

Solid State 1 HW1

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1

We use the distance convention relative to the distance between the centers of adjacent cubes. The first four terms of the Madleung constant are then:

$$T1 : \frac{8}{\sqrt{3/4}} = 9.24 \quad (0.1)$$

$$T2 : -6 \quad (0.2)$$

$$T3 : \frac{-12}{\sqrt{2}} = -8.48 \quad (0.3)$$

$$T4 : \frac{24}{\sqrt{11/4}} = 14.47 \quad (0.4)$$

Alternatively, using the nearest-neighbor distance as 1:

$$T1 : 8 \quad (0.5)$$

$$T2 : -\frac{6}{\sqrt{2}} = -4.24 \quad (0.6)$$

$$T3 : -\frac{12}{2} = -6 \quad (0.7)$$

$$T4 : \frac{24}{\sqrt{11/2}} = 10.23 \quad (0.8)$$

The series is converging.

2

We use the Lennard-Jones potential with parameters $\epsilon = 50, \sigma = 2.74$. The total potential energy is given by Kittel 3.11:

$$U_{tot} = 2N\epsilon \left\{ \sum_j \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_{ij}R} \right)^6 \right\} \quad (0.9)$$

For the fcc and bcc crystals the constants are the same, and only the structure-dependent sums are different. For the fcc crystal:

$$\sum_j p_{ij}^{-12} \equiv p_{ij}^{-12} = 12.13 \quad (0.10)$$

$$\sum_j p_{ij}^{-6} \equiv p_{ij}^{-6} = 14.45 \quad (0.11)$$

For the bcc crystal:

$$\sum_j p_{ij}^{-12} \equiv p_{ij}^{-12} = 9.11 \quad (0.12)$$

$$\sum_j p_{ij}^{-6} \equiv p_{ij}^{-6} = 12.25 \quad (0.13)$$

The cohesive energy depends on the lattice distance R . The equilibrium value of R can be evaluated from the derivative of the potential energy:

$$\frac{dU}{dR} = 2N\epsilon \left\{ -\sigma^{12} (p_{ij})^{-12} 12R^{-12} + \sigma^6 (p_{ij})^{-6} 6R^{-7} \right\} = 0 \quad (0.14)$$

$$R_0 = \sigma \left\{ \frac{2p_{ij}^{-12}}{p_{ij}^{-6}} \right\}^{1/6} \quad (0.15)$$

The equilibrium value R_0 is 1.0902 for the fcc structure and 1.0684 for the bcc structure. We can now calculate the cohesive energies of the Ne structures:

$$U_{fcc} = -4.30341(2N\epsilon) \quad (0.16)$$

$$U_{bcc} = -4.1181(2N\epsilon) \quad (0.17)$$

$$\frac{U_{bcc}}{U_{fcc}} = 0.9569 \quad (0.18)$$

3

4

The cohesive energy per molecule of an ionic crystal (ignoring the repulsive term) is:

$$U_{tot} = -\frac{aq^2}{R} \quad (0.19)$$

For both Ba^+O^- and Ba^{++}O^- the internuclear distance is 2.76\AA and the Madelung constant is 1.75. For Ba^+O^- $q = e$, while for Ba^{++}O^- $q = 2e$.

Calculating the energies in SI and then converting to eV:

$$U_{Ba+O-} = -\frac{1}{4\pi\epsilon_0} \frac{ae^2}{R_0} = 1.46e^{-18}J = -9.12eV \quad (0.20)$$

$$U_{Ba++O--} = -\frac{1}{4\pi\epsilon_0} \frac{a(2e)^2}{R_0} = 5.84e^{-18}J = -36.48eV \quad (0.21)$$

A configuration will be stable if the cohesive energy plus the electron affinity of the negative ion are greater than the ionization potential of the positive ion. For Ba+O-, the configuration energy is $(-9.12 - 1.5 + 5.19 = -5.43eV)$ so the configuration is stable. For Ba++O- the configuration energy is $(-36.48 + 9 + 9.96 = -17.52eV)$ so it is stable as well. Since the lowest energy configuration is Ba++O- we expect that to be the valence configuration found in the BaO crystal.