



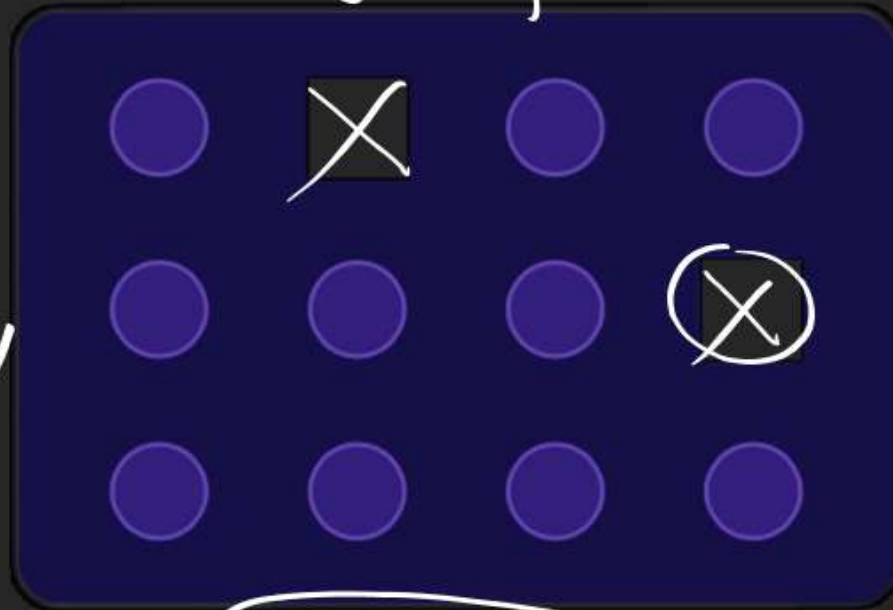


Stoichiometric defect \therefore formula of the compound remains same

SOLID STATE

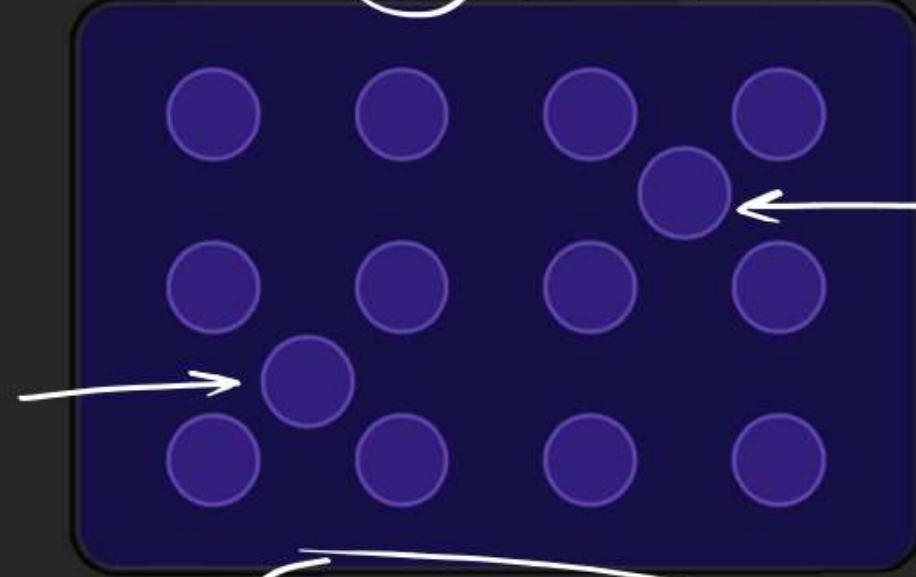
① Vacancy defect

density ↓

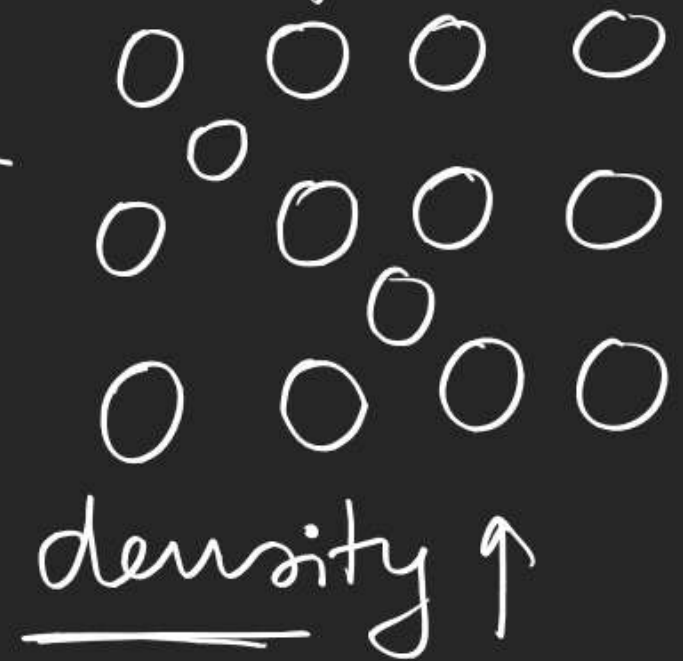


Vacancy defects

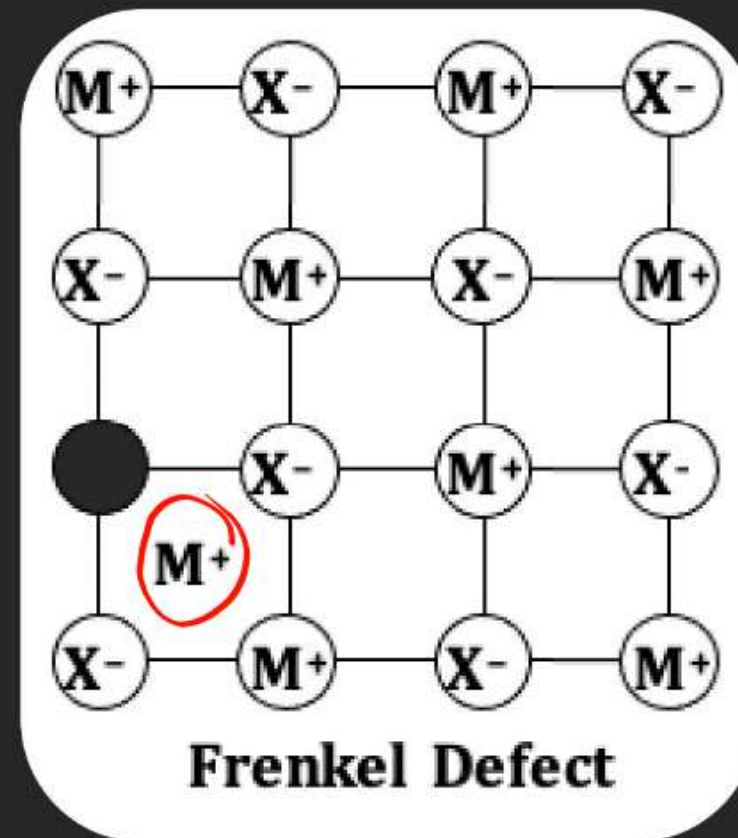
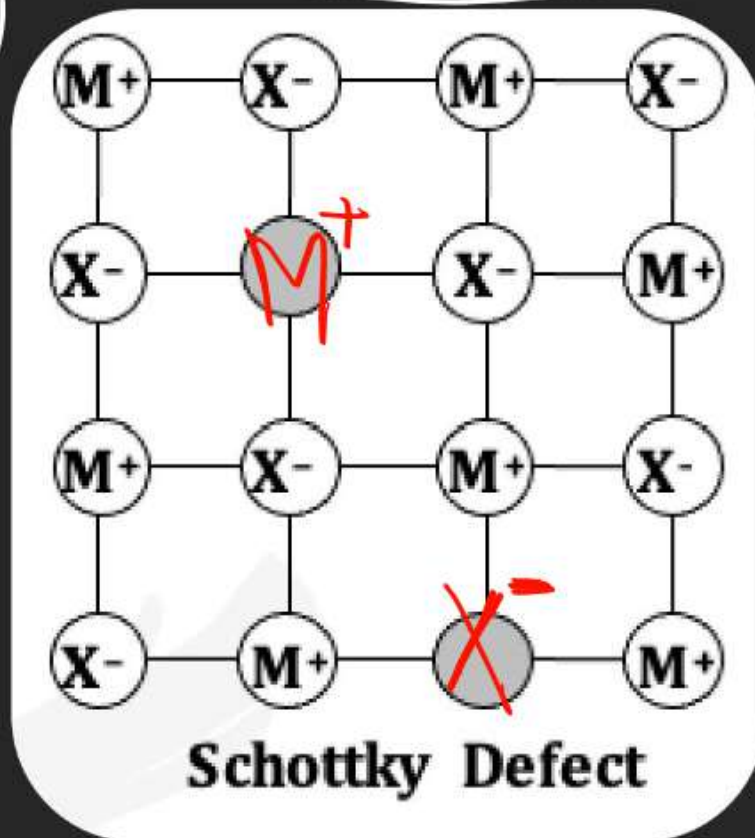
② Interstitial defect



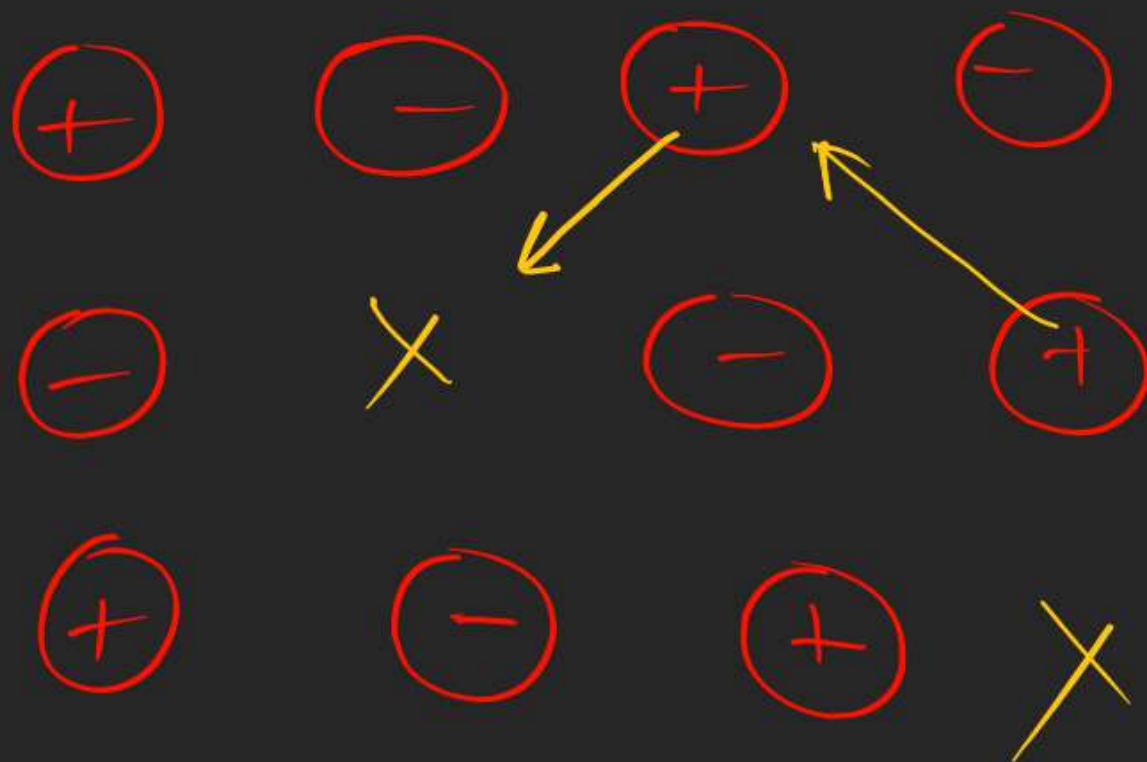
Interstitial defects



CaF_2



Schottky defect \rightarrow exist in ionic compounds



density \downarrow

electrical conductivity \uparrow

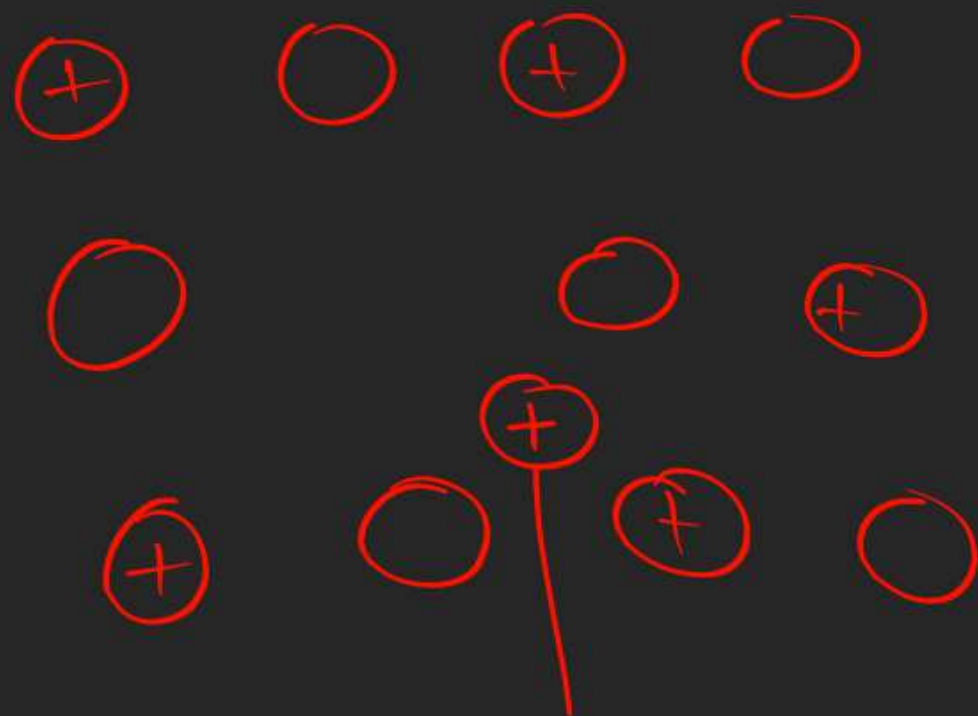
\rightarrow In high coordination compounds

e.g. CsCl

NaCl
KCl

AgBr

Frenkel defect : \rightarrow dislocation defect



Vacancy
cum
Interstitial
defect

Cation

density — Same

electrical
conductivity \uparrow

\rightarrow Mainly observed in
low co-ordination no.
compound e.g. ZnS



Non-stoichiometric defect $\therefore \rightarrow$

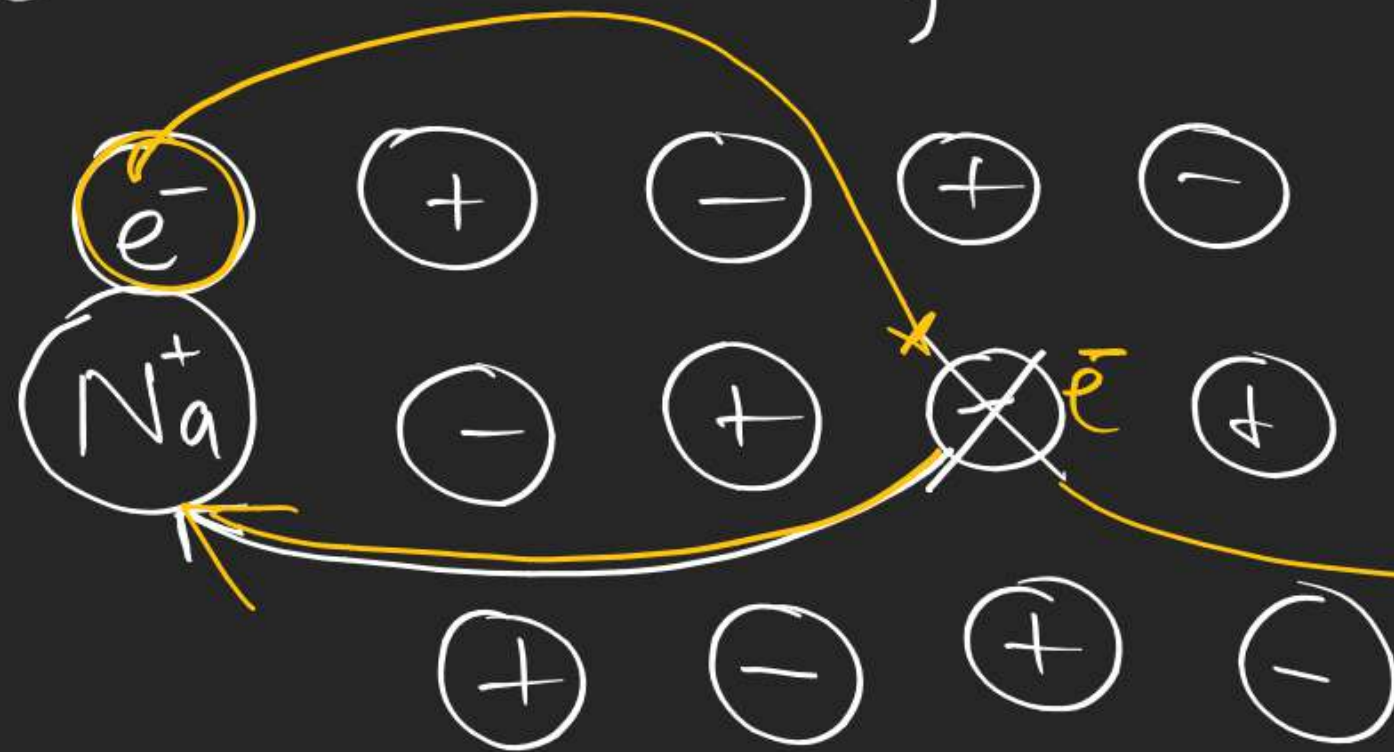
Cation-metal ion

① Metal excess defect

② metal deficiency defect



① Metal excess defect due to anionic vacancies



density \downarrow
electrical conductivity \uparrow

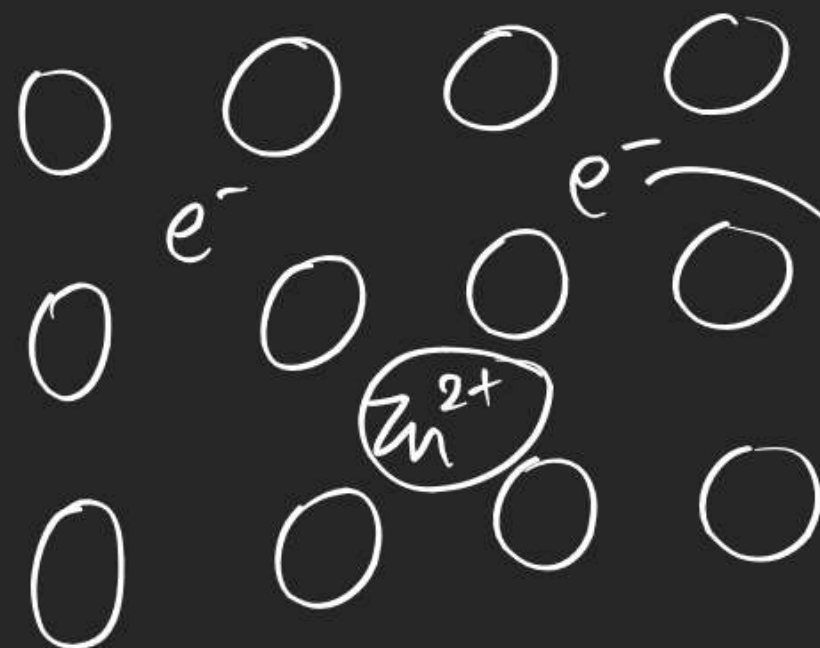
F-centre

Farbe
(Colour)

- NaCl — Yellow
- LiCl — Pink
- KCl — Violet (lilac)

⑪ Metal excess defect due to extra metal ion

e.g. ZnO



density \uparrow
electrical conductivity

F-centre

$\text{ZnO} \rightarrow \text{yellow}$

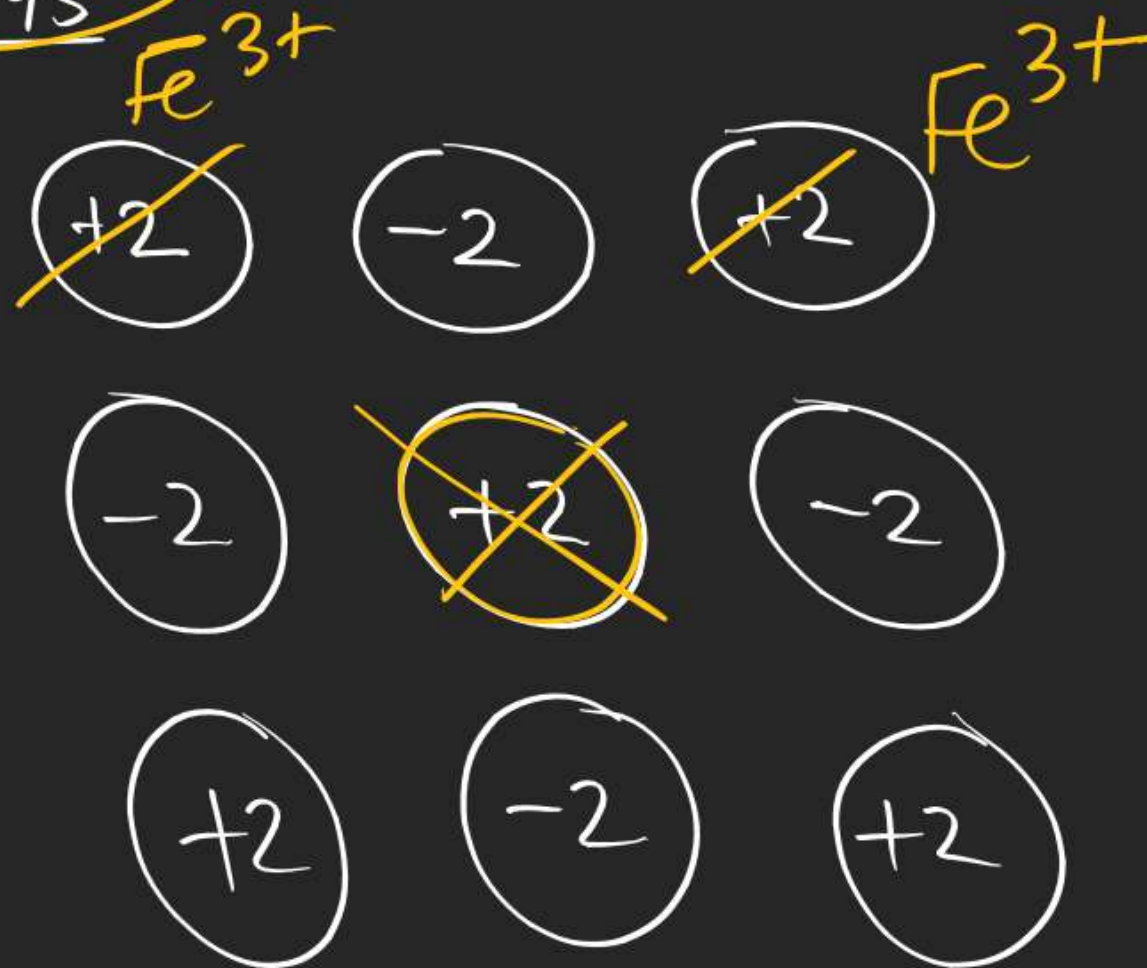
③ Metal deficiency defect due to missing cation

e.g. $\text{Fe}_{0.95}\text{O}$

Fe^{2+}

Fe^{3+}

Vacant



Fe^{2+}

Fe^{3+}

Sn^{2+}

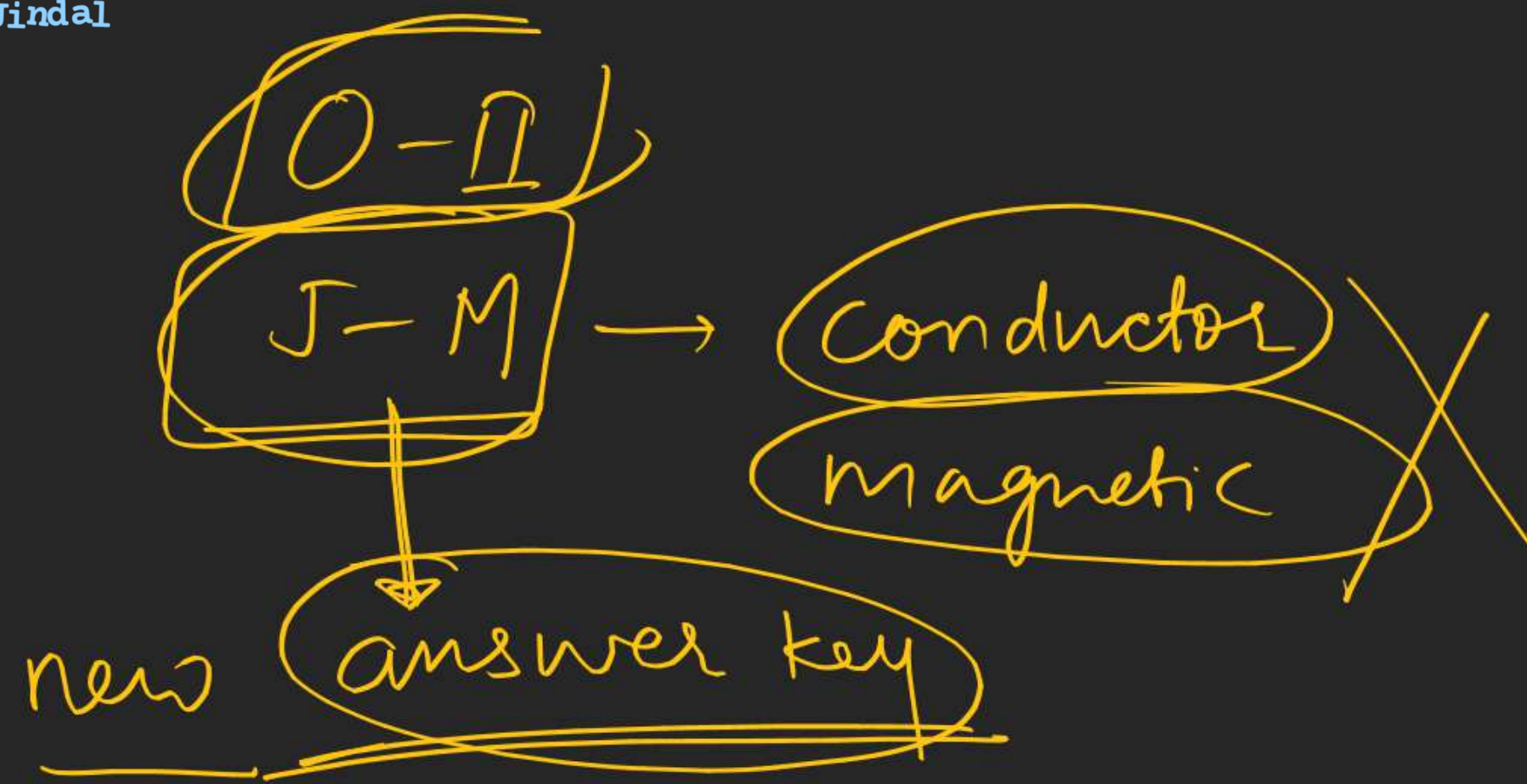
Sn^{4+}

Pb^{2+}

Pb^{4+}

1 Vacancy $\Rightarrow +2$

$2 \text{Fe}^{2+} \rightarrow 2 \text{Fe}^{3+}$



SOLID STATE



An F-centre in a crystal

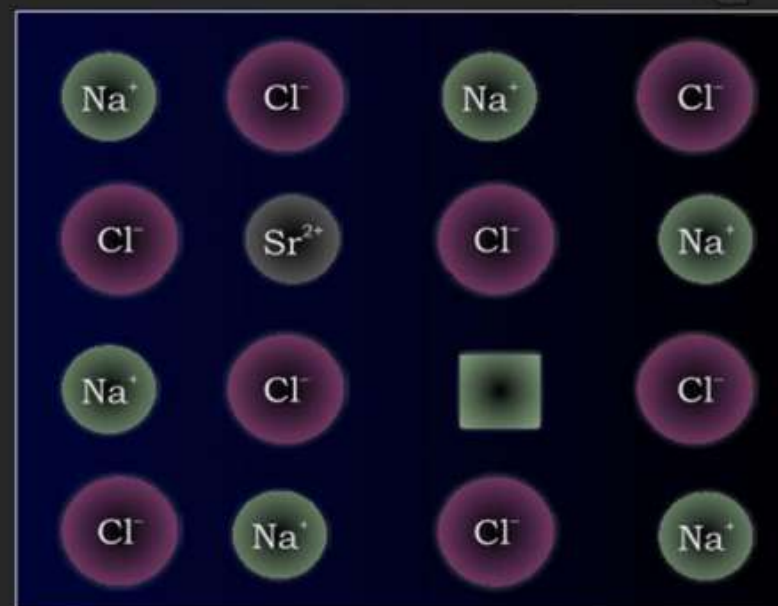


Fig. 1.31: Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}