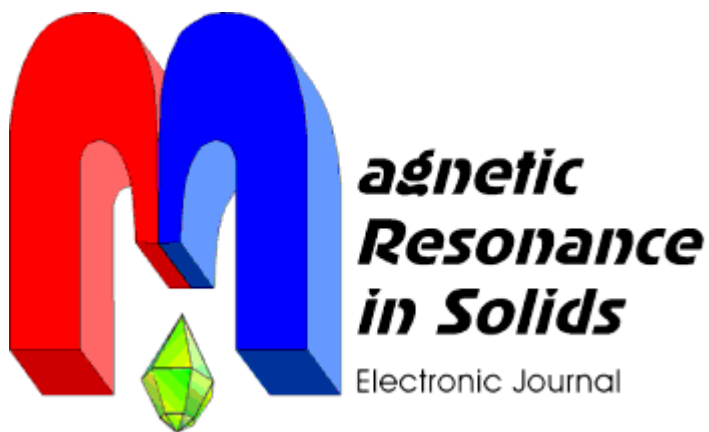


**Temperature Effects in the FMR spectra of Magnetic Nanoparticles
Dispersed in Polymer Film and Viscous Fluid**

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Temperature Effects in the FMR spectra of Magnetic Nanoparticles Dispersed in Polymer Film and Viscous Fluid

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Temperature dependences of ferromagnetic resonance spectra of nanoparticles of magnetite dispersed in polyethylene glycol films and nickel in vaseline oil have been studied. Sharp changes in spectra position (g -value) and linewidth have been found for both systems in the temperature interval 60 – 100 K above glass transition point. These effects have not been observed for polyethylene glycol films prepared under external magnetic field. It has been shown that the effects observed are connected with formation of anisotropic aggregates from nanoparticles under magnetic field action. The main factors determining the temperature of spectra parameters changes are the matrix viscosity, particles translational mobility and spectrum sweeping time.

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Keywords: magnetite nanoparticles, nickel nanoparticles, nanoparticles dispersions, polyethylene glycol films, vaseline oil, ferromagnetic resonance, temperature effects, nanoparticles aggregation.

1. Introduction

Ferromagnetic resonance (FMR) technique has been productively used for studying of magnetic nanoparticles [1-10]. It was found that the shape, width and position of FMR line depend on the particle size, shape, magnetic moment and uniformity of internal magnetic fields. These dependences allow one to get information about dimensional characteristics of nanoparticles [2,3], and also about nature of their distribution over the matrix, aggregate formation, their shape and orientation. At present it is difficult to imagine integrated study of systems containing magnetic nanoparticles (composite materials, biological systems) without the FMR data. There are two main reasons which inhibit the development of this technique: complexity of the line shape analysis and the lack of experimental material.

The main goal of this work is to study the temperature changes in the FMR spectra of magnetic nanoparticles: ferrous-ferric oxide (magnetite) and nickel, dispersed in polyethylene glycol (PEG) and vaseline oil, respectively.

2. Experimental

Magnetite nanoparticles were obtained by the interaction of ferrous and ferric salts solutions in water by the procedure developed in [11]. Phosphate-citrate buffer with pH = 4 was used for particles stabilization. The size distribution of particles was characterized by Gaussian distribution with the center at 17 nm and standard deviation of 12 nm according to photonic correlation spectrometry data. Polyethylene glycol in amount of 2 vol.% was dissolved in the hydrosol contained 0.001-0.2 vol.% of magnetite. Then the solution was dried on glass substrate at room temperature for several days. Polymer film dimensions were 18 by 5 mm and ca. 5 μm in thickness. The samples were placed into the cavity of spectrometer in plastic holders. The plane of the polymer films was parallel to the direction of external magnetic field.

Nickel particles were obtained by soda treatment of nickel chloride in solution. The precipitate was filtrated, dried and reduced by hydrogen at temperatures 400-600 $^{\circ}\text{C}$ during 30 minutes. The specific surface area of the particles equals to 48.5 m^2/g according to the results of low-temperature adsorption of nitrogen vapors. The average size of nickel particles calculated from specific surface area and nickel density (8.9 g/cm^3) was ca. 14 nm. The particles were dispersed in vaseline oil by ultrasonic treatment. Their concentration in the dispersion was about 6 mg/ml .

Ferromagnetic resonance spectra were registered in the temperature interval of 173-363 K with step 10 K using X-band "Bruker" (EMX-8/2.7) spectrometer. The spectra sweep time was 3 min and the gap between two nearest sweeping was 5 min. The temperature maintained with the accuracy of 0.5 K.

3. Results

FMR spectra of nanoparticles dispersed in polymer matrix

The spectra of PEG films formed under different conditions and containing 5 vol.% of magnetite nanoparticles are presented on Figure 1a. The films prepared by solvent evaporation in the absence of external magnetic field give nearly symmetric FMR lines with the peak-to-peak width $\Delta H_{pp} \approx 830$ G (Fig. 1a, Table 1). The films drying in magnetic field of 1500 G leads to the line shape distortion, its broadening and splitting, so that an additional line appears in the low-field part of spectrum. This line is an identifying feature for anisotropic aggregates of magnetic particles (Fig. 1a, curve 3) [10]. Exposition of dried films in magnetic field at room temperature during 5 days also leads to the spectra splitting (Table 1).

Temperature dependences of spectra parameters

The linewidth, ΔH_{pp} , position of the line in magnetic field, H_{centr} , its asymmetry, α , and also number of lines are the basic characteristic features of FMR spectra. The ratio of low-field and high-field part widths of spectrum at half-height was used as asymmetry parameter. Let us give consideration to behavior of these parameters with temperature for PEG films containing 5 vol.% of magnetite (Fig. 2 and 3, Table 1).

If heating and cooling processes for dried films are realized in magnetic field of spectrometer (spectra are registered periodically in the field interval of 2000-5000 G), we can see the following linewidth changes: ΔH_{pp} decreases with temperature and when the temperature decreases this value rises (Fig.2). Such behavior of curves is easily explained by particle magnetic moment decreasing under heating. It is characteristically for temperature dependences obtained that for one conditions of film preparation and treatment heating and cooling curves coincide and for other conditions the curves differ. For the samples dried in the external magnetic field both curves coincide (Fig. 2b). Here, ΔH_{pp} is the distance between low-field and high-field peaks. For the samples which were not previously magnetically treated the behavior of

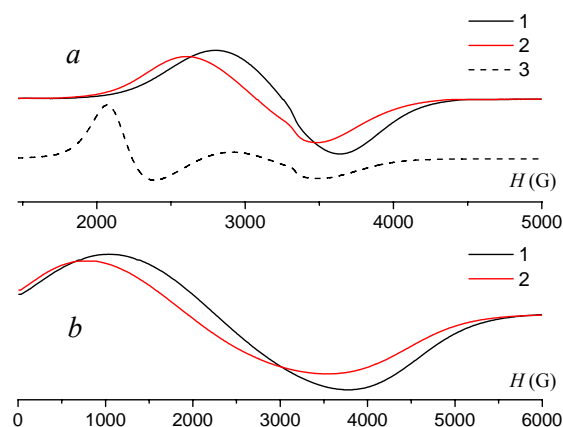


Fig.1. FMR spectra of PEG film containing 5 vol.% of magnetite nanoparticles at 293 K (a) and nickel nanoparticles in vaseline oil (b).
 a: 1 – the film prepared in zero magnetic field, 2 – the same film after heating up to 363 K with consequent cooling, 3 – PEG film prepared in magnetic field;
 b: 1 – the sample before treatment in the magnetic field of spectrometer, 2 – the sample after treatment in the magnetic field of spectrometer.

temperature dependences for heating and cooling are not the same (Fig. 2a).

Table 1. Values of linewidth, ΔH_{pp} , the shift of its position in magnetic field of spectrometer, δH_{centr} , temperature intervals of the shift, ΔT , and asymmetry parameter, α , in relation to sample preparation conditions

Sample preparation	ΔT (K)	δH_{centr} (G)	$\Delta H_{pp}, \pm 10$ G Before/after heating in spectrometer magnetic field at 293 K	$\alpha \pm 0,02$ after heating in spectrometer magnetic field ($T=293$ K)
Dried in zero magnetic field at room temperature	303-338 K	150	830 / 860	1.11
Dried in magnetic field at room temperature	293-323 K	5	Two lines appear in spectrum	
The film dried in zero magnetic field at room temperature was held in magnetic field during 5 days	283-313 K	60	870/915	1.44

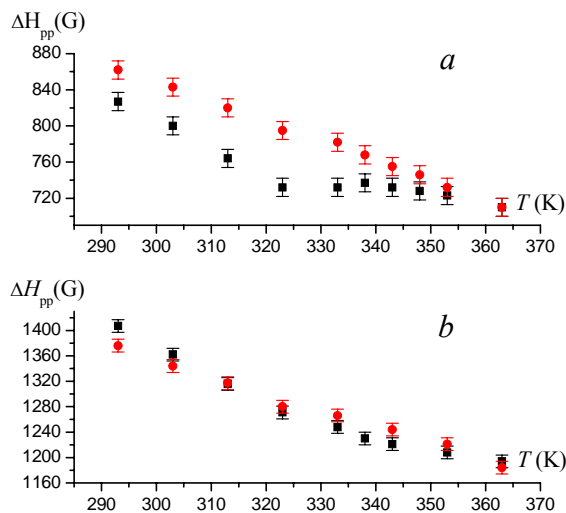


Fig.2. Temperature dependences of FMR linewidth for magnetite nanoparticles in PEG films, prepared in zero magnetic field (a) and in magnetic field (b). ■ – heating of the sample, ● – its cooling.

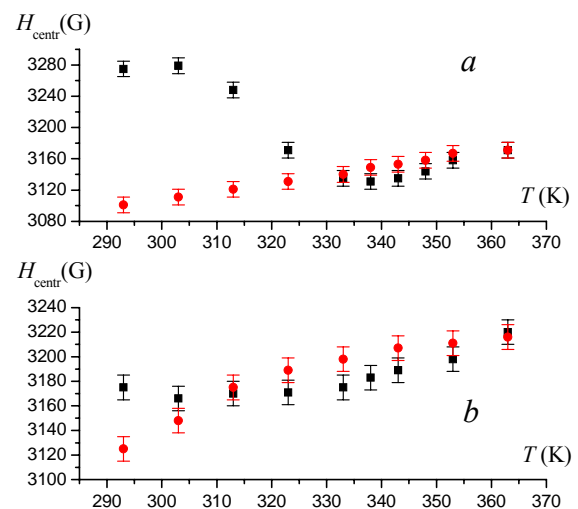


Fig.3. Temperature dependences of FMR spectrum position, H_{centr} , of magnetite nanoparticles in PEG films, prepared in zero magnetic field (a) and in magnetic field (b). ■ – heating of the sample, ● – its cooling.

Heating of the samples in magnetic field is accompanied by line broadening (Table 1). If the magnetic field is applied at the stage of film formation from solution then as it was mentioned before the spectra split into two lines. All the linewidth changes observed may be interpreted by nonuniformity of nanoparticles distribution and their aggregation in the samples. This nonuniformity appeared on the stage of solvent evaporation. When the temperature rises up to 323 K, change of the slope for the temperature dependence of linewidths takes place (Fig. 2a) It is caused by competition of two processes. One of them is decreasing of particle magnetic moment with heating. And the other is aggregation of particles under the influence of the spectrometer magnetic field. The first process leads to narrowing and the second to broadening of linewidth.

More pronounced effects appear on temperature dependences of FMR line position in the field (the x-intercept) (Fig. 3). When the films which were not previously exposed to magnetic treatment are heated in the field of spectrometer, sharp shift of spectrum position (δH_{centr}) to the low fields takes place in the temperature interval 303-343 K. The magnitude of the shift achieves the value of 150 G and depends on the conditions of film formation and treatment (Table 1) whereas the cooling leads to linear dependences of the line position. The temperature dependences of line position of succeeding “heating-cooling” cycles coincide completely and there are no jumps on these curves. For the films which were prepared in magnetic field, the magnitude of δH_{centr} (the x-intercept of central-peak) sharply decreases (Table 1) and vanishes. Therefore, it is obvious that jumps on the curve $H_{centr} = f(T)$ are concerned with the magnetic field influence. Notice that observable effects are reproduced in the wide interval of magnetite nanoparticles concentrations (0.05-9 vol.%).

These results make two questions arise: could the observed features be connected with transitions in magnetite or with matrix properties? To answer the first question we will analyze the results for the second particles dispersion – nickel in vaseline oil. The spectra are presented on Figure 1b.

The same effects were detected in this system. Jumps on the temperature dependences of H_{centr} for nickel dispersion under heating in the field of spectrometer are also observed but at more low temperatures 263-323 K (Fig. 4).

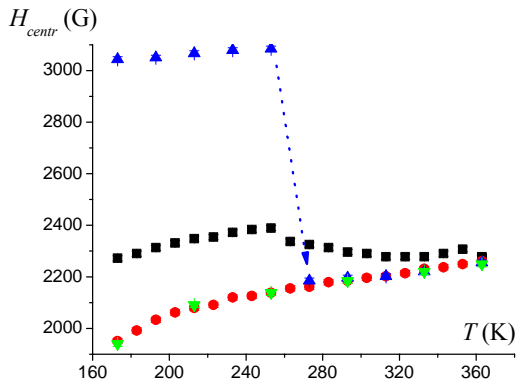


Fig.4. Temperature dependence of H_{centr} for nickel nanoparticles in vaseline oil. Square points – the first heating, round points – the first cooling, rhombs – the line position after 90° turn of the sample at 170 K. ■ – heating of the sample, ● – its cooling; ▲ – heating of the sample after turning round on 90° , ▼ – its cooling.

by aggregation of particles in matrix under the influence of magnetic field. Evidently, dipole-dipole interaction between particles is more intense in aggregates. It is also clear that the rate of this process is controlled by nanoparticle translational mobility. Linear aggregates formation occurs more intensive in the case when the time during which the particles overcome the distance d between them (the translational mobility correlation time, τ_t) becomes comparable with the spectrum registration time (~ 180 s). I.e., the following condition takes place:

$$\tau_t = \frac{\pi\eta r d^2}{kT} \leq 180 \text{ s}, \quad (1)$$

where η is viscosity, r is the average radius of particles [12].

Thus, the temperature at which we see the bends on the dependences $\Delta H_{pp} = f(T)$ and jumps of $H_{centr} = f(T)$ for particles of given size depends on medium viscosity, particles concentration and spectrum sweeping time.

Resonance conditions for linear aggregates and shape of spectra

It is clear that we have taken into account nanoparticles aggregation to explain the character of FMR spectra parameters changing with temperature and the effect of magnetic field on this process. Aggregation of particles with magnetic moment leads to increasing of local magnetic fields, line broadening and changing of line shape, symmetry and line position in magnetic field (g-value). If the arrangement of particles in assemblies characterized by high symmetry, the lines have Gaussian shape [13,14]. Deviation from symmetry leads to appearance of asymmetric lines in spectrum [9].

Aggregate symmetry is disturbed in the systems with sufficiently high molecular mobility (liquids, melts and possibly rigid porous systems). The aggregates disposed in external magnetic field elongate in the direction of magnetic field lines [15]. In this case it becomes possible to observe additional maxima in the FMR spectra [9]. Resonance condition for elongate anisotropic aggregates includes a factor connected with demagnetizing pole influence [16,17,18]. Approximating linear aggregate of particles by endless cylinder we can use the following equations of FMR theory:

$$\omega / \gamma = H_{res} + 2\pi M_s, \quad (2)$$

$$(\omega / \gamma)^2 = H_{res} (H_{res} - 2\pi M_s), \quad (3)$$

where ω is microwave frequency, γ – gyromagnetic ratio for electron, H_{res} – resonance field strength, 4π – magnetic anisotropy constant, M_s – saturation magnetization of particles.

Eq.(2) holds when the cylinder is situated parallel to the field direction. According to Eq.(2) the resonance field decreases by the value $2\pi M_s$. Eq.(3) is valid for perpendicular orientation of the cylinder. According to Eq.(3) resonance field increases.

Due to the fact that equations for various orientations of nanoparticle aggregates are different, it is interesting to analyze the spectra for diverse mutual orientations of linear aggregates and magnetic field. For this aim the dispersion of nickel nanoparticles in vaseline oil placed into quartz tube with spherical end was heated in the field of spectrometer up to the temperatures at which linear aggregate formation is completed (340-360 K). Then the temperature was decreased lower than oil glass transition temperature (203 K) and the tube was turned round on 90° . Line center position sharply moves to the high field and this shift exceeds 1 kG (Fig.4). According to the equations (2) and (3) this shift may occur when magnetization of dispersion, M_s , is equal to ~ 115 G. When this sample is heated, sharp shift of line to the low field at 253-273 K is observed. The obtained result is explained in the following way. When the frozen dispersion

of nanoparticles is rotated linear aggregates orientate perpendicular to field force lines and their resonance takes place in the field predicted by Eq. (3). When the sample is heated, the condition of fast translational mobility (1) is performed and anisotropic aggregates rearrange in the direction of field. Therefore, the system reverts to the state that it had before the tube rotation. In this case the line position again corresponds to Eq. (2).

4. Conclusion

The analysis of results obtained in this study coupled with ferromagnetic resonance equations leads to the following explanation of the observed effects. If magnetic nanoparticles dispersions in solid and viscous matrices undergo heat treatment in magnetic field linear aggregates of particles form. Their axis is orientated parallel to force lines of field. The rate of this process depends on particle size, their concentration, magnetic moment and dispersion medium viscosity. For dispersions examined in this study the temperature interval of linear aggregate formation lies 60-100 K above glass-transition temperature ($T_g \sim 210$ K for PEG; $T_g = 203$ K for vaseline oil). Resonance lines shift, increasing of line asymmetry, appearance of additional peaks are features of this process. Non-uniform distribution of nanoparticles over the sample may be a significant factor especially in polymer matrix. High local concentrations of particles contribute to their aggregation; magnetic field just deforms the aggregates symmetry elongating them along force lines. When the samples are cooled in the magnetic field the formed nanoparticle structures freeze. This is the reason why there are no anomalies on temperature dependences in repeated heating-cooling cycles. Preliminary exposition of the samples in magnetic field leads to the same result.

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