Werkgroep 9 Fysica van de Vaste Stof– 3 febr 2011 **UITWERKINGEN**

Opgave 1: Nulpuntsenergie van LiF tov statische potentiele energie

Potentiele energie per 'molecuul"(LiF eenheid), zie Kittel H3, Eq 20

$$U = z\lambda e^{-R/\rho} - \frac{\alpha e^2}{4\pi\varepsilon_0 R}$$

De totale energie per LiF bij de evenwichts-naaste-buur afstand R0 $\left.\frac{\partial U}{\partial R}\right|_{R=R_0}$ waarvoor wordt dan

$$U_{tot} = -\frac{\alpha e^2}{4\pi\varepsilon_0 R_0}(1 - \rho/R_0)$$

Met z = 6, R_0 = 0.2014 nm, $z\lambda = 0.296 \times 10^{-15}$ J, en ρ = 0.0291 nm, geeft dat $U_{tot} = -1.7 \times 10^{-18}$ J

De dynamische of nulpuntsenergie wordt gegeven door (zie college)

$E_0 = \frac{9}{8}\hbar\sqrt{k/m}$ waarbij de veerconstante k de tweede afgeleide is van de potentiele energie waarin elk ion zich bevindt.

Dit is $$U_i = \tfrac{1}{2}\left(z\lambda e^{-R/\rho} - \frac{\alpha e^2}{4\pi\varepsilon_0 R}\right)$$

En dus $$k = \left.\frac{\partial^2 U}{\partial R^2}\right|_{R=R_0} = \frac{z\lambda}{\rho^2}e^{-R_0/\rho} - \frac{2\alpha e^2}{4\pi\varepsilon_0 R^3} = \frac{\alpha e^2}{4\pi\varepsilon_0 \rho R_0^2}(1 - 2\rho/R_0)$$

Als ik het goed heb uitgerekend krijg ik voor het Li^+ – ion (m = 7 amu) 1.71 x 10^{-20} J,
en voor het F- - ion (m = 19 amu) : 1.04 x 10-20 J, zodat de verhouding

$\frac{E_0}{U_{tot}} = \frac{1.71 + 1.04}{170} = 1.6\%$ De correctie is dus vrij klein, maar blijkt significant, omdat de meetnauwkeurigheid zo goed is.

Opgave 2: Bulkmodulus van NaCl

Solution: NaCl Bulk Modulus

Using the interaction potential given in the problem, the total energy of the system is written as

$$U = N\left(-\frac{e^2}{r}\sum\frac{\pm 1}{\rho_{ij}} + \frac{\alpha}{r^n}\sum\frac{1}{\rho_{ij}^n}\right) \tag{12.4}$$

where $\rho_{ij} = r_{ij}/r$, and $r = 2.10$ Å is the distance between Na and Cl first nearest neighbors. The first sum is for alternating charged ions (Na^+ and Cl^-); it yields, by definition, the Madelung constant, $M = 1.748$ (Ashcroft and Mermin [2, p. 405]). The second sum results in $\alpha\sum 1/\rho_{ij}^n = C$.

Pressure is given by $P = -\frac{\partial U}{\partial V}$. The volume is $V = 2Nr^3$. Therefore $\mathrm{d}V = 6Nr^2\mathrm{d}r$, and we can solve for the pressure,

$$P = -\frac{1}{6Nr^2}\frac{\partial}{\partial r}N\left(-Me^2\frac{1}{r} + \frac{C}{r^n}\right) \tag{12.5}$$

$$= -\frac{1}{6r^2}\left(ME^2\frac{1}{r} - \frac{nC}{r^{n+1}}\right) \tag{12.6}$$

The equilibrium lattice parameters are determined at $P = 0$ ($P = 1$ atm is essentially zero). Note that this is equivalent to finding a minimum in $U(r)$:

$$0 = \frac{Me^2}{r_0^2} - \frac{nC}{r_0^{n+1}} \tag{12.7}$$

The compressibility is determined from

$$B = -V\frac{\partial P}{\partial V} = 2Nr^3\frac{1}{6Nr^2}\frac{\partial}{\partial r}\frac{1}{6r^2}\left(ME^2\frac{1}{r} - \frac{nC}{r^n}\right) \tag{12.8}$$

$$= \frac{1}{18}r\frac{\partial}{\partial r}\left(Me^2\frac{1}{r^4} - \frac{nC}{r^{n+3}}\right) \tag{12.9}$$

$$= \frac{1}{18}\left(\frac{n(n+3)}{r_0^{n+3}}C - Me^2\frac{4}{r_0^4}\right) \tag{12.10}$$

Using Equations 12.7 and 12.10, we have two equations from which to solve for two unknowns, C and n. We can rewrite Equation 12.7 as

$$\frac{C}{r_0^{n+3}} = Me^2\frac{1}{nr_0^4} \tag{12.11}$$

and Equation 12.10 becomes

$$B = \frac{Me^2}{18}\left(\frac{n(n+3)}{n} - 4\right)\frac{1}{r_0^4} \tag{12.12}$$

$$= \frac{1}{18}Me^2\frac{1}{r_0^3}(n-1) \tag{12.13}$$

We have separated out the terms because we know that $\phi_{\text{Coulomb}} = e^2A/(4\pi\varepsilon_0 r_0)$, and therefore we can obtain

$$n = 1 + \frac{18r_0^3 B}{\phi_{\text{Coulomb}}} \tag{12.14}$$

Using the values given in the problem, $\phi_{\text{Coulomb}} = 8.53$ eV and

$$n = 1 + \frac{18\cdot(2.82\times10^{-8}\text{ cm})^3\cdot 2.4\times10^{11}\text{ dyn cm}^{-2}}{8.53\cdot1.6\times10^{-12}} = 8.1 \tag{12.15}$$

From Equation 12.7 we can see that

$$\phi_{\text{Coulomb}} = \frac{nC}{r_0^n} \quad\longrightarrow\quad C = \frac{\phi_{\text{Coulomb}}r_0^n}{n} \tag{12.16}$$

so $C = 1.05$ eV$\cdot$(4436 Å)$^{8.1}$ = 4660 eVÅ$^{8.1}$. To obtain α from C, we have to calculate $\sum\frac{1}{\rho_{ij}^n}$. There are six first neighbors, which have $\rho_{ij} = 1$, 12 second nearest neighbors ($\rho_{ij} = \sqrt{2}$), eight third nearest-neighbors ($\rho_{ij} = \sqrt{3}$), ...

$$\sum\frac{1}{\rho_{ij}^n} = 6 + 12\frac{1}{2^{4.05}} + 8\frac{1}{3^{4.05}} + \cdots = 6.81 \tag{12.17}$$

Therefore,

$$\alpha = \frac{C}{6.81} = 684\text{ eVÅ}^{8.1} \tag{12.18}$$