T.D.C. Part I ; Chem (Hons)
Paper II ; Gen & Org Chem

Unit 3 — Crystal Structure of Compound

① Rock salt structure :-

NaCl (1:1 type)

(a) Co-ordination no of Na+ = 6
" " " " Cl- = 6

Hence NaCl possess 6:6 co-ordination of ions thus Na+ and Cl- occupy octahedral hole.

(b) Effective no. →

$n_+(NaCl) = 4$

$n_-(Cl) = 4$

i.e 4 Na+ and 4 Cl- ions are present per unit cell. Thus each ion has 6 fold.

(c) Radius ratio :-

$\frac{r_+}{r_-} = 0.926$

Which is greater than 0.414 for C.N = 6. Thus arrangement of ions are octahydral.

(d) By X-ray analysis →

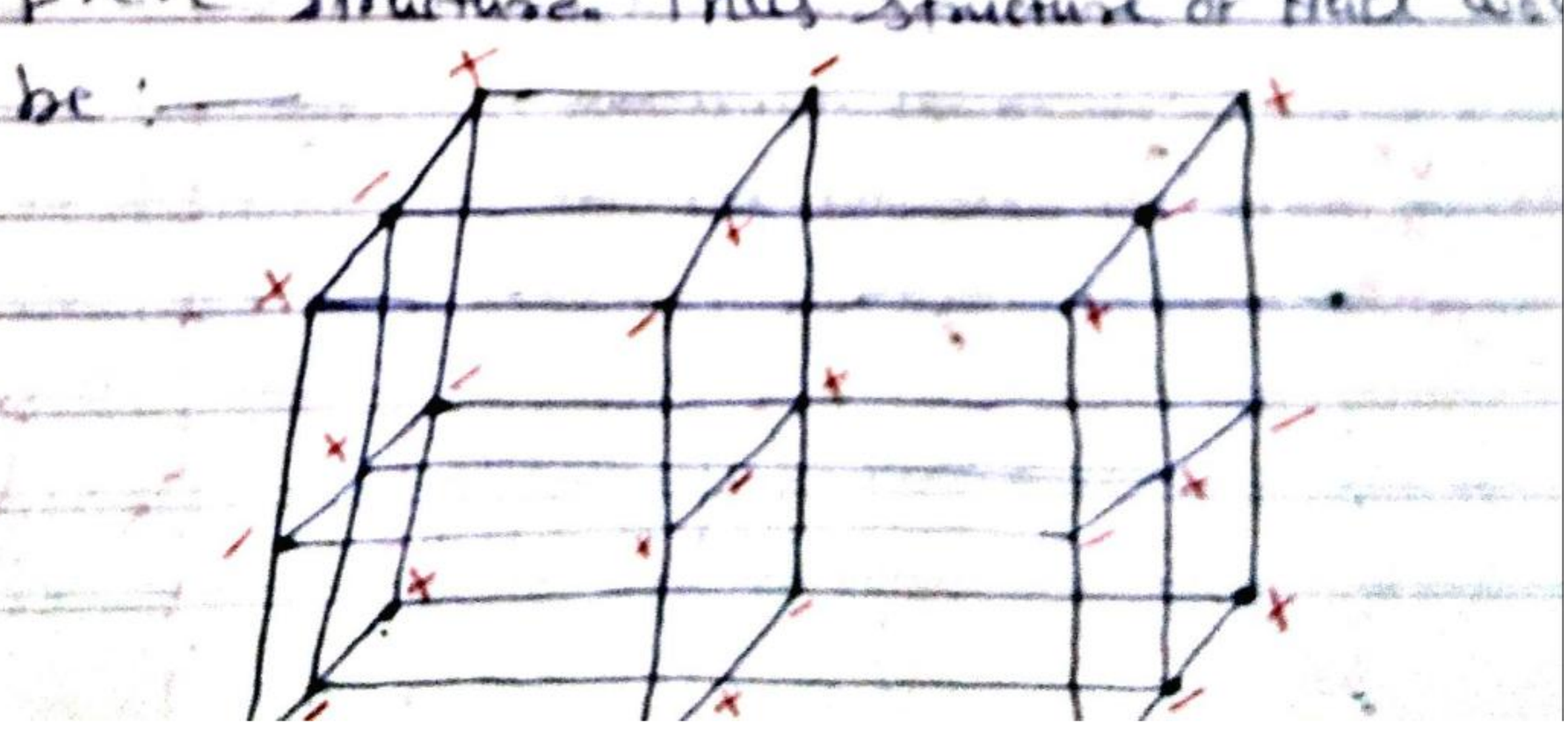
$d_{100} = d_{110} = d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

$= 1 : \frac{\sqrt{2}}{2} : \frac{2\sqrt{3}}{3}$

$= 1 : \frac{1.414}{2} : \frac{2 \times 1.732}{3}$

$= 1 : 0.707 : 1.151$

Which is the ratio, for F.C.C structure. Thus structure of NaCl will be :-



[illegible] structure [illegible]

[illegible]

[illegible] at the centre of the cube [illegible] body centre [illegible]

No. of positive ions = [illegible]

No. of negative ions = [illegible]

Effective no. of [illegible] ions,

[illegible]

[illegible]

[illegible]

Sodium chloride has the formula of NaCl and crystal is said to be stoichiometric.

Diamond

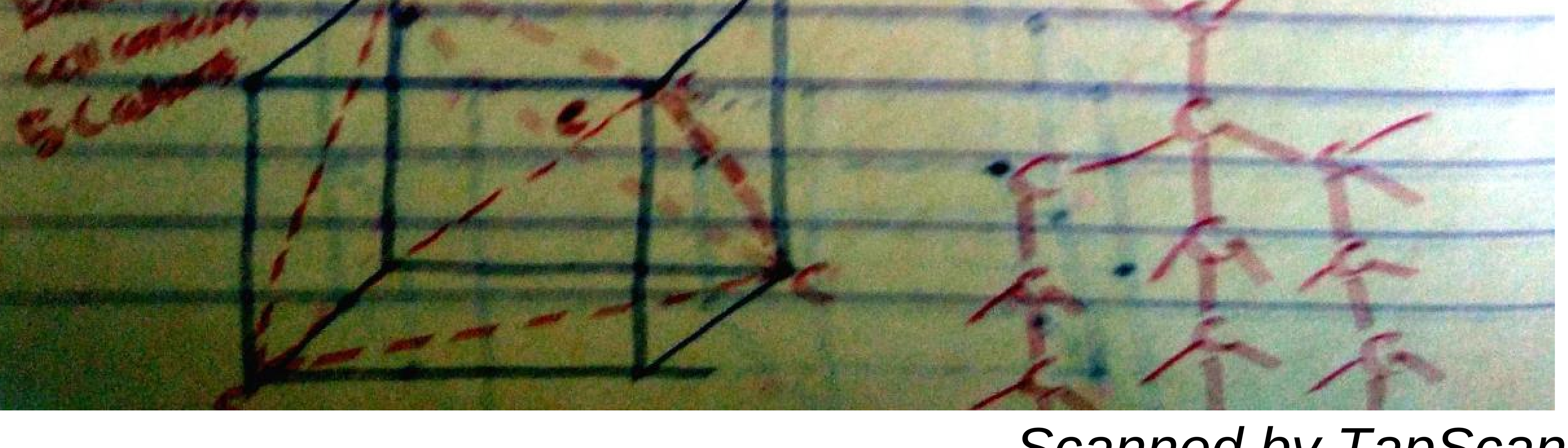
(a) Co-ordination no. of C = 4,

i.e. its arrangement is tetrahedral.

(b) Effective no. of C = 8

which suggests tetrahedral [illegible]

Thus C atoms occupy alternate corners of cube and the tetrahedral hole.



In diamond C is sp^3 hybridised and C-form 4 tetrahedral co-valent bond with four outer C-atoms This results the formation of three dimensional — infinite polymer.

The m.p of diamond involved the breaking of strong C–C co-valent bond which extend over all direction. So, that the m.p of diamond is usually about 3600°C.

CaCl2

CaCl2 has rutile structure (TiO_2).

(i) C.N of Ca^{++} = 6

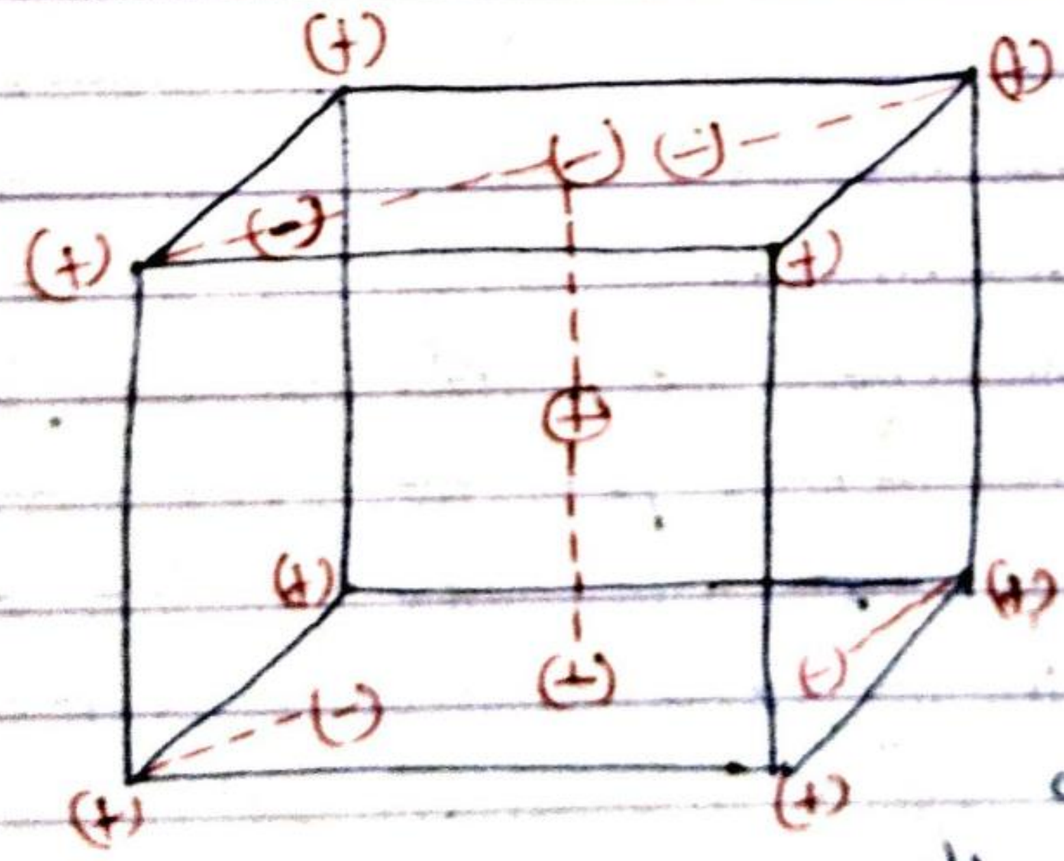
" " " Cl^- = 3.

∴ Ca^{+2} lies in octahydral hole and Cl^- lies at the centre of a triangle surrounded by the ions.

(ii) $\frac{r_+}{r_-}$ is between 0.41 to 0.73

(iii) Two pairs of -ve ions are co-planer and lie on 11 face ~~dig~~ diagonals.

The str. would be



+ve ions are at the corners and at the centre of the octahydral surrounded by six -ve ions at the corners of a slightly distorted octahydral.

CaF_2 (Fluorite structure)

(i) c.N of Ca^{+2} = 8

c.N of F^- = 4

Thus there is 8:4 coordination

of ions i.e Ca^{+2} has B.C.C structure and

F^- lie in tetrahydral hole.

(ii) Effective no. of Ca^{+2}.

$n^+ = 4$

Effective no of F^-

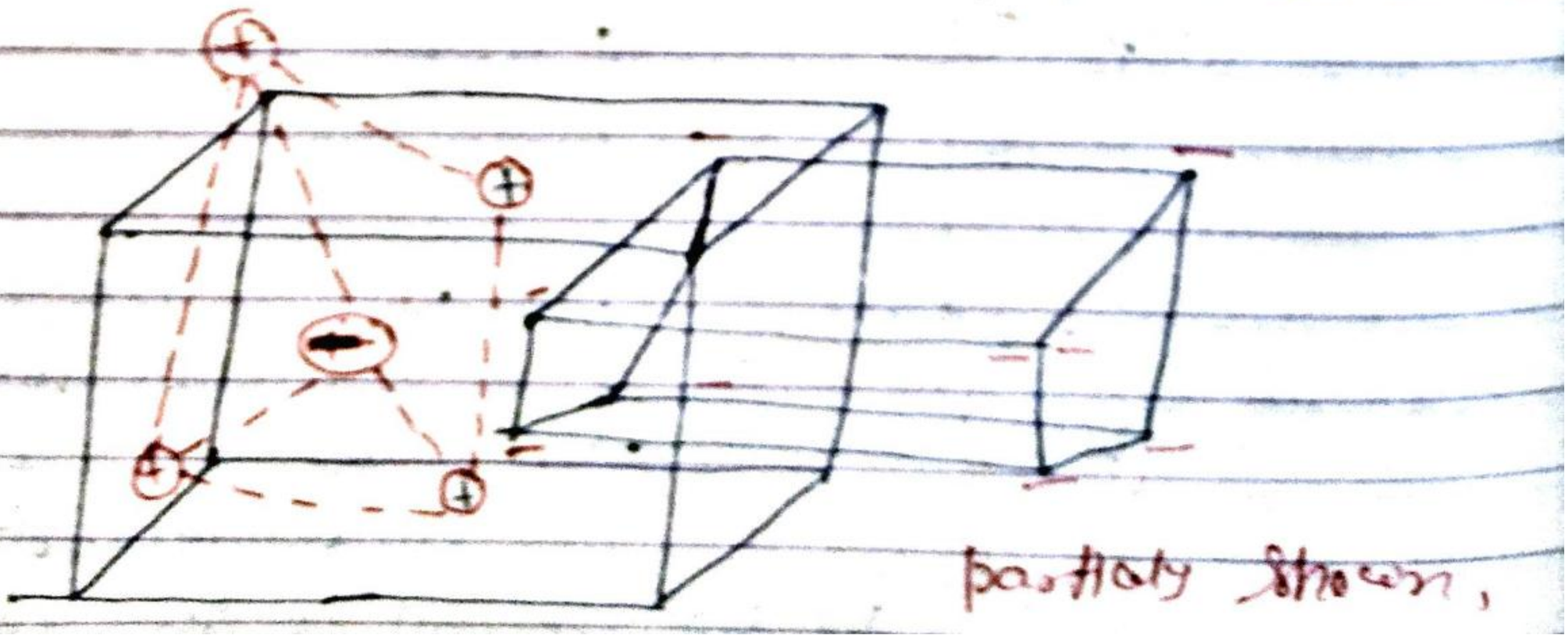
$n^- = 8$.

i.e +ve ion have F.C.C str. and -ve ions are in the tetrahedral holes formed within the unit cell.

(iii) $\frac{r^+}{r^-} > 0.732$ which is the limiting value of C.N = 8

Thus +ve ion is at the body centre and -ve ions at the corners in B.C.C arrangement

(iv) +ve ions are in C.C.P, this suggests F.C.C str. for +ve ion. These results lead to the following str. of CaF_2.



partly shown.

+ve ions are at the corners & and face centred and -ve ions occupy the tetrahedral holes formed by one Ca^{+2} ion at the corners and 3 Ca^{+2} ion at the adjacent face centres. There are 8 such holes. All the 8 holes are occupied by the F^- ions. F^- ion thus formed a simple cube with a +ve ion at its body centre. F^- ions are thus on body diagonals of the cube, each at the Quarter length of the diagonal from a corner.

In an unit cell,

no. of Ca^{+2} ion = 8 + 6 = 14

" " F^- " = 8.

Thus effective no. of +ve ions.

$$n^+ = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 3 + 1 = 4$$

Effective no. of -ve ion

$$= 8 \times 1 = 8.$$

$$\therefore \frac{n^+}{n^-} = \frac{4}{8} = \frac{1}{2}.$$

Thus the formula of is CaF_2 and the crystal is stoichiometric.

(Li_2O) < LiO_2 Antifluoride Str. >

(i) C.N of $Li^+ = 4$

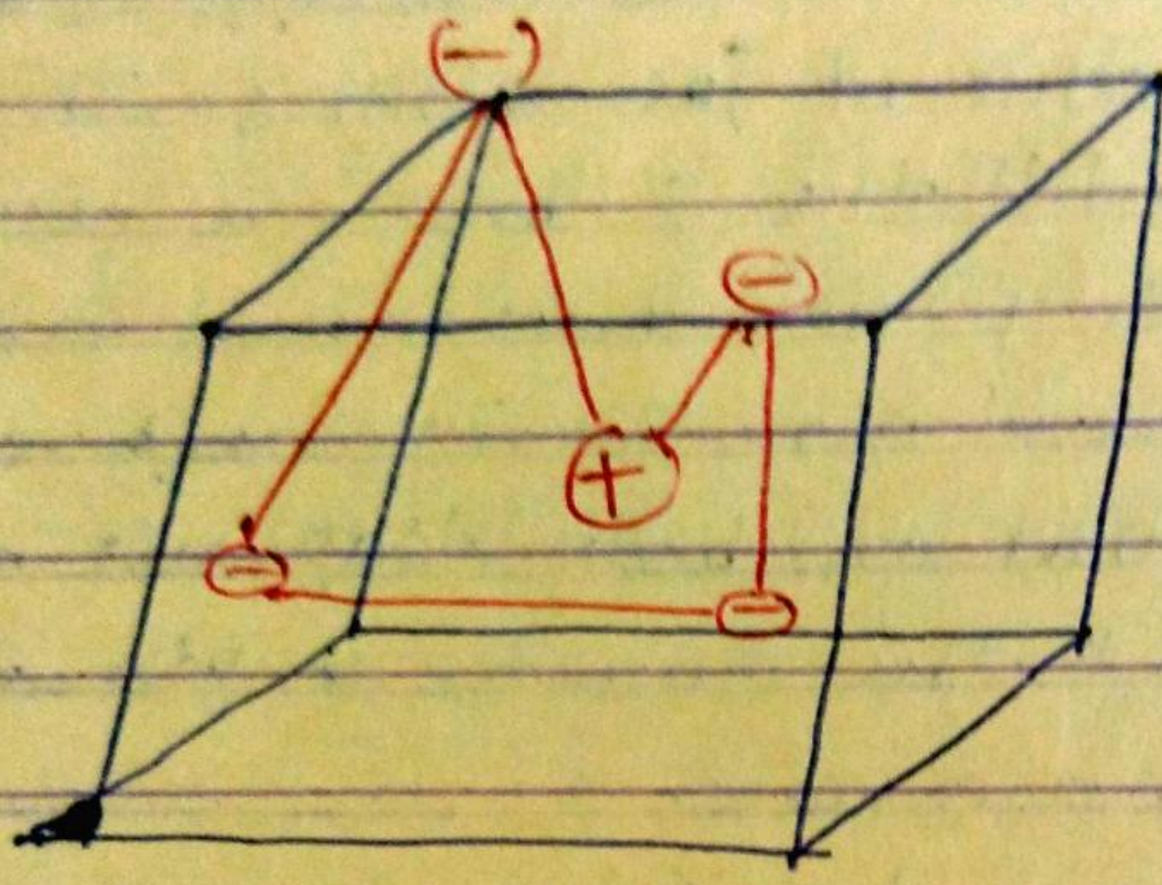
C.N of $O^{-2} = 8$.

This is 4:8 co-ordination of ions, Li^+ is lies in tetrahydral hole a O^{-2} are at the body centre of a cube corner of which are occupied by +ve ions.

(ii) Effective no. of Li^+ $(n^+) = 8$

O^{-2} $(n^-) = 1$

Thus O^{-2} has F.C.C arrangement. Thus Structure of Li_2O is



partially shown.

(iii) O^{-2} ion occupy 8 corner and 6 face centre of a cube. Li+ ions are in tetrahydral holes formed by O^{-2} ion at a corner and 3 adjacent face centre. All the 8 tetrahydral holes are occupied.