Physics 460 Hmwk #3 Solutions

1. Kittel 3-2

For bcc

$$U_{tot} = \frac{1}{2} N \cdot (4\epsilon) \left[\sum_j{}' \left(\frac{\sigma}{P_{ij}R}\right)^{12} - \sum_j{}' \left(\frac{\sigma}{P_{ij}R}\right)^{6} \right]$$

$$= 2N\epsilon \left[9.11418 \left(\frac{\sigma}{R}\right)^{12} - 12.2533 \left(\frac{\sigma}{R}\right)^{6} \right]$$

for bcc $\sum_j{}' P_{ij}^{-12} = 9.11418$. $\sum_j{}' P_{ij}^{-6} = 12.2533$

$$U'_{tot}(R_0) = -2N\epsilon \left[12 \cdot 9.11418 \cdot \frac{\sigma^{12}}{R^{13}} - 6 \cdot 12.2533 \frac{\sigma^6}{R^7} \right) = 0$$

$$\Rightarrow \left(R_0/\sigma\right)^6 = \frac{12 \cdot 9.11418}{6 \cdot 12.2533} \Rightarrow R_0 = 1.06844$$

bcc: $U_{tot}(R_0) = -2N\epsilon \cdot 4.1184$

The result for fcc is $U_{tot}(R_0) = -2.15 (4N\epsilon)$ Kittel's eq 3-16

$$\therefore \frac{bcc}{fcc} \simeq 0.958$$

2. Kittel 3-4

In this problem, we need to investigate whether Na^+Na^- crystal (in NaCl structure) is stable.

From table 5, Ionization energy for Na is 5,14eV

From table 4 in chapter 1, nearest-neighbor distance for Na is $\overset{R_0}{\overset{\shortparallel}{3,659\ \text{Å}}}$

α in NaCl structure = 1,747565

$$\therefore \frac{U_{tot}}{N} = -\frac{\alpha q^2}{R_0}\left(1-\frac{\rho}{R_0}\right) = -\frac{1.7476}{3,659}\, 2\cdot 0,529 \overset{/\!/ 13,6\text{ev}}{\left(\frac{e^2}{2\cdot 0,529}\right)} \left(1-\frac{\rho}{R_0}\right)$$

$$= -6,873\text{eV}\left(1-\frac{\rho}{R_0}\right)$$

$$\underset{\text{gas}}{\text{Na}} + 5,14\text{eV} \longrightarrow \underset{\text{gas}}{\text{Na}^+} + e^-$$

$$\underset{\text{gas}}{\text{Na}} + e^- \longrightarrow \underset{\text{gas}}{\text{Na}} + 0,78\text{eV}$$

$$\underset{\text{gas}}{\text{Na}^+} + \underset{\text{gas}}{\text{Na}^-} \longrightarrow \underset{\text{crystal}}{\text{Na}^+\text{Na}^-} + 6,873\left(1-\frac{\rho}{R_0}\right)\text{ eV}$$

$$\underset{\text{gas}}{\text{Na}} + \underset{\text{gas}}{\text{Na}} \longrightarrow \underset{\text{crystal}}{\text{Na}^+\text{Na}^-} + \left(6.873\left(1-\frac{\rho}{R_0}\right) - 4,36\right)\text{eV}$$

ρ is usually of order $0,1 R_0$, putting $\rho \doteq 0,1 R_0$

$6,873(1-0,1) - 4,36 = \underline{1,826\text{ eV}}$ (per pair)

$\therefore$ Cohesive energy relative to separated atom is 0,913 eV/atom,

Comparing to the table of cohesive energies, we have for the metallic Na: 1,113 eV/atom, which is more stable.

3 Kittel 3-6

From table 7,

$$z\lambda = 2,05\times10^{-8}\ \mathrm{erg}\ , \quad \rho = 0,326\ \mathrm{Å}$$

where z is the number of nearest neighbors in NaCl structure, i.e $z=6$

$$\therefore\ \lambda = \frac{2,05}{6}\times10^{-8}\ \mathrm{erg} = \frac{2,05}{6}\times10^{-8}\cdot\frac{1}{1,602\times10^{-12}}\ \mathrm{eV} = 2,133\times10^{3}\ \mathrm{eV}$$

In cubic ZnS structure, $z=4$

From eq. (3-23) in Kittel,

$$R_0^2\exp(-R_0/\rho) = \rho\alpha q^2/z\lambda\ ,$$

we can determine the value of R_0 (Note $\alpha = 1,6381$)

$$R_0^2\, e^{-\frac{R_0}{0,326\ \mathrm{Å}}} = 0,326\ \mathrm{Å}\cdot1,6381\cdot\frac{1}{4\cdot2,133\times10^{3}\ \mathrm{eV}}\ \frac{e^2}{\mathrm{Å}}\ \mathrm{Å}$$

Note $\frac{1}{2}\frac{e^2}{0,529\ \mathrm{Å}} = 13,6\ \mathrm{eV}$

$$= 0,326\cdot1,6381\cdot\frac{1}{4\cdot2,133\times10^{3}}\ 2\cdot0,529\cdot13,6\ \mathrm{Å}^2$$

$$= 9,006\times10^{-4}\ \mathrm{Å}^2$$

R_0 can be solved to be $3,003$ Å (neglecting those unreasonable solutions)

Thus

$$\frac{U_{tot}}{N} = -\frac{\alpha e^2}{R_0}\left(1-\frac{\rho}{R_0}\right) = -\frac{1,6381}{3,003}\cdot2\cdot0,529\cdot13,6\cdot\left(1-\frac{0,326}{3,003}\right) = -6,997\ \mathrm{eV}$$

For a mole,

$$U_{tot} = -6,022\times10^{23}\cdot6,997\ \mathrm{eV} = -6,022\times10^{23}\cdot6,997\cdot1,602\times10^{-19}\cdot\frac{1}{4,18}\ \mathrm{cal}$$

$$= -1,601\times10^{5}\ \mathrm{cal} = \underline{-160,1\ \mathrm{kcal}}$$

as compared to the value <u>161,6 kcal</u> calculated for KCl in NaCl structure (table 7)

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From eq. 3-20 in Kittel

$$U_{tot}(R) = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right)$$

$$U'_{tot}(R) = N\left(-\frac{z\lambda}{\rho} e^{-R/\rho} + \frac{\alpha q^2}{R^2}\right) \qquad U'_{tot}(R_0) = 0 \Rightarrow z\lambda = \frac{\rho\alpha q^2}{R_0} e^{R_0/\rho} \text{ —— ①}$$

$$U''_{tot}(R) = N\left(\frac{z\lambda}{\rho^2} e^{-R/\rho} - 2\frac{\alpha q^2}{R^3}\right)$$

Then by ① $U''_{tot}(R_0) = N\left(\frac{\alpha q^2}{\rho R_0^2} - 2\frac{\alpha q^2}{R_0^3}\right) = \frac{N\alpha q^2}{R_0^3}\left(\frac{R_0}{\rho} - 2\right)$

Suppose we compress the crystal

$R_0 \to R_0 - \Delta R$ where $\Delta R / R_0 = \frac{1}{3}\delta$ (or $V_0 \to V_0 - \Delta V$, $\frac{\Delta V}{V_0} = \delta$)

The work done,

$$\Delta U_{tot} = U_{tot}(R_0 - \Delta R) - U(R_0) \simeq \overset{0}{\overset{/\!/}{U'_{tot}(R_0)}}\Delta R + \frac{1}{2}U''_{tot}(R_0)\Delta R^2$$

$$\frac{\Delta U_{tot}}{N} = \frac{1}{2}\frac{\alpha q^2}{R_0}\left(\frac{R_0}{\rho} - 2\right)\frac{1}{9}\delta^2 \text{ —— ②}$$

From the definition of bulk modulus B, $u = \frac{1}{2}B\delta^2$ where u is the energy density, so we have to divide ② by the volume (V_0) occupied a pair of ions.

$$\therefore \frac{\Delta U_{tot}}{N \cdot V_0} = \frac{1}{2}\frac{1}{V_0}\frac{\alpha q^2}{R_0}\left(\frac{R_0}{\rho} - 2\right)\frac{1}{9}\delta^2 \Rightarrow B = \frac{1}{V_0}\frac{\alpha q^2}{R_0}\left(\frac{R_0}{\rho} - 2\right)\frac{1}{9}$$

(If we're considering the NaCl like structure, a unit cell has volume $(2R_0)^3 = 8R_0^3$ and 4-pairs $\Rightarrow$ So the volume occupied by a pair is $2R_0^3 = V_0$

But if we're consider the ZnS like structure, a unit cell has volume $\left(\frac{4R_0}{\sqrt{3}}\right)^3$ and 4 pairs $\Rightarrow V_0 = \frac{16}{3\sqrt{3}}R_0^3$ per pair

In ZnS like structure, KCl has $\alpha = 1.6381$ $R_0 = 3.003$ Å, $\rho = 0.326$ Å, $q = e$

$$B = \frac{1}{\frac{16}{3\sqrt{3}}(3.003\text{Å})^3}\frac{1.6381}{3.003}\cdot 2\cdot 0.529\boxed{\frac{e^2}{2\cdot 0.529\text{Å}}}^{/\!/\,13.6\,ev}\cdot\left(\frac{3.003}{0.326} - 1\right)\frac{1}{9}\frac{ev}{(\text{Å})^3}$$

$$= 0.08588 \times 1.602 \times 10^{-19}\ \text{joule} \times \frac{1}{10^{-30}}\frac{1}{m^2} = 1.376 \times 10^{+10}\ N/m^2$$

$\leftarrow 1.376 \times 10^{10}\ N/m^2$