

## Answer Set 4 Physics 240B

**A&M 19.2** CsCl structure: the small atom, at the body-centered site, fits in the gap formed by the large atoms at the corner sites. Consider a cross-section of the cube parallel to the (1 1 0) plane. This is a rectangle with sides  $2r_>$  and  $2\sqrt{2}r_>$ . At maximum  $r_<$ , the diagonal has length  $2r_> + 2r_<$ . Then  $2r_> + 2r_< = \sqrt{4r_>^2 + 8r_>^2} = 2\sqrt{3}r_>$ , so  $r_>/r_< = 1/(\sqrt{3}-1) = (\sqrt{3}+1)/2 = 1.366$ . Zincblende: refer to Figure 4.18. Each atom sits within a regular tetrahedron, of side  $a/\sqrt{2}$ , of atoms of the other species. The inner atom stops mattering if the atoms at the tetrahedron corners touch. This means  $r_> = a/2\sqrt{2}$ . To get the smaller atom's maximum radius, consider when a sphere centered at  $(\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$  just touches a sphere of radius  $r_>$  centered at the origin. This gives  $r_< = \sqrt{3}a/4 - a/2\sqrt{2} = (\sqrt{3} - \sqrt{2})a/4$ . The ratio is  $r_>/r_< = \sqrt{2}/(\sqrt{3} - \sqrt{2}) = 2 + \sqrt{6}$ .

1. a) Note that you have to be *extremely* careful to keep the terms in the sum ordered correctly, so that the crystal is always neutral. Otherwise you can come up with all manner of wrong answers, thanks to the conditionally convergent series. The energetics are not identical for the + and - ions, so calculate both. I did it in C, and you can check out my code. (You can do each sum in under 5 lines.) I get energy  $-2.08 \frac{Q^2}{a}$  for each positive charge and  $-0.693 \frac{Q^2}{a}$  for each negative charge. The total is  $-3.47 \frac{Q^2}{a}$  per unit cell.
  - b) First sum the repulsive energies over all pairs. (Half) the sum on pairs that involve a particular positive ion is  $1 + \frac{1}{3^9} + \frac{1}{4^9} + \frac{1}{5^9} + \frac{1}{7^9} + \frac{1}{8^9} + \frac{1}{9^9} + \dots = 1.00006$ . The equivalent (half)-sum over all pairs that involve a particular negative ion gives  $0.502A$ . The total repulsive energy per unit cell is then  $\frac{2.004A}{a^9}$ . Minimizing the total energy,  $U(a) = \frac{2.004A}{a^9} - \frac{3.47Q^2}{a}$ , with respect to  $a$  gives  $a_o = 1.23(\frac{A}{Q^2})^{1/8}$ .
  - c) If the spacing becomes  $a_o(1+\delta)$ , then the energy is  $U(a_o(1+\delta)) = \frac{2.004A}{a_o^9(1+\delta)^9} - \frac{3.47Q^2}{a_o(1+\delta)}$ . Expanding this in powers of  $\delta$  gives the equilibrium energy as the zero order term, zero as the first order term (since the expansion is around the equilibrium point), and  $\frac{2.004A}{a_o^9}(45\delta^2) - \frac{3.47Q^2}{a_o}\delta^2 = 4(3.47)\frac{Q^2\delta^2}{a_o^2}$ . This is the work per unit cell. Dividing by  $4a_o$  gives the work per length,  $3.47Q^2\delta^2/a_o^2$ .
2. The easiest solution is to use A&M (20.8), which gives the minimum energy in terms of the sums  $A_6$  and  $A_{12}$  of a crystal structure,  $U_{eq} = -\frac{\epsilon A_6^2}{2A_{12}}$ . Reading the sums off Table 20.2 gives  $U_{bcc}/U_{fcc} = (12.25)^2(12.13)/(9.11)(14.45)^2 = 0.957$ , which is a significant but not mammoth energy difference.
3. a) The zero-point energy should have more influence in two dimensions than in three. Its magnitude decreases by a factor of 2/3, but the number of neighbors (which determines the total strength of the attractive interaction) decreases faster. The noble gases crystallize into fcc, the best packing in 3D, which has 12 nearest neighbors. The best 2D packing has only 6.
  - b) Graphite changes everything. It adds an additional force, the graphite-helium interaction, which totally throws off the near-balance between zero-point and van der Waals interactions. In fact 2D helium solidifies on graphite even though 3D helium only solidifies under pressure.