

this procedure, the fractional charges in the unit cell will add up to integer charges at their correct positions.

The value of the sum fluctuates considerably, but when the sum has covered a “charge neutral” amount of the crystal, the convergence is fast.¹ The crucial step was using a building block which did not have dipole moment. Our calculated Madelung constant for NaCl is 1.75 in agreement with the known result (Ashcroft and Mermin [1] p. 405).

Similarly, the fulleride crystal was constructed from a $q = +3$ charge at (0,0,0), $q = -1/2$ charges at the (-1/2,0,0) and (1/2,0,0) points, and $q = -1$ charges at (1/4,1/4,1/4) and (-1/4,-1/4,-1/4). Again, this is not a very symmetric arrangement, but it has zero dipole moment and does the job.

The resultant Madelung constant of Rb_3C_{60} is 11.04.

2.2 Solution: NaCl Bulk Modulus

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

$$U = N \left(-\frac{e^2}{r} \sum \frac{\pm 1}{\rho_{ij}} + \frac{\alpha}{r^n} \sum \frac{1}{\rho_{ij}^n} \right), \quad (\text{II.2.4})$$

where $\rho_{ij} = r_{ij}/r$ and $r = 2.10 \text{ \AA}$ 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, $M = 1.748$.² The second sum results in $\alpha \sum \frac{1}{\rho_{ij}^n} = C$.

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

$$P = -\frac{1}{6Nr^2} \frac{\partial}{\partial r} N \left(-Me^2 \frac{1}{r} + \frac{C}{r^n} \right) \quad (\text{II.2.5})$$

$$= -\frac{1}{6r^2} \left(ME^2 \frac{1}{r} - \frac{nC}{r^{n+1}} \right). \quad (\text{II.2.6})$$

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

$$0 = \frac{Me^2}{r_0^2} - \frac{nC}{r_0^{n+1}}. \quad (\text{II.2.7})$$

¹ The distribution of charges over a cubic unit cell, as described by Ashcroft and Mermin [1] p. 404, requires more attention when creating the unit cell. On the other hand, these unit cells form a simple cubic lattice.

² See Ashcroft and Mermin [1] p. 405.

The compressibility is determined from

$$B = -V \frac{\partial P}{\partial V} = 2Nr^3 \frac{1}{6Nr^2} \frac{\partial}{\partial r} \frac{1}{6r^2} \left(ME^2 \frac{1}{r} - \frac{nC}{r^n} \right) \quad (\text{II.2.8})$$

$$= \frac{1}{18} r \frac{\partial}{\partial r} \left(Me^2 \frac{1}{r^4} - \frac{nC}{r^{n+3}} \right) \quad (\text{II.2.9})$$

$$= \frac{1}{18} \left(\frac{n(n+3)}{r_0^{n+3}} C - Me^2 \frac{4}{r_0^4} \right) . \quad (\text{II.2.10})$$

Using Eqs. II.2.7 and II.2.10, we have two equations from which to solve for two unknowns, C and n . We can rewrite Eq. II.2.7 as

$$\frac{C}{r_0^{n+3}} = Me^2 \frac{1}{nr_0^4} , \quad (\text{II.2.11})$$

and Eq. II.2.10 becomes

$$B = \frac{Me^2}{18} \left(\frac{n(n+3)}{n} - 4 \right) \frac{1}{r_0^4} \quad (\text{II.2.12})$$

$$= \frac{1}{18} Me^2 \frac{1}{r_0^3} (n-1) . \quad (\text{II.2.13})$$

We have separated out the terms because we know that $\phi_{\text{Coulomb}} = \frac{e^2 A}{4\pi\epsilon_0 r_0}$, and therefore we can obtain

$$n = 1 + \frac{18r_0^3 B}{\phi_{\text{Coulomb}}} . \quad (\text{II.2.14})$$

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

$$n = 1 + \frac{18 \cdot (2.82 \times 10^{-8} \text{ cm})^3 \cdot 2.4 \times 10^{11} \frac{\text{dyn}}{\text{cm}^2}}{8.53 \cdot 1.6 \times 10^{-12}} = 8.1 . \quad (\text{II.2.15})$$

From Eq. II.2.7 we can see that

$$\phi_{\text{Coulomb}} = \frac{nC}{r_0^n} \rightarrow C = \frac{\phi_{\text{Coulomb}} r_0^n}{n} , \quad (\text{II.2.16})$$

so $C = 1.05 \text{ eV} \cdot (4436 \text{ \AA})^{8.1} = 4660 \text{ eV \AA}^{8.1}$. 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 ($\rho_{ij} = \sqrt{3}$), ...:

$$\sum \frac{1}{\rho_{ij}^n} = 6 + 12 \frac{1}{2^{4.05}} + 8 \frac{1}{3^{4.05}} + \dots = 6.81 . \quad (\text{II.2.17})$$

Therefore,

$$\alpha = \frac{C}{6.81} = 684 \text{ eV \AA}^{8.1} . \quad (\text{II.2.18})$$