MATRL 218/CHEM277: Assignment 6

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1. The one dimensional chain compound K_2PtBr_4 has square planes of $PtBr_4^{2-}$ forming chains that are linked through Pt–Pt bonds. Describe the crystal field splitting, and sketch schematic density of states. What does the dispersion along the Pt–Pt bonds look like and which orbital is involved? Is K_2PtBr_4 a metal? How can it be made into a metal.

2. FeS_2 (fools gold) has the pyrite structure (octahedral Fe) and because of a bond between the two S atoms (characterized by a short S–S distance), it can be formulated $Fe^{2+}[S_2]^{2-}$. Magnetic measurements suggest that the compound is non-magnetic.

   (a) Sketch out the crystal field (showing t_{2g} and e_g levels) and fill them with the correct number of electrons.

   (b) Sketch out schematic densities of states showing Fe d states and S p states. Do you expect a metal or an insulator?

   (c) What do you expect the situation in CoS_2 to be? It has the same crystal structure.

3. What does the concept of the divergence of susceptibility mean to you. When does the susceptibility diverge for a Curie paramagnet. Explain what happens when (i) ferromagnetic interactions are present, and (ii) antiferromagnetic interactions are present, using the concept of an internal field. Make sketches for all cases.

4. Sketch the magnetic densities of state for antiferromagnetic $LaCrO_3$ (perovskite), and ferromagnetic CrO_2 (rutile).

5. 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). Assume that A is tetrahedral and B (Fe^{3+}) is octahedral.

6. 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.

7. 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.

8. $BaMO_3$ (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.

9. 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