Assignment 4  
Due Thursday, April 15, 2010

Problems from Orchard’s *Magnetochemistry*:

Chapter 1: Exercises 2, 4, 5b,c,d,e

Chapter 2: Exercises 2, 4, 5

Chapter 3: Exercises 1a,b,c,e, 3a,b,c, 4, 6, 9a,b

Chapter 4: Exercises 3 (carefully reread section 3.4), 5, 10

Chapter 5: Exercises 1, 2 (Hint: think about CFSEs), 10a,b,c,d, 11

(1) (a) For an $S = \frac{3}{2}$ molecule with axial symmetry, draw the ZFS/Zeeman splitting diagram and the expected form of the $\chi T$ vs. $T$ plot if the zero-field splitting parameter is negative ($D < 0$). Be sure that your $\chi T$ vs. $T$ sketch includes the correct zero-temperature intercept and high-temperature asymptotic limit.

(b) Confirm your results from part (a) using a graphing program (Excel will do) to plot $\chi T$ vs. $T$ from 0 to 300 K for $D/k_B = -2K$. Label the values at the high and low-temperature extremes (just as was done in plots supplied in your notes) and explain the significance of those values in terms of the values expected for Curie-Law cases.

(2) Compute the effective magnetic moments for the following free ions (the ground states will be sufficient).

- (a) Gd$^{3+}$
- (b) Mn$^{2+}$
- (c) Fe$^{2+}$
- (d) Pr$^{3+}$
- (e) Er$^{3+}$

(3) Use a simple “rectangular DOS” model of for molybdenum metal in which the $5s$ band is 20 eV wide and the $4d$ band is 8 eV wide (see figure) and the densities of states are constant within these intervals. Assuming the Zeeman splitting for the band electrons is the same as for free electrons (i.e., the $g$-value is 2.0), give an estimate of the magnitude of the Pauli paramagnetism for molybdenum. Compare your result to the magnitude of Curie-Law paramagnetism.

(4) We have discussed saturation measurements of paramagnetic compounds, which are carried out at high fields and low temperatures ($\mu_B H \gg k_B T$). For cases where spin-only magnetism applies, like octahedral Cr$^{3+}$ complexes, high-spin Fe$^{3+}$ (Mn$^{2+}$) complexes, or...
Gd$^{3+}$ complexes, the saturation magnetizations are respectively 3.0 $\mu_B$, 5.0 $\mu_B$, and 7.0 $\mu_B$ per ion. If ferromagnetic gadolinium metal is placed in high magnetic field at low temperature, conditions where the $f$ magnetic moments are maximally aligned, the magnetization is also close to 7.0 $\mu_B$ per Gd atom. However, if one calculates the effective magnetic moments of these ions in the usual higher temperature regime where the Curie law applies ($k_B T \gg \mu_B H$), one will obtain $g_e[S(S+1)]^{1/2} \mu_B = 3.87 \mu_B$, 5.91 $\mu_B$, and 7.94 $\mu_B$, respectively. What explains the apparent discrepancies; why are the effective magnetic moments larger than the saturation magnetizations per ion/atom?

(5) In lecture, the effects of orbital contributions for ‘T-terms’ in octahedral complexes were discussed (and some graphs from Figgis & Hitchman, “Ligand Field Theory and its Applications”, Chapter 9 were presented). The ‘E-terms’ were not discussed – and for good reason. Figgis discusses such cases qualitatively and explains why this is so (Section 9.3).

(a) Show whether a $^2E$ term split in first order by spin-orbit coupling.

(b) In your own words, supply an explanation for why Figgis & Hitchman don’t treat ‘E-terms’. (Hint: What is the angular momentum $z$-component for the two $e_g$ orbitals?)

(6) Because of the effects of spin-orbit coupling, the Eu$^{3+}$ ion is expected to have a diamagnetic ground state, despite the fact that it has 6 unpaired $4f$ electrons.

(a) Follow the discussion given in an early atomic structure lecture to show how the ground state term is split by spin-orbit coupling (draw a complete splitting diagram for all the J-states that emerge from the ground state term, complete with expected energies of the of the splittings in terms of $\lambda$, the spin-orbit coupling parameter (see lecture notes).

(c) The experimentally observed energy levels for this term are given in the accompanying table. Compute an estimate for $\lambda$ (and $\zeta$) from this data.

(d) Because the energy level spacings are not much larger than $k_B T$ at room temperature and above, europium(3+) compounds are not typically observed to be diamagnetic. Use Boltzmann statistics and a spreadsheet (like Excel) to plot the expected magnetic moment from these energy levels (don’t forget the correct level degeneracies, expected $g_J$ values, and magnetic moments). [Note: This will only give an order-of-magnitude estimate in actual compounds because the crystal field splittings of the $f$-levels also contributes.]