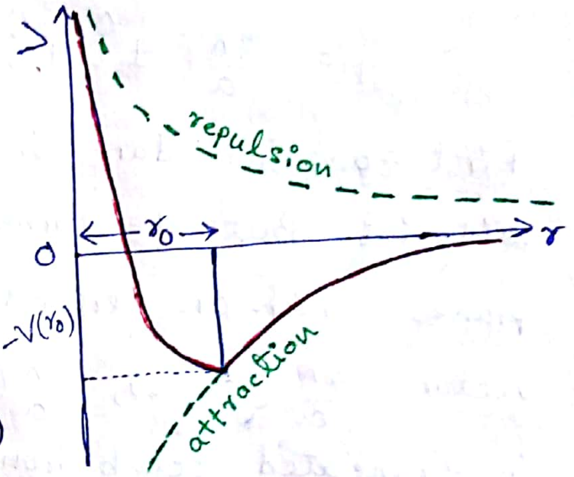
Crystal Bonding

The ability to hold the atoms / ions together is called bonding. Atoms vibrate in lattice & nucleus due to heavy mass is almost at rest. So electrostatic interaction happen between electron cloud & distribution of electron leads to 5 types of bonding due to (a) "attractive force" of negatively charged electron cloud of one atom with positive nuclear charge of other atom (b) "repulsive force" of overlapping negatively charged electron clouds & positively charged nucleus of two atoms.

"spring effect" → attraction → repulsion.

$F = -\frac{dV}{dr}$ attractive force = negative potential.

repulsive force = positive potential.



cohesive / binding energy $V(r_0)$ (negative)

dissociation energy $-V(r_0)$ (positive)

Cohesive energy of a solid is the energy that will be given out in forming a crystal by bringing neutral atoms from ∞ to equilibrium separation r_0.

Suppose $V_{attractive} \propto r^{-m}$ & $V_{repulsive} \propto r^{-n}$

$$\therefore \text{ Cohesive energy } V = V_{attractive} + V_{repulsive} = -Ar^{-m} + Br^{-n}$$

$$\text{\& force } F = -\frac{dV}{dr} = mAr^{-(m+1)} - nBr^{-(n+1)}$$

$$\text{at } r = r_0,\ F = 0 = mAr_0^{-(m+1)} - nBr_0^{-(n+1)}.$$

$$\text{or } r_0^{m-n} = \frac{A}{B}\frac{m}{n}$$

Then equilibrium potential energy $V(r_0) = -Ar_0^{-m} + Br_0^{-n}$

$$= -Ar_0^{-m}\left(1 - \frac{B}{A}r_0^{m-n}\right) = -Ar_0^{-m}\left(1 - \frac{m}{n}\right).$$

For V to be minimum, it must be concave upwards curvature,

$$\left.\frac{d^2V}{dr^2}\right|_{r=r_0} > 0 \quad \text{or} \quad \left[-m(m+1)A r^{-(m+2)} + n(n+1)B r^{-(n+2)}\right]_{r=r_0} > 0$$

$$\text{or} \quad -m(m+1) + n(n+1)\frac{B}{A} r_0^{m-n} > 0$$

$$\text{or} \quad -\cancel{m}(m+\cancel{1}) + \cancel{n}(n+\cancel{1})\frac{\cancel{m}}{\cancel{n}}\cancel{\frac{B}{A}}\cancel{\frac{A}{B}} > 0$$

$$\text{or} \quad n-m > 0 \quad \text{or} \quad n > m.$$

Thus to form a chemical bond, we always need repulsive force be of shorter range than attractive force.

<u>Types of bonding</u> 5 types of bonding exist

(a) Ionic bond (transfer of valence electron) : NaCl, LiF.

(b) Covalent bond (sharing of valence electrons) : Diamond, SiC.

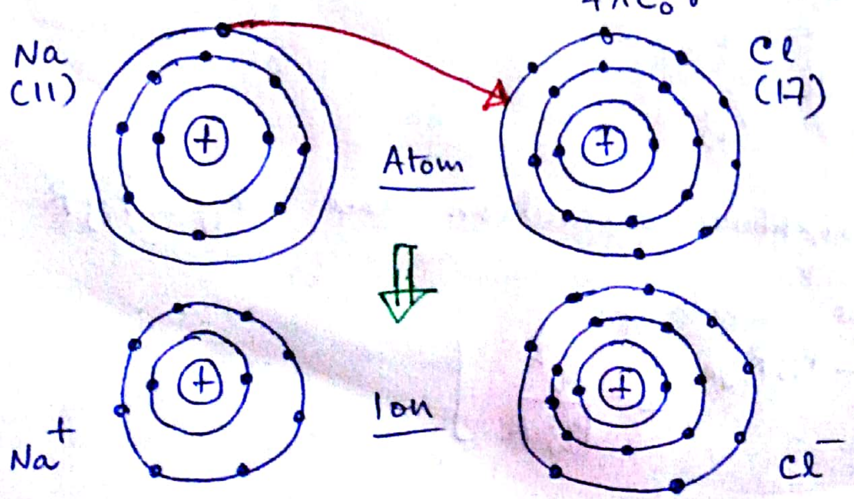
(c) Metallic bond (free nature of valence electron) : Cu, Ag, Fe

(d) Hydrogen bond ($V \propto -r^{-2}$) : Ice

(e) van der Waal's bonding (dipole-dipole interaction)

<u>Ionic / Electrovalent Bonding</u>

Transfer of electrons from an electropositive element to electronegative element, to create +− ion. Electronegative element of large electron affinity accomodate extra added electron to complete outermost valence orbit to stabilize. Oppositely charged ions attract $V_{attraction} = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}$



Na + ionisation energy (5.1 eV) $\rightarrow Na^+ + e^-$

$Cl + e^- \rightarrow Cl^-$ + electron affinity (3.6 eV)

$\therefore Na + Cl + 1.5\,eV \rightarrow Na^+ + Cl^-$

$Z_1 = Z_2 = 1.$

So potential energy $V = -\frac{e^2}{4\pi\epsilon_0 r_0} = \frac{-(1.6\times10^{-19})^2}{4\pi\times 8.85\times10^{-12}\times 2.4\times10^{-10}}$
($r_0 = 2.4$ Å)

$$= -\frac{9.6\times10^{-19}}{1.6\times10^{-19}} \text{ eV} = -6 \text{ eV}.$$

So net energy released $= 5.1 - 3.6 - 6 = -4.5$ eV.

Cohesive energy Binding energy calculated by Born & Madelung in 1910 extended by Mayer.

assumptions : (a) Ionic crystals are formed by positive & negative ions with spherical charge distribution. (b) Force of attraction depends on inter-ionic distance & isotropic (orientation independent), (c) Electrostatic interaction (Madelung energy $V_a = -\frac{\alpha q^2}{4\pi\epsilon_0 r}$, α = Madelung constant) contributes to cohesive energy

According to Born-Madelung theory interaction energy U_i on ion i due to all j other ions, $U_i = \sum_{j\neq i} U_{ij}$

U_i consists of two parts :

1. Short range central field repulsive potential βr_{ij}^{-n} between + & - ions which was modified by $\lambda e^{-r_{ij}/\rho}$, λ = strength, ρ = range of interaction (screened Coulomb)
2. Attractive or repulsive long ranged coulomb force with energy $\pm \frac{q^2}{r_{ij}}$

$$\therefore U_i = \sum_{j\neq i}\left[\lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}\right]$$

If R is the nearest neighbour separation then $r_{ij} = p_{ij} R$ where p_{ij} is a dimensionless quantity.

$$\text{Then } U_i = \sum_{j\neq i}\left[\lambda e^{-p_{ij}R/\rho} \pm \frac{q^2}{p_{ij}R}\right]$$

$$= Z\lambda e^{-R/\rho} \pm \sum_{j\neq i} \frac{q^2}{p_{ij}R} = Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}$$

where Z is number of nearest neighbour of i^{th} ion & $\alpha = \pm\sum \frac{1}{p_{ij}}$ is called Madelung constant

If the crystal contain $2N$ ions or N molecules, then

$$U_{total} = N U_i = N\left[Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right]$$

at equilibrium distance $R = R_0$, $\frac{dU_{total}}{dR} = 0$

or $-\frac{Z\lambda}{\rho} e^{-R_0/\rho} + \frac{\alpha q^2}{R_0^2} = 0$ or $\boxed{e^{-R_0/\rho} = \frac{\rho\alpha q^2}{Z\lambda R_0^2}}$

$$\therefore U_{total} = N\left[\cancel{Z\lambda} \frac{\rho\alpha q^2}{\cancel{Z\lambda} R_0^2} - \frac{\alpha q^2}{R_0}\right] = -\underbrace{\frac{N\alpha q^2}{R_0}}_{\text{Madelung energy}} \underbrace{\left(1 - \frac{\rho}{R_0}\right)}_{\text{contribution from short range repulsion}}$$

$$U_i = -\frac{\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right),$$

or in SI units, $\boxed{U_i = -\frac{\alpha q^2}{4\pi\epsilon_0 R_0}\left(1 - \frac{\rho}{R_0}\right)}$

as $\frac{\rho}{R_0} \to 0$ repulsive interaction is very short range.

In $\alpha = \sum \pm \frac{1}{p_{ij}}$, $+$ is used for $+$ive ion & $-$ for $-$ive ion if i^{th} ion is $-$ive. & we consider repulsive interaction effective for nearest neighbours only.

Madelung constant for a 1D lattice

$$+ \; - \; + \; - \; + \; \overset{\leftrightarrow R}{\ominus} \; + \; - \; + \; - \; + \; -$$

reference

$$\alpha = \sum_{j\neq i} \pm \frac{1}{p_{ij}}, \quad \frac{\alpha}{R} = \sum_{j\neq i} \pm \frac{1}{p_{ij}R} = \pm\sum_{j\neq i} \frac{1}{r_{ij}}$$

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

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

$\uparrow$ due to both side of reference ion

but $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$

if $x = 1$, $\ln 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots$

$\therefore \alpha = 2\ln 2 = 1.38$

Madelung constant for NaCl crystal

Nearest neighbour to $-$ive (reference) ion $=$ 6 $+$ive ions with $P_{ij} = p = 1$. 12 $-$ive ions at $p = \sqrt{2}$. 8 $+$ive ions at $p = \sqrt{3}$. 6 $-$ive ions at $p = \sqrt{4}$ & so on

$$\alpha = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \cdots = 1.748$$

Bigger α, more cohesive energy, greater stability of structure

Cohesive energy for repulsive core potential $\propto r^{-n}$

$$V_i = V_{attractive} + V_{repulsive} = -\frac{\alpha q^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

at $r = r_0$, V is minimum, $\left.\frac{dV}{dr}\right|_{r=r_0} = 0 = \frac{\alpha q^2}{4\pi\epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$

$$\therefore B = \frac{\alpha q^2 r_0^{n-1}}{4\pi\epsilon_0 n}$$

$$\therefore V_i = -\frac{\alpha q^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

& for 2N molecules, $V_{tot} = -\frac{N\alpha q^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$

for NaCl, $\alpha = 2\ln 2$, $\boxed{V_{tot} = -\frac{2Nq^2 \ln 2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)}$.

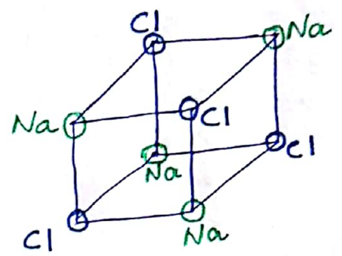
Bulk modulus of Ionic crystals

Volume strain $= \frac{dV}{V}$, change in pressure dp, Bulk modulus

$B = -\left.\frac{dp}{dV/V}\right|_{R=R_0}$. Using 1^{st} law of thermodynamics, $dQ = dU + pdV$

or $\frac{dU}{dV} = -p \quad (dQ=0)$ or $\frac{d^2U}{dV^2} = -\frac{dp}{dV}$.

$$\therefore B = V \left.\frac{d^2U}{dV^2}\right|_{R=R_0}$$



Volume occupied by $\frac{1}{2}$ molecule $\rightarrow R_0^3$

volume occupied by 1 molecule $\rightarrow 2R_0^3$

volume occupied by N molecule $\rightarrow 2NR_0^3$. (equilibrium separation)

(2N ions)

volume of unit cell $\rightarrow (2R_0)^3 = 8R_0^3$ because $a = 2R_0$

$$V = 2NR^3, \quad \frac{dV}{dR} = 6NR^2 \quad \text{and} \quad \left.\frac{dU}{dR}\right|_{R=R_0} = 0$$

$$\therefore \frac{d^2U}{dV^2} = \frac{d}{dV}\left(\frac{dU}{dV}\right) = \frac{d}{dV}\left(\frac{dU}{dR}\cdot\frac{dR}{dV}\right) = \frac{d}{dV}\left(\frac{dU}{dR}\right)\cdot\frac{dR}{dV} + \frac{dU}{dR}\cdot\frac{d^2R}{dV^2}$$

$$= \frac{d}{dR}\left(\frac{dU}{dR}\right)\frac{dR}{dV}\cdot\frac{dR}{dV} + \frac{dU}{dR}\cdot\frac{d^2R}{dV^2} = \frac{d^2U}{dR^2}\cdot\left(\frac{dR}{dV}\right)^2 + \cancelto{0}{\frac{dU}{dR}}_{R=R_0}\cdot\frac{d^2R}{dV^2}$$

$$\therefore \left.\frac{d^2U}{dV^2}\right|_{R=R_0} = \frac{d^2U}{dR^2}\cdot\left(\frac{dR}{dV}\right)^2 = \frac{1}{(6NR_0^2)^2}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}$$

$$\therefore B = V\left.\frac{d^2U}{dV^2}\right|_{R=R_0} = 2NR_0^3\,\frac{1}{36N^2R_0^4}\left.\frac{d^2U}{dR^2}\right|_{R=R_0} = \frac{1}{18NR_0}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}$$

We learned that $U_{total} = N\left[Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right]$

$$\therefore \frac{dU_{total}}{dR} = -\frac{NZ\lambda}{\rho}e^{-R/\rho} + \frac{N\alpha q^2}{R^2}$$

$$\frac{d^2U_{total}}{dR^2} = \frac{NZ\lambda}{\rho^2}e^{-R/\rho} - \frac{2N\alpha q^3}{R^3}, \quad \text{also} \quad e^{-R_0/\rho} = \frac{\rho\alpha q^2}{Z\lambda R_0^2}$$

$$\therefore B = \frac{1}{18NR_0}\left[\frac{NZ\lambda}{\rho^2}e^{-R_0/\rho} - \frac{2N\alpha q^3}{R_0^3}\right] = \frac{1}{18\cancel{N}R_0}\left[\frac{\cancel{NZ\lambda}}{\cancel{\rho^2}}\,\frac{\cancel{\rho}\alpha q^2}{\cancel{Z\lambda}R_0^2} - \frac{2\cancel{N}\alpha q^3}{R_0^3}\right]$$

$$\boxed{B = \frac{\alpha q^2}{18R_0^4}\left(\frac{R_0}{\rho} - 2\right)}$$

From B & R_0, range of repulsive interaction can be calculated.