Materials 218/UCSB: Assignment VI

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1. CoS_2 has the pyrite structure (octahedral Co) and because of a bond between the two S atoms (characterized by a short S-S distance), can be formulated $Co^{2+}[S_2]^{2-}$. 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 Co d states and S p states. Do you expect a metal or an insulator ?

2. TiS_2 has the layered CdI_2 structure, and there are no short S-S distances.

   (a) What is the oxidation state of Ti ?

   (b) Sketch out schematic DOS showing Ti d states and S p states. Do you expect an metal or an insulator ?

   (c) TiS_2 shows metallic conductivity. Suggest a possible origin ?

3. Sketch isotherms of the van der Waals equation of state:

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

   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 $p - V_M$ isotherms of 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:

   `http://www.mrl.ucsb.edu/~seshadri/Periodic/index.html`

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. $BaTiO_3$ is a ferroelectric but $BaSnO_3$ is not. Can tolerance explain this (calculate t) ? If it cannot, provide an alternate suggestion.