Chapter 12

A crystalline solid consists of a large number of atoms arranged in a regular array.

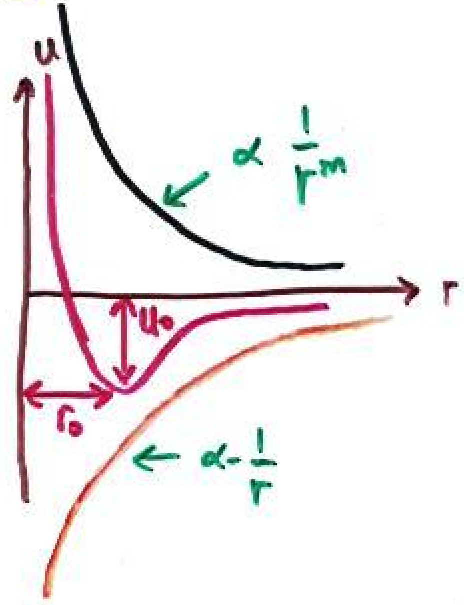
Bonding mechanisms in solids are:

Ionic solids such as NaCl crystal. The total potential energy per ion pair is:

$$U = \underbrace{-\alpha \frac{ke^2}{r}}_{\text{attraction term}} + \underbrace{\frac{B}{r^m}}_{\text{repulsion term}}$$

α

α: Madelung Constant



at $r=r_0$: $U \rightarrow U_0 = -\alpha \frac{ke^2}{r_0}\left(1-\frac{1}{m}\right)$

U_o: "ionic cohesive energy" of the solid is the energy required to pull the solid apart into its constituent ions.

"The atomic cohesive energy" is the energy required to pull the solid apart into its constituent atoms.

Ionic crystals are fairly hard, high melting points, strong cohesive energies.

Covalent solids such as diamond in which atoms are covalently bonded. They are very hard, high melting points and high cosehive energies.

Metallic solids are held together by metallic bonds which arises from the attractive force between the positive ion cores and the negative electron "gas". They are softer and have high electrical and thermal conductivity

Molecular solids are held together by Vander Waals or dipole-dipole forces. They generally have low melting points and low cohesive energies.

Drude and Tompson proposed the classical free-electron model of metals to calculate the electrical and thermal conductivities.

According to their model, the electrical conductivity σ is given by

$$\text{\# of free electrons/cm}^3 \longrightarrow \quad \sigma = \frac{n e^2 L}{(3 k_B T m_e)^{1/2}} \longleftarrow \text{mean free path}$$

temperature (K)

and the resistivity ρ is given by

$$\rho = \frac{1}{\sigma} = \frac{\sqrt{3 k_B m_e}}{n e^2 L} \sqrt{T} \propto \sqrt{T}$$

However experimental measurements shows that

$\rho \propto T$!

furthermore σ calculated is different from σ measured by one order of magnitude!

If L is replaced by the quantum mean free path and v_{rms} is replaced by the Fermi velocity $\Rightarrow$ $\sigma_{measured} = \sigma_{calculated}$!

How to calculate the number of free electrons / cm³.

$$V = \frac{m}{\rho} = \frac{\overset{\overset{1}{\shortparallel}}{n}\, M}{\rho} = \frac{M\,(g/mole)}{\rho\,(g/cm^3)} \Rightarrow cm^3/mole$$

volume of one mole

$$n = \frac{N_A\,(electrons/mole)}{V\,(cm^3/mole)} \Longrightarrow \left(\frac{electrons}{cm^3}\right)$$

Example: $\underline{\underline{Cu}}$

$M = 63.5\ g/mole$

$\rho = 8.95\ g/cm^3$

$$n = N_A \times \frac{\rho}{M} = 6.02\times10^{23} \times \frac{8.95}{63.5} \simeq 8.5\times10^{22}\ e^-/cm^3.$$