FMR STUDY OF γ-Fe$_2$O$_3$ AGGLOMERATED NANOPARTICLES IN GLUE

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Abstract. Three samples containing γ-Fe$_2$O$_3$ magnetic nanoparticles (with an average size of about 10 nm) forming agglomerates of different sizes in glue were prepared. Samples 1, 2, and 3 contained agglomerates with average sizes of 1.5 mm, 0.5 mm and 0.2 mm, respectively. At room temperature the position of the ferromagnetic resonance (FMR) line was centered at about $g_{eff} \sim 2$ what was essentially different from the position of the FMR line found for small size agglomerates. The temperature dependence of the FMR spectra was carried out in the 90-300K range. Very interesting behavior of the FMR spectral parameters (g_{eff}-factor, linewidth, integrated intensity) was observed. It was found that the temperature dependence of the g_{eff}-factor could be described by a simple function $c_1 + c_2/T$, while the linewidth varied with temperature as $c_3 \exp(-c_4 T)$. The interplay of the dipole and the demagnetization fields, depending on the agglomerate size, determined the values of the FMR spectral parameters as well as their thermal dependence.

1. INTRODUCTION

Magnetic nanoparticles have been the focus of intense research due to their size dependent properties and numerous applications [1-13]. Maghemite (γ-Fe$_2$O$_3$) is one of the most studied representatives of iron oxides which exhibits ferromagnetic behaviour below around 1000K. However, its physical properties are not well understood because the γ-phase of an iron oxide is metastable and it is hard to grow single crystals. Interest in maghemite nanoparticles extends into many areas of science and technology. They are particularly attractive in biomedicine, where they were first used as a contrast agent in magnetic resonance imaging. They have also been used in many other biomedical applications, such as drug targeting, immunoassays, molecular biology, DNA purification, cell separation and purification and hyperthermia therapy. In industry, they are currently applied in magnetic recording, magnetic refrigeration, magnetic printing, sealing, damping, sensing, catalysis, ion recovery, magnetic membranes and other applications. Apart from their industrial value, maghemite nanoparticles are of great interest in earth and planetary sciences as well as in life sciences.

The magnetic behaviour of disordered assemblies of ferromagnetic nanoparticles with volume distribution and randomly oriented easy axes represents a complex and challenging problem. The difficulty is due to the coexistence of surface effects

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and magnetic interparticle interactions. Due to the surface spin disorder, the whole set of exchange coupled spins, i.e., the particle, forms a many-state system with multiminima potentials in the energy configuration space, similar to another magnetic system with many degrees of freedom - spin glasses. The dipolar interparticle interaction induces frustration in the particle assembly which is also present in spin-glass systems. These interactions modify the particle energy barriers which become interdependent, influencing many essential characteristics, e.g., the blocking temperature.

The ferromagnetic resonance (FMR) is a unique method for studying interactions between magnetic nanoparticles embedded in different matrices. Relatively narrow FMR lines at high temperatures produced by maghemite could facilitate a better understanding of the dynamical processes between the matrix and magnetic moments. The observed shift of the resonance field connected with an internal magnetic field gives information about intra- and inter-agglomerate interactions, as well as about the role of demagnetization processes. The internal magnetic field acting on magnetic nanoparticles strongly depends on the concentration and size of agglomerates [12-16]. A study of magnetic nanoparticles or agglomerates in different matrices has shown that the resonance FMR field at room temperatures differs considerably and that larger magnetic agglomerates could create a smaller resonance field [17].

The aim of this report is to study the temperature dependence of FMR spectra of TEC 4185H glue filled with nanoparticles of γ-Fe₂O₃ in agglomerates of different sizes in order to find a correlation between the FMR parameters and the agglomerate's size. Knowledge of this relationship for a specific type of nanoparticles could be very helpful in forecasting possible physical properties of the studied nanosystems. Glue was chosen as a matrix because it offered a medium easily accommodating magnetic particles without inhibiting their movements.

2. EXPERIMENTAL

Three samples of magnetic nanoparticles (with an average size of 10 nm) of γ-Fe₂O₃ in agglomerated form (size 1.5 mm – sample 1, 0.5 mm – sample 2, and below 0.2 mm – sample 3) dispersed in glue in form of a thin film of TEC 4185H modified acrylic were prepared. The process of preparation has been described previously [18,19]. The TEC 4185H glue
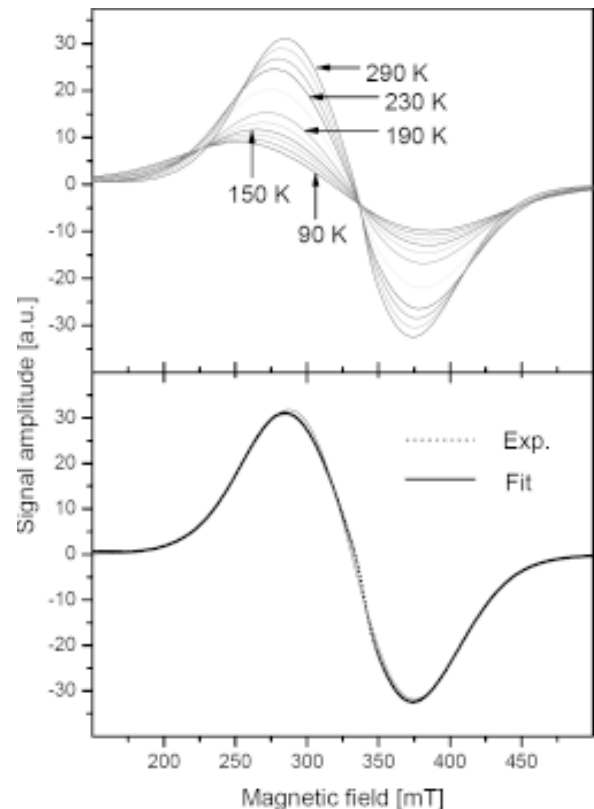

Fig. 1. FMR spectra of sample 1: selection of spectra registered at different temperatures (top panel); comparison of experimental and fitted spectrum at 290K (bottom panel).

was synthesized from modified acrylic PSA with the following constituents: 51.0 wt.% 2-EHA, 45.5 wt.% BA, 3.5 wt.% AA with 30.0 wt.% of polyterphene phenolic resin added to the polymer mass.

The FMR measurements were carried out on a conventional X-band (ν = 9.4 GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation. The measurements were performed in the temperature range of 90 to 300K using an Oxford nitrogen flow cryostat. A square-shaped sample with the dimensions of 3.0×3.0×1.0 mm cut out from a polymer sheet was attached to a sample holder made of a quartz rod 4 mm in diameter. The sample holder was accommodated in the TE_{102} cavity center, i.e., at the local maximum of the microwave magnetic component H_1 and in the nodal plane of the electric component E_1. Prior to the measurements, samples were magnetized by a steady magnetic field of 1.6 T to saturate any domain structure.
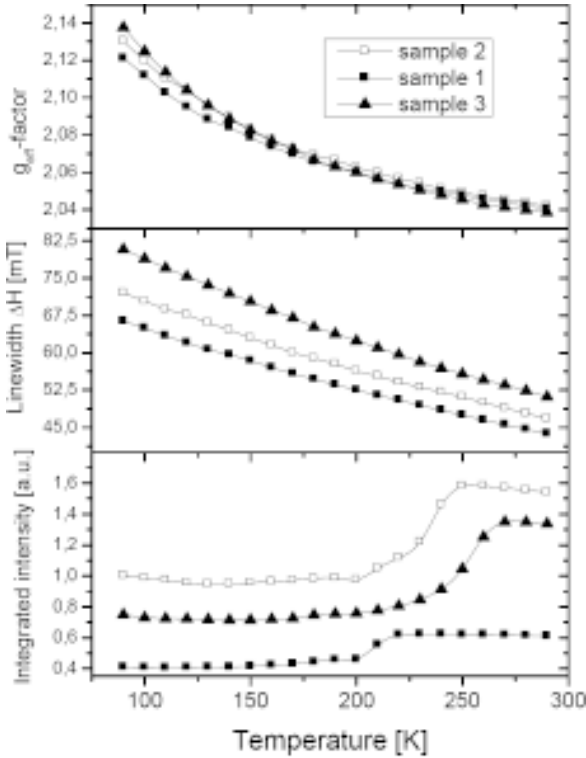
Fig. 2. Temperature dependence of FMR parameters for the three investigated samples: effective g_{eff}-factor (top panel), linewidth (middle panel), integrated intensity (bottom panel).

3. RESULTS AND DISCUSSION

Fig. 1 (top panel) presents the FMR spectra taken at different temperatures for sample 1. A slightly asymmetrical and very intense FMR line was recorded for all three investigated samples. The registered FMR spectra showed a similar temperature dependence and the same resonance field at room temperature as those reported in [17]. The FMR line was fitted by the Gaussian lineshape function and the result for T=290K is shown in Fig. 1 (bottom panel). The fitting could be regarded as satisfactory for all the three samples at all the applied temperatures. The observed slight asymmetry of the FMR line suggests that the signal could be composed of two components. The nanoparticles for which the applied magnetic field is parallel to the easy axis of magnetization produce one component line while the nanoparticles with an easy axis perpendicular to the applied field generate a component at a higher resonance field.

The following spectral parameters were calculated to describe the FMR spectra of γ-Fe$_2$O$_3$ ag-

glomerates dispersed in glue: the effective g_{eff}-factor, the linewidth (half width at half height) ΔH, and the integrated intensity. The effective g_{eff}-factor was calculated from the equation, $h\nu=g_{eff}\mu_B H_r$, where H_r is the effective resonance field. The FMR integrated intensity, defined as the area under the absorption resonance curve, is proportional to the imaginary part of the complex magnetic susceptibility. Fig. 2 shows the temperature dependence of these three calculated parameters: the effective g_{eff}-factor (top panel), the linewidth (middle panel), and the integrated intensity (bottom panel). All parameters depend strongly on temperature. The temperature dependence of the resonance field H_r and the linewidth ΔH is very similar to that reported for other nanoparticle systems, i.e., H_r decreases (g_{eff}-factor increases) and ΔH increases as the temperature decreases.

The resonance field shifts towards the lower magnetic field with decreasing temperatures (g_{eff}-factor increases). This temperature dependence of the g_{eff}-factor could be approximated quite well by the following function: $g_{eff}(T)=c_1+c_2/T$, where c_1 and c_2 are constants (see Fig. 3). This relation holds for the high temperature region which in the case of sample 1 spans the 300-140K range, a wider 300-120K range for sample 2, and extends to the whole investigated 300-90K range for sample 3. The value of $c_1=2.00(1)$ is the same for all the three samples, while c_2 is sample dependent. The value of c_2 is equal to 11.7(1)K, 12.7(1)K, and 13.2(1)K for samples 1, 2, and 3, respectively. It could be easily noticed that the value of c_2 increases with the diminishing size of maghemite agglomerates. It means that there is a more pronounced temperature change of the g_{eff}-factor for smaller agglomerates than for larger ones.

The temperature dependence of the linewidth ΔH for the three investigated samples (Fig. 2, middle panel) shows a substantial increase in the linewidth with lowering temperature. This is an indication of a superparamagnetic regime of the maghemite nanoparticle spin system. In that regime thermal fluctuations average out random magnetic fields produced by nanoparticles leading to the narrowing of the resonance line. The following observation is also evident: the smaller the agglomerates, the broader the resonance line. This clearly indicates that the magnetic dipole-dipole interaction between agglomerates plays a decisive role in controlling the linewidth of the FMR line. It was also found that the temperature dependence of linewidth could be very well approximated by the following equation: $\Delta H(T)=c_3 exp(-c_4 T)$, where c_3 and c_4 are constants
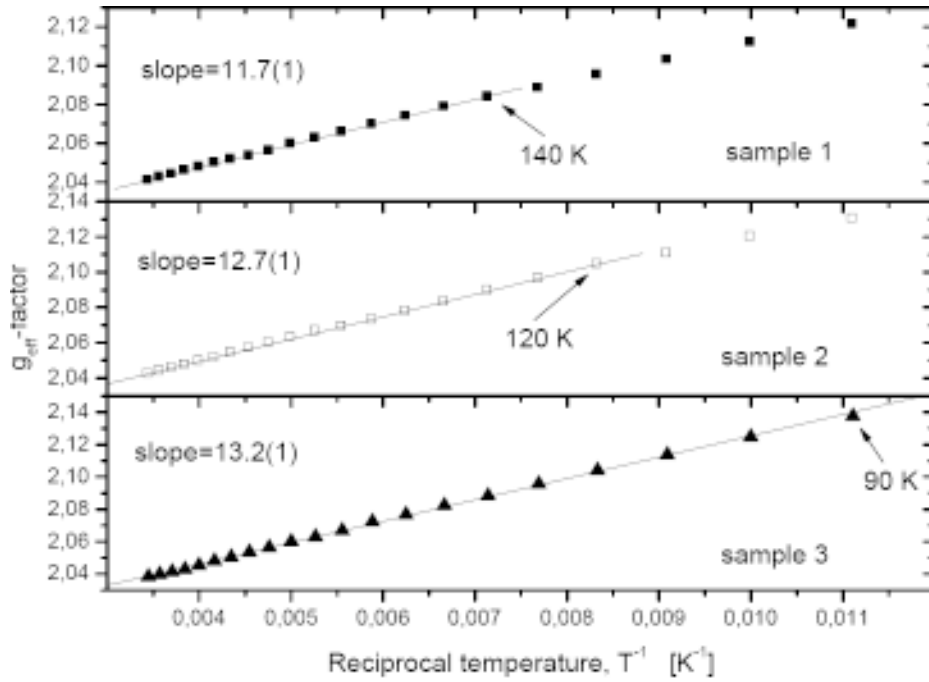
Fig. 3. The g_{eff}-factor dependence on the reciprocal temperature for samples 1, 2, and 3. This functional dependence has been fitted with a linear function with a given value of the slope in an appropriate temperature range (indicated).

(see Fig. 4). This dependence holds for the whole studied temperature range 90-300K. The values of c_3 and c_4 are sample dependent and the value of c_4 correlates well with the size of the investigated agglomerate. For samples 1, 2, and 3 the calculated value of c_4 is 0.00214(1), 0.00207(1), and 0.00229(1), respectively. Thus it could be concluded that the bigger the agglomerate, the smaller the value of c_4. Therefore, the temperature decrease of the linewidth is smaller for larger agglomerates.

The temperature dependence of the integrated intensity for the three samples is presented in Fig. 2 (bottom panel). The most characteristic feature of this plot is a jump of the integrated intensity in a specific temperature range different for each sample. If the temperature in the middle of that temperature range is taken as a characteristic jump temperature T_j for an examined sample than for the values 210K, 225K, and 255K are obtained samples 1, 2, and 3, respectively. It could be noticed that the value of T_j decreases with an increase in the maghemite agglomerate size. As far as the amplitude of the jump is concerned, it is rather small for large agglomerates in sample 1, while the jump amplitude increases for smaller agglomerates in samples 2 and 3. A strong temperature dependence of the in-

tegrated intensity for smaller agglomerates could be connected with the reorientation processes.

A double logarithmic plot of linewidth ΔH versus the shift of resonance field $\delta H_r = H_r(T)-H_r(\infty)$ was proposed to reveal different possible temperature ranges of relaxation processes (see Fig. 5). $H_r(\infty)$ is the resonance field in the limit of very high temperatures. According to the model of Nagata and Ishihara the shift in the resonance field δH_r is due to the demagnetizing fields of nonspherical samples [20]. In the theory of Nagata and Ishihara the shifts of the resonance line δH_r and the linewidth ΔH are related by $\delta H_r = \Delta H^n$. The plot of $\ln(\delta H_r)$ *vs.* $\ln(\Delta H)$ for our three investigated samples is shown in Fig. 5. Any detected change of slope on this type of plot should be a sign of a relaxation type variation in the studied samples. A closer inspection of Fig. 5 reveals the existence of only one temperature range for all the three samples. Moreover, a slop of the $\Delta H(\delta H_r)$ dependence is the same for all the studied samples and is equal to $n = 4.0(1)$. It is only for sample 3, for temperatures higher than 260K that the experimental points seem to depart from the linear regression.

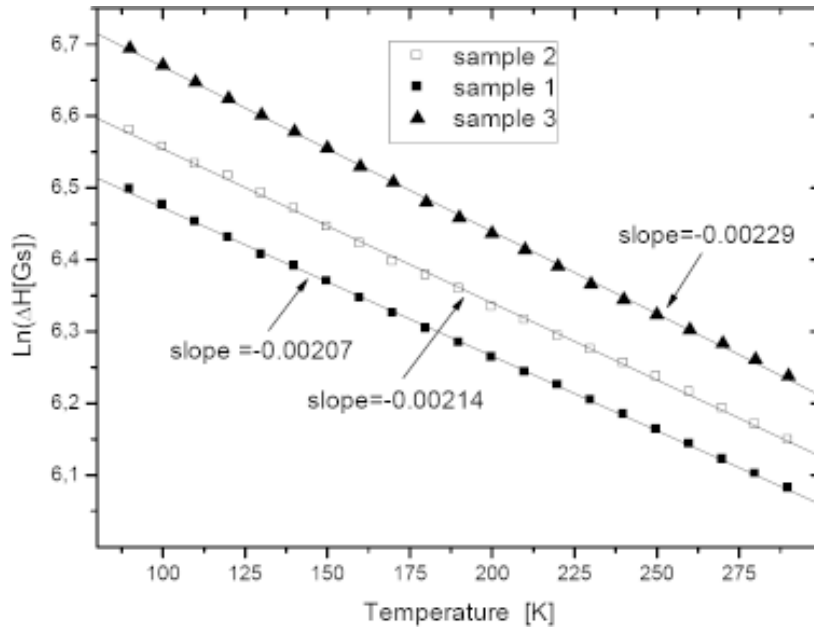The values of the resonance field and the linewidth for sample 3 are almost the same as for γ-

Fig. 4. Temperature dependence of the linewidth logarithm for the three investigated samples. The solid lines are the best fits to the experimental points with the slopes indicated.
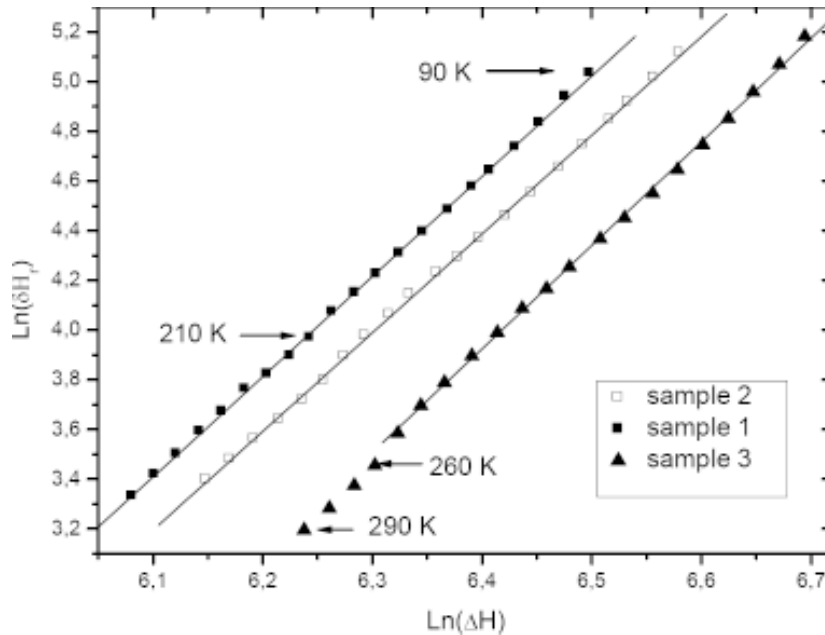

Fig. 5. Double logarithmic plot of linewidth ΔH *vs.* resonance line shift $\delta H_r = H_r(T) - H_r(\infty)$ for the three studied samples. The solid lines are the best linear fits to the experimental points

Fe_2O_3 large agglomerates of nanoparticles embedded in a polymer matrix [14]. At high temperatures, the gradient $\Delta H_r/\Delta T$ is about 1.5 times greater than for small-size aggregates of γ-Fe_2O_3 [13,15,16]. The FMR resonance condition could be written in the following form: $h\nu = g_{eff}\mu_B H_r$, where h is the Planck constant, ν is the resonance frequency, μ_B is the Bohr magneton. The resonance field could be cre-

ated as a result of the following magnetic interactions: $H_r = H_o + H_{dip} + H_{dem} + H'_{dip}$, where H_o is the applied external magnetic field, H_{dip} is an internal magnetic field of dipole-dipole interaction between agglomerates, H_{dem} is an internal magnetic field from the demagnetization, H'_{dip} is an internal magnetic field from the dipole-dipole interaction between magnetic nanoparticles. The last three terms are very

small at high temperatures and only the terms H_{dip} and H_{dem} are important for our samples. The interplay of the dipole and the demagnetization fields, depending on the agglomerate size, determines the values of the FMR spectral parameters and their thermal dependence in the 90-300K range for the γ-Fe$_2$O$_3$ magnetic nanoparticles.

4. CONCLUSIONS

A strong temperature dependence of the FMR spectra of γ-Fe$_2$O$_3$ magnetic nanoparticles forming large size agglomerates was recorded. It was found that the temperature dependence of the g_{eff}-factor could be described by a simple function c_1+c_2/T, while the linewidth varied with temperature as $c_3 exp(-c_4 T)$. A correlation between parameters in these functions and the sizes of agglomerates was established. It was determined that the relaxation process in all three studied samples was of the same kind. The magnetic dipole interaction and the demagnetization field played an important role in shaping the FMR parameters for the studied agglomerates.

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