Contrast Agents for MR Imaging: Enhanced T_2 Relaxivity of Zn-Doped Maghemite-Magnetite Nanoparticles

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The effect of Zn-doping into originally spinel structure of Fe_3O_4 on stoichiometry, ^{57}Fe hyperfine parameters and magnetic response is investigated by means of liquid-helium temperature in-field Mössbauer spectroscopy (up to 6 Tesla) and temperature-dependent SQUID magnetometry. While for bulk material, Zn atoms preferably occupy tetrahedral (A) positions, the situation in nanocrystals may differ in dependence on their diameter as well as the method of preparation. Distribution of non-magnetic Zn cations within the tetrahedral (A) and octahedral [B] sites significantly influences the predominant A-B magnetic interactions, causing the change in magnetic structure.

The nanoparticles (NPs) of $Zn_xFe_{3-x}O_4$ with x being 0, 0.05 and 0.36 as determined by X-ray fluorescence spectroscopy, are synthetized by controlled two-step thermal decomposition [1]. The particles' morphology and size distribution as observed via transmission electron microscopy corresponds well to the log-normal distribution. Mean diameters and polydispersity indices are d_0=11.3 nm and σ=0.39 for x=0; d_0=10.6 nm and σ=0.19 for x=0.05; NPs with x=0.33 have bimodal distribution with d_{01}=5.1 nm and σ_1=0.15 and d_{02}=14.4 nm and σ_2=0.06, respectively. The spinel structure is confirmed by X-ray diffraction.

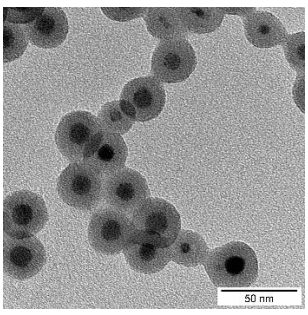

Figure 1. Representative TEM bright field image of $Zn_{0.36}Fe_{2.64}O_4$@SiO_2 NPs with 8.8(8)nm wide shell layer.

The subsequent coating of $Zn_{0.36}Fe_{2.64}O_4$ magnetic cores by silica shell of varying thickness provides colloidally stable particles whose transverse relaxivity (r_2) is analyzed with respect to the applied magnetic field in the range from 0.5 to 11.75 T. The iron concentration (resp. magnetically active atoms) in aqueous suspensions is accurately determined by atomic absorption spectroscopy. The highest observed r_2 value of about 324 Fe $mM^{-1}s^{-1}$ is relatively higher than those previously reported for undoped magnetite NPs [2].

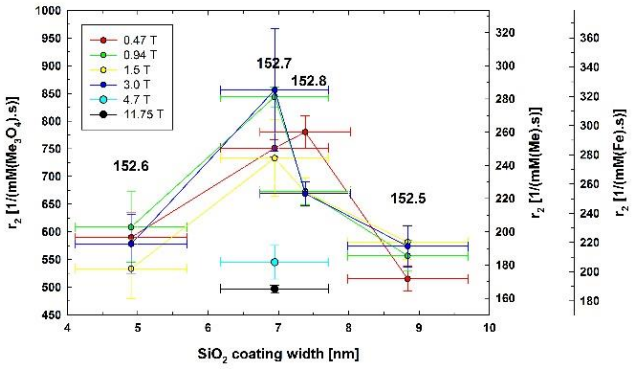

Figure 2. Transversal relaxivity r_2 of $Zn_{0.36}Fe_{2.64}O_4$@SiO_2 NPs versus silica coating thickness for different external magnetic fields, *Me* stands for all metallic atoms in the structure. Connecting lines are only guide for the eye.

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References

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