

PHY 491, Homework 8
November 11, 2011

Problem 8.1

Problem #2, Chapter 3

Compares the subtle difference between different types of crystal structures for Lennard Jones solids.

$$E_{coh} = 4\varepsilon \left(\frac{C_2^2}{8C_1} \right)$$

$$C_1 = \sum_j \frac{1}{p_{ij}^{12}} = 12.13188 (FCC); 9.11418 (BCC)$$

$$C_2 = \sum_j \frac{1}{p_{ij}^6} = 14.45392 (FCC); 12.2533 (BCC)$$

$$E_{coh} = 4\varepsilon(2.1525); FCC$$

$$E_{coh} = 4\varepsilon(2.0592); BCC$$

$$\frac{(E_{coh})_{BCC}}{(E_{coh})_{FCC}} = \frac{2.0592}{2.1525} = 0.957$$

Problem 8.2

Problem #3, Chapter 3

$$\frac{E_{coh}}{mole} = 4\varepsilon(2.1525)N_A = 4 * 50 * 10^{-16} erg * \frac{10^{-7}J}{erg} * 6.022 * 10^{23}$$

$$\frac{E_{coh}}{mole} = 2.592 kJ$$

Problem 8.3

Problem #5, Chapter 3

Nice problem involving Madelung energy and repulsive energy for a 1-dimensional ionic crystal

$$U = N \left[\frac{zA}{R^n} - \frac{\alpha q^2}{R} \right]; \alpha = 2 \ln 2; z = 2$$

$$\frac{dU}{dR} = 0; R_0^{n-1} = \frac{2nA}{\alpha q^2}$$

$$U(R_0) = \frac{N}{R_0} \left[\frac{2A}{R_0^{n-1}} - \alpha q^2 \right]$$

$$U(R_0) = -\frac{2N \ln 2 q^2}{R_0} \left[1 - \frac{1}{n} \right]$$

Now we can expand $U(R)$ near $R=R_0$. The linear terms vanish because the first derivative of $U(R)$ vanishes at R_0 . The quadratic term is the first correction.

$$U(R) = U(R_0(1+\delta)) = N \left[\frac{zA}{R_0^n (1+\delta)^n} - \frac{\alpha q^2}{R_0(1+\delta)} \right]$$

$$U(R) = U(R_0(1+\delta)) = U(R_0) + \frac{1}{2} N \delta^2 \frac{(n-1)q^2 \ln 2}{R_0}$$

$$\frac{U(R)}{2N} = \frac{U(R_0)}{2N} + \frac{1}{2} C \delta^2; C = \frac{(n-1)q^2 \ln 2}{R_0}$$

Problem 8.4

Problem #7, Chapter 3

Nice problem about ionic solids and the stable ionic configuration.

We have to first calculate the Madelung energy when the charges are ± 1 (in units of electron charge) and when ± 2 . Here we will calculate energy/molecule, U/N , because we will correct for ionization energy and electron affinity for a molecule.

Madelung energy (ignore short range repulsion which is about 10% correction).

We will write the charge $q = \epsilon \epsilon_0$; $\epsilon = 1, 2$

FCC lattice

$$\frac{U}{N} = -\frac{\alpha q^2}{R_0} = -\frac{1.747565}{2.76} \left(\frac{e^2}{1.4^0} \right) \epsilon^2; \epsilon = 1, 2$$

$$\frac{U}{N} = -8.61 \text{ eV}; \epsilon = 1 \tag{1}$$

$$\frac{U}{N} = -34.44 \text{ eV}; \epsilon = 2 \tag{2}$$

Clearly the +2.-2 charge state has lower (more attractive and hence large cohesive energy) energy. But we have to compare this energy with that for isolated neutral Ba and O atoms.

Cohesive energy calculation

Charge states are +1,-1 ($\epsilon=1$)

$$\begin{aligned}Ba + 5.19 \text{ eV} &= Ba^{1+} + e \\O + e &= O^{1-} + 1.5 \text{ eV} \\Ba + O &= Ba^{1+} + O^{1-} + (1.5 - 5.9) \text{ eV}\end{aligned}\tag{3}$$

Using Eq.1 and Eq. 3, the cohesive energy of $Ba^{1+}O^{1-}$ is given by

$$E_{coh} = 8.61 - 4.1 = 4.51 \text{ eV}$$

Now consider the charge +2,-2

$$\begin{aligned}O + 2e &= O^{2-} + (1.5 - 9.0) \text{ eV} \\Ba + (5.19 + 9.96) \text{ eV} &= Ba^{2+} + 2e\end{aligned}$$

Putting these two equations together

$$Ba + O = Ba^{2+} + O^{2-} - 22.65 \text{ eV}\tag{4}$$

Using Eq.2 and Eq.4, the cohesive energy of $Ba^{2+}O^{2-}$ is given by

$$E_{coh} = 34.44 - 22.65 = 11.79 \text{ eV}$$

Cohesive energy of $Ba^{2+}O^{2-}$ is larger than that of $Ba^{1+}O^{1-}$. So the stable compound is indeed $Ba^{2+}O^{2-}$.