Ionic Crystals

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May 11, 2020

The cohesive energy of a crystal is defined as the energy that must me added to separate its components into neutral free atoms at rest, at infinite separation with the same electronic configuration. Lattice energy is defined as the energy that must be added to a crystals to separate its component ions into free ions at rest at infinite separation.

1 Ionic Crystals

Ionic crystals are made up of positive and negative ions. The ionic bond is a result of the electrostatic interaction of oppositely charged ions. The ionic crystals normally occur in two crystal structures, the sodium chloride and cesium chloride structures.

The electronic configuration of all ions of an ionic crystal corresponds to inert gas atoms. Inert gas atoms have closed shells with spherically symmetric charge distribution. The charge distribution of each ion in an ionic crystal is expected to have approximately spherical symmetry, with some distortions in the regions of contact with the neighbouring atoms. This has been confirmed with X-ray diffraction studies.

1.1 Electrostatic Energy or Madelung Energy

The long-range interaction between ions with charge $\pm q$ is the electrostatic interaction $\pm\frac{q^2}{4\pi\epsilon_0 r}$, attractive between ions of opposite charge and repulsive between ions of same charge. The ions in the crystal arrange themselves such that the attractive forces balance the repulsive forces between the ion cores. The main contribution to the binding energy of ionic crystals is electrostatic and is called Madelung energy. If U_{ij} is the interaction

energy between ions i and j, we define a sum U_i which includes all interactions involving the ion i:

$$U_i = \sum_i {}' U_{ij} \tag{1}$$

where the summation includes all ions except j=i. We suppose that U_{ij} may be written as the sum of a central repulsive potential of the form $\lambda \exp(-r/\rho)$, where λ and ρ are empirical parameters, and a coulomb potential $\pm \frac{q^2}{4\pi\epsilon_0 r}$

$$\therefore U_{ij} = \lambda \exp(-\frac{r_{ij}}{\rho}) \pm \frac{q^2}{4\pi\epsilon_0 r} \tag{2}$$

where + sign is taken for like charges and – sign for unlike charges. The repulsive term describes the fact that each ion resists overlap with the electron distribution of neighbouring ions.

λ and ρ are constants to be defined from observed values of the lattice constant and compressibility. ρ is a measure of the range of the repulsive interaction; when $r = \rho$ the repulsive interaction is reduced to e^{-1} of the value at $r = 0$. neglecting surface effects, the total lattice energy U_{tot} of a crystal composed of N molecules or 2N ions can be written as

$$U_{tot} = NU_i \tag{3}$$

Here N, rather than 2N occurs, because we must count a pair of interactions only once or each bond only once.

The total lattice energy is defined as the energy required to separate the crystal into individual ions at an infinite distance apart. Let us introduce a quantity p_{ij} such that

$$r_{ij} = p_{ij} R \tag{4}$$

where R is the nearest neighbour separation in the crystal. If we include the repulsive interaction only among nearest neighbours

$$U_{ij} = \begin{cases} \lambda \exp(-\frac{R}{\rho}) - \frac{q^2}{4\pi\epsilon_0 R}, & \text{(nearest neighbours)} \\ \pm \frac{q^2}{p_{ij} 4\pi\epsilon_0 R}, & \text{(otherwise)} \end{cases} \tag{5}$$

Thus

$$U_{tot} = NU_i = N(Z\lambda e^{(-\frac{R}{\rho})} - \frac{\alpha q^2}{4\pi\epsilon_0 R}) \tag{6}$$

where Z is the number of nearest neighbours of any ion and

$$\alpha = \sum_j{}' \frac{(\pm)}{p_{ij}} \equiv \text{Madelung Constant} \tag{7}$$

For a stable crystal α should be positive. If we take the reference ion as a negative charge, the plus sign will apply to positive ions and minus sign to negative ions. An equivalent definition is

$$\frac{\alpha}{R} = \sum_j{}' \frac{(\pm)}{r_j} \tag{8}$$

where r_j is the distance of the j^th ion from the reference ion and R is the nearest neighbour distance. The value of α will depend on whether it is defined in terms of nearest neighbour distance R or in terms of lattice parameter 'a'. At the equilibrium separation $\frac{dU_{tot}}{dR}|_{R=R_0} = 0$

$$N\frac{dU_i}{dR} = -\frac{NZ\lambda}{\rho}\exp(-\frac{R}{\rho}) + \frac{N\alpha q^2}{4\pi\epsilon_0 R^2} = 0 \tag{9}$$

$$R_0^2 \exp(-\frac{R_0}{\rho} = \frac{\rho\alpha q^2}{4\pi\epsilon_0 Z\lambda} \tag{10}$$

This determines the equilibrium separation R_0, if parameters ρ, λ of the repulsive interaction are known.

The total lattice energy of the crystal of 2N ions at their equilibrium separation R_0 may be written as using eqn 6 and eqn 10

$$U_{tot} = N(Z\lambda\frac{\rho\alpha q^2}{Z\lambda R_0^2} - \frac{\alpha q^2}{4\pi\epsilon_0 R_0})$$

$$U_{tot} = -\frac{N\alpha q^2}{4\pi\epsilon_0 R_0}(1 - \frac{\rho}{R_0}) \tag{11}$$

The term $-\frac{N\alpha q^2}{4\pi\epsilon_0 R_0}$ is the madelung energy

1.2 Computation of Madelung Constant

Compute madelung constant for the infinite line of ions of the alternating sign.

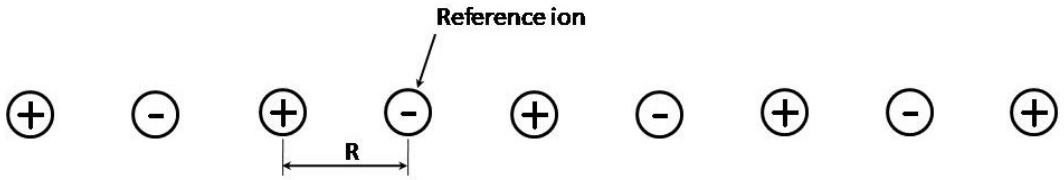

Figure 1: Linear ion Chain

Let us pick a negative ion as a reference ion and let R denote the distance between adjacent ions. Then

$$\frac{\alpha}{R} = \sum_j{}' \frac{(\pm)}{p_{ij}}$$

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

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

The factor of 2 comes because there are 2 ions, one to the left and one to the right at equal distace r_j. Using the expression of $\ln(1+x)$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$$

Put x=1,

$$\ln(2) = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots$$

$\therefore$ Madelung constant for one dimensional chain is

$$\alpha = 2\ln(2)$$

1.2.1 Madelung Constant of NaCl crystal

Consider a central Na^+ ion as reference ion having positive charge on it. This ion is surrounded by 6 Cl^- ions as first nearest neighbours, 12 Na^+ ions as second nearest neighbours and so on. Madelung constant can be written as summation series

$$\alpha = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \cdots$$

which converges to 1.74756.