



Physical Metallurgy Principles

Chapter 3. CRYSTAL BINDING



Crystal Binding

Crystalline Solid

- a. Ionic
- b. Van der waals
- c. Covalent
- d. metallic

Internal Energy

- ① Lattice E : Lattice E is defined as the potential energy due to the electrostatic attractions and repulsions that exert on one another.
- ② Thermal E : There is the thermal energy of the crystal, associated with the vibrations of the atoms about their equilibrium lattice positions.

At $0K$, thermal E can be neglected.

Crystal Binding

Born Theory

Attractive force

$$f = \frac{ke_1e_2}{(r_{12})^2} \qquad \phi = \frac{ke_1e_2}{r_{12}}$$

Total P.E. of a single ion in NaCl type

$$\phi = \phi_M + \phi_R \qquad \phi = -\frac{Az^2e^2}{r} + \frac{Be^2}{r^n}$$

For 1 mole of NaCl

$$U = -\frac{ANz^2e^2}{r} + \frac{NBe^2}{r^n}$$

For single ion of NaCl X-tal

$$\phi_M = -\frac{e^2A}{r} \qquad (\because z^2 = 1)$$

Crystal Binding

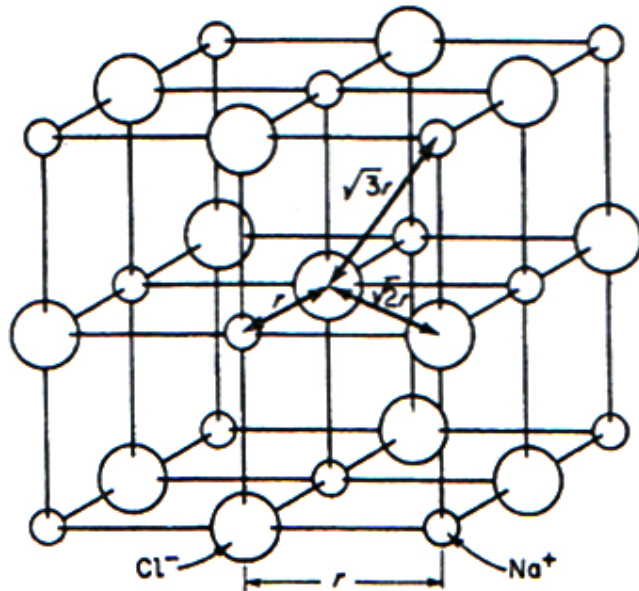


Fig. 3.4. Interionic distances in the sodium chloride lattice.

Around each negative chlorine ion there 6 positive sodium atoms at a distance of r .

\therefore Total attractive energy between Cl and Na is,
$$-\frac{6e^2}{r}$$

The next closest ions to a given chlorine ion are 12 other negatively charged chlorine ions at a distance $\sqrt{2}r$.

\therefore repulsive energy $\cong \frac{12e^2}{\sqrt{2}r}$

Following this there are 8 sodium ions at a distance of $\sqrt{3}r$, 6 chlorine ions at $\sqrt{4}r$, 24 sodium atoms at $\sqrt{5}r$, etc.

Crystal Binding

$$\therefore \phi_M = -\frac{6e^2}{\sqrt{1}r} + \frac{12e^2}{\sqrt{2}r} - \frac{8e^2}{\sqrt{3}r} + \frac{6e^2}{\sqrt{4}r} - \frac{24e^2}{\sqrt{5}r} \dots\dots\dots$$

OR,

$$\phi_M = -\frac{Ae^2}{r} = -\frac{e^2}{r} [6 - 8.45 + 4.62 - 3.00 + 10.7\dots\dots]$$

$\therefore A$ (madelung number) = 1.7476 for NaCl

$$\therefore \phi_M = -\frac{1.7476e^2}{r}$$

Ex) CsCl $A=1.7626$

Zns $A=1.6381$

Crystal Binding

Repulsive energy for a single ion

$$\phi_R = \frac{Be^2}{r^n}$$

In this term the two quantities, B and n, must be evaluated. This can be accomplished with the aid of two experimentally determined quantities: r_0 , the equilibrium interionic separation at 0K; and K_0 , the compressibility of the solid at 0K.

($r_0 = 0.282\text{nm}$ for NaCl, XRD)

$$\begin{aligned} \textcircled{1} \text{ At } r_0, \quad \sum f_i (\text{net force}) &= 0 \\ \therefore \left(\frac{d\phi}{dr} \right)_{r=r_0} &= \frac{d}{dr} \left(-\frac{Ae^2}{r} + \frac{Be^2}{r^n} \right) = 0 \end{aligned}$$

$$\textcircled{2} \quad K_0 = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Crystal Binding

Re) The subject of material science

$$\phi(\Delta r) = \phi_{r=r_0} + \left(\frac{d\phi}{dr} \right)_{r=r_0} \Delta r + \frac{1}{2} \left(\frac{d^2\phi}{dr^2} \right)_{r=r_0} \Delta r^2 + \dots$$

$$\therefore \phi(\Delta r) = \phi_{r=r_0} + \frac{1}{2} \left(\frac{d^2\phi}{dr^2} \right)_{r_0} \Delta r^2$$

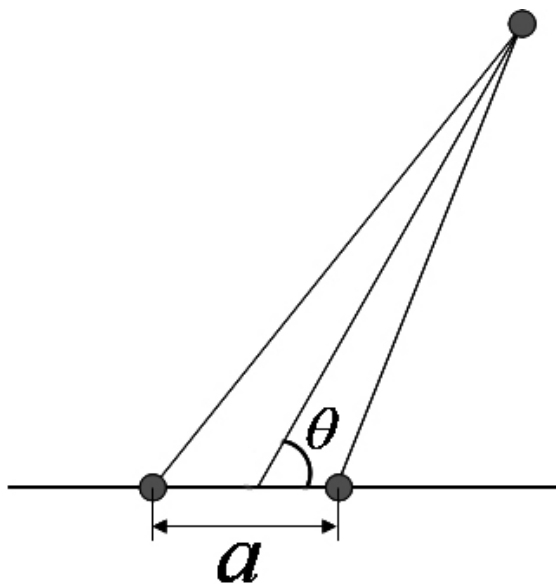
$$force = - \frac{d\phi(\Delta r)}{d(\Delta r)} = - \left(\frac{d^2\phi}{dr^2} \right)_{r_0} \Delta r$$

Elastic modulus

Crystal Binding

Van Der Waals Crystals

Van der waals force ← Nonsymmetrical charge distribution



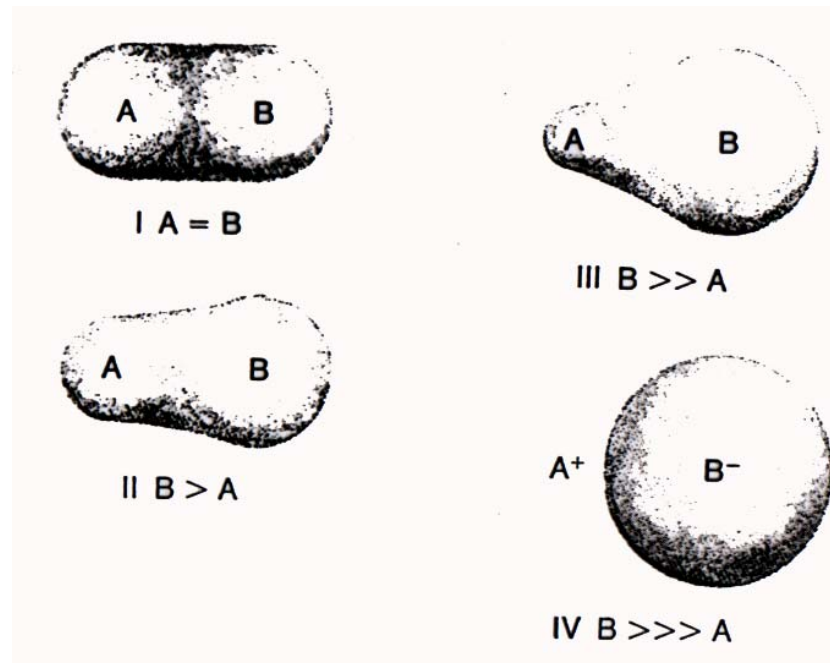
$$E_r = \frac{2e_1 a \cos \theta}{r^3}$$

$$E_\theta = \frac{2e_1 a \sin \theta}{r^3}$$

$$\left. \begin{array}{l} E_r \\ E_\theta \end{array} \right\} \rightarrow E \propto \frac{\mu}{r^3}$$

$$\mu \text{ (dipole moment)} = e_1 \cdot a$$

Crystal Binding

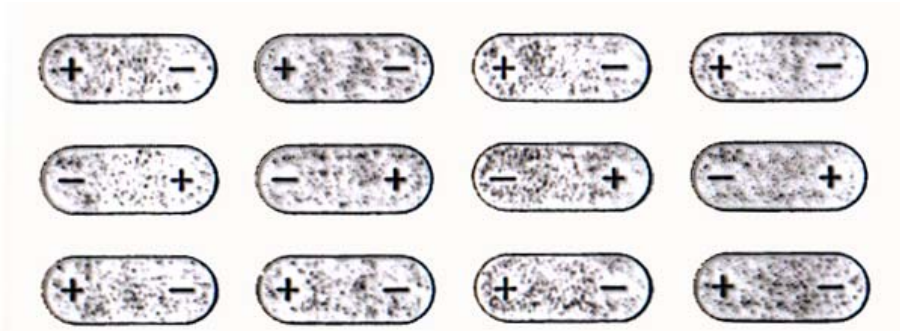


Electron sharing as a function of electronegativity differences

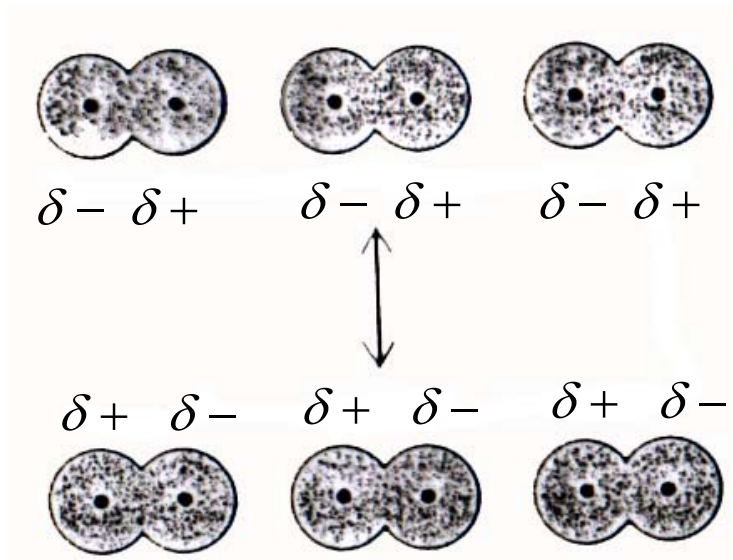
Because of unequal sharing of the electrons and the molecular shape, the electron cloud is not distributed symmetrically about the atoms on the molecule.

Dipole

Crystal Binding



Orientation of polar molecules in crystal



The origin of van der waals force

Dipole- Dipole

Attraction



Van der waals force

Crystal Binding

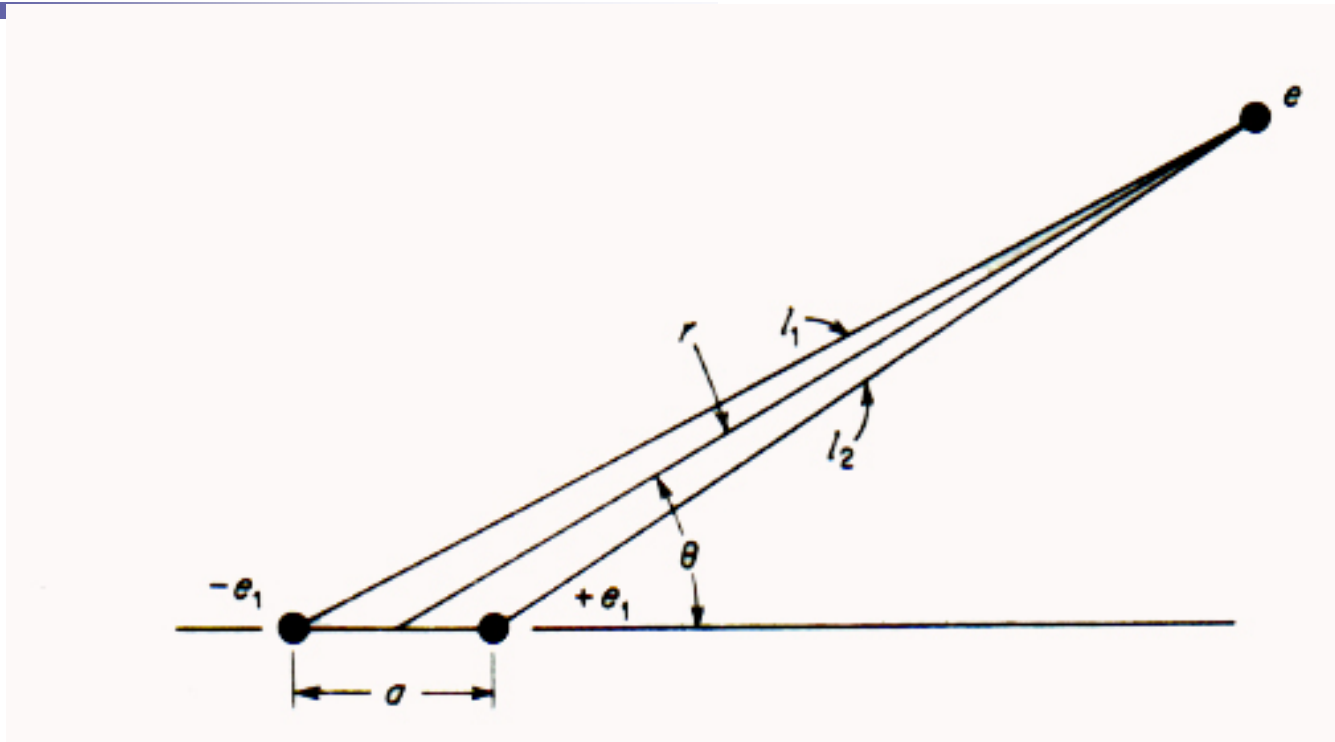


Fig. 3.6 An electrical dipole

$$F = - \frac{e_1 e}{l_1^2} + \frac{e_1 e}{l_2^2}$$

Crystal Binding

Induced Dipoles

$$\mu_I = \alpha E$$

$$\phi \approx \alpha \frac{\mu^2}{r^6}$$

Debye Frequency

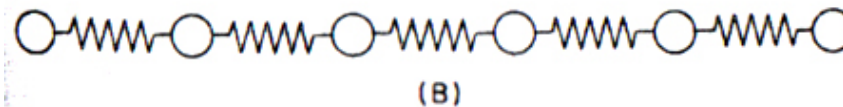
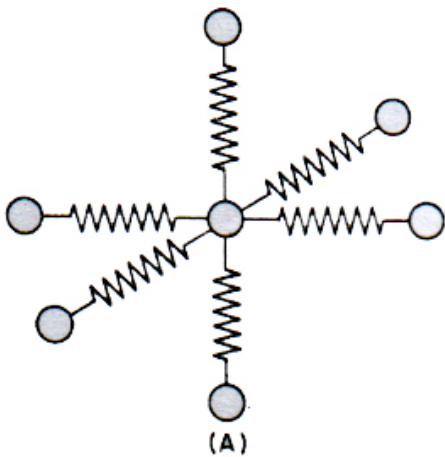


Fig. 3.8

(A) Debye model of a simple cubic crystal pictures an atom as a joined to its neighbors by springs.

(B) A one dimensional crystal model.

$$\lambda_{\min} = 2a \quad \therefore v_m = \frac{v}{\lambda} \quad (v : \text{the velocity of the shortest sound waves})$$

Crystal Binding

Zero Point Energy

In the case of linear array of N_x atoms, there will $\frac{1}{2}N_x$ wavelengths when the array vibrates at its maximum frequency.

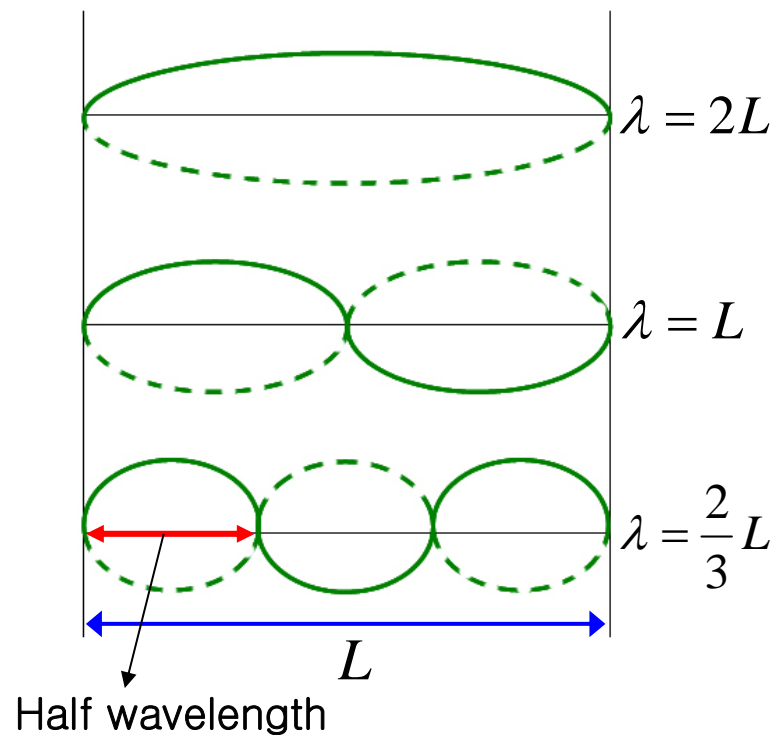
In the three-dimensional case the number of modes possessing frequencies in the range ν to $\nu + d\nu$ is given by

$$f(\nu)d\nu = \frac{9N}{\nu_m^3} \nu^2 d\nu$$

$$\therefore E_z = \int_0^{\nu_m} f(\nu) \frac{h\nu}{2} d\nu = \frac{9}{8} N h \nu_m$$

Crystal Binding

Standing waves in a string



In a simple string, the number of harmonics is theoretically infinite, and there is not lower limit for the wavelengths that might be obtained, but this is not true when a series of masses connected by springs are caused to vibrate.

The minimum wavelength is obtained when neighboring atoms vibrate against each other. (Fig. 3.9)

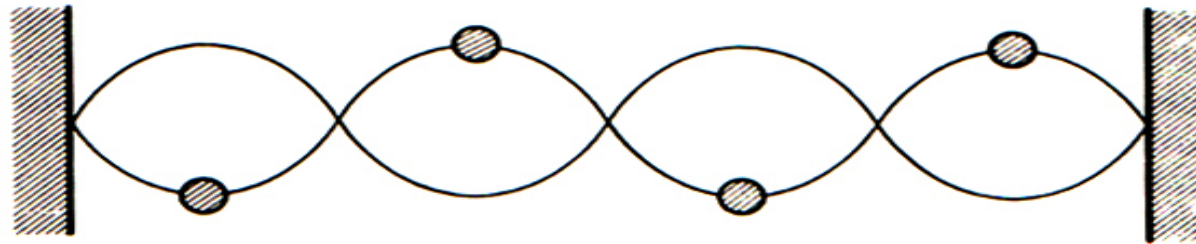


Fig. 3.9. The highest frequency vibration mode for and an array of four masses.

$$\lambda_{\min} = 2a \quad (a : \text{the interatomic spacing})$$

$$\therefore v_m = \frac{v}{\lambda} \quad (v : \text{the velocity of the shortest sound waves})$$