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Superspin Glass State in MgFe₂O₄ Nanoparticles

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Abstract

MgFe₂O₄ nanoparticles were prepared at different annealing temperature of 400, 450 and 500 °C. Transmission electron microscope image show that powders consist of ~ 8 nm particles. Scanning electron microscope image show aggregation of particles and formation of large particles with size of 20-100 nm. Obtained nanoparticles were superparamagnetic at room temperature. A broad peak (Tp) was observed in temperature dependant AC magnetic susceptibility curves. The Tp increased by increasing the annealing temperature, as a result of increase in particles size. The effective anisotropy constant estimated about 2 (to 3) × 10⁵ erg/cm³. The aggregation caused high interparticles interactions and consequently the total energy barrier between equilibrium states increased. Analysis of frequency dependence AC magnetic susceptibility showed presence of superspin glass state at low temperatures.

Keywords: Mg-Ferrite; Nanoparticle; Superparamagnetism; Superspin glass; Interactions.

1. Introduction

Magnetic interactions have important contribution to the different properties of nanoparticles system. By changing of the coercivity and anisotropy, interactions can alter the relaxation time and dynamics of superspins. There are various reports which have studied the effect of interactions on magnetic properties of single domain particles. Based on these studies, three classes of nanoparticles have known, depending on interactions strength. (I) Non interacting superparamagnetic (SPM) particles which are usually seen in diluted nanoparticles inside a fluid, Dormann et al. (1999). For these systems, the relaxation time obeys the Néel-Brown law, Dormann et al. (1999). (II)
The SPM nanoparticles with intermediate interactions strength. Here, the interactions energy is not enough to lead an ordered (or collective disordered) state, but can change the physical properties of system, such as average blocking temperature and coercivity, Vargas et al. (2005). (III) Highly interacting nanoparticles which is divided into two subclasses. Nanoparticles with random orientations of easy axis, has usually seen in systems with distribution of particles size. Interactions in these systems can lead to a frustrated superspin glass (SSG) state at low temperatures, Aslibeiki et al. (2010). In the case of identical particles with same orientation of easy axis, a long range ferromagnetic order can be formed which is called super-ferromagnetism (SFM). Since each of these magnetic states has different properties, hence determining the type of interactions is an important subject in the field of nanomagnetism.

On the above basis, we studied the effect of magnetic interactions on spin dynamic properties of MgFe$_2$O$_4$ nanoparticles synthesized by thermal decomposition method. Samples with different particles sizes were obtained at different annealing temperatures and then the magnetization and interparticles interactions were investigated.

2. Experimental

MgFe$_2$O$_4$ nanoparticles were prepared with a simple thermal decomposition method. Briefly, magnesium nitrate, iron nitrate, and citric acid powders were mixed. The powders were ball milled in a planetary ball mill for 1 h using agate balls. The ball milled powders were annealed in the ambient air at different temperatures; 400 °C (sample Mg400), 450 °C (sample Mg450), 500 °C (sample Mg500) for 1 h. Morphology of samples were studied using a Hittachi S-4160 field emission scanning electron microscope (FESEM) and a JEM-2100 transmission electron microscope (TEM). Dynamic magnetic properties of samples were studied through AC magnetic susceptibility measurements at different frequencies in a Lake Shore susceptometer (Model 7000).

3. Results and discussion

Figure 1a shows FESEM image of Mg500 sample. The powders consist of particles with size of ≤ 100 nm. The observed particles are too large (for spinel ferrites) to be considered as single domain particles.

The TEM image in Fig. 1b shows that the average size of particles is about 8 nm. Therefore, the large particles in FESEM image should be aggregates of ultrafine particles. Formation of nano-aggregates can influence magnetic the properties of ferrite samples. The aggregated particles can show high interactions energy which can lead to different magnetic order at low temperatures.
Figure 2 shows real ($\chi'$) and imaginary ($\chi''$) parts of the AC magnetic susceptibility of samples as a function of temperature in an AC field of 10 Oe and frequency of 333 Hz. There is a peak in both parts of susceptibility at TP which is called peak temperature. The TP is not identical to blocking temperature (TB) because of presence of interactions, particle size distribution and also the field and frequency dependence behavior. Generally, TP and TB are related together by: TP = $\alpha + \beta$ TB, where the parameters $\alpha$ and $\beta$ are constants, Madsen et al. (2008). Although TP is not exactly the blocking temperature of superspins, but as like as TB it is a size dependent parameter and increases by increasing the size of particles. Increase of TP from 167 to 243 K (for $\chi''$) by increasing the annealing temperature from 400 to 500 °C is a result of particles size increasing. For noninteracting particles, the TB has linear relation with particles volume. In addition to the size, magnetic interparticles interactions influence the effective energy barrier between equilibrium states and then change the position of TP.

Fig. 2. Temperature dependence (a) real and (b) imaginary parts of AC magnetic susceptibility of MgFe$_2$O$_4$ nanoparticle at frequency of 333 Hz and AC field of 10 Oe.

To further investigate the type of interactions and also dynamic magnetic-relaxation behavior of the ferrite samples, frequency dependent AC susceptibility was measured in an AC field of 10 Oe and frequencies of 33, 111, 333, 666 and 1000 Hz. The real part of the AC susceptibility of the Mg450 sample was shown in Fig. 3a as a function of temperature. From Fig. 3a, it is evident that the TP is frequency dependent and it shifts towards higher temperatures by increasing the applied frequency.

To determine the interactions strength in the samples, the following models were used:

\[ \tau = \tau_0 \exp\left(\frac{E_a}{k_B T_B}\right) \]  

\[ \tau = \tau_0 \exp\left(\frac{E_a}{k_B (T_B - T_0)}\right) \]

**Néel-Brown**

**Vogel-Fulcher**

(a) (b)
\[ \tau = \tau_0 \left( \frac{T_B}{T_g} - 1 \right)^{-z} \]

Critical slowing down

\[ C = \frac{\Delta T_B}{T_B \Delta (\log_{10} f)} \]

Model independent parameter

where \( \tau_0 \) is in the range of \( 10^{-9} \text{-} 10^{-13} \) s for SPM systems, and \( \tau \) is related to measurement frequency as \( \tau = \frac{1}{2\pi f} \). Energy barrier, \( E_a \) can be assumed to be proportional to particle volume (V) by \( E_a = K_{\text{eff}} V \), where \( K_{\text{eff}} \) is effective magnetic anisotropy constant.

For noninteracting isolated nanoparticles, the frequency dependence of \( T_B \) is given by Eq. 1 which is known as the Néel-Brown model. For weakly interacting magnetic nanoparticles, the frequency dependence of \( T_B \) is given by the Vogel-Fulcher law given in Eq. 2. The \( T_0 \) is an effective temperature which represents the existence of the interaction between nanoparticles. The Eq. 3 shows critical slowing down model of spin glasses which gives reasonable values for strongly interacting nanoparticles. In this model, the \( T_g \) is value of \( T_B \) in the zero frequency and the exponent \( z \nu \) has been reported to be between 4 to 12 for spin glasses. Parameter \( C \) (Eq. 4) is another factor to classify the observed blocking/freezing process. Dormann et al. distinguished three different types of dynamical behavior based on the values of \( C \): (1) \( 0.13 \leq C \) for noninteracting particles, (2) \( 0.05 \leq C < 0.13 \) in the medium interaction regime, and (3) \( 0.005 \leq C < 0.05 \) for spin glasses, Dormann et al. (1999), Dormann et al. (1997).

The obtained values of fit parameters with Eq. 1-3 are collected in table 1. As an example the Fig. 3b shows best fits of experimental data with Eq. 3. Results show that, the Néel-Brown model gives unphysical values for \( \tau_0, E_a \). The obtained parameters of Vogel-Fulcher model is rather reasonable than those of Néel-Brown. This result confirms presence of interparticles interaction in the samples. From the obtained \( E_a \) we estimate the effective
anisotropy constant to be about 2 to $3 \times 10^5$ erg/cm$^3$ which is in good agreement with those reported for soft ferrite nanoparticles, Vargas et al. (2011). The model independent C parameter (~ 0.03) is in the range of those reported for spin glasses, Dormann et al. (1999), Dormann et al. (1997). Also as it is evident from table 1 the critical slowing down model well justified the experimental data and $z\nu$ values are in the range of spin glasses. These results confirm formation of a frustrated superspin glass state in these samples. Similar behaviour was observed in MnFe$_2$O$_4$, MnFe$_2$-xAgxO$_4$ and Fe$_3$O$_4$ nanoparticles prepared with similar method, Aslibeiki et al. (2012a), Aslibeiki et al. (2012b), (2013), Aslibeiki et al. (2010).

### Table 1. The parameter C and the best fit parameters obtained from Néel-Brown, Vogel-Fulcher and Critical slowing down models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Mg400</th>
<th>Mg450</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model-independent</td>
<td>C</td>
<td>0.032</td>
<td>0.030</td>
</tr>
<tr>
<td>Néel-Brown</td>
<td>$\tau_0$ (s)</td>
<td>$1.03 \times 10^{-14}$</td>
<td>$6.76 \times 10^{-15}$</td>
</tr>
<tr>
<td></td>
<td>$E_v/k_B$ (K)</td>
<td>16863</td>
<td>17691</td>
</tr>
<tr>
<td>Vogel-Fulcher</td>
<td>$\tau_0$ (s)</td>
<td>$1.19 \times 10^{-8}$</td>
<td>$4.91 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$E_v/k_B$ (K)</td>
<td>529</td>
<td>434</td>
</tr>
<tr>
<td></td>
<td>$T_0$ (K)</td>
<td>190</td>
<td>203</td>
</tr>
<tr>
<td>Critical slowing down</td>
<td>$\tau_0$ (s)</td>
<td>$1.38 \times 10^{-8}$</td>
<td>$2.57 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$z\nu$</td>
<td>6.57</td>
<td>5.99</td>
</tr>
<tr>
<td></td>
<td>$T_g$ (K)</td>
<td>210</td>
<td>221</td>
</tr>
</tbody>
</table>

### 4. Conclusion

In summary, the MgFe$_2$O$_4$ nanoparticles were synthesized by a simple thermal decomposition method. AC magnetic susceptibility measurements showed a peak which was corresponded to blocking temperature. The peak shifted toward higher temperatures with increasing the particles size. The critical slowing down model showed formation of superspin glass-like behaviour at low temperatures in the samples.

### References