Novel Magnetic Properties of Gd Substituted Mn-Zn Ferrites Nanoparticles: Modeling T2 Variation with Temperature

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Introduction: We investigate the thermal behavior (18 ~ 58 ^oC) of NMR relaxation induced by novel magnetic nanoparticles (NP) synthesized for use as hyperthermia and MRI contrast agents. Fitting hysteresis data to a single Langevin function (SLF) reveals that the expected decrease of the saturation magnetization (M_s) with temperature is also accompanied by an unexpected increase of the average magnetic moment of the particle μ. Several investigations have reported similar results for ferritin and small NP due to thermoinduced magnetization or the presence of moment distribution[1,2]. We present a new model to explain the increase of μ with temperature which can explain the MRI relaxation data fitted with the Motionally Averaged Regime[3] (MAR) model.

Materials & Methods: Chemical co-precipitation is used to synthesize $Mn_{0.5}Zn_{0.5}Gd_{0.02}Fe_{1.98}O_4$ NP. We measured its physical, chemical, magnetic, and NMR relaxation properties as detailed elsewhere[4]. Both magnetization and NMR relaxation measurements were made at different temperatures from which M_s, μ, *T1*, and *T2* (@1.5T) were obtained. The magnetization data *M(H,T)* is fitted to SLF: $M(H,T)=M_s\ L(\mu_0\mu H/kT)$ with $L(x)=coth(x)-1/x$. We have also examined other fitting functions that include a second superparamagnetic (SPM) component and/or a linear paramagnetic component given by the susceptibility χ: $M(H,T) = M_s\ L(\mu_0\mu H/kT) + \chi H$ (SPM + Paramagnetic – eq. 1); or (2 SPM's + Paramagnetic – eq. 2) $M(H,T)=M_{s1}\ L(\mu_0\mu_1 H/kT)+M_{s2}\ L(\mu_0\mu_2 H/kT)+\chi H$. They take into account the non-saturated magnetization component that keeps rising at large *H* using χH (e.g. ferritin[5]) and also the existence of a second magnetization phase attributed to the surface layer (eq. 2) of the particle or to isolated spin groups of different magnetization.[6]

Results: The variation of both fitted parameters (SLF) with temperature is shown in Fig. 1. For our sample, both additional models (eq. 1 and 2) were unnecessary and produced negligible additional magnetization terms beyond the first component as shown in Table 1, i.e. a single Langevin term represented the data accurately. All errors associated with the fit (SSE and RMSE) were much smaller for the single fit than the other types (data not shown). In order to explain the increase in magnetic moment with temperature we propose that additional spin contribution is generated at the surface shell layer due to increased particle volume caused by thermal expansion. The increase in the surface layer volume, and hence its magnetization, can be bigger than that of the core due to its larger surface coefficient of thermal expansion.[7]

We implemented this model to fit T2 data as shown in Fig. 2 (concentrations [C2]=0.03 and [C4]=0.12 m*M*/kg Fe). Our samples fall within the MAR regime[3] with $1/T2 = (64\ N_A\ 4\pi/10^6\ D)\ [C]\ (\gamma\mu_0/45)^2\ r^5\ M^2$. *D* is diffusion coefficient; *r* is radius of NP; and *M* is magnetization. We use temperature dependent values for *r* and *M* as extracted from the hysteresis measurements (assuming constant NP mass density). Furthermore, *r* is adjusted to take into account effects due to NP agglomeration and non-magnetic part of the NP cluster by the packing factor ($\alpha^{1/3}$).[4,8] A single value for α yields close agreement between model and data for all NP concentrations and temperatures. Radius range (~ 40^{o}C) is 20.3 to 23.1 nm while *M* decreases from 71 to 58 (x10^3 J/T/m^3).

Table 1. Parameters for the three magnetization models show that a Single Langevin fit is adequate for this sample. The units are: T (k); M_S (emu/g); and μ (BM).

	Single		Langevin + Paramagnetic			Double Langevin + Paramagnetic				
T	M_s	μ	M_s	μ	χ	M_{s1}	M_{s2}	μ_1	μ_2	χ
50	25.15	1677	25.15	1677	2.7E-14	25.15	22.67	1677	2.61E-06	4.41E-14
100	23.16	3951	23.16	3951	3.3E-14	23.16	3.09E-13	3951	5.45E-03	2.22E-14
200	18.19	10731	18.25	10281	2.3E-14	18.2	7.58E-13	10676	2.36E-03	2.22E-14
300	12.8	20988	12.8	20988	2.4E-14	12.8	2.33E-14	20988	7.89E-06	2.22E-14

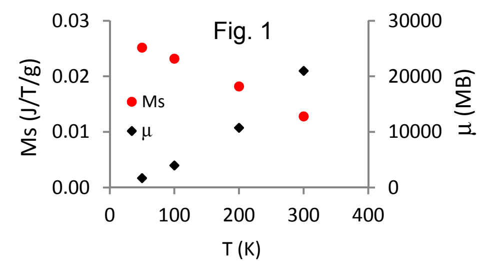
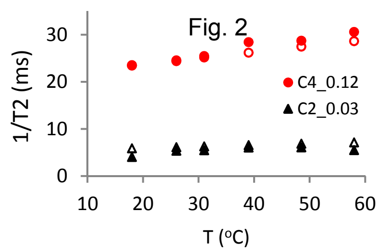


Fig. 1. The increase in μ is attributed to particle volume expansion with *T*. Hysteresis data yield increasing particle radius *r* & decreasing magnetization *M*.

Fig. 2. Extracted variable NP radius is used to fit the *T2* data for all six NP concentrations and four temperatures. Only two values for [C] are shown here.



Conclusions: We attribute the simultaneous decrease of M_s and increase of μ with temperature to inter-particle interaction, particularly as this will increase with increasing μ. There may also be particles that have lost their magnetic properties due to intensified structural defects and changes in crystal morphology and structure, or the substitution of non-magnetic ions instead of the magnetic ions[9] with temperature. The modeling of *T2* variation with temperature depends critically on particle size and also on *M*. A new model is presented to explain the anomalous behaviour of μ that relies on increasing *NP volume* with *T*. Only when variation of *r*, μ, and *M* is taken into account a successful fitting to the *T2* data is achieved. This enables correct characterization of contrast agent effect on the MR image.

References: **1.** Mørup S et al. PRL 92, 217201; 2004. **2.** Silva NJ et al. PRB 71, 184408; 2005. **3.** Laurent S et al. Chem. Rev. 108, 2064; 2008. **4.** Issa B et al. JMRI 34, 1192; 2011. **5.** Makhlouf SA et al. PRB 55, R14717; 1997. **6.** Bulte JWM at al. MRM 42, 379; 1999. **7.** Pigozzi G et al. Nanotechnology 20, 245704; 2009. **8.** Noginova N et al. JPCM 25, 255301; 2009. **9.** Harris JGE et al. PRB 60, 3453; 1999.

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