

# Physics 460 Hmwk #3 Solutions

1. Kittel 3-2

For bcc

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

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

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

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

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

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

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

$$\therefore \frac{\text{bcc}}{\text{fcc}} \approx 0.958$$

## 2. Kittel 3-4

In this problem, we need to investigate whether

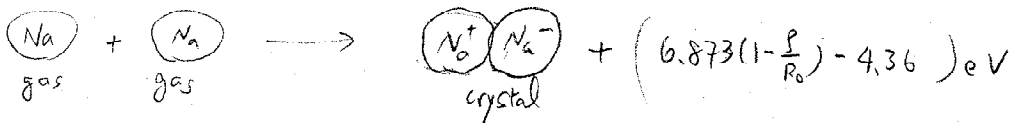
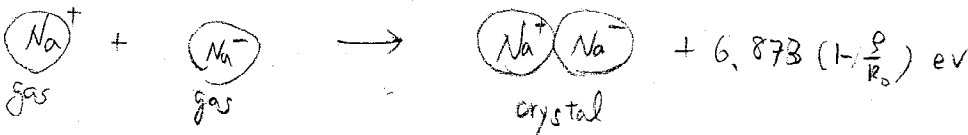
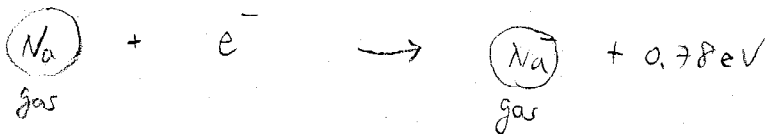
$\text{Na}^+ \text{Na}^-$  crystal (in NaCl structure) is stable.

From table 5, ionization energy for Na is 5.14 eV

From table 4 in chapter 1, nearest-neighbor distance for Na is  $3.659 \text{ \AA}$   
 $\alpha$  in NaCl structure = 1.747365

$$\begin{aligned} U_{\text{lat}}/N &= -\frac{\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0}\right) = -\frac{1.74736}{3.659} \cdot 2.0529 \left(\frac{e^2}{2.0529}\right) \left(1 - \frac{\rho}{R_0}\right) \\ &= -6.873 \text{ eV} \left(1 - \frac{\rho}{R_0}\right) \end{aligned}$$

$\nearrow 13.6 \text{ eV}$



$\rho$  is usually of order  $0.1 R_0$ , putting  $\rho \approx 0.1 R_0$

$$6.873(1 - 0.1) - 4.36 = \underline{1.826 \text{ eV}} \quad (\text{per pair})$$

$\therefore$  Cohesive energy relative to separated atom is  $0.913 \text{ eV/atom}$

Comparing to the table of cohesive energies, we have for the metallic Na:

$1.113 \text{ eV/atom}$ , which is more stable.

3 Kittel 3-6

From table 7,

$$z \lambda = 2.05 \times 10^{-8} \text{ eV} \quad , \quad \rho = 0.326 \text{ \AA}$$

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

$$\therefore \lambda = \frac{2.05}{6} \times 10^{-8} \text{ eV} = \frac{2.05}{6} \times 10^{-8} \cdot \frac{1}{1.602 \times 10^{12}} \text{ eV} = 2.133 \times 10^3 \text{ eV}$$

In cubic ZnS structure,  $z = 4$ .

From eq. (3-23) in Kittel,

$$R_0^2 \exp(-R_0/\rho) = \rho \alpha \frac{e^2}{z \lambda}$$

We can determine the value of  $R_0$ . (Note  $\alpha = 1.6381$ )

$$\begin{aligned} R_0^2 e^{-\frac{R_0}{0.326 \text{ \AA}}} &= 0.326 \text{ \AA} \cdot 1.6381 \cdot \frac{1}{4 \cdot 2.133 \times 10^3 \text{ eV}} \cdot \frac{e^2}{\text{\AA}} \\ &= 0.326 \cdot 1.6381 \cdot \frac{1}{4 \cdot 2.133 \times 10^3} \cdot 2.0529 \cdot 13.6 \text{ \AA}^2 \\ &= 9.006 \times 10^{-4} \text{ \AA}^2 \end{aligned}$$

Note  $\frac{1}{2} \frac{e^2}{0.529 \text{ \AA}} = 13.6 \text{ eV}$

$R_0$  can be solved to be  $3.003 \text{ \AA}$  (neglecting those unreasonable solutions)

Thus

$$\frac{U_{\text{tot}}}{N} = - \frac{\alpha e^2}{R_0} \left(1 - \frac{\rho}{R_0}\right) = - \frac{1.6381}{3.003} \cdot 2.0529 \cdot 13.6 \cdot \left(1 - \frac{0.326}{3.003}\right) = -6.997 \text{ eV}$$

For a mole,

$$\begin{aligned} U_{\text{tot}} &= -6.022 \times 10^{23} \cdot 6.997 \text{ eV} = -6.022 \times 10^{23} \cdot 6.997 \cdot 1.602 \times 10^{-19} \cdot \frac{1}{4.18} \text{ cal} \\ &= -1.601 \times 10^5 \text{ cal} = \underline{\underline{-160.1 \text{ Kcal}}} \end{aligned}$$

as compared to the value 161.6 Kcal calculated for KCl in NaCl structure (table 7)

4

From eq. 3-20 in Kittel

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

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

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

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

Suppose we compress the crystal

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

The work done,

$$\Delta U_{\text{tot}} = U_{\text{tot}}(R_0 - \Delta R) - U_{\text{tot}}(R_0) \approx U''_{\text{tot}}(R_0) \Delta R + \frac{1}{2} U''''_{\text{tot}}(R_0) (\Delta R)^2$$

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

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.

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

(If we're considering the NaCl like structure, a unit cell has volume

$$(2R_0)^3 = 8R_0^3 \quad \text{and} \quad 4 \text{ pairs} \Rightarrow \text{So the volume occupied by a pair is } 2R_0^3 = V_0$$

But if we're consider the ZnS like structure, a unit cell has volume

$$\left( \frac{4R_0}{\sqrt{3}} \right)^3 \quad \text{and} \quad 4 \text{ pairs} \Rightarrow V_0 = \frac{16}{3\sqrt{3}} R_0^3 \quad \text{per pair}$$

In ZnS like structure, KCl has  $\alpha = 1.6381$ ,  $R_0 = 3.003 \text{ \AA}$ ,  $\rho = 0.326 \text{ \AA}$ ,  $q = e$ 

$$B = \frac{1}{\frac{16}{3\sqrt{3}} (3.003 \text{ \AA})^3} \cdot \frac{1.6381}{3.003} \cdot 2 \cdot 0.529 \cdot \frac{e^2}{2 \cdot 0.529 \text{ \AA}} \cdot \left( \frac{3.003}{0.326} - 2 \right) \cdot \frac{1}{9} \cdot \frac{\text{eV}}{(\text{ \AA})^2}$$

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

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