Experiment 11
Ferrite Magnetic Nanoparticles for Ferrofluids*

***Lab follows the protocol published online by the University of Wisconsin MRSEC**

Introduction

A major thrust of modern chemistry has been nanoscience, one aspect of which is the synthesis of smaller and smaller solids of precisely controlled size. One major driving force for the field of nanotechnology is the semiconductor industry, where the power of a CPU is limited by the number of transistors that can fit on a chip. When the dimensions of a material drop below ~20nm, the physical properties of at the nanoscale begin to differ from that of the bulk material.

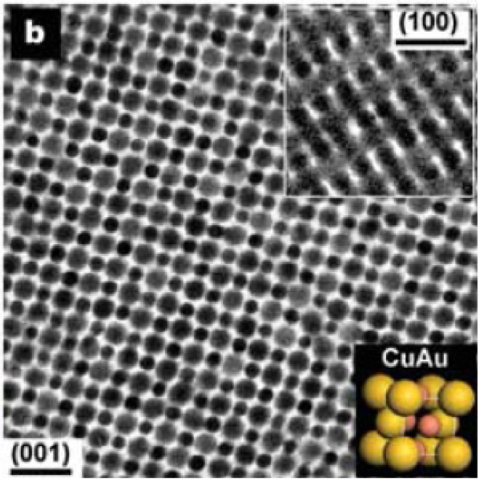

Figure 1. Ordered array of large PbSe (7.6nm) and small Au (5.0nm) nanoparticles adopt the specific structure of the CuAu alloy studied at IBM for magnetic applications. (Murray et. al, Nature, 439, p. 55, 2006)

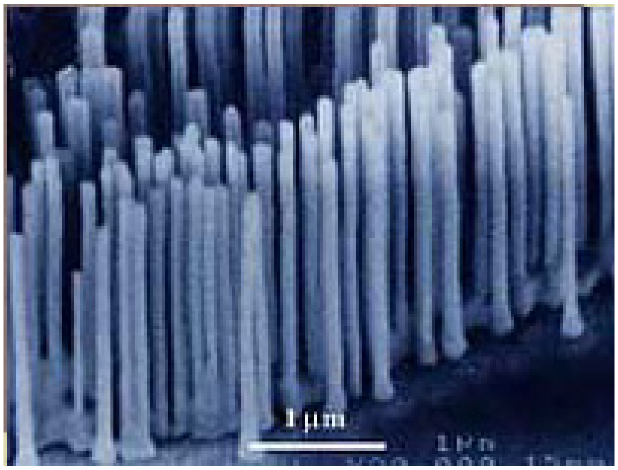

Figure 2. ZnO nanowire UV lasers of about 100nm diameter and 10μm length synthesized at Berkeley. (Yang et al, Science, 292, p. 1897, 2001).

Ferrite is the name given to the spinel structure of formula Fe_3O_4. The proper mineral name of this compound is magnetite, though you may also have heard it called by the name lodestone, which describes a magnetized piece of magnetite. It is very difficult to convince all of the individual spins in a bulk sample of magnetite to co-align, and it has been hypothesized that this only occurs in nature via lightening strikes. However, once a piece of magnetite has been turned into lodestone, it is virtually impossible to demagnetize the sample without resorting to heating the sample to high temperatures (> 500 °C). This is in sharp contrast to typical “soft” ferromagnetic materials such as iron (Fe), which can be trivially demagnetized.

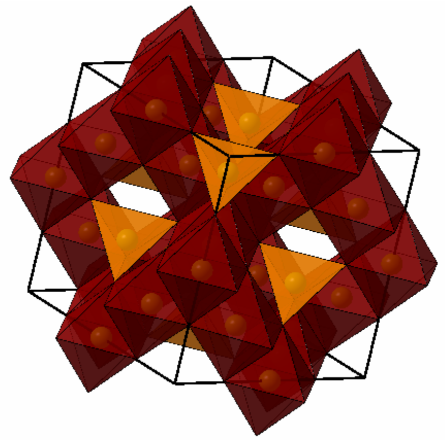

Figure 3. Spinel structure, with tetrahedral and octahedral Fe coordination.

Ferromagnets are materials where all of the individual spins aligned in the same direction, resulting in a greatly magnified sample magnetization. Antiferromagnets are materials where the individuals spins are arranged in an opposing manner, resulting in a cancellation of their contributions, and a greatly suppressed magnetization. Ferrite is an example of a ferrimagnet, which contains aspects of both ferromagnets and antiferromagnets. Ferrite has a large magnetization (like a ferromagnet), yet it is difficult to reorient its magnetization (like an antiferromagnet). This makes ferrite a “hard” ferromagnet, and an ideal permanent magnet.

When hard magnets such as the ferrite spinels are synthesized as nanoparticles, it becomes possible to suspend them in liquid (something that cannot be done with the bulk material). If ferrite nanoparticles are coated with a cationic detergent, they will be unable to tightly agglomerate, and behave like a ferromagnetic fluid, or “ferrofluid”. Applications of ferrofluids include high-vacuum rotating seals and vibrational dampers in speakers.

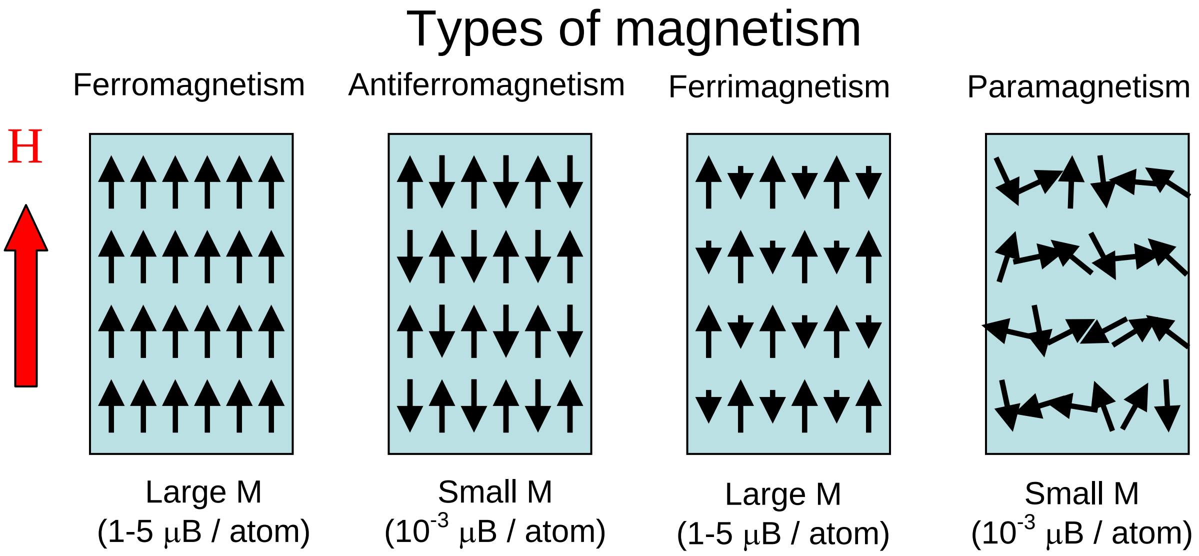

Figure 4. Primary arrangements of magnetic spins within solids. All types of long range ordering (ferro-, ferri-, and antiferromagnetism) will become disordered at high temperatures, resulting in paramagnetism.

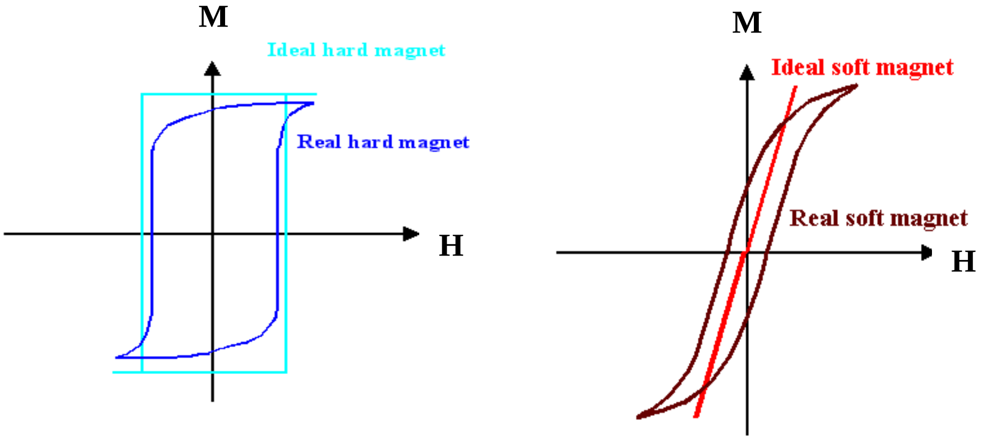

Figure 5. Behavior of hard ferromagnets (left) and soft ferromagnets (right). Ferrimagnets can behave in a similar manner, but are much more likely to be “hard” than “soft”.

Preparation Fe_3O_4 nanoparticles

Caution: Do not let your synthesis product come into direct contact with the magnets. Due to their small size, it is very difficult to remove nanoparticles from magnets. Also, both the starting materials and products are capable of staining fabric, so work carefully to avoid splashing.

Add 4 mL of 1M $FeCl_3$ (in 2M HCl) and 1 mL of 2M $FeCl_2$ (in 2 M HCl) to a large beaker. Using a stir-bar, continuously mix these solutions while slowly carrying out a dropwise addition of 50 mL of 1M NH_3 using a buret. Although you may initially see a brown precipitate forming, the desired product is black. If necessary, add additional NH_3 to obtain a black product if the original 50 mL does not suffice.

After your addition is complete, turn of the stirrer and immediately use a strong magnet to move the stir-bar most of the ways up the side of the beaker. Once it is raised above the level of the liquid, grab it with a gloved hand to prevent the stir-bar from directly touching the magnet and contaminating it with your nanoparticles.

Allow the magnetite to settle to the bottom of the beaker. Although magnetite is substantially more dense than water ($\rho \sim 5$ g/cm^3, and more dense than metallic titanium), this process may take a while since the extremely small particles are very susceptible to the effects of Brownian motion. You can substantially speed up the settling process by placing a strong magnet underneath your beaker, demonstrating the magnetic nature of these particles. Once the settling is complete, pour off as much of the remaining liquid as you can.

Transfer your product to a weigh boat, using squirts of water from a Pasteur pipette to aid the process. Rinse three times, using squirts of water for the cleaning, and using a strong magnet under the boat to hold your particles in place while the excess water is poured off after each rinse.

Finally, add a minimal amount (1-2 mL) of a 25% solution of the surfactant tetramethylammonium hydroxide to resuspend the nanoparticles. Using a glass rod, stir in the surfactant for ~1 min to ensure that it is well dispersed. You should now be able to observe spiking of the ferrofluid if you hold a magnet under your suspension. If the solution is too liquid too exhibit spikes, you can hold the solid material in place with a magnet while pouring off excess liquid. Demonstrate the behavior of your ferrofluid to a TA before disposing of your product.