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## **EXAFS and XANES of Magnetic Nanoparticles**

S. Calvin, E. E. Carpenter, V. G. Harris (NRL) and S. A. Morrison (GWU)

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**Introduction:** In recent years, increasing attention has been focussed on magnetic nanoparticles, both because they possess enhanced properties for traditional magnetic application such as high frequency electronics, and because they show promise for novel applications such as pharmaceutical delivery and biological sensors [1]. The nature of these materials, however, often makes characterization by conventional techniques such as x-ray diffraction (XRD) problematic. X-ray absorption spectroscopy (XAS), which is element specific and does not require long-range order, is an ideal complement to traditional probes.

**Methods and Materials:** In this study, all nanoparticulate samples were synthesized using the reverse micellar method [2]. Two main classes were investigated: mixed spinel nanoparticles, in particular manganese zinc ferrites (MZFOs); and nanoparticles with metallic iron cores and passivating oxide shells.

The MZFOs were investigated by fitting the Fourier transforms of the extended x-ray absorption fine structure (EXAFS) of the manganese, zinc, and iron K-edges to theoretical standards generated by FEFF8 [3]. The three edges were fit simultaneously and the fits were constrained by the stoichiometry as determined by inductively coupled plasma atomic emission spectroscopy, allowing parameters that often show high correlations in single-spectrum EXAFS fits to be decoupled. The results were checked on ceramic standards of known structure. The nanoparticles were 10-15 nm in size as determined by transmission electron microscopy (TEM) and XRD.

The core/shell particles posed a more difficult analysis problem, since only one edge (the iron K-edge) was available for XAS and at least two phases were present. To begin the analysis, x-ray absorption near-edge structures (XANES) of three bulk materials thought to be similar to the constituents of the nanoparticles were collected: a composite of bcc iron and fcc nickel, an iron-nickel fcc alloy, and a mixture of iron oxides. These spectra were then used to deduce the fraction of oxide present in the samples. Finally, the results were used as a constraint for fitting the EXAFS of the samples to theoretical standards generated by FEFF8. TEM showed that the particles typically exhibited cores about six nanometers in diameter with a shell a few nanometers thick.

**Results:** Spinel materials have two sublattices on which cations can reside; the EXAFS analysis could determine the distribution of each element between these sublattices with an accuracy that was typically better than 10% [4]. Zinc in the nanoparticles was found to reside almost exclusively in sites tetrahedrally coordinated by oxygen, while the distribution of manganese and iron between tetrahedrally and octahedrally coordinated sites was strongly dependent on synthesis conditions [5].

The core/shell particles were found in almost all cases to have an amorphous or mixed phase oxide shell on a metal core. The structure of the metal core varied depending on the surfactant used to form the micelles: a nonionic surfactant produced cores which were amorphous, but loosely based on a close-packed structure, while a cationic surfactant produced cores which included bcc iron crystals as well as some of the amorphous phase. Other synthetic variables had relatively little effect.

**Conclusions:** Analysis of XAS yielded structural details of novel magnetic nanoparticles that would otherwise have been difficult to obtain. In the case of the MZFOs, samples synthesized under similar conditions exhibited different magnetic behavior even though the structure appeared very similar to XRD. An EXAFS analysis applied to the three metal edges simultaneously revealed that the differences were due to the distribution of iron and manganese ions over the available lattice sites. Likewise, XAS confirmed the successful synthesis of passivated iron nanoparticles, and determined that the structure of the metallic core was dependent on the surfactant used to form the micelles.

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