

CHAPTER 3

1. $E = (\hbar^2/2M) (2\pi/\lambda)^2 = (\hbar^2/2M) (\pi/L)^2$, with $\lambda = 2L$.

2. bcc: $U(R) = 2N\varepsilon[9.114(\sigma/R)^{12} - 12.253(\sigma/R)^6]$. At equilibrium $R_0^6 = 1.488\sigma^6$, and $U(R_0) = 2N\varepsilon(-2.816)$.

fcc: $U(R) = 2N\varepsilon[12.132(\sigma/R)^{12} - 14.454(\sigma/R)^6]$. At equilibrium $R_0^6 = 1.679\sigma^6$, and $U(R_0) = 2N\varepsilon(-4.305)$. Thus the cohesive energy ratio bcc/fcc = **0.956**, so that the fcc structure is more stable than the bcc.

3. $|U| = 8.60 N\varepsilon$
 $= (8.60)(6.02 \times 10^{23})(50 \times 10^{-16}) = 25.9 \times 10^9 \text{ erg/mol}$
 $= 2.59 \text{ kJ/mol}$.

This will be decreased significantly by quantum corrections, so that it is quite reasonable to find the same melting points for H₂ and Ne.

4. We have $\text{Na} \rightarrow \text{Na}^+ + e - 5.14 \text{ eV}$; $\text{Na} + e \rightarrow \text{Na}^- + 0.78 \text{ eV}$. The Madelung energy in the NaCl structure, with Na⁺ at the Na⁺ sites and Na⁻ at the Cl⁻ sites, is

$$\frac{\alpha e^2}{R} = \frac{(1.75) (4.80 \times 10^{-10})^2}{3.66 \times 10^{-8}} = 11.0 \times 10^{-12} \text{ erg},$$

or 6.89 eV. Here R is taken as the value for metallic Na. The total cohesive energy of a Na⁺ Na⁻ pair in the hypothetical crystal is 2.52 eV referred to two separated Na atoms, or 1.26 eV per atom. This is larger than the observed cohesive energy 1.13 eV of the metal. We have neglected the repulsive energy of the Na⁺ Na⁻ structure, and this must be significant in reducing the cohesion of the hypothetical crystal.

5a.

$$U(R) = N \left(\frac{A}{R^n} - \frac{\alpha q^2}{R} \right); \quad \alpha = 2 \log 2 = \text{Madelung const.}$$

In equilibrium

$$\frac{\partial U}{\partial R} = N \left(-\frac{nA}{R_0^{n+1}} + \frac{\alpha q^2}{R_0^2} \right) = 0; \quad R_0^n = \frac{nA}{\alpha q^2},$$

and

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

b.
$$U(R_0 - R_0 \delta) = U(R_0) + \frac{1}{2} \frac{\partial^2 U}{\partial R^2} R_0 (R_0 \delta)^2 + \dots,$$

bearing in mind that in equilibrium $(\partial U / \partial R)_{R_0} = 0$.

$$\left(\frac{\partial^2 U}{\partial R^2} \right)_{R_0} = N \left(\frac{n(n+1)A}{R_0^{n+2}} - \frac{2\alpha q^2}{R_0^3} \right) = N \left(\frac{(n+1)\alpha q^2}{R_0^3} - \frac{2\alpha q^2}{R_0^3} \right)$$

For a unit length $2NR_0 = 1$, whence

$$\left(\frac{\partial^2 U}{\partial R^2} \right)_{R_0} = \frac{\alpha q^2}{2R_0^4} (n-1); \quad C = R_0^2 \left. \frac{\partial^2 U}{\partial R^2} \right|_{R_0} = \frac{(n-1)q^2 \log 2}{R_0^2}.$$

6. For KCl, $\lambda = 0.34 \times 10^{-8}$ ergs and $\rho = 0.326 \times 10^{-8}$ Å. For the imagined modification of KCl with the ZnS structure, $z = 4$ and $\alpha = 1.638$. Then from Eq. (23) with $x \equiv R_0/\rho$ we have

$$x^2 e^{-x} = 8.53 \times 10^{-3}.$$

By trial and error we find $x \approx 9.2$, or $R_0 = 3.00$ Å. The actual KCl structure has $R_0(\text{exp}) = 3.15$ Å. For the imagined structure the cohesive energy is

$$U = \frac{-\alpha q^2}{R_0} \left(1 - \frac{p}{R_0} \right), \quad \text{or} \quad \frac{U}{q^2} = -0.489$$

in units with R_0 in Å. For the actual KCl structure, using the data of Table 7, we calculate $\frac{U}{q^2} = -0.495$,

units as above. This is about 0.1% lower than calculated for the cubic ZnS structure. It is noteworthy that the difference is so slight.

7. The Madelung energy of $\text{Ba}^+ \text{O}^-$ is $-\alpha e^2/R_0$ per ion pair, or -14.61×10^{-12} erg = -9.12 eV, as compared with $-4(9.12) = -36.48$ eV for $\text{Ba}^{++} \text{O}^-$. To form Ba^+ and O^- from Ba and O requires $5.19 - 1.5 = 3.7$ eV; to form Ba^{++} and O^- requires $5.19 + 9.96 - 1.5 + 9.0 = 22.65$ eV. Thus at the specified value of R_0 the binding of $\text{Ba}^+ \text{O}^-$ is 5.42 eV and the binding of $\text{Ba}^{++} \text{O}^-$ is 13.83 eV; the latter is indeed the stable form.

8. From (37) we have $e_{xx} = S_{11}X_x$, because all other stress components are zero. By (51), $3S_{11} = 2/(C_{11} - C_{12}) + 1/(C_{11} + C_{12})$.

$$\text{Thus } Y = (C_{11}^2 + C_{12}C_{11} - 2C_{12}^2)/(C_{11} + C_{12});$$

further, also from (37), $e_{yy} = S_{21}X_x$,

$$\text{whence } \sigma = e_{yy}/e_{xx} = S_{21}/S_{11} = -C_{12}/(C_{11} + C_{12}).$$

9. For a longitudinal phonon with $\mathbf{K} \parallel [111]$, $u = v = w$.

$$\omega^2 \rho = [C_{11} + 2C_{44} + 2(C_{12} + C_{44})]K^2/3,$$

$$\text{or } v = \omega/K = [(C_{11} + 2C_{12} + 4C_{44}/3\rho)]^{1/2}$$

This dispersion relation follows from (57a).

10. We take $u = -w$; $v = 0$. This displacement is \perp to the [111] direction. Shear waves are degenerate in this direction. Use (57a).

11. Let $e_{xx} = -e_{yy} = \frac{1}{2}e$ in (43). Then

$$U = \frac{1}{2}C_{11}(\frac{1}{4}e^2 + \frac{1}{4}e^2) - \frac{1}{4}C_{12}e^2$$

$$= \frac{1}{2}[\frac{1}{2}(C_{11} - C_{12})]e^2$$

so that $\left(\frac{\partial^2 U}{\partial R^2}\right)_{R_0} = N\left(\frac{n(n+1)A}{R_0^{n+2}} - \frac{2\alpha q^2}{R_0^3}\right) = N\left(\frac{(n+1)\alpha q^2}{R_0^3} - \frac{2\alpha q^2}{R_0^3}\right)$ is the effective shear

constant.

12a. We rewrite the element $a_{ij} = p - \delta_{ij}(\lambda + p - q)$ as $a_{ij} = p - \lambda' \delta_{ij}$, where $\lambda' = \lambda + p - q$, and δ_{ij} is the Kronecker delta function. With λ' the matrix is in the “standard” form. The root $\lambda' = R\rho$ gives $\lambda = (R - 1)p + q$, and the $R - 1$ roots $\lambda' = 0$ give $\lambda = q - p$.

b. Set

$$u(\mathbf{r}, t) = u_0 e^{i[(K/\sqrt{3})(x+y+z) - \omega t]},$$

$$v(\mathbf{r}, t) = v_0 e^{i[\dots]},$$

$$w(\mathbf{r}, t) = w_0 e^{i[\dots]},$$

as the displacements for waves in the [111] direction. On substitution in (57) we obtain the desired equation. Then, by (a), one root is

$$\omega^2 \rho = 2p + q = K^2(C_{11} + 2C_{12} + 4C_{44})/3,$$

and the other two roots (shear waves) are

$$\omega^2 \rho = K^2(C_{11} - C_{12} + C_{44})/3.$$

13. Set $u(\mathbf{r}, t) = u_0 e^{i(\mathbf{K} \cdot \mathbf{r} - t)}$ and similarly for v and w . Then (57a) becomes

$$\omega^2 \rho u_0 = [C_{11}K_y^2 + C_{44}(K_y^2 + K_z^2)]u_0$$

$$+ (C_{12} + C_{44})(K_x K_y v_0 + K_x K_z w_0)$$

and similarly for (57b), (57c). The elements of the determinantal equation are

$$M_{11} = C_{11}K_x^2 + C_{44}(K_y^2 + K_z^2) - \omega^2 \rho;$$

$$M_{12} = (C_{12} + C_{44})K_x K_y;$$

$$M_{13} = (C_{12} + C_{44})K_x K_z.$$

and so on with appropriate permutations of the axes. The sum of the three roots of $\omega^2 \rho$ is equal to the sum of the diagonal elements of the matrix, which is

$(C_{11} + 2C_{44})K^2$, where

$$K^2 = K_x^2 + K_y^2 + K_z^2, \text{ whence}$$

$$v_1^2 + v_2^2 + v_3^2 = (C_{11} + 2C_{44})/\rho,$$

for the sum of the (velocities)² of the 3 elastic modes in any direction of K.

14. The criterion for stability of a cubic crystal is that all the principal minors of the quadratic form be positive. The matrix is:

$$\begin{matrix} C_{11} & C_{12} & C_{12} & & & & \\ C_{12} & C_{11} & C_{12} & & & & \\ C_{12} & C_{12} & C_{11} & & & & \\ & & & C_{44} & & & \\ & & & & C_{44} & & \\ & & & & & C_{44} & \end{matrix}$$

The principal minors are the minors along the diagonal. The first three minors from the bottom are C_{44} , C_{44}^2 , C_{44}^3 ; thus one criterion of stability is $C_{44} > 0$. The next minor is $C_{11} C_{44}^3$, or $C_{11} > 0$. Next: $C_{44}^3 (C_{11}^2 - C_{12}^2)$, whence $|C_{12}| < C_{11}$. Finally, $(C_{11} + 2C_{12})(C_{11} - C_{12})^2 > 0$, so that $C_{11} + 2C_{12} > 0$ for stability.