MATRL 218/CHEM277: Assignment 5

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1. The susceptibility of a Curie paramagnet at 0 K diverges. What does this mean. Explain how an internal field (the Θ 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 $A^{2+}Fe_2^{3+}O_4$. 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 $SrTiOi_3$ 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_Cs: $BaTiO_3 > BaZrO_3 \sim BaHfO_3$. 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