

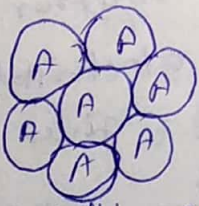
Crystal Binding

~~Crystal~~ What holds crystal together?

Main contribution \rightarrow The attractive electrostatic interaction between the negative charges of the electrons and the positive charges of the nuclei is largely responsible for the cohesion of solids.

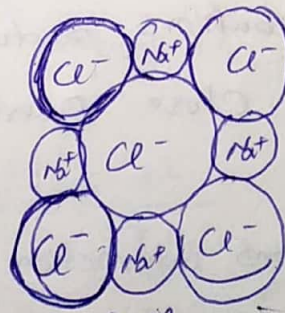
Cohesive energy: — Energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation, with the same electronic configuration.

Ionic crystal \rightarrow Lattice energy: — Energy that must be added to the crystal to separate its component ions into free ions at rest at infinite separation.

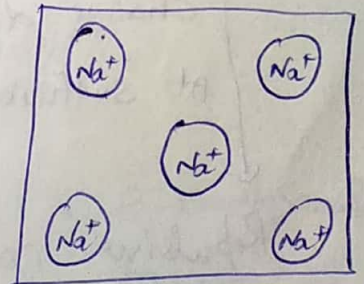


Crystalline Argon
(Vander Waals)

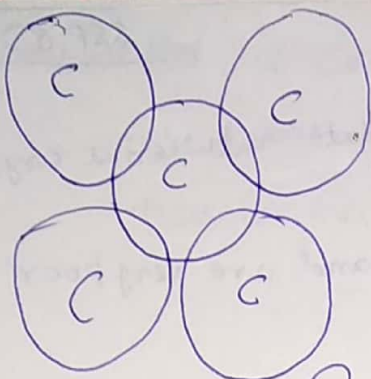
(i)



NaCl (ionic) (ii)



Sodium
(metallic) (iii)



Diamond (iv)
(Covalent)

In (c) the valence electrons are taken away from each alkali atom to form a communal electron sea in which the positive ions are dispersed

Crystal of Inert gases \rightarrow outermost shell completely filled

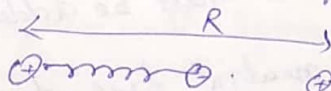
Distribution of e^- charge in free atom is spherically symmetric

\rightarrow In the crystal the inert gas atoms pack together as closely as possible. \rightarrow Crystal structures are all cubic closed packed (fcc), except He^3, He^4 .

In crystal cohesive energy of an atom is only 1 percent or less of the ionization energy of an atomic electron \Rightarrow not much energy is available to distort the free atom charge distributions. Part of this distortion gives the Van der Waals interaction.

Van der Waals interaction = London interaction = induced dipole-dipole interaction

Two neutral atoms induce dipole moment each other



gives rise to a attraction interaction energy

$$\Delta U = -\frac{A}{R^6}$$

} Two identical linear harmonic oscillator

R = separation b/w two oscillators

Repulsive interaction \rightarrow As two atoms come close together their charge distributions gradually overlap \rightarrow changing electrostatic energy
At sufficiently close overlap energy is repulsive given by

$$\frac{B}{R^{12}}, B = +ve \text{ const}$$

Repulsive Coulomb interaction

+ Pauli exclusion principle

For two atoms total Pot energy at separation R

$$V(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right] \quad \text{--- (1)}$$

↑
Lennard Zone Potential

Here $A = 4\epsilon\sigma^{12}$
 $B = 4\epsilon\sigma^6$

For N atoms in crystal (neglecting K.E. of the inert gas)

$$U_{tot} = \frac{1}{2} N (4\epsilon) \left[\sum_j \left(\frac{\sigma}{P_{ij}R}\right)^{12} - \sum_j \left(\frac{\sigma}{P_{ij}R}\right)^6 \right] \quad \text{--- (2)}$$

$P_{ij}R \rightarrow$ distance b/w reference atom i and any other atom j .
 $\frac{1}{2}$ factor \rightarrow to compensate for counting twice each pair of atoms.

$$\frac{dU_{tot}}{dR} \Big|_{R=R_0} = 0 \quad \text{gives} \quad \frac{R_0}{\sigma} = 1.09$$

↑
eq^m distance

Cohesive energy \rightarrow At absolute zero and at zero pressure.

at R_0
$$U_{tot}(R_0) = -(2.15)(4N\epsilon) \quad \text{--- same for all inert gases}$$

Ionic Crystals :- Made up of +ve & -ve ions.

Inert gas atoms have closed shells and the charge distributions are spherically symmetric. We expect that the charge distributions on each ion in an ionic crystal will have approximately spherical symmetry with some distortion near the region of contact with neighbouring atoms

[Na^+ , Ar \rightarrow same electronic configuration etc.]

Main contribution to binding energy (in Ionic crystal) is electrostatic energy called Madelung energy.

$$U_{ij} = \sum_{j \neq i} V_{ij} \quad \text{--- Interaction energy b/w ions } i \text{ \& } j$$

↑
all interactions involving the ions

$$V_{ij} = \lambda \exp\left(\frac{-\gamma V_j}{\rho}\right) \pm \frac{q^2}{\gamma V_j}$$

↑
Central field
repulsive Pot.

↑
Coulomb
Pot.

$\lambda, \rho \rightarrow$ empirical parameters
 $\left. \begin{matrix} + \rightarrow \text{like charges} \\ - \rightarrow \text{unlike } \end{matrix} \right\}$ (in cgs)

$P \rightarrow$ measure of the range of the repulsive interaction
 at $r=P \rightarrow$ repulsive interaction reduced to e^{-1} of the value at $r=0$.

For N molecules (NaCl crystal) or $2N$ ions.

$$U_{tot} = N U_i$$

, N not $2N \rightarrow$ count each pair only once

Again $r_{ij} = P_{ij} R$,

$R = nm$. separation in the crystal.

CGS
$$U_{ij} = \begin{cases} 2 \exp(-\frac{R}{P}) - \frac{q^2}{R} & (nm) \\ \pm \frac{1}{P_{ij}} \frac{q^2}{R} & \text{else} \end{cases}$$

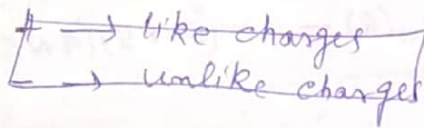
$$U_{tot} = N U_i = N \left(2 \exp(-R/P) - \frac{\alpha q^2}{R} \right)$$

$Z = \#$ of nns of any ion

$$\alpha = \sum_j' \frac{\pm}{P_{ij}}$$

\equiv Madelung const.

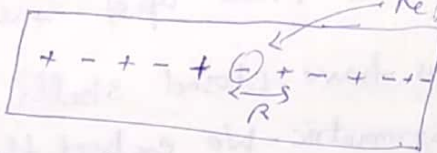
$\sum_j' \frac{1}{r_{ij}}$ sumⁿ $i \neq j$



$\alpha \rightarrow +ve$

evaluation of α

for 1d chain



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

$r_j =$ distance of j th ion from reference ion R

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

$$\frac{\alpha}{R} = 2 \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \dots \right] \Rightarrow \alpha = 2 \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right)$$

$$\alpha = 2 \ln 2$$

Here if we take reference ion as $-ve$, ~~ext~~ Plus sign will apply to $+ve$ ions & minus sign to $-ve$ ions.

In 3-D series presents greater difficulty