ionization energy $Na \rightarrow Na^+$: 5.14 eV Table 5

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electron affinity $Cl \rightarrow Cl^-$: 3.61 eV table 6

Madelung constant NaCl $\alpha = 1.747565$ p. 65

R_0 nearest neighbor distance = 2.820 Å table 7

ρ repulsive parameter = 0.321 Å table 7

Ionic $U = \sum \left[-\frac{q^2 \alpha}{R} + z\lambda e^{-\frac{R}{\rho}} \right]$

(z ↑ coordination number)

Coulomb energy $= -\frac{k_e q^2}{R_0} = -5.1063 \text{ eV}$

$k_e = 8.987 \times 10^9 \ldots$ $q = e = 1.60219 \times 10^{-19}$ C

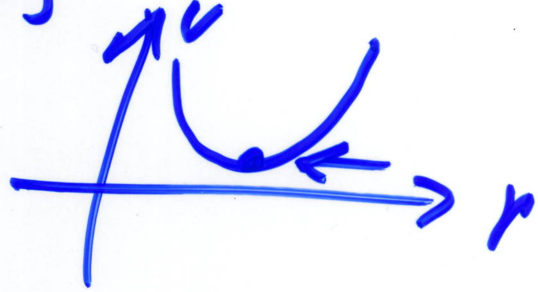
$$\text{Madelung energy} = -\frac{k_e q^2 \alpha}{R_0} = -8.9236\ eV$$

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

Eq 3-24

↑

V at minimum



$$\text{Lattice energy} = -7.9078\ eV$$

This is the difference between

Na^+ ⟷ ∞ Cl^- and  NaCl

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Cohesive energy

= |Lattice energy| − ionization energy + electron affinity

$= +7.9078\ eV - 5.14\ eV + 3.61\ eV$

$= \underline{6.378\ eV}$

Covalent Crystals

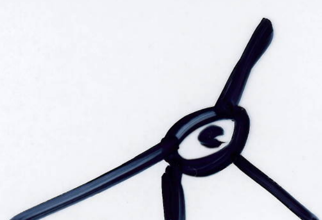
Bond is formed from 2 electrons, one from each atom.

electron spins are antiparallel
↑↓ (Pauli exclusion)

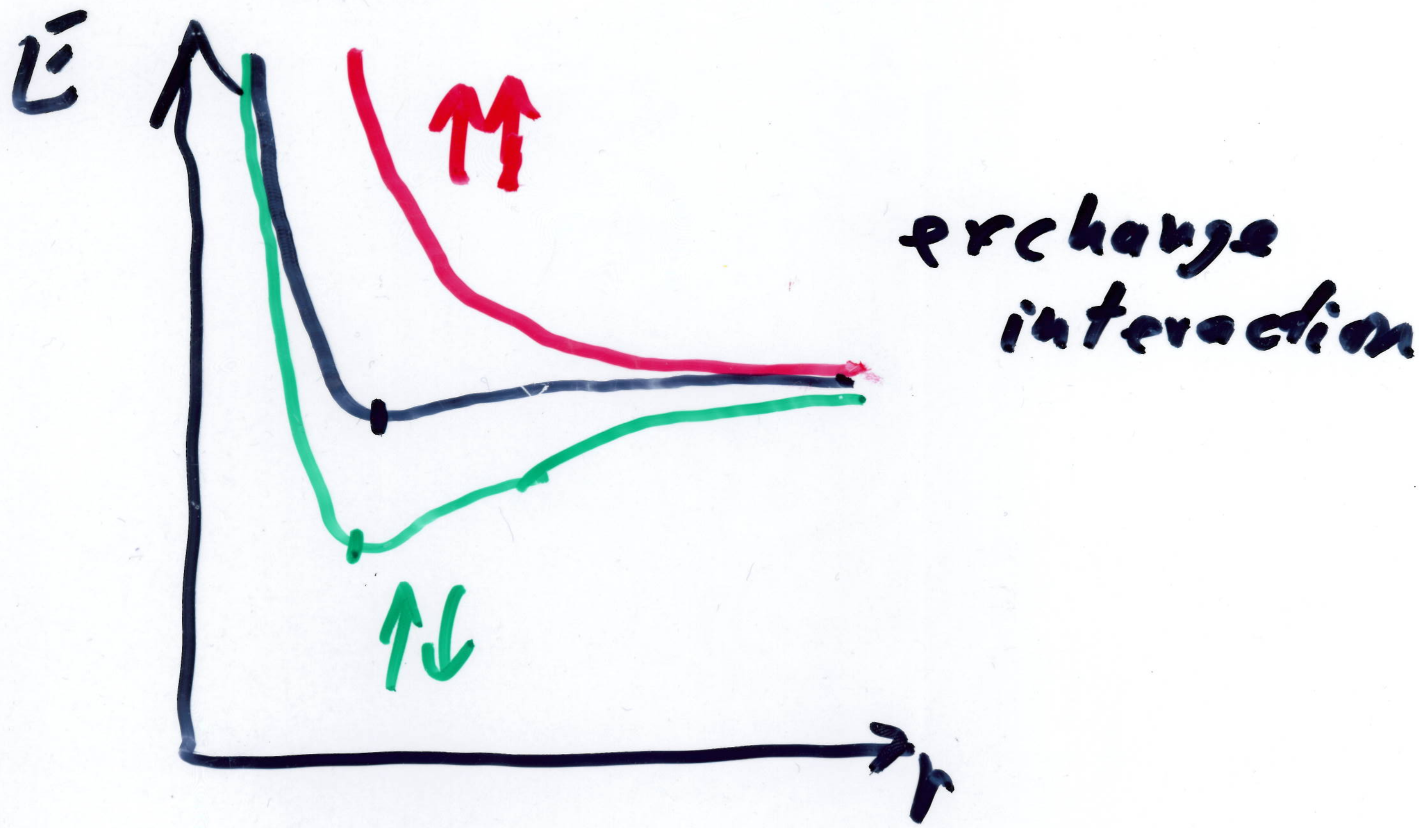
Covalent bonds are very strong like ionic bonds, not like the weak van der Waals bonds.

Real materials - bond is some fraction ionic, some fraction covalent.

Covalent bonds are highly directional → low packing fraction

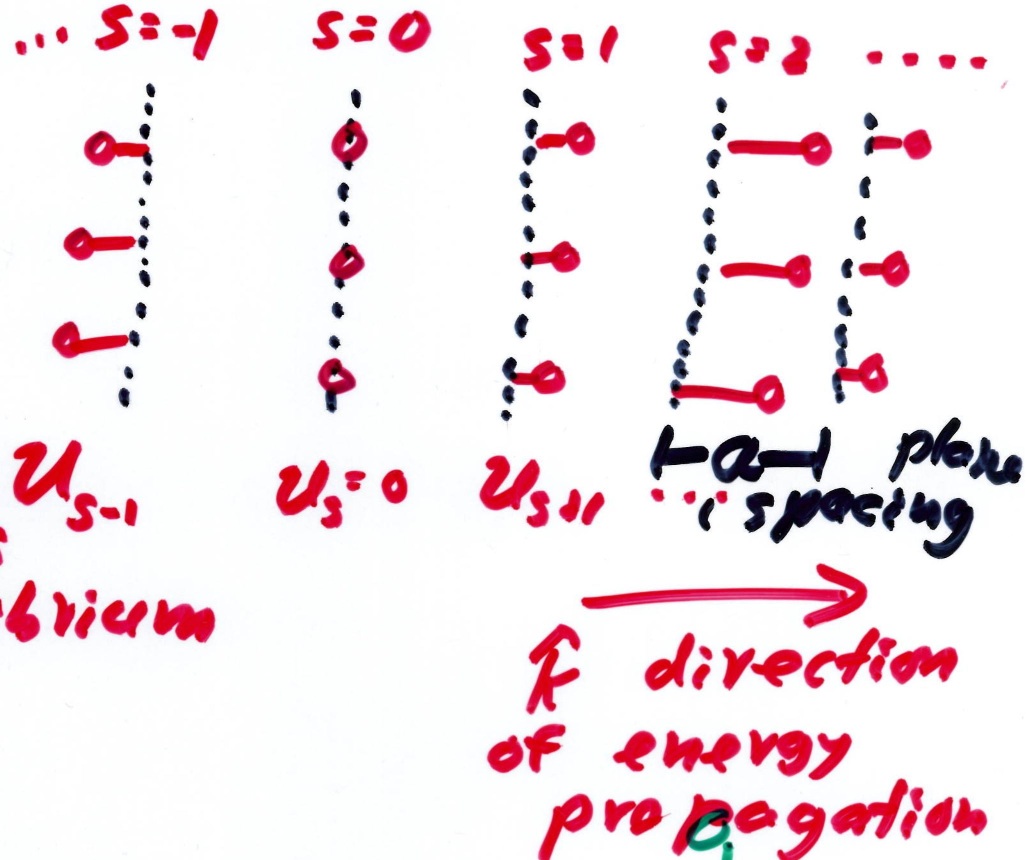


34% vs. 74% for fcc


E
↑↑
↑↓
r
exchange interaction

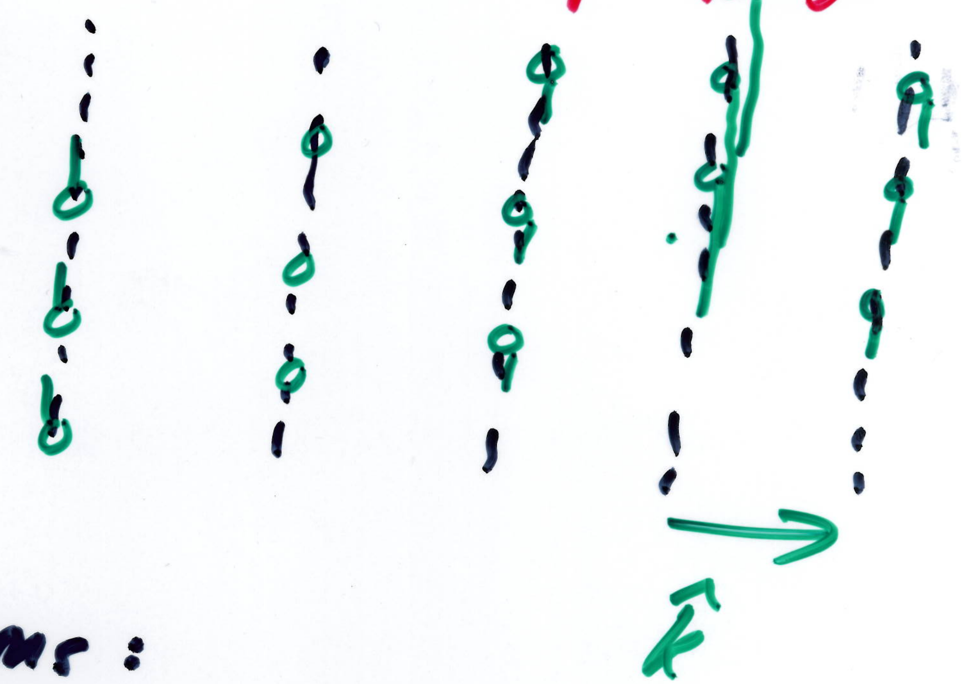
Phonons

Longitudinal wave



displacements from equilibrium

Transverse wave



Assumptions:

- nearest neighbor interaction <u>only</u>.
- force on a given atom is proportional to the displacement. Hooke's law.

Generic Potential

taylor expand around minimum

(choose = 0)

$$U(r) = \cancel{U_0} + \cancel{\frac{dU}{dr}}(r-r_0) + \frac{1}{2!}\frac{d^2U}{dr^2}\cdot(r-r_0)^2$$

($\frac{dU}{dr} \to 0$ at minimum)

$$= C\,u^2 + \cdots$$

↑ spring constant

Force on an atom in the s-plane

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)$$

$$M\frac{d^2u_s}{dt^2} = C\left[u_{s+1} - 2u_s + u_{s-1}\right]$$

Difference (not differential) equation.

Expect sinusoidal waves time dependence $e^{-i\omega t}$

$$u_s \propto e^{-i\omega t} \qquad \frac{d^2 u_s}{dt^2} = -\omega^2 e^{-i\omega t} = -\omega^2 u_s$$

time part

$$M \frac{d^2 u_s}{dt^2} = C\left[u_{s-1} - 2u_s + u_{s+1}\right]$$

$$-M\omega^2 u_s = C\left[u_{s-1} - 2u_s + u_{s+1}\right]$$

---

space part

$$u_s = A e^{ikx_s} = A e^{ikas}$$

$$u_{s+1} = A e^{ika(s+1)} = A e^{ikas} \cdot e^{ika}$$

$$u_{s-1} = A e^{ikas} \cdot e^{-ika}$$

$$-M\omega^2 A e^{ikas} = C e^{ikas} A \left[e^{-ika} - 2 + e^{ika} \right]$$

$$-M\omega^2 = C\left[2\cos(ka) - 2\right]$$

$$\omega^2 = \frac{2C}{M}\left[1 - \cos(ka)\right]$$

$$\omega^2 = \frac{4C}{M} \sin^2(ka)$$

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin(ka) \right|$$

Dispersion relation