MatSci 193/203 Homework 5

Graphite, Carbon Nanotubes, Ionic Crystals

Due Wednesday, November 13, 2013 at 5pm outside of Durand 110 or emailed to duerloo .at. stanford.edu

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1 Graphite structures

Determine and draw a unit cell for all possible graphite structures that have a stacking sequence repeat pattern of three layers or fewer. Recall that the interlayer interactions are relatively weak, making many stacking sequences similar in energy and potentially experimentally relevant. Assume that the carbon atoms are located only at close-packed A, B, or C sites in each basal plane. How many such unique structures are there?

2 Nanotube diameter

Given the positive integers n and m that characterize the chiral vector of a nanotube and the carbon-carbon bond distance a, find an approximate expression for the diameter of the tube.

3 Boron nitride

(a) BN is an interesting III-V material because it can assume a 2D planar form like graphene with 2 atoms per unit cell. Draw a few unit cells of this form of BN. Treat it as a 2D structure (monolayer). Give the atom positions and lattice vectors, i.e. enough information to uniquely specify the structure.

(b) What do you expect the dominant type of bonding to be in this 2D structure?

(c) If the bonding were purely ionic in nature, what would be the range of radius ratio between B and N to give a planar form according to the radius ratio rules? Given the location of B and N on the periodic table, do you believe that the atoms are likely to exhibit a radius ratio in the range you calculated above? Check your answer by looking at a table of radii.

(d) A variety of bulk, 3D forms of BN exist, including a so-called A-A′ layered structure which can be described by a hexagonal Bravais lattice. This structure consists of stacked BN 2D layers such that B and N atoms alternate along the [0001] direction. Draw a unit cell for this structure.

(e) Show by putting arrows in your drawing above how the atoms can shift to become a hexagonal symmetry tetrahedral semiconducting structure. Write the Miller vector of the each of the atomic displacements. Give the name of this tetrahedral structure.

4 Prediction of the ionization state of an ionic crystal

Barium oxide has the NaCl structure. Estimate the cohesive energies per molecule of the hypothetical crystals $Ba^{+}O^{-}$ and $Ba^{++}O^{--}$ referred to separated neutral atoms. The observed nearest-neighbor internuclear distance is R_0=0.276 nm; assume that this is independent of the ionization state. The first and second ionization potentials of Ba are 5.19 and 9.96 eV. The electron affinities of the first and second electrons added to the neutral oxygen atom are 1.5 and -9.0 eV. Which valence state do you predict will occur? Neglect the repulsive portion of the energy.

5 Can a crystal of a single atom type be ionic?

It is possible (although not usually considered) that a crystal of a single atom type, e.g. Na, can exist in an ionic form. In such a form, electrons would transfer from some atoms to other atoms to form both positive and negative ions. Such a process could conceivably result in a greater cohesive energy if the gain in electrostatic energy exceeds the energy cost of electron transfer. Following the example in class, evaluate the stability of such a form of Na in the NaCl structure relative to the cohesive energy of metallic sodium (1.113 eV/atom). Evaluate the energy at the observed interatomic distance in metallic sodium, and use 0.78 eV as the electron affinity of Na. Assume $\rho = 0.3$Å.

6 Critical ionic radius ratios

(a) Compute the critical radius ratio for 4, 6, 8, and 12-fold coordination in ionic structures. Give the radius ratios ranges in which you would expect to see structures of these coordinations.

(b) Given ionic radii from tables (e.g. from class handouts), calculate the expected CsCl lattice constant. How does it compare to the experimental value? Do you think this is good agreement or not? What are potential sources of error?

(c) Compute the radius ratio for CsCl, GaAs, and LiF and determine the structure predicted using the radius ratio criterion. Do these predictions agree with experiments? Based on the locations of these compounds on the periodic table, would you expect the radius ratio rule to apply to these compounds?

(d) What different pairs of coordination numbers are consistent with the stoichiometry of an A_3B_4 compound? What are the permissible ranges for radius ratios for such a compound if A atoms are tetrahedrally coordinated?

7 Ionic crystal structures

For the following crystals, describe the structure in terms of fcc, hcp, and cubic lattices and their interstitials. Sketch each structure and use a visualization program (e.g. http://www.chemtube3d.com/solidstate/_table.htm) to confirm your sketches. List the lattice vectors in a conventional notation.

(a) NaCl

(b) CaF_2

(c) Na_2O

(d) NiAs

(e) CdI_2

(f) $BaTiO_3$