MADELUNG CONSTANT :-

The principal contribution to the cohesive energy of an ionic crystal is the electric potential energy ϕ_a due to the electrostatic force of Coulomb attraction given by

$$\phi_a = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r^2} = -\frac{\alpha e^2}{4\pi\epsilon_0 r}$$

where $Z_1 e$ is the charge, say on the +ve ion, $Z_2 e$ is the charge on the −ve ion separated by a distance r and α is a dimensionless constant known as Madelung constant.

To find the value of Madelung Constant α, we use the relation for potential energy per ion pair. This relation is given by $U_{tot} = \frac{\alpha q^2}{r_0}\left(1 - \frac{\rho}{r_0}\right)$ where α is a constant, known as Madelung Const. q is the charge on each ion, ρ is a constant giving a measure

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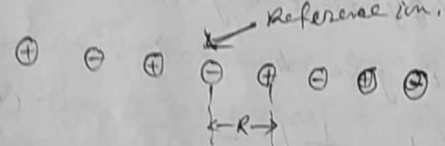
of the range of repulsive interaction and r_0 the equilibrium distance between the ions.

The Madelung Const. $\alpha = \sum \left(\frac{\pm 1}{P_{ij}}\right)$ where P_{ij} is a dimensionless quantity given by the relation

$$r_j = P_{ij} R \, .$$

R being the nearest neighbour separation in the crystal.

Letus choose an infinite line of ions of alternate sign in one dimension as shown in the fig.



Let us consider a negative ion as a reference ion and let R be the distance between the adjacent ions. Then we can write

$$\frac{\alpha}{R} = \sum_j \pm \left(\frac{1}{R P_{ij}}\right) = \sum_j \pm \left(\frac{1}{r_j}\right) \longrightarrow (1)$$

where r_j is the distance of the jth ion from the reference ion. We can also write

$$\frac{\alpha}{R} = 2\left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \cdots\right]$$

$$\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right] \text{ --- } (2)$$

~~Here~~ all the ions are taken into consideration. The factor 2 occurs because there are two ions, one to the left and other to the right of the reference ion at the same distance.

We know that $\log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4}$

If we put $x=1$, the form of above equation becomes

$$\log 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots \longrightarrow (3)$$

using (3) in (2)

$$\alpha = 2\log 2$$

$$= 2 \times 0.69 = 1.38$$

Thus the Madelung Constant of one dimensional infinite line of ions of alternating sign is 1.38.

In one dimension it is easy to evaluate Madelung const, but in three dimension it is very difficult because series presents greater difficulty in three dimension. These difficulty can be seen in Nacl structure.

MADELUNG CONSTANT FOR NACL CRYSTAL :-

$\left(\alpha = \sum \frac{\pm 1}{p_{ij}}\right)$

In Nacl structure the nearest neighbours w.r.t -ve reference ion are six positive ions at $p_{ij} = p = 1$, Contributing $\frac{6}{1}$ to α. There are 12 -ve ions at $p = \sqrt{2}$, Contributing $\frac{-12}{\sqrt{2}}$ to α. Also there are 8 +ve ions at $p = \sqrt{3}$, Contributing $\frac{8}{\sqrt{3}}$. Further there are six -ve ions at $p = \sqrt{4}$, giving $\frac{-6}{\sqrt{4}}$. Next there are 24 +ve ions at $p = \sqrt{5}$ giving $\frac{24}{\sqrt{5}}$ and so on. Hence the Madelung Constant

$$\alpha = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{8}} \cdots$$

$$= 6 - 8.485 + 4.18 - 3.000 + 10.733$$

$$= 1.75$$

~~It is clear that the Con~~ which is close to the accurate value $\alpha = 1.7475$ for Nacl.

BONDING