MATRL 218/CHEM277: Assignment 5

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Due date: March 11th 2008

1. The susceptibility of a Curie paramagnet at 0 K diverges. What does this mean. Explain how an internal field (the $\Theta$ in the Curie-Weiss law) shifts the temperature at which such divergence is observed to positive values (ferromagnetic interactions) or to negative values (antiferromagnetic interactions).

2. Consider various spinel ferrites $A^{2+}Fe^{3+}_2O_4$. For the A ions Mn, Co, or Ni, calculate the numbers of unpaired electrons per spinel formula unit if the spinels are all ferrimagnetic (the moments on the A atom and Fe point in opposite direction’s). Keep in mind that A is tetrahedral and B ($Fe^{3+}$) is octahedral.

3. Sketch isotherms of the van der Waals equation of state (per mole):

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

Show that for some of the isotherms, there are regions that are unstable. How is this corrected? Explain the nature of flat regions in the corrected plot.

4. Use the perovskite tolerance factor (which you must calculate) to explain why $CaTiO_3$ and $SrTiO_3$ are different from $BaTiO_3$ in that the first two compounds do not display ferroelectricity. Radii for calculating $t$ can be obtained from the Seshadri group web page. Remember to pick the correct charge states and coordination numbers.

5. $BaMO_3$ ($M = Ti, Zr, Hf$) display the following trend in the paraelectric-ferroelectric $T_C$’s: $BaTiO_3 > BaZrO_3 \sim BaHfO_3$. Calculate the perovskite tolerance factors for these three compounds, and use these to explain the trend.

6. How would you describe the following phase transitions in crystal-chemical terms:

(a) The complete slowing down of reorientation in solid $C_{60}$ at low temperatures.

(b) The transition from cubic perovskite to tetragonal perovskite in $PbTiO_3$

(c) The change on going from the perovskite structure to the tetragonal tungsten bronze (ttb) structure