MATRL 218/CHEM 227: Assignment 4

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1. In class, we examined the band structure of a square lattice of s orbitals. Sketch out the band structure of a *rectangular* lattice of s orbitals with a and b as the lattice parameters and $a < b$. Remember that $X(0, \frac{\pi}{a})$ and $Y(\frac{\pi}{b}, 0)$ will not be degenerate. Sketch the DOS alongside.

2. Sketch the band structure of square lattice of p_x and p_y orbitals, with the DOS alongside.

3. Sketch the most bonding and the most antibonding crystal orbitals formed from sp^2 orbitals on carbon in graphite. Do the same for p_z orbitals.

4. Sketch the most antibonding sp^3 crystal orbital for (a few) Si atoms within the unit cell of diamond Si. Why is molten Si metallic, while crystalline Si is insulating.

5. FeS_2 (fool's 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.

6. 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 ?