Ch. 19
Ch. 20

Classification of solids

Lecture 10

Bindings

Type	Forces	Potential shape	Example
Metallic	Coulomb + Pauli principle		Na
Ion	Electrostatic	$\pm \frac{1}{r}$	NaCl
Covalent	Orbital overlap	directional "bonds" 	C (diamond)
Molecular	× Permanent dipole × Induced dipole (van der Vaal)	$\frac{1}{r^{12}} - \frac{1}{r^6}$ core repulsion / dipole	He

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Covalent crystals

Orbitals share electrons

{ bonding orbitals filled
{ antibonding orbitals empty

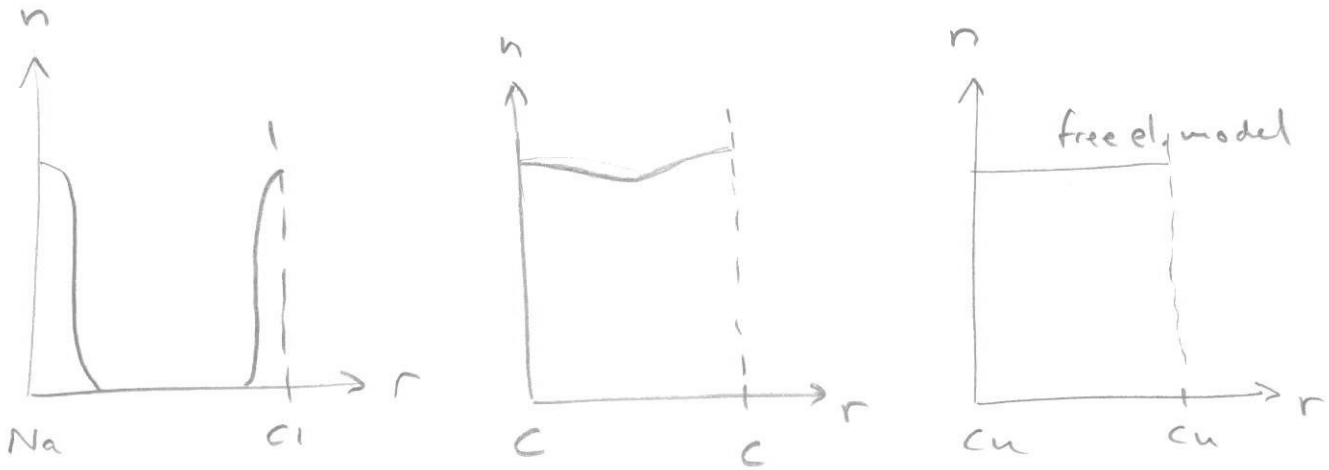
Ex. Diamond 

4 bonding directions
2el at each bond (one from each atom)

sp^3-hybridization

1 s-orbital } ⇒ 4 sp^3 orbitals
3 p-orbitals }

Characteristic electron density between nearest neighbors



Ion binding — Repulsive term: core shells overlap → short-range force $\left(\sim \frac{1}{r^{12}}\right)$

Attractive: Electrostatic energy

$$\mathcal{E} = \frac{e^2}{4\pi\varepsilon_0} \sum_\nu \frac{(\pm 1)}{r_\nu} = \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{R_0} \sum \frac{(\pm 1)}{r_\nu'}$$

(±1): attractive or repulsive term

r_ν': normalized distance

$\sum \frac{(\pm 1)}{r_\nu'} = \alpha$ Madelung constant

$\sum_\nu$: sum over all ions

r_ν: distance between ions

R_0: nearest neighbor distance

$$\alpha = \left\{ \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \cdots \right\}$$

Bad way of summing → edge effects due to surface charge

Charge-neutral summing

$\Longrightarrow$ $\alpha = 1.747$ for NaCl, for instance.

Van der Waals binding

Electrical field due to dipole (dipole) $\sim \frac{P_1}{r^3}$

The field polarizes a second dipole

$$P_2 = \alpha \cdot E \sim \frac{\alpha P_1}{r^3}$$

(α: polarizability)

Energy due to dipole-dipole interaction

$$\varepsilon \sim \frac{P_1 P_2}{r^3} \sim \alpha \cdot \frac{P_1^2}{r^6}$$

Atoms $\langle p_1 \rangle = \langle p_2 \rangle = 0$ time averages

Molecular binding potential

$$U(r) = -\frac{C_1}{r^6} + \frac{C_2}{r^{12}}$$

"Lennard-Jones potential"

$-\frac{C_1}{r^6}$: Van der Waal

$\frac{C_2}{r^{12}}$: ion core overlap

Derivative with respect to r

$$\frac{dU}{dr} = 0 \Longrightarrow \text{binding distance } r_0$$

$$U(r_0) \Longrightarrow \text{binding energy}$$

Metallic bonding

$$\varepsilon = \varepsilon_a + \varepsilon_r + \varepsilon_{kin}$$

attractive	repulsive	kinetic
$\varepsilon_a < 0$	$\varepsilon_r > 0$	$\varepsilon_{kin} > 0$
Coulomb (ion)	within el. gas	kinetic energy of the valence electrons
$\sim \frac{1}{r}$	$\sim \frac{1}{r}$	$\sim \frac{1}{r^2}$
(ions do not sense each other)		

$$n = \frac{N}{V} = \frac{N_{ions} \cdot z}{V}$$ (z: valence)

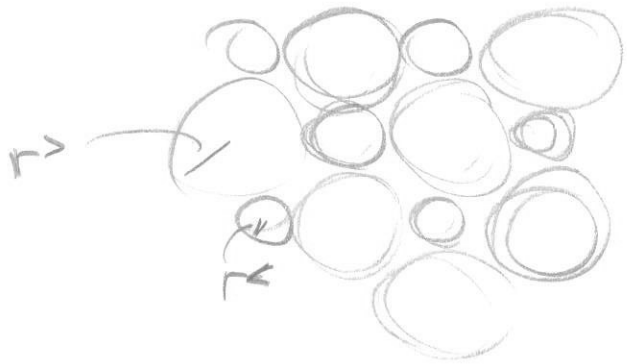
$$k_F = (3\pi^2 n)^{1/3} \implies k_F^3 \sim \frac{1}{V}$$

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} \implies \varepsilon_F \sim \left(\frac{1}{V}\right)^{2/3} \sim \frac{1}{r^2}$$

$$\frac{d\varepsilon}{dr} = 0 \quad \text{gives} \quad r_0$$

Ionic radii

Ionic crystals ~ hard spheres



ions with closed shells

⇓

hard to let electron enter because high energy of free orbitals

Ion size mainly given by d-band.

Negative ions typically larger.

Nearest neigbor distance = $r^< + r^>$

Unless $r^<$ so small that the ions cannot touch at all

("lattice of touching $r^>$-ions")