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Site Determination of Zn Doping in Protein Encapsulated $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ Nanoparticles

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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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