###### Synthesis and Characterization of Magnetic Spinel Nanoparticles

*Read the following article.*

Sun, Shouheng; Zeng, Hao; Robinson, David B.; Raoux, Simone; Rice, Philip M.; Wang, Shan X.; Li, Guanxiong “Monodisperse MFe2O4 (M = Fe, Co, Mn) Nanoparticles” *J. Am. Chem. Soc.* **2004**, *126*, 273-279.

*Work the following problems on a separate sheet of paper to turn in:*

1. The article describes the synthesis of a group of iron oxide nanoparticles that share a common structure called the spinel structure.

(a) What is the general formula of the spinel materials formed in this work? Indicate the oxidation state of each element. Use M to indicate the metal ion that varies.

(b) Using the description of the spinel structure given in the article’s introduction, draw a layer diagram for the oxide ions. Indicate the location of the tetrahedral and octahedral holes created by the oxide lattice.

(c) In the spinel structure, the Fe3+ ions fill some of the octahedral holes and the M2+ ions fill some of the tetrahedral holes. Would you predict this behavior given what you know about trends in ionic radii and the relative sizes of the holes? Explain.

2. Draw the chemical structures of each of the metal precursors, 1,2-hexadecanediol, oleic acid, and oleylamine. Which serves as the reducing agent? the capping agent(s)?

3. Draw *d*-orbital energy diagrams for each metal ion in the three types of nanoparticles and count the number of unpaired electrons in each ion. Do not forget to take into account each ion’s ligand environment.

4. The magnetic properties of the nanoparticles are presented in Figures 6 and 8. The figures show the nanoparticles’ magnetization (y-axis) vs the applied magnetic field (x-axis) as the field is applied and then removed. The width of the hysteresis loop (or magnetization curve) is a measure of the extent to which the particle remains magnetized after a magnetic field is removed. This property is called the coercivity.

1. Which nanoparticles were determined to be superparamagnetic? Fill in the drawings below to show the alignment (or lack thereof) of unpaired spins in a superparamagnetic material at different temperatures and in the presence and absence of a magnetic field. The first two are done for you.

|  |  |  |
| --- | --- | --- |
|  | **no magnetic field** | **magnetic field applied** |
| **10 K** |  |  |
| **300 K** |  |  |

(b) Which nanoparticles were determined to be ferromagnetic? Fill in the drawings below to show the alignment (or lack thereof) of unpaired spins in a ferromagnetic material at different temperatures and in the presence and absence of a magnetic field. The diagram given as an example shows the individual magnetic domains (or regions of magnetic spin alignment) found in a ferromagnetic material.

|  |  |  |
| --- | --- | --- |
|  | **no magnetic field** | **magnetic field applied** |
| **10 K** |  |  |
| **300 K** |  |  |

(c) Rank the nanoparticles from most to least magnetic. Does the order match what you would predict based on the total number of unpaired electrons per formula unit? What justification do the authors give for the observed magnetic properties?