HW 4	**Inorganic Materials Chemistry**	**Name:**	
Points:	**C7780**	**Date due:**	**Dec. 12, 2013**
Max. 100 points	**Fall 2013**	**A**	

1. (50 pts) Use the ligand field theory to explain why Mn_3O_4 is a normal spinel while Fe_3O_4 is an inverse spinel. Hint: draw diagrams of energy levels of d-electrons for ions in tetrahedral and octahedral sites, use approximation $\Delta_T = 4/9\ \Delta_O$, consider all MO_4 and MO_6 moieties as high spin complexes, calculate ligand field stabilization energy in terms of Δ_O for both normal and inverse arrangement of ions, compare them and find which is more stable.

2. (50 pts) Although hexagonal wurzite (W) and cubic sphalerite (S, also called zincblende) structures are often very close in energy and many compounds that exhibit one structure also exhibit the other, the wurzite structure is often preferred by compounds having appropriate radius ratios and high ionicities. For example, the wurzite structure is strongly preferred for ZnO. Could the preference for the wurzite structure in such cases be merely due to the slightly higher value of the wurzite Madelung constant (A_W = 1.6413 vs. A_S = 1.6381)? Please assume that wurzite and sphalerite structures of ZnO are in equilibrium with one another at room temperature:

Equilibrium: ZnO (wurtzite) $\rightleftarrows$ ZnO (sphalerite) K_{eq}

Calculate the value of the equilibrium constant (K_{eq}) assuming that $\Delta G^0 = \Delta L = L_S - L_W$. Recall that $\Delta G^0 = -RT \ln K_{eq}$. Use ionic radii of 0.74 Å and 1.26 Å for Zn^{2+} and O^{2-}, respectively. What is the ratio of moles of wurzite ZnO crystals to moles of sphalerite ZnO crystals at equilibrium? N_A = Avogadro constant, d = interionic distance, L = lattice enthalpy, n = Born exponent (use value of 8).
Use Born–Lande equation for the lattice enthalpy L:
$4\pi\varepsilon_0 = 1.11\ 10^{-10}\ C^2J^{-1}m^{-1}$

$$L = N_A A \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{1}{n}\right)$$