Magnetic Behavior in Manganese Nanoparticles

Research on the magnetic properties of ubiquitous elements such as manganese will have almost endless applications—from engineering to electronics to environmental protection.

Manganese is present in rail switches, tools, axes, safes, batteries, and an additive in unleaded gasoline. Manganese works with several enzymes in the body and is a required trace element for all known living organisms. Manganese ore is often found in combination with iron ore.

Both manganese and iron have magnetic properties. Andy Christianson, a Shull Fellow at ORNL who is interested in the physics of manganese oxide (MnO) nanoparticles, explains the different magnetic properties of both elements.

"If I pick up a piece of iron, it may not act magnetic because the domains are pointing in different directions," Christianson says, explaining that a domain contains electrons that spin in one direction, either up or down. "If a strong magnetic field is applied to the iron piece, the domains line up in the same direction and an external magnetic field results."

Manganese is antiferromagnetic. In materials that exhibit antiferromagnetism, the magnetic moments of atoms or molecules, usually related to the spins of electrons, align in a regular pattern with neighboring spins (on different sublattices) pointing in opposite directions. Like ferromagnetism, antiferromagnetism is a manifestation of ordered magnetism.

Christianson is looking for evidence that the magnetic behavior of bulk MnO is different from that of MnO nanoparticles. ORNL's Sheila Baker is working on synthesizing MnO nanoparticles in a uniform size—about 8 nanometers across. If bulk MnO has long-range antiferromagnetism, Christianson believes that some MnO nanoparticles could exhibit a different magnetic or nonmagnetic property from what is detected.

"MnO is a classic antiferromagnetic system," Christianson says, adding that he uses neutrons to detect magnetic excitations, or spin waves. "We picked manganese oxide because we wanted to start with a material as simple as possible."

Neutron scattering is the best method for measuring spin waves, Christianson says. "Neutrons will scatter from spin waves. Neutrons entering a sample will either create a spin wave or destroy a spin wave in the material before being deflected toward a detector."

A relationship exists between the energy of a spin wave and its wavelength: as a spin wave's energy decreases, its wavelength gets larger.

"If the energy is small enough, the spin wave would have a wavelength that is bigger than the nanoparticle, which is impossible," Christianson says with a smile. "What we expect is a gap in the spin wave spectrum that is due to this size effect."

The MnO nanoparticles are encapsulated in a hollow aluminum tube filled with helium. Christianson then cools down the sample to find the temperature at which the antiferromagnetic order appears. Below that temperature he can detect spin waves using neutron scattering.

During cooling of the nanoparticles, the helium gas transfers heat evenly, keeping the nanoparticles at the same temperature. Christianson and his colleague Mark Lumsden have cooled the MnO nanoparticles down to their antiferromagnetic ordering temperature of 118 kelvin (room temperature is 300 kelvin).

Using a helium-3 refrigerator, the scientists have cooled the sample all the way down to

500 millikelvin, or 0.5 kelvin, just barely above absolute zero. At this extremely low energy for the spin waves, they have tried to measure a gap in the wavelength spectrum.

"We want to track the magnetic properties of the nanoparticles, such as the ordering temperature at which they become antiferromagnetic and begin producing spin waves, as a function of particle size," Christianson says.

Christianson, Lumsden, Baker, and their colleagues Steve Nagler and William Heller have not yet published any papers, but they have a lot of interesting preliminary data. They obtained their data from the HB-1A Triple-Axis Spectrometer and the GP-SANS instrument at HFIR, a chopper spectrometer at the NIST, and the Backscattering Spectrometer at SNS, "from which we obtained interesting data that we don't understand," Christianson says.

An important part of this study is the synthesis of nanoparticles of different sizes for comparison. Sheila Baker has been synthesizing 8-nanometer MnO nanoparticles and capping them with hairlike organic ligands that have two purposes: (1) they allow the chemist control over size and (2) they protect each nanoparticle from contaminants that could alter its size and composition.

Another group of scientists not associated with ORNL studied MnO nanoparticles embedded in porous glass. Finding that the nanoparticles have a higher ordering temperature than does bulk manganese, the scientists speculated that pressure from the glass could have raised the temperature at which the particles magnetically order. The ORNL group found that the MnO nanoparticles capped with organic ligands have a slightly lower ordering temperature than bulk manganese—the lowest of the three cases.

Mark Lumsden (left) and Andy Christianson (right) examine a sample of a new FeAs-based superconductor.

"It's as if our nanoparticles are under negative pressure," Christianson says. "It may be that the lower the pressure is on manganese oxide molecules, the lower is the magnetic ordering temperature."

Transmission electron microscopy (TEM) images of the nanoparticles Baker makes show the size distribution—the percentages of nanoparticles that are slightly larger or smaller than the desired size. X-ray diffraction experiments also confirm that the nanoparticle consists of MnO instead of other manganese oxide states (such as Mn_2O_3). In conjunction with TEM data, they can determine whether the nanoparticles are single crystalline.

Next steps for the team include continuing to improve the size distribution of the nanoparticles and replacing the hydrogen in the organic ligand caps with deuterium. Because deuterium has a smaller incoherent cross section, ligands made with it will produce less background noise.