

Magnetic resonance study of γ -Fe₂O₃ nanoparticles dressed in oxygen based free radicals*

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Two composites consisting of γ -Fe₂O₃ (maghemite) nanoparticles covered by two different oxygen-based free radicals derived from a 4-(methylamino)phenol sulphate and 8-hydroxy-1,3,6-trisulfonic trisodium salt acid were prepared and investigated by the magnetic resonance method in the 4 – 300 K range. Both composites displayed broad and very intense ferromagnetic resonance (FMR) lines originating from γ -Fe₂O₃ agglomerated nanoparticles. The FMR spectrum was fitted satisfactorily at each temperature by two Landau-Lifshitz functions reflecting the existence of magnetic anisotropy in the investigated system. The temperature dependence of the obtained FMR parameters (resonance field, linewidth, integrated intensity) was studied and the results were interpreted in terms of magnetic interactions between free radicals and nanoparticle agglomerates. A comparison with previously studied similar systems containing maghemite nanoparticles was made and conclusions about the role of free radicals were drawn.

Keywords: *magnetic nanoparticles; maghemite nanoparticles; magnetic resonance*

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1. Introduction

Maghemite (γ -Fe₂O₃) is the most frequently studied representative of iron oxides which exhibits ferromagnetic behavior below 1000 K. The strong magnetic behavior of γ -Fe₂O₃ is due to its spinel structure with two magnetically nonequivalent interpenetrating sublattices. Interest in maghemite nanoparticles extends into many areas in science and technology. Magnetic nanoparticles of γ -Fe₂O₃ are widely used in various biomedical and biological applications including enhancement of magnetic resonance imaging contrast, biomagnetic separations, hyperthermia treatment, magnetic drug targeting and many more [1]. An extensive use of maghemite nanoparticles in medicine

originates from their nontoxicity, biocompatibility, biodegradability, low particle dimension, large surface area and suitable magnetic properties [2]. In industry they are applied in magnetic recordings, magnetic printing, sensing, catalysis, ion recovery, magnetic membranes and other applications

Organic molecular networks containing free radicals in their framework are very interesting systems from the scientific and technological point of view, especially in the presence of localized magnetic moments introduced by magnetic nanoparticles [3–11]. Localized magnetic moments could form a correlated spin system at high temperatures which could be attractive in problems connected with spintronics and in the explanation of some important magnetic interactions in the living matter [12]. The study of electron paramagnetic resonance/ferromagnetic resonance (EPR/FMR) spectra from these systems has shown that a correlated spin system coexisting with an ultra low concentration of magnetic clusters could form a very interest-

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ing physical state [8, 9]. The concentration of magnetic nanoparticles essentially influences the spin reorientation processes and the magnetic compensation could change the spin of the correlated system. Recently, a multi-functional phosphotriazine-based polymer has been developed and used as a matrix for embedding γ -Fe₂O₃ nanoparticles, that exhibits high antibacterial and antifungal activity [10].

In this study we report the temperature dependence of the FMR spectra of two composite samples composed of γ -Fe₂O₃ nanoparticles covered by oxygen based free radicals derived from a 4-(methylamino)phenol sulphate and 8-hydroxy-1,3,6-trisulfonic trisodium salt acid. The FMR parameters (resonance field, linewidth, integrated intensity) will be calculated and their temperature dependence will be studied in order to gain knowledge on the influence of free radicals on the magnetic nanoparticles system. The obtained results will be discussed and compared with previous studies on maghemite nanoparticles embedded in different matrices.

2. Experimental

The precursor molecules of 8-hydroxy-1,3,6-trisulfonic trisodium salt and 4 (methylamino)phenol sulphate were obtained from Aldrich. Composite 1 was prepared in the following way: 1 g of p-methylaminophenol sulfate and 1 g of ferric chloride hexahydrate were added to 20 ml of polyethylene glycol 200 (designated as Sample 1). The mixture became colored upon heating in order to dissolve the organic material. One gram of powdered KOH was added to it and the mixture refluxed for 2 h. After cooling, 30 ml of alcohol was added to the resulting solution, and the precipitated solid was isolated by centrifugation, washed with 2 × 25 alcohol and dried in air. The corresponding composite from the precursor of 8-hydroxy-1,3,6-pyrenetrisulfonic acid, trisodium salt, was prepared in an analogous manner using 300 mg of the precursor and 300 mg of ferric chloride hexahydrate (designated as Sample 2). Thus, the two samples under study consisted of maghemite nanoparticles, forming a

core, dressed by oxygen based free radicals derived from the oxidative action of trivalent iron during the preparation of maghemite nanoparticles.

The magnetic resonance spectra were recorded using standard X-band spectrometer Bruker E 500 ($\nu = 9.4$ GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with an NMR magnetometer. The measurements were performed in the temperature range from 4 to 300 K using an Oxford helium-flow cryostat.

3. Results and discussion

In Fig. 1a few of the registered magnetic resonance spectra (in the first derivative mode) of both samples are presented. At each temperature a strong, broad and slightly asymmetric line is observed. In Sample 1, an additional narrow spectrum in the low temperature range is registered (see inset in Fig. 1a). The intense, broad line is attributed to the superparamagnetic resonance of maghemite nanoparticles in an agglomerated form while the additional narrow line seen at low temperatures in Sample 1 is most probably due to the EPR of isolated iron ions in the ⁶S_{5/2} state. In the high spin ground state of the Fe³⁺ ion, there is no first order spin-orbit interaction and the g-factor is expected to lie near the free electron value of 2, what is in fact observed. No apparent signal could be attributed to free radicals in both samples.

A few different line shapes have been proposed for the description of magnetic resonance spectra of magnetic nanoparticles in the superparamagnetic phase [13]. In case of our spectra a satisfactory result of the fittings was achieved by using two Landau-Lifshitz (LL) lines. The following equation for the absorption LL lineshape could be used in case of linear polarization of the microwave field and for a perfect ferromagnet [13]:

$$\chi''(B) = A \frac{B_r^2 [(B_r^2 + \Delta B^2) B^2 + B_r^4] \Delta B}{[B_r^2 (B - B_r)^2 + B^2 \Delta B^2] [B_r^2 (B + B_r)^2 + B^2 \Delta B^2]} \quad (1)$$

where A is an amplitude, B_r is the intrinsic resonance field and ΔB is the intrinsic linewidth. The

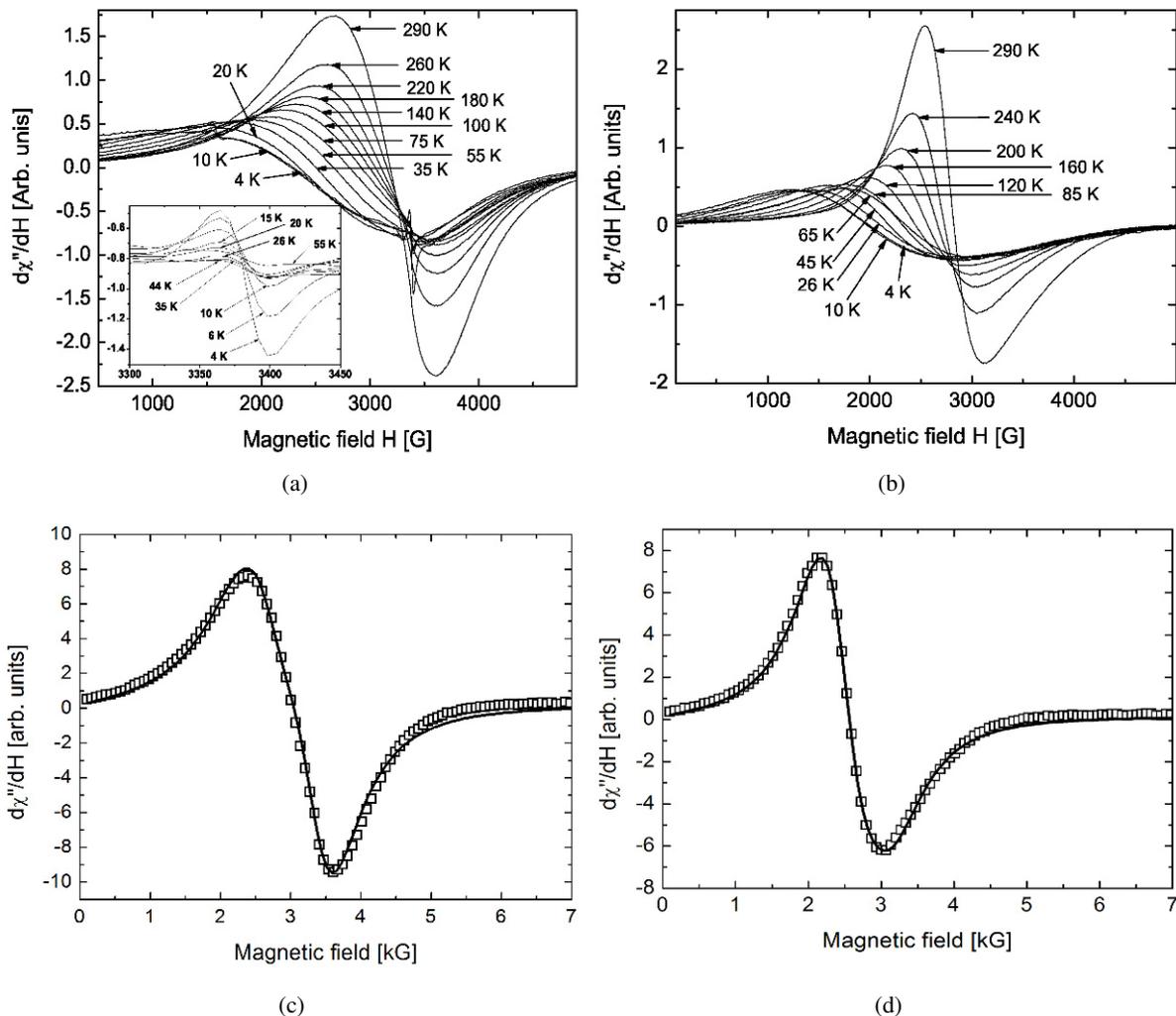


Fig. 1. Magnetic resonance spectra of investigated samples at different temperatures and an example of spectra fittings with two Landau-Lifshitz components: (a) FMR spectra of Sample 1; (b) FMR spectra of Sample 2; (c) fitting of experimental spectrum of Sample 1 at 160 K (open squares) with the sum of two Landau-Lifshitz components (solid line); (d) fitting of experimental spectrum of Sample 2 at 160 K (open squares) with the sum of two Landau-Lifshitz components (solid line). The inset in (a) shows the EPR line due to free radicals.

observed spectrum is in fact the sum of many individual LL lines produced by individual nanoparticles with a randomly oriented anisotropy axis. We have approximated the overall spectrum with only two components that correspond to two orientations (parallel and perpendicular) of an external magnetic field with respect to the effective anisotropy axis. This is a fairly coarse approximation of a complicated situation, but it could provide information on the degree of magnetic anisotropy in our nanoparticle systems. An example of fittings

for both samples is presented in Figs. 1c and d for spectra taken at 160 K. The fitted spectra are reasonably close to the experimental ones and a better fitting is hardly to be expected under the approximations that have been done.

The values of amplitude, intrinsic resonance field B_r and the intrinsic linewidth ΔB for each component could be determined from the fittings at a particular temperature. Moreover, another important parameter, the integrated intensity, I_{int} , could be calculated. The integrated intensity, defined as

$I_{int} = A \cdot (\Delta B)^2$, is proportional to the magnetic susceptibility at microwave frequency of the spin system under study.

In Fig. 2 the temperature dependence of the resonance field B_r for both components in Sample 1 (upper panel) is presented. The lower panel in Fig. 2 shows the same dependence on the reciprocal temperature scale. Two temperature regimes are easy to recognize – the high and low-temperature ranges. In the high temperature range, above 20 K, the resonance field increases with a temperature increase while in the low temperature range, below 20 K, the line shifts towards higher magnetic fields with a temperature decrease. It could be also noticed that a change of the line shift (temperature gradient of resonance line shift, $\partial B_r / \partial T$) takes places at about 100 K in the high temperature range – the line shift is bigger below that temperature. Typical behavior observed for many kinds of magnetic nanoparticles is a shift of the resonance line towards smaller magnetic fields on cooling the sample from RT [14–21].

Fig. 3 presents the temperature dependence of linewidth ΔB for both components in Sample 1. The upper axis shows this dependence on the reciprocal temperature scale. Decreasing the temperature from RT causes both linewidths to increase and the rate of linewidth change varies in the high and low temperature ranges. Below ~ 10 K the temperature change of the linewidth reverses and both components are getting narrow on sample cooling.

In Fig. 4 the temperature variation of the integrated intensity I_{int} is presented. Close to RT, the integrated intensity decreases slightly on cooling, reaching a minimum at about ~ 200 K. Down to 100 K the change of I_{int} is insignificant, but below ~ 100 K a strong increase in I_{int} on cooling is observed. At about ~ 35 K a change of $\partial I_{int} / \partial T$ is noticeable (see Fig. 4a). There are two temperature ranges where the Curie-Weiss law, $I_{int}(T) \sim 1/(T - T_0)$, holds: in the high-temperature range, $35 \text{ K} < T < 140 \text{ K}$, with $T_0 = 0(2) \text{ K}$, and in the low-temperature range, $T < 35 \text{ K}$, with $T_0 = -25(2) \text{ K}$. The minus sign of the Curie-Weiss constant T_0 in the latter case indicates antiferromagnetic interactions in the spin system. These temperature ranges are easily recognized in Fig. 4b,

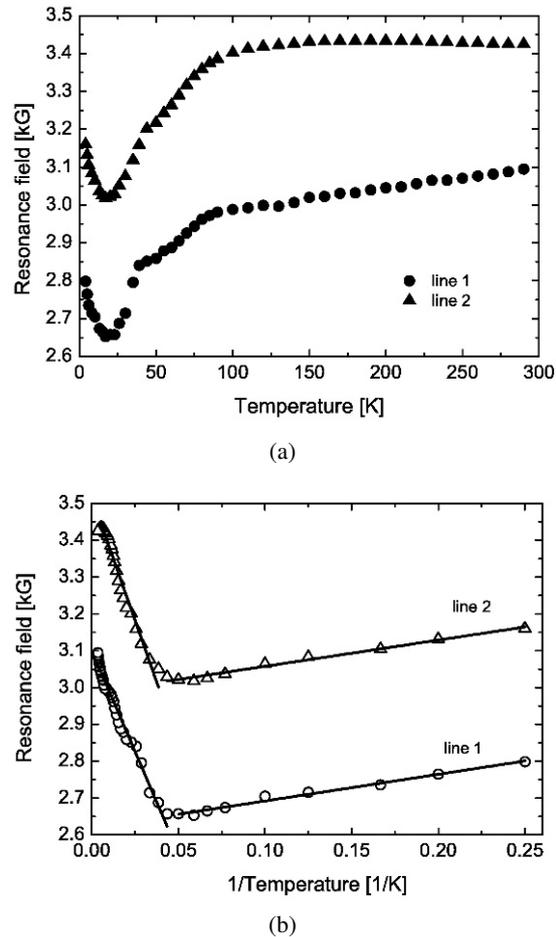


Fig. 2. (a) Temperature dependence of resonance fields for both components in Sample 1. (b) The same dependence on the reciprocal temperature scale.

where the temperature dependence of the product $I_{int} \cdot T$, that is proportional to the square of an effective magnetic moment, is presented.

The temperature dependences of resonance fields, linewidths and integrated intensities for both components in Sample 2 are presented in Figs. 5, 6, 7. The resonance fields of lines 1 and 2 decrease with the temperature decrease in the whole investigated temperature range, except perhaps at the lowest temperature of 4 K (Fig. 5). In comparison with Sample 1, the temperature range where B_r increases with a decrease in temperature is absent or shifted down below 4 K. Another difference between two investigated samples worth stressing is the magnetic anisotropy field δB_a , calculated as the difference between the resonance fields of both

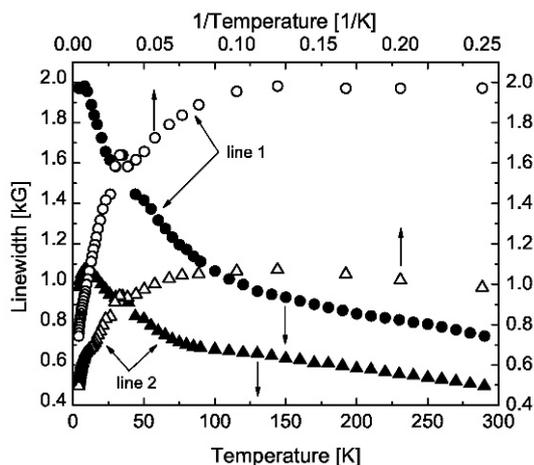
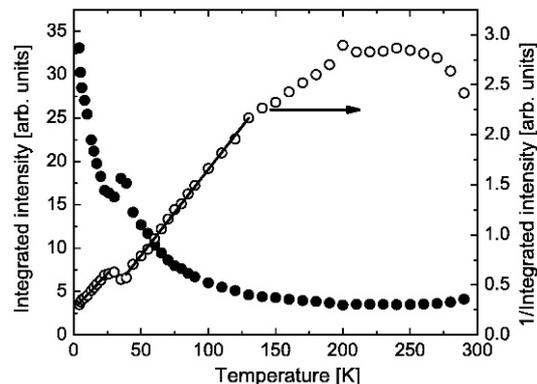


Fig. 3. Temperature dependence of linewidths for both components in Sample 1. The upper axis shows this dependence on the reciprocal temperature scale.

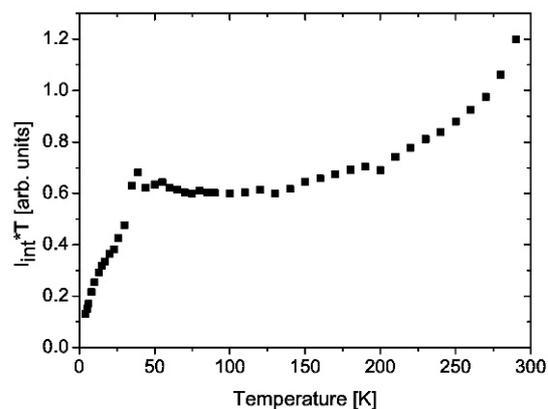
components, $\delta B_a = B_r(\text{line 1}) - B_r(\text{line 2})$. This anisotropy field is connected with the anisotropy of an internal magnetic field in the studied sample. In Sample 1 the anisotropy field $\delta B_a = 0.4(1)$ kG near RT and it has approximately the same value in the 4–300 K range, while in Sample 2 the anisotropy field $\delta B_a = 0.4(1)$ kG close to RT but increases to 0.6(1) kG at low temperatures. This is the consequence of stronger dependence of B_r on temperature in Sample 2 in comparison with Sample 1.

The temperature dependence of linewidths of two components in Sample 2 is presented in Fig. 6. Both component lines display a very similar $\Delta B(T)$ dependence. In comparison with Sample 1 the low temperature decrease of ΔB with a decrease in temperature is not visible in Sample 2. Thus, the anisotropy in linewidths of both components, associated with relaxation processes, must be much smaller in Sample 2 in comparison with Sample 1.

The temperature dependence of the integrated intensity I_{int} of Sample 2 is presented in Fig. 7. The whole $I_{int}(T)$ dependence could be divided into three temperature ranges. In the high temperature range, $T > 200$ K, there is a minimum in this dependence, similarly as was observed in Sample 1. A decrease in an effective magnetic moment with a decrease in temperature (Fig. 7b) indicates the existence of a dominating antiferromagnetic interaction in this temperature range. In the intermediate tem-



(a)

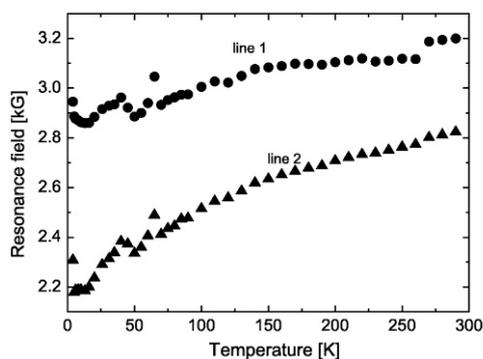


(b)

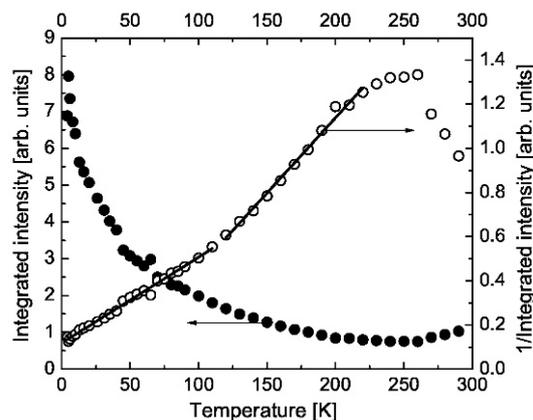
Fig. 4. (a) Temperature dependence of integrated intensity of FMR spectrum in Sample 1. The left axis presents the reciprocal of the integrated intensity. (b) Temperature dependence of the product $T \cdot I_{int}$ in Sample 1.

perature range ($100 \text{ K} < T < 200 \text{ K}$) I_{int} increases with a temperature decrease and the Curie-Weiss law holds with $T_0 = 30(3)$ K indicating prevalence of ferromagnetic interaction. In the low temperature range ($T < 100 \text{ K}$) the Curie-Weiss law with $T_0 = -40(3)$ K is fulfilled what demonstrates the existence of an effective antiferromagnetic interaction. In Fig. 7b the change of the interactions type at temperature of about ~ 100 K can be clearly recognized.

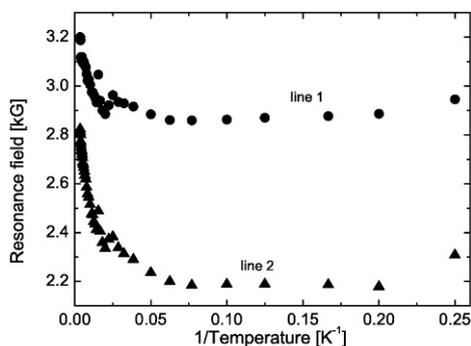
The absence of EPR lines due to the free radicals present in our samples could be explained by their very strong interaction with the nanoparticles resulting in a very short relaxation time of



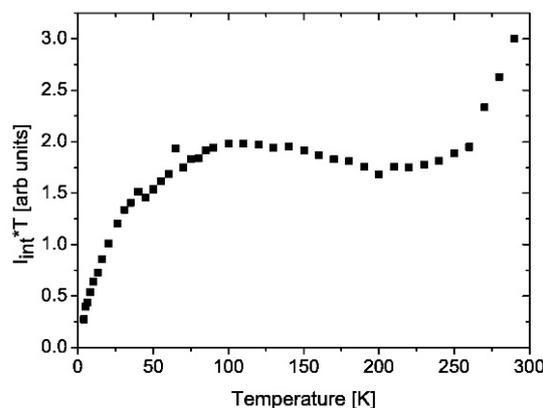
(a)



(a)



(b)



(b)

Fig. 5. (a) Temperature dependence of the resonance fields for both components in Sample 2. (b) The same dependence on the reciprocal temperature scale.

Fig. 7. (a) Temperature dependence of integrated intensity of FMR spectrum in Sample 2. The left axis presents the reciprocal of the integrated intensity. (b) Temperature dependence of the product $T \cdot I_{int}$ in Sample 2.

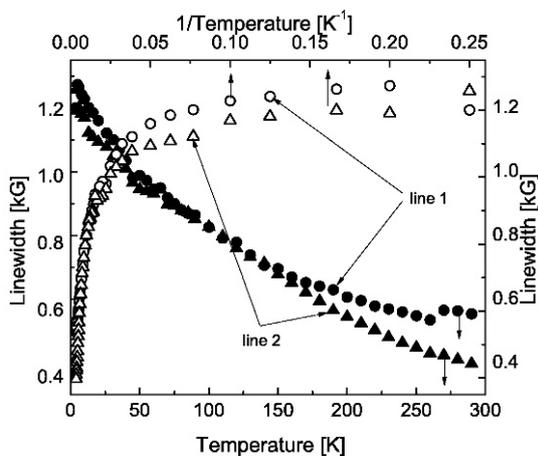


Fig. 6. Temperature dependence of linewidths for both components in Sample 2. The upper axis shows this dependence on the reciprocal temperature scale.

the energy flow from the free radical spins to the maghemite spins. This causes such strong broadening of the EPR lines from free radicals so as to make them unobservable in microwave spectroscopy.

It would be instructive to compare the results of the present study with previous research on maghemite nanoparticles embedded in different matrices. In [18] two samples containing maghemite nanoparticles dispersed in a multiblock copolymer matrix were studied. The temperature dependence of the resonance field for the sample designated in that paper as II (with small nanoparticles, no agglomeration) is very similar (e.g. change

of $\partial B_r/\partial T$ at ~ 100 K, the presence of the low temperature upturn) to that what is observed in the present Sample 1. The low temperature upturn of $\partial B_r/\partial T$ was explained by freezing of the surface spins of maghemite nanoparticles. On the other hand, the behavior of Sample I (agglomerated nanoparticles) is very similar to the present Sample 2 (e.g. absence of the low temperature upturn). As far as the temperature dependence of linewidths is concerned, there is a similarity between Sample I (in [18]) and Sample 1 in this paper (e.g. a decrease in the linewidth on cooling in the low temperature range) and between Sample II (in [18]) and Sample 2 in this paper (e.g. a continuous increase in the linewidth with a temperature decrease).

In [22] maghemite nanoparticles (5 wt.% and 10 wt.%) capped with oleic acid were embedded into PMMA polymer chains and studied by FMR and DSC methods. The FMR lines were analyzed in terms of two (Gaussian) components. In the high temperature range, $T > 200$ K, an increase in the integrated intensity with a temperature increase was observed like in our samples. This effect was greater in the sample with bigger concentration of nanoparticles, hence, it was attributed to the dipole-dipole interaction of maghemite nanoparticles. The temperature dependence of the resonance fields and linewidths was similar to what was registered in our Sample 2, but the integrated intensity behaved like in our Sample 1.

Taking into account the similarities and differences between our samples and the previously studied systems the following picture of the γ -Fe₂O₃ nanoparticles covered by two different oxygen-based free radicals emerges. Maghemite nanoparticles in Sample 1 are probably smaller or less agglomerated than in Sample 2. This is evidenced by different thermal behavior of the resonance fields of both components forming the overall FMR spectrum. There is also a difference in the coupling strength between the surface of a nanoparticle and free radicals. In Sample 1 this coupling seems to be weaker than in Sample 2 which influences the temperature dependence of the FMR linewidths. In Sample 1 freezing of the surface nanoparticles spins seems to occur at the lowest temperatures but in Sample 2 stronger coupling with free radicals

prevents this from happening. This strong coupling in Sample 2 might be also responsible for the ferromagnetic interaction in the intermediate temperature range observed in this sample. As a result, the role of free radicals might be as important a factor as the degree of agglomeration of nanoparticles.

4. Conclusions

Two samples of magnetic nanoparticles covered by free radicals were prepared and investigated by magnetic resonance spectroscopy in the 4 – 300 K temperature range. Very intense and broad resonance lines were recorded in both samples. They were fitted by two different LL lines reflecting the presence of magnetic anisotropy in the spin system. The temperature dependences of FMR spectra parameters: resonance fields, linewidths, integrated intensities were analyzed and compared to the thermal behavior of these parameters in other systems containing maghemite nanoparticles in different matrices. The role of free radicals in determination of the FMR parameters was evaluated and compared with other important factors establishing the FMR spectrum.

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