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Authors

Pool, V.
Klem, M.
Holroyd, J.
et al.

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Site Determination of Zn Doping in Protein Encapsulated $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ 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 $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ 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 straightforward explanation for the moment decrease is that Zn substitutes preferentially into the octahedral B-site as a Zn^{2+} cation, generating a mixed spinel.

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