Site Determination of Zn Doping in Protein Encapsulated $Zn_xFe_{3-x}O_4$ Nanoparticles

V. Pool; [1, 4]; *M. Klem;* [2, 4]; *J. Holroyd;* [1]; *H. Li;* [1, 4]; *T. Harris;* [2, 4]; *E. Arenholz;* [5]; *T. Douglas;* [2, 4]; *M. Young;* [3, 4]; *Y. U. Idzerda;* [1, 4];

1. Dept. of Physics, Montana State University, Bozeman , MT, USA.
2. Dept. of Chem. and Biochem., Montana State University, Bozeman , MT, USA.
3. Dept. of Plant Sciences and Pathology, Montana State University, Bozeman , MT, USA.
4. Center for Bio-inspired Nanomaterials, Montana State University, Bozeman , MT, USA.
5. Advanced Light Source, Lawrence Berkeley Nat. Lab., Berkeley, CA, USA.

Abstract Body: There are numerous applications for magnetic nanoparticles that would benefit from control of the particle moment without size modification. Doping non-magnetic Zn into iron oxide nanoparticles alters the overall moment, allowing for tunability of the material. For Fe_3O_4, this control will depend on which Fe-site that the Zn dopant atom substitutes into. In this study, the X-ray absorption spectra of the Fe and Zn L-edges for 8 nm Fe_3O_4 nanoparticles grown inside 12 nm ferritin protein cages with 10%, 15%, 20% and 33% zinc doping, shows that the Zn is substitutional as Zn^{2+}. In addition, by performing frequency dependent ac-susceptibility measurements and angle-dependent electron magnetic resonance measurements, we determine that the anisotropy constants for $Zn_xFe_{3-x}O_4$ nanoparticles are substantially enhanced from the bulk values. Using X-ray magnetic circular dichroism (XMCD), it is possible to obtain the net magnetic moment per iron lattice site as a function of Zn concentration (which cannot be done with traditional magnetometry due to mass normalization problems). The XMCD of the nanoparticles displays a linear decrease with Zn-doping in sharp contrast to the initial increase present in the bulk system. The most straight-forward explanation for the moment decrease is that Zn substitutes preferentially into the octahedral B-site as a Zn^{2+} cation, generating a mixed spinel.

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.