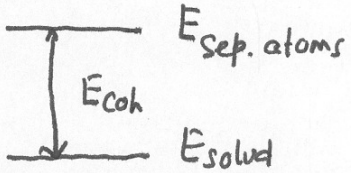
Chapters 3, 4, 5*, 12, 15

Chapter 3 : Crystal Binding

T=0; Lowest energy structure ; Crystalline?
(No rigorous proof)

Cohesive energy of solids

$$E_{coh} = E_{\substack{separated \\ Atoms}} - E_{solid} > 0$$



If $E_{coh} < 0$: crystal is not stable
Falls apart.

Units: $\frac{eV}{atom}$ or $\frac{eV}{molecule}$, $\frac{J}{mole}$, $\frac{Kcal}{mole}$ $\quad Kcal = 10^3$ cal.

Types of solids depending on the nature of binding (bonds)

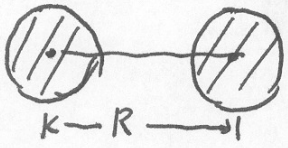
① Raregas solid : Very small E_{coh}
② Ionic
③ Metallic
④ Covalent

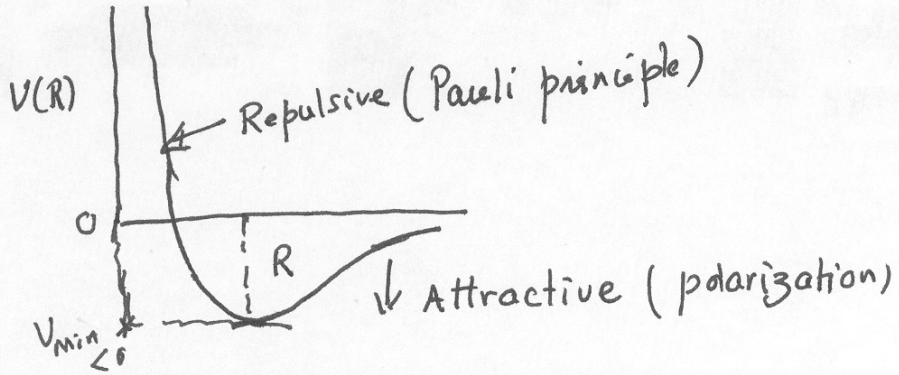
} A solid can have a mixture of these bonds.

①	E_{coh}	③	E_{coh}	T_m	④	E_{coh}	T_m
He	X	Li	1.63	(453.7K)	C	7.37	(
Ne	0.02	Na	1.113		Si	4.63	(1687K)
Ar	0.08	K	0.934		Ge	3.85	
Kr	0.116	Rb	0.852		Sn	3.14	(505.1 K)
Xe	0.160 (161.4K)	Cs	0.804	(301.6K)			
Rn	0.202						
	Increase			Decrease			Decrease

Melting Temp: $\propto E_{cohesive}$

Physics of ① Rare-gas solid (van der Waals bond)





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

(Lennard Jones Potential)
6-12 Potential

ϵ : Energy scale

σ : Length scale

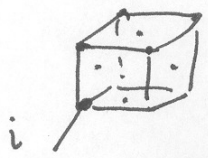
	$\epsilon(10^{-15}$ erg)	$\sigma(\text{Å})$
Ne	50	2.74
Ar	167	3.40
Kr	225	3.65
Xe	320	3.98

Calculation of E_{coh} & Equilibrium lattice constant for LJ or vander Waals solids.

Structure: FCC (Bravais lattice)

$$E = \frac{1}{2}\sum_{i}\sum_{j\neq i} V(R_{ij}) = \frac{1}{2}N\sum_{j}{}' V(R_{ij}) \qquad '\Rightarrow j\neq i$$

$$= \frac{1}{2}N \cdot 4\epsilon \sum_{j}{}' \underbrace{\left[\left(\frac{\sigma}{R_{ij}}\right)^{12} - \left(\frac{\sigma}{R_{ij}}\right)^{6}\right]}_{S}$$



Write: $R_{ij} = R p_{ij}$: R = nearest neighbor (nn) distance (length scale)

$$S = \left(\frac{\sigma}{R}\right)^{12}\sum_{j}{}' \frac{1}{(p_{ij})^{12}} - \left(\frac{\sigma}{R}\right)^{6}\sum_{j}{}' \frac{1}{(p_{ij})^{6}}$$

: For nn $p_{ij} = 1$

Geometry: (FCC) $C_1 = \sum_j{}' \frac{1}{p_{ij}^{12}} = 12 + ? + \ldots = 12.13188$
(nn) (nnn)

$$C_2 = \sum_j{}' \frac{1}{p_{ij}^{6}} = 14.45302$$

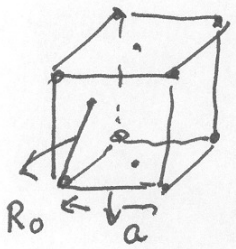
$$E = N \cdot 2\epsilon \left[\frac{C_1 \sigma^{12}}{R^{12}} - \frac{C_2 \sigma^{6}}{R^{6}} \right] \equiv U_{tot}$$

For equilibrium

$$\frac{dU_{tot}}{dR} = 0 = N2\epsilon \left[-\frac{12 C_1 \sigma^{12}}{R^{13}} + \frac{6 C_2 \sigma^{6}}{R^{7}} \right]$$

$$= N2\epsilon \frac{\sigma^6}{R^7} \left[-12 C_1 \left(\sigma/R\right)^6 + 6 C_2 \right]$$

$$\left(\sigma/R_0\right)^6 = \frac{6 C_2}{12 C_1} \Rightarrow \boxed{\left(\frac{R_0}{\sigma}\right) = 1.09}$$



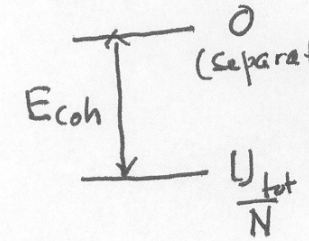
Eq. lattice constant $a = \sqrt{2}\, R_0 = (\sqrt{2})(1.09)\,\sigma$

Energy at equilibrium.

$$U_{tot} = 2N\epsilon \left[C_1 \left(\sigma/R_0\right)^{12} - C_2 \left(\sigma/R_0\right)^{6} \right]$$

$$= 2N\epsilon \left[C_1 \cdot \left(\frac{C_2}{2C_1}\right)^2 - C_2 \left(\frac{C_2}{2C_1}\right) \right]$$

$$= -2N\epsilon \left(\frac{C_2^2}{4C_1}\right) \qquad |U_{el}|/|U_{att}| = \frac{1}{2}$$



$$\frac{U_{tot}}{N} = -4\epsilon \left(\frac{C_2^2}{8C_1}\right) = -(4\epsilon)(2.15) = -8.60\epsilon$$

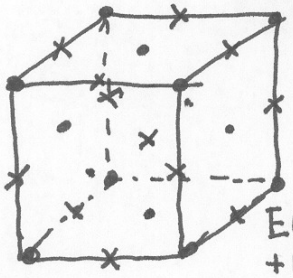
$\boxed{E_{coh} = 8.60\,\epsilon}$ WHY?

Compare E_{coh} with expt.

	E_{coh} (eV/atom) exp.	8.60ϵ	$(Th - Exp)/Th$	
Ne	0.02	0.027	26%	Quantum Effects
Ar	0.08	0.090	11%	
Kr	0.116	0.121	4%	
Xe	0.202	0.173	7%	

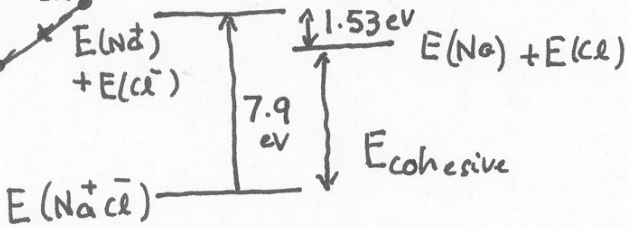
Binding of Ionic Solids

Look at an example: $NaCl \Rightarrow Na^+ Cl^-$



Crystal structure:

Two interpenetrating fcc lattice



(All energies are per molecule)

$$E_{cohesive} = (7.9 - 1.53) = 6.37 \text{ eV/molecule}$$

More about 1.53 eV

$E(Na) + 5.14\,eV = E(Na^+) + e$: Ionization energy of Na atom

$E(Cl) + e = E(Cl^-) + 3.61\,eV$: Electron affinity of Cl atom.

$$E(Na) + E(Cl) + e + 5.14\,eV = E(Na^+) + E(Cl^-) + e + 3.61\,eV$$

$$\therefore \quad E(Na) + E(Cl) = E(Na^+) + E(Cl^-) + (3.61 - 5.14)\,eV$$

$$\boxed{E(Na) + E(Cl) = E(Na^+) + E(Cl^-) - 1.53\,eV}$$

Lattice energy $E(Na^+Cl^-)$

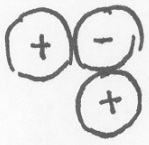
N molecules : 2N ions

U_+ = Energy of +ive ions

U_- = Energy of -ive ions

$$U_{tot} = \frac{1}{2}\left[NU_+ + NU_-\right]$$

Assume: Nearest neighbor repulsion



$U_+ = U_-$

Consider the i^{th} site (can be either + or - ion)

$$U_+ = U_- = U_i = \sum_j{}' U_{ij}$$

$q_i = \pm q$

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}$$

cgs unit

SI $q^2/4\pi\epsilon_0 r_{ij}$

↓ Short range repulsion

↓ Long (very) range attraction and repulsion

(2-parameters.

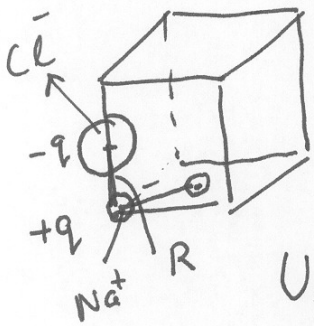
(ϵ, σ) ↑ Lennard Jones Potential } λ: energy scale

ρ: length scale

only operates between (nn)

$$U_{ij} = \lambda e^{-R/\rho} - q^2/R \qquad (nn)$$

$$= \pm \frac{q^2}{p_{ij} R} \qquad (others)$$



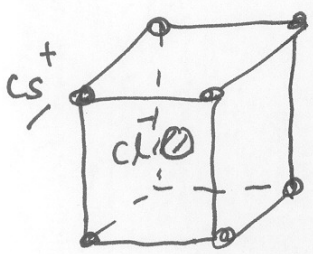
$p_{ij} = 1$ nn

$p_{ij} = \sqrt{2}$ nnn

$$U_{tot} = NU_i = N\left[z\lambda e^{-R/\rho} - \alpha \frac{q^2}{R}\right]$$

z = # nearest neighbors

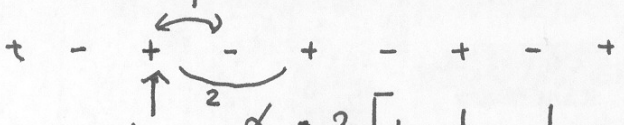
$$\alpha = \sum_j{}^{\pm} \frac{(\pm)}{p_{ij}} = \text{Madelung Constant}$$



FCC: $z = 12$, α_{NaCl}

BCC: $z = 8$ α_{CsCl}

Madelung Constant



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

$$\boxed{\alpha = 2\ln 2}$$

$$\ln(1+x) = x - x^2/2 + x^3/3 \cdots$$

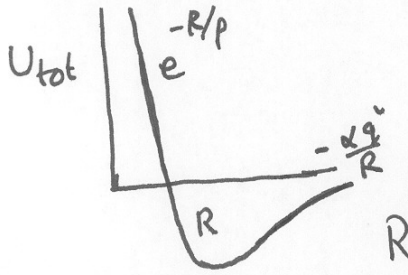
Need special tricks to calculate α.
(Ewald summation)

Structure	α
NaCl	1.747565
CsCl	1.762675
ZnS (zinc blende)	1.6381

Energy minimum / Lattice energy

$$\frac{dU_{tot}}{dR} = 0 = N\left[z\lambda e^{-R/\rho}\left(-\frac{1}{\rho}\right) + \alpha\frac{q^2}{R^2}\right] = 0$$

$$\frac{z\lambda}{\rho} e^{-R_0/\rho} = \alpha\frac{q^2}{R_0^2}$$



$$R_0^2 e^{-R_0/\rho} = \frac{\alpha q^2 \rho}{z\lambda} \Rightarrow \boxed{\left(\frac{R_0}{\rho}\right)^2 e^{-R_0/\rho} = \alpha\cdot\left(\frac{q^2}{\rho}\right)\frac{1}{z\lambda}}$$

$F\left(\frac{R_0}{\rho}\right)$

↙ min. energy

$$\frac{U_{tot}}{N} = z\lambda e^{-R_0/\rho} - \alpha q^2/R_0$$

$$= \alpha\rho\frac{q^2}{R_0^2} - \alpha\frac{q^2}{R_0}$$

$$= -\frac{\alpha q^2}{R_0}\left[1 - \frac{\rho}{R_0}\right]$$

$$= \left(\frac{U_{tot}}{N}\right)_{\text{Madelung (Attractive)}} + \left(\frac{U_{tot}}{N}\right)_{\text{Repulsion}}$$

Numerical Results (Table 7)

	ρ (Å)	R_0 (Å)	$-U_{tot}^{Th}$	$-U_{tot}^{Exp}$ ($T=0$)
LiF	0.291	2.014	242.2	246.8
NaCl	0.321	2.820	178.6	185.3
KBr	0.336	3.298	154.5	159.3
RbI	0.348	3.671	139.6	144.9

Kcal/mole

$T = 300K$

$$\frac{\rho}{R_0} \simeq 0.1$$

Pretty good! (within a few %)

Summary

1. Dominant energy in binding of ionic solids Madelung energy ~~~~
2. Repulsive energy ~ 10%. (Compare with Lennard Jones system)
3. For $E_{cohesive}$: Correct for $E(Na^+) + E(Cl^-)$

$= E(Na) + I + E(Cl) - A$

$(I - A)$ $E(Na^+) + E(Cl^-)$ / $E(Na) + E(Cl)$

I: Ionization en. of Na

A: Electron aff. Cl