DYNAMIC EFFECTS OF DIPOLAR INTERACTIONS ON THE SPECIFIC LOSS POWER OF Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$

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ABSTRACT

In this work, isothermal magnetization and initial dc susceptibility of spheroidal, nearly monodisperse Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles (typical diameter: 20 nm) prepared by a hydrothermal route have been measured between 10 and 300 K. The high-temperature inverse magnetic susceptibility was always found to follow a linearly temperature dependence. The deviation from the standard superparamagnetic behavior is related to dipolar interaction among nanoparticles. The results are well explained using interacting superparamagnetic model, which is basically a mean field theory. As a consequence, the dipolar interaction affected the specific loss power of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$

Keywords: magnetic nanoparticles, interacting superparamagnetic model, spinel.

1. INTRODUCTION

In recent years, magnetic fluid hyperthermia (MFH) therapy has been considered as a promising therapy for cancer treatment [1]. In the MFH therapy, energy dissipated from magnetic nanoparticles (MNPs) in an alternating magnetic field can be used to locally raise the temperature more above physiological temperature (37°C), in targeted tumor tissues, thereby destroying them without harm to surrounding healthy tissue [2]. The large specific loss power (SLP) is the key required characteristic for clinical hyperthermia. The magnetic fluid containing MNPs with large SLP can minimize the dose of MNPs, which applied to the patient body, while maintaining enough heat to kill the cancer cell. Zinc ferrite (ZnFe$_2$O$_4$) and manganese ferrite (MnFe$_2$O$_4$) nanoparticles are among the most biocompatible agents for MFH. These particles are
typically coated with a biocompatible polymer to prevent their aggregation and biodegradation for in vivo applications [3]. Up to now, theoretical descriptions of magnetic fluids are based on models consisting of non-interacting particles [4]. Therefore, such behavior has typically been not observed experimentally in both suspension [5] and biological systems [6]. In the absence of magnetic fields, interparticle interactions can produce clustering and formation of structures in suspension [4]. In fact, influence of dipolar interactions on the heating capacity is not so clear and apparently contradictory results have been reported [7]. The experimental studies regarding an increase [6], a decrease [8] or a non-monotonic [4] variation of SLP with dipolar interactions have been reported. From the point of view of theory, most theoretical works agree that SLP tend to decrease in the presence of strong interactions [4] although a limited increase in a restricted range of MNPs concentration has also been reported [8]. One of the existing approaches is the interacting superparamagnetic (ISP) model [9], which is particularly suitable to account for the effect of dipolar interactions on otherwise superparamagnetic nanoparticles. In this work, we show that the dynamical aspects of dipolar interaction actually play a major role on the specific loss power of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles.

2. EXPERIMENTAL

Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles (NPs) having mean diameter of about 20 nm were prepared by a hydrothermal process employing a Teflon lined stainless steel autoclave. More detailed information on the synthesis of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ NPs is available in ref. [10]. FeCl$_3$, MnCl$_2$, ZnCl$_2$, HCl and NaOH (Merck 99.9 %) were used as received. The FeCl$_3$, MnCl$_2$, and ZnCl$_2$ were dissolved in aqueous hydrochloric acid solution, and then the sodium hydroxide was slowly added into the solution. The reaction mixture was stirred for about 30 min. Finally, the solution was transferred into a Teflon lined stainless-steel autoclave with a filling degree of 80 %. After heating at 180 °C for 12 h, the autoclave was cooled down to room temperature. The products were washed several times with hot de-ionized water and acetone and finally dried in an oven at 80 °C for 5 h. A X-ray diffractometer (XRD) D 5000 with CuK$\alpha$ ($\lambda = 0.15406$ nm) radiation was used to determine crystal structure and to estimate grain sizes of the samples. The particle size of sample was determined by using X-ray diffraction and transmission electron microscopy (TEM) (JEOL, JEM-1010). All magnetic measurements were carried out on Quantum Design Physical Property Measurement System (PPMS) system. A homemade unit, in which a RDO generator produced AC magnetic field with the amplitude in the range 50 – 80 Oe at a fixed frequency of 178 kHz, was utilized to measure the magnetic inductive heating of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$. The temperature change of the fluid was directly monitored by dipping an optical sensor into the fluid. The concentrations of the fluid, NPs dispersed in water, were 3 mg/mL, 5 mg/mL and 7 mg/mL.

3. RESULTS AND DISCUSSION

The XRD pattern of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles is shown in Fig. 1 where clear peaks corresponding to Bragg diffraction from (220), (311), (222) (400), (422), (333), (440), (620) and (533) planes. It is well concord with standard JCPDS (No. 10-0319). No other oxide (Fe$_2$O$_3$) or impurity peaks were observed which infers the phase purity of the Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$. In addition, the calculated lattice constant of 8.430 Å reveals the cubic structure of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$. Using Scherrer’s equation, the calculated crystallite size is 20 nm for the high intensity (311) plane. The size, shape and morphologies of the Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles were further determined.
by TEM. The TEM image (Fig. 2a) evidenced that the particles are having almost spherical in shape. The mean particle size was estimated to be 20 nm, which is close to that obtained from the XRD data, suggesting that each particle here is a single nano-crystallite.

![TEM Image](image)

**Figure 1.** X-ray diffraction patterns of the Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ sample.

![XRD Patterns](image)

**Figure 2.** TEM image and particle size histograms of the Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ sample.

Figure 3a presents the zero-field-cooled (ZFC) magnetization profile of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles under an applied field of 100 Oe. The Curie temperature ($T_C$) was estimated to be 450 K. It should be noticed that $T_C$ value of our sample are much higher than the reported $T_C$ value of its bulk counterpart (343 K) [11]. However, no finding the appearance of blocking temperature ($T_B$) in sample, which can be due to the existence of strong interparticle interactions origin from the multi-domain behavior of the sample. Therefore, to test this hypothesis of our system, we have estimated critical diameter for single domain by following equation [12],

$$D_{cr} = \frac{9w_p}{2\pi M_s^2}$$

(1)

in which $D_{cr}$ is the critical diameter, $w_p$ is the energy density of the magnetic domain and $M_s$ is the spontaneous magnetization. It is clear that the particles can be considered as single domain when particle size is smaller than $D_{cr}$. Because the Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ ferrite is a crystal with a
cubic symmetry, the energy density of the magnetic domain can be calculated by following expression [12]

$$w_p = 2k_BT_CK_1/a^{1/2}$$  \(\text{(2)}\)

where \(k_B\) is the Boltzmann constant, \(T_C\) is the Curie temperature, \(K_1\) is the magnetocrystalline anisotropy constant, and \(a\) is the crystalline lattice constant. By substituting \(K_1 = 3.8 \times 10^4\) erg/cm\(^3\) [13], \(T_C = 343 K\) [10], \(k_B = 1.38 \times 10^{-16}\) erg/K, and calculated lattice constant \(a = 8.45 \times 10^{-8}\) cm, we obtained \(w_p = 0.226\) erg/cm\(^2\). Putting in \(M_s = 418 G\) [14] into Eq. (2), \(D_{cr} = 15.5\) nm is obtained. The fact that this value is smaller than the experimental value (20 nm) indicates the multi-domain nature of the sample.

Figure 3. The plot of dc magnetization vs. temperature (a) and inverse susceptibility plotted as a function of the quantity \(T/M_s^2\) for \(\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4\) sample (b). Straight lines are fits to high-temperature data.

As known, in paramagnetic regime, where the magnitude of the magnetic moments associated to magnetic ions does not change with temperature, the physically significant information can be extracted plotting \(1/\chi\) as a function of temperature by the Curie-Weiss law [9]:

$$\frac{1}{\chi} = 3Nk_BT - \frac{T-\theta}{M_s^2}$$  \(\text{(3)}\)

in which, \(N\) is the number of MNPs per unit volume and the saturation magnetization is \(M_s = N\mu\). This was done in Fig. 3b for our sample. The curve shows that the ideal Curie-Weiss law correspondence for a linear behavior is indeed measured at high temperature and deviations from linearity at very low temperatures, which can be ascribed to some type of particle blocking. The straight line constantly intercept the temperature axis estimating the positive value of \(\theta\), implies a predominant ferromagnetic interaction among magnetic moments. The origin of the ferromagnetic interaction is attributed to dipolar coupling. Therefore, in this case, it could be of interest to check for the presence of dipolar interactions between the \(\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4\) MNPs to better predict the magnetic response of this sample. A comprehensive analysis of the possible presence of dipolar interactions was carried out with the help of a mean-field model, recently proposed by Allia et al. [9]. The use of this model could allow us to estimate dipolar interactions at a temperature region, in which the so-called interacting superparamagnetic (ISP) regime describes the behavior of interacting nanomagnets. It is well-known that in superparamagnetic nanoparticles, their hysteretic magnetization curves are well described in terms of Langevin functions and in some cases, the classical “superparamagnetic” scaling law of the reduced magnetization \(M/M_s\) with \(M_s(H/T)\) has been approximately observed; at low temperatures,
deviations from the $M_s(H/T)$ law in samples containing chemically homogeneous particles are usually ascribed to single-particle blocking and of random, collective interactions among particles [15].

Figure 4. Reduced magnetization for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ sample, measured at seven different temperatures, and plotted as a function of $M_s(H/T)$ (a) and $H/M_s$ (b). Dark line is the fitting of M(H) curves to a Langevin function.

Figure 4 shows the reduced magnetization as a function either of $M_s(H/T)$ (Fig. 4a) and $H/M_s$ (Fig. 4b). It is clearly that our sample don’t obey the classical “superparamagnetic” scaling law. This analysis confirms the inner coherence of the ISP model. On the other hand, the ISP model could be used to describe for the real magnetic interaction behavior of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles. In the case of magnetic nanoparticles with the interacting superparamagnetic behavior, the magnetization vs. magnetic field can be described by a modified Langevin function [9]:

$$M = M_s L \frac{\mu H}{k_B (T + T^*)}$$  \hspace{1cm} (4)

in which $M_s = N\mu$ is the saturation magnetization, $k_B$ is Boltzmann constant, $T^*$ is related to the dipolar energy $\varepsilon_D$ through the relation [9],

$$\varepsilon_D = k_B T^*$$  \hspace{1cm} (5)

The best fits with Eq. (4) to the data are shown by the lines in Fig. 4b, proving the validity of the ISP approach. However, in order to gain a deeper insight on this problem, we determined the value of the effective magnetic anisotropy constant ($K_{eff}$) from the magnetization data at 10 K using the law of approach to saturation [16]:

$$M = M_s \left( 1 - \frac{B}{H} - \frac{c}{H^2} + \chi_f H \right)$$  \hspace{1cm} (6)

where $M_s$ is the saturation magnetization, $\chi_f$ is the high-field susceptibility, and $B$ is function of $M_s$ and $K$, and is given by the following expression [15]:

$$B = \frac{4K_{eff}^2}{15M_s^2}$$  \hspace{1cm} (7)

From the magnetization curves near the saturation region, $B$ may be deduced. Using Eq. (7), $K_{eff}$ may be calculated from the above expression. The values of $K_{eff}$ is found to be $1.13 \times 10^6$ erg/cm$^3$, which is larger than the estimated value for bulk ferrite ($8.5 \times 10^5$ erg/cm$^3$ [17]). This increase in the effective anisotropy can be associated with the enhanced surface anisotropies in
the nanoparticles. A further confirmation of the veracity of the anisotropy constant value was obtained from the values of $H_c$ at 10 K. For example, for an assembly of noninteracting randomly oriented single-domain cubic particles the value of coercivity can be determined by the expression $H_c = 0.64K_{eff}/M_s$, while for uniaxial particles $H_c = 0.98K_{eff}/M_s$. The values of $H_c$ are 1498 Oe and 2247 Oe by the law of approach to saturation, respectively. Variations with respect to these theoretical values can be associated, for example, with interparticle interactions [15].

In order to study the AC magnetic heating characteristic of $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles, the dependence of the heat generation on altering the applied magnetic fields of the sample was measured at fixed frequencies of 178 kHz and under different magnetic field amplitudes from 40 to 80 Oe. The strength and frequency of the applied AC magnetic field is chosen so that the high values of SAR is achieved maintaining the safety limit for application in hyperthermia treatment ($H_f \leq 5 \times 10^9 \text{Am}^{-1}\text{s}^{-1}$) [7]. The experiments were performed for 25 min with nanoparticles at three different concentrations, viz. 3.0, 5.0, and 7.0 mg/mL. The Specific Absorption Rate for the nanoparticles can be determined using the following expression,

$$SLP = \frac{C_i m_i}{m} \frac{dT}{dt}$$

where $C_i$ is the specific heat capacity of the $i^{th}$ component in ferrofluid, $m_i$ is the mass of component ($\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles and water, respectively), $m$ is the mass of the $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles in ferrofluid and $dT/dt$ is the initial slope of the time dependent of temperature curve. In these experiments, we used the linear relations in ranges 0 – 5 minutes intervals in order to calculate $dT/dt$. The results for temperature rise are shown in Fig. 5. It can be seen that in low applied field (40, 50 Oe), after about 20 minutes of heating, the temperature of the sample comes to saturation, however, a sharp increase in temperature is noticed for higher strength of the applied field. This shows that power loss due to Brownian relaxation dominates at smaller applied field (40, 50 Oe), while that due to Neel’s relaxation favors comparatively at larger applied field (60, 70 and 80 Oe). The initial temperature rising rate and SLP of samples was listed in Tab. 1.

<table>
<thead>
<tr>
<th>Applied field (Oe)</th>
<th>$dT/dt$ (°C/s)</th>
<th>SLP (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 mg/mL</td>
<td>5 mg/mL</td>
</tr>
<tr>
<td>40</td>
<td>0.0033</td>
<td>0.0132</td>
</tr>
<tr>
<td>50</td>
<td>0.0131</td>
<td>0.0175</td>
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<td>60</td>
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<td>70</td>
<td>0.0338</td>
<td>0.0479</td>
</tr>
<tr>
<td>80</td>
<td>0.0421</td>
<td>0.0545</td>
</tr>
</tbody>
</table>

As can be seen from Table 1, values of $dT/dt$ for $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ NPs fluids increases as almost a linear trend with the ferrite concentration. In addition, it is interesting that when increasing $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ NPs concentration in fluids, the SLP values light decrease, which could be related to effect of interparticle interactions. To analyze the effect of dipolar interaction...
between colloidal clusters on the SLP of magnetic fluids, we focus on fluids with low aggregation. As shown in Table 1, the highest SAR value is 58.7 W/g for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ NPs fluids with concentration of 3 mg/mL and decreasing with the increasing of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ NPs concentration. The increasing of SLP value when decreasing concentration of Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ NPs fluids was revealed in the recent report of Presa et al. [18]. They suggest that magnetic interactions take place inside a particle (magnetic cluster) seem to be responsible for the changing of SLP value. For superparamagnetic fluids, hysteresis is vanished, SLP value was dominated by Néel and Brown relaxation loss. The particle-particle interactions strongly effect on the Néel relaxation time of heating dissipation, resluting in decreasing SLP value when increasing strength of interactions [19, 20]. In our case, we may imply that the heating capacity was effected by the interactions between magnetic colloidal clusters. These interactions not only affect on the relaxation of each moment in Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ particles (Néel relaxation), but also impact strongly on rotation of each clusters that mean impact on Brownian relaxation loss. When decreasing Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ concentration the distance between clusters increases and reduces strength of dipole interactions so that the rotation of clusters smoother that make the Brown relaxation processes more convenient. At this time the contribution of Brown relaxation loss on heating dissipation is dominated. The increasing of SLP value with the decreasing Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ NPs concentration is as consequence of Brown loss contribution. We imply that magnetic interaction between clusters plays an importance role in heating capacity of magnetic fluid because it affects directly on Brown loss. The effect of the dipolar interaction on the specific absorption rate of iron oxide nanoparticles have been described in previous works [21, 22]. Furthermore, there are also interesting reports on the impact of particle interactions on the collective behavior of multicore nanoparticles ferrofluids for hyperthermia [23, 24]. The magnetic ordering and exchange interactions within the multicore nanostructures may lead to increase a tenfold of SLP for multicore nanoparticle systems with respect to that of single core materials as recent report of Lartigue et al. [23]. However, further studies are necessary to describe how magnetic interaction between clusters effect on each heating dissipation loss.

![Figure 5](image-url)  
*Figure 5. (a)–(c) Temperature vs. time curves for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles with different concentrations (3, 5, and 7 mg/ml). The fixed frequency is 178 kHz and the applied fields are 40, 50, 60, 70 and 80 Oe.*

4. CONCLUSION

In summary, we studied the role of the magnetic interaction between magnetic clusters on heating dissipation of magnetic fluid of prepared Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles in an alternating field. Our results implied that magnetic interactions between magnetic clusters affect directly to the large value of the SLP for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ fluids. Reducing Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ nanoparticles concentration in fluid means decreasing dipolar interaction between colloidal particles and help
colloidal particles move easier in fluid. Therefore, SAR achieved higher value at lower concentration. Maximum SAR of 58.7 W/g is achieved in the AC magnetic field of 80 Oe while the frequency is set to 178 kHz. Thus, these nanoparticles could also be used as effective heat mediator in AC induction heating.

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