Chapter 3.
Crystal Binding and Elastic Constants.

Argon	: Van der waals
Sodium chloride	: ionic
Sodium	: metallic
Diamond	: covalent
H_2O	:Hydrogen Bonding

Crystal of inert gases.

:charge가 symmetric하다.

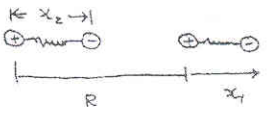
원래 symmetric하다.

cohesive energy는 ionization energy의 1%정도이다.

Van der waals force에 의해 결정구조를 이룸.

Induced dipole moment가 attractive interaction의 원인.

Model.



$$H_0 = \frac{1}{2m}p_1^2 + \frac{1}{2}cx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}cx_2^2$$

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$$

if $|x_1|, |x_2| \ll R$이면,

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R(1+\frac{x_1-x_2}{R})} - \frac{e^2}{R(1+\frac{x_1}{R})} - \frac{e^2}{R(1-\frac{x_2}{R})}$$

$$\simeq \frac{e^2}{R} + \frac{e^2}{R}\left[1-\left(\frac{x_1-x_2}{R}\right)+\left(\frac{x_1-x_2}{R}\right)^2\right] - \frac{e^2}{R}\left[1-\frac{x_1}{R}+\left(\frac{x_1}{R}\right)^2\right] - \frac{e^2}{R}\left[1+\frac{x_2}{R}+\left(\frac{x_2}{R}\right)^2\right]$$

$$= \frac{e^2}{R}\left[-\frac{x_1-x_2}{R} + \frac{x_1^2-2x_1x_2+x_2^2}{R^2} + \frac{x_1}{R} - \frac{x_1^2}{R^2} - \frac{x_2}{R} - \frac{x_2^2}{R^2}\right]$$

$$= -\frac{e^2}{R^3}2x_1x_2$$

이 Hamiltonian을 diagonalize하자.

$$x_s = \frac{1}{\sqrt{2}}(x_1+x_2)\ ;\ x_a = \frac{1}{\sqrt{2}}(x_1-x_2)$$

$$x_1 = \frac{1}{\sqrt{2}}(x_s+x_a)\ ;\ x_2 = \frac{1}{\sqrt{2}}(x_s-x_a)$$

$$p_1 = \frac{q}{\sqrt{2}}(p_s+p_a)\ ;\ p_2 = \frac{1}{\sqrt{2}}(p_s-p_a).$$

total Hamiltonian.

$$H = \frac{1}{2m}p_1^2 + \frac{1}{2}Cx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}Cx_2^2 - \frac{2e^2x_1x_2}{R^3}$$

$$= \frac{1}{2m}\frac{1}{2}[(p_s+p_a)^2 + (p_s-p_a)^2] + \frac{1}{2}C\frac{1}{2}[(x_s+x_a)^2 + (x_s-x_a)^2] - \frac{2e^2 \cdot \frac{1}{2}(x_s^2-x_a^2)}{R^3}$$

$$= \frac{1}{2m}[p_s^2+p_a^2] + \frac{1}{2}C[x_s^2+x_a^2] - \frac{e^2}{R^3}(x_s^2-x_a^2)$$

$$= \left[\frac{1}{2m}p_s^2 + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{1}{2m}p_a^2 + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2\right]$$

two free...

$$\omega = \sqrt{\frac{C \pm \frac{2e^2}{R^3}}{m}} = \sqrt{\frac{C}{m}\left(1 \pm \frac{2me^2}{R^3C}\right)}$$

$$= \omega_0\left(1 \pm \frac{me^2}{R^3C} - \frac{1}{8}\left(\frac{2me^2}{R^3C}\right)^2 \cdots\right)$$

$$\triangle U = \frac{\hbar}{2}(\triangle\omega_s + \triangle\omega_a)$$

$$= \frac{\hbar}{2}\omega_0\left(-\frac{1}{4}\right) \cdot \frac{4m^2e^4}{R^6C^2}$$

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

Attraction force에 의해 dipole-dipole interaction

A의 값 $\sim \hbar\omega_0\alpha^2$

Repulsive interaction.

Pauli exclusion principle.

total potential energy.

$$U(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$ Lennard－Jones potential.

$4\varepsilon\sigma^6 \equiv A, 4\varepsilon\sigma^{12} \equiv B.$

ε과 σ는 gas phase에서 얻는다.

또는 expulsion을 $\lambda \cdot \exp(-R/\rho)$

ρ: measure of the range of the interaction

Equilibrium lattice constant.

$$U_{tot} = \frac{1}{2}N \cdot (4\varepsilon) \cdot \left[\sum_j{}'\left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j{}'\left(\frac{\sigma}{p_{ij}R}\right)^{6}\right]$$

p_{ij}: distance between reference atom i and any other atom j.

fcc: $\sum p_{ij}^{-12} = 12.13188$, $\sum p_{ij}^{-6} = 14.45392.$ hcp: 12.13229, 14.45489. bcc: 9.11418, 12.2533.

$$\frac{dU_{tot}}{dR}=0 \quad =-2N\varepsilon\left[12\cdot(12.13)\cdot\frac{\sigma^{12}}{R^{13}}-6\cdot 14.45\cdot\frac{\sigma^{6}}{R^{7}}\right]$$

$$\text{where}\frac{R_0}{\sigma}=1.09$$

observed value.

	Ne	*Ar*	*Kr*	*Xe*
$\frac{R_0}{\sigma}$	1.14	1.11	1.10	1.09

Cohesive energy.

$$U_{tot}=2N\varepsilon\left[12.13\cdot\left(\frac{\sigma}{R}\right)^{12}-14.45\left(\frac{\sigma}{R}\right)^{6}\right]$$

$$U_{tot}(R_0)=-2.15\cdot 4\cdot N\cdot\varepsilon$$

Quantum mechanical correction

28, 10, 6, 4 %

Ne, Ar, Kr, Xe

가벼우면 correction 크다.

Ionic crystals

$Li: 1s^2 2s$ $\quad Li^+: 1s^2$

$F: 1s^2 2s^2 p^5$ $\quad F^-: 1s^2 2s^2 2p^6$

Helium and *Neon*

$Na+5.14eV \rightarrow Na^+ + e^-$

$e^- + Cl \rightarrow Cl^- + 3.61eV$

$Na^+ Cl^- \rightarrow Na^+ Cl^- + 7.9eV$

서로 *neutral*로 있는 것보다 얼마나 안정되어 있나

$$Na+Cl\rightarrow Na^+ + Cl^- + 7.9 + 3.61 - 5.14$$

$$\rightarrow Na^+ + Cl^- + 6.4eV$$

Electrostatic or Madelung Energy.

$$U_i = \sum_j U_{ij}$$

$j=i$ 빼놓고 모두 더한다

*Repulsive interaction*을 *nearest nbd*에만 적용

$$U_{ij} = \lambda \exp\left(-\frac{R}{\rho}\right) - \frac{q^2}{R} \quad (nearest\ \ nbd)$$

$$\text{or} = \pm \frac{1}{p_{ij}} \frac{q^2}{R} \quad (otherwise)$$

$$U_{tot} = NU_i$$

$$= N\left(z\lambda e^{\frac{R}{\rho}} - \frac{\alpha q^2}{R} \right)$$

$$\alpha \equiv \sum{}' \frac{\pm 1}{p_{ij}} \equiv \text{Madelung constant}$$

At equilibrium

$$\frac{dU_{tot}}{dR} = 0$$

$$N\frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho} \exp(-R/\rho) + \frac{N\alpha q^2}{R^2} = 0$$

$$\therefore R_0^2 \exp(-R_0/\rho) = \rho\alpha q^2/2\lambda$$

$$U_{tot} = N\left(z\lambda e^{-R_0/\rho} - \frac{\alpha q^2}{R_0} \right) \quad \text{at equilibrium}$$

$$= N\left(z\lambda \cdot \frac{\rho\alpha q^2}{z\lambda R_0^2} - \frac{\alpha q^2}{R_0} \right)$$

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

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

Evaluation of the Madelung constant

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

$$\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots \right] = 2\ln 2 \cong 1.386$$

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

Covalent crystals.

Covalent band:

electron forming the bond tend to be partially localized in the region between two atoms joined by the bond

가장 강할 때: spin이 반대방향일 때... Pauli의 배타원리에 의해.

spin-dependent coulomb energy:exchange energy.

예 Cl_2 거리 2Å

Ar Solid 3.76Å

C, Si, Ge: 4개의 전자가 모자란다.

electron contribution of carbon : $1S^2 2S^2 2P^2$

tetrahedral system: $1S^2 2S^2 2P^3$

binding energy of Metal

Metals alkali metal < alkali Halaid.

Metal: highly conductive, 한 원자당 1개 내지는 2개의 자유전자

conduction elenctron의 K.E.가 낮게 하기 위해서 interatomic distance가 크다. binding은 약하다.

transition metal: inner electron shell에 의해 binding이 된다.

d-electron의 binding은 세다.

Hydrogen bonds.

hydrogen bond: ionic in character

most electronegative atoms.

Atomic Radii.

atom 사이거리는 X-ray로 10^{-5}정도까지 잰다.

A가 얼마이고 B가 얼마인지... answer no.

not rigid spherical boundary

그러나 interatomic spacing을 예측할 수 있다.

NaF: Na^+ 0.97Å
F^- 1.36Å ∴2.33Å,

interatomic spacing 2.32Å

$Na + F$ = 2.58Å 보다 훨씬 정확.

diamond에서 C사이의 거리: 1.54Å 그반은 0.77Å

Si의 반은 1.17Å

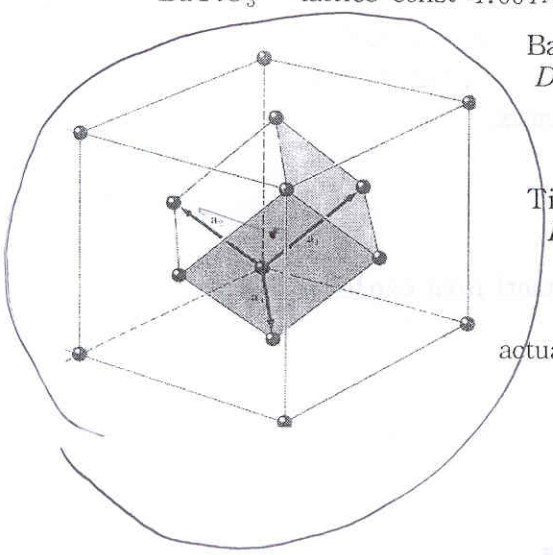
SiC : 1.94Å인데, 1.89Å(exp)와 거의 비슷

Ionic Crystal Radii에서 거리 구하는 법

$D_N = R_C + R_A + \Delta_N$

$BaTiO_3$ lattice const 4.004 Å

Correction for the coordination number



BaO

$D_{12} = 1.35 + 1.40 + 0.19 = 2.94$ Å

$\Delta_{12} = 0.19$

or $a = 4.16$ Å

TiO contact에 의하면

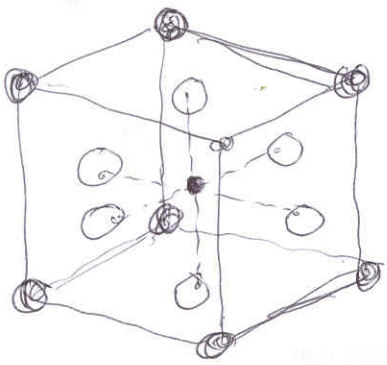
$D_6 = 0.68 + 1.40 = 2.08$ $\Delta_6 = 0$

$a = 4.16$ Å

actual estimate: 이것보다 작다.

bonding이 (100%) ionic이 아니고,

partially covalent이다.



$Ti \; Ba \; O_3$