FMR STUDY OF CARBON COATED COBALT NANOPARTICLES DISPERSED IN PARAFFIN

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Abstract. Agglomerated cobalt magnetic nanoparticles coated with carbon dispersed in paraffin matrix were prepared. Two samples with different carbon to cobalt content (25%C-75%Co and 50%C-50%Co), dispersed at low concentration in paraffin (about 0.5%) were studied. Temperature dependence of the FMR (ferromagnetic resonance) spectra were recorded in the temperature range from 90K to room temperature (RT). Both samples showed very intense and broad asymmetric FMR resonance line arising from cobalt nanoparticles. The dipole reorientational processes of the magnetic nanoparticles were strongly influenced by their concentration. The FMR spectra showed strong temperature dependence with extremum at about 200K but with opposite thermal behavior for both samples. The integrated intensity of the FMR line showed thermal conduct similar to that observed in materials with the blocking temperature.

1. INTRODUCTION

The study of magnetic interactions, especially between magnetic nanoparticles or clusters, embedded in dielectric matrices could be very useful in the characterization of physical properties of various materials, especially exhibiting unusual behavior [1-8]. Their remarkable magnetic properties [9] have been exploited in many applications in engineering, technology and medicine. [1-4,10-21]. The macroscopic physical properties of nanostructured magnetic systems and their application are strongly dependent on the type and strength of magnetic coupling [5-7,9]. Magnetic interactions could be very effectively investigated by using the ferromagnetic resonance (FMR) technique. This method allows characterization of different critical processes (phase transitions, crossovers) of the matrices filled with magnetic nanoparticles (e.g. γ-Fe_2O_3, Fe_3O_4, α-Fe, Fe_3C or Co) [5-7,9,22,23]. The temperature dependence of the FMR spectra of magnetic nanoparticles and agglomerates in different matri-

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ces could shed light on very important dynamical processes in the lattice, on the magnetic interactions and the ordering phenomena.

The purpose of this work is to report the results of the investigation of the temperature dependence of FMR spectra of two paraffin samples. The samples contained cobalt nanoparticles coated with carbon and embedded at low concentration of 0.5% in paraffin matrix. These two samples differed in carbon to cobalt ratio. The obtained thermal dependence of the FMR spectral parameters will be used for magnetic characterization of the investigated samples.

2. EXPERIMENTAL

The detailed description of the whole process of preparation of nanocrystalline carbon-coated cobalt nanocapsules has been presented previously [24,25]. Two samples with carbon-cobalt nanocapsules in ratio 25:75 (sample I) and 50:50 (sample II) were prepared and were used as the filler in paraffin at concentration of about 0.5%.

The FMR spectra were recorded using standard X-band spectrometer - Bruker E 500 (ν=9.5 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The measurements were performed in the temperature range from 100 to 290K using an Oxford nitrogen flow cryostat. The samples, containing about 10 mg of paraffin with magnetic nanoparticles, were placed into 5 mm diameter quartz tubes. Before proper measurements the samples were subjected several times to alternating magnetic field (amplitude 1.5 T) to eliminate

demagnetization fields. After this procedure the FMR spectra did not show any dependence on the direction of change of applied magnetic field. During thermal measurements the samples were initially cooled down to 100 K in magnetic field ~10 mT and measurements were taken at progressively increasing temperatures.

3. RESULTS AND DISCUSSION

The XRD patterns of samples I and II indicate on the existence of face-centered cubic (*fcc*) β-Co and hexagonal closed-packed (*hcp*) α-Co phases where the first exists above 422 °C – as that form is not stable at room temperature [26]. The use of structural promoters could help to stabilize the β-Co form in the obtained samples. The cobalt crystallites are very sensitive to oxidation, especially in contact with air and hence the metal particles were coated with carbon which protected the surface against oxidation. Furthermore, the samples were embedded into paraffin. As a result, in the diffraction patterns (XRD) a wide peak, characteristic of cobalt oxide was not visible and the peak characteristic of graphite was not observed. HRTEM images showed that the nanoparticles were composed of a metallic core and a carbon shell. The carbon shell in nanocapsules has a crystalline graphite structure and the thickness of the coating shell is about 10 nm. The width of these nanotubes equals 25 nm and at the ends of this carbon structures some cobalt crystallites are visible.

Figs. 1 and 2 present the temperature dependence of the FMR spectra for two samples of carbon-coated cobalt nanocapsules embedded in par-
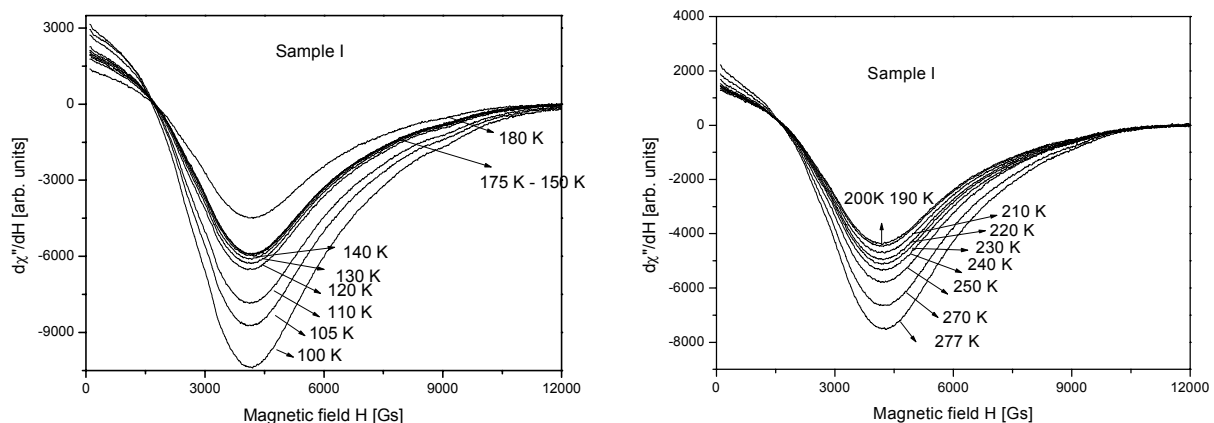

Fig. 1. Temperature dependence of the FMR spectra for sample I. Left panel *T*<185K, right panel *T*>185K.
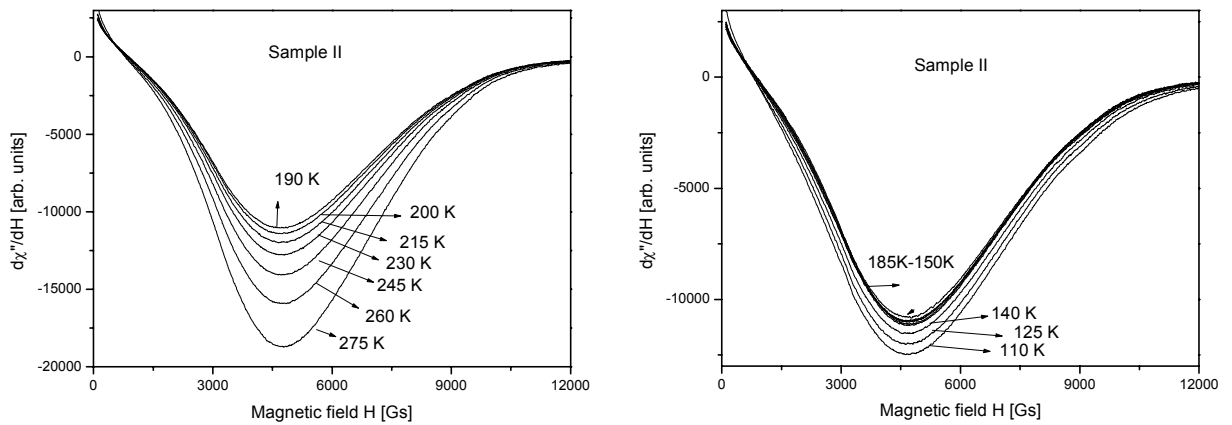
Fig. 2. Temperature dependence of the FMR spectra for sample II. Left panel *T*>190K, right panel *T*<195K.

affin with different concentration of carbon. The concentration of magnetic nanoparticles inside the matrix was homogenous because the FMR spectra taken from different parts of a large parent sample were almost identical. In this work the following parameters will be introduced to describe the FMR line arising from the cobalt nanoparticles: H_0 is the magnetic field where the resonance line amplitude is zero, the linewidth H_R is the difference between magnetic fields referring to minimum position of the line and H_0, the integrated intensity $I \cdot (H_R)^2$ (where I is the value of resonance line amplitude) [27]. Both samples showed very intense and broad asymmetric FMR resonance line arising from cobalt nanoparticles. The FMR spectra showed strong temperature dependence. Figs. 3

and 4 present the temperature dependence of the integrated intensities and the magnetic field H_0 for both samples.

The intensity of the FMR spectra decreased with decreasing temperatures and the minimal values were recorded at about 170-200K for sample I (Fig. 3a) and 150-200K for sample II (Fig. 4a). A broader plateau in intermediate temperature range observed for sample II could be related to stronger dipole interaction for a sample with greater concentration of magnetic nanoparticles. Thermal dependence of the integrated intensity showed conduct similar to observed in materials with the blocking temperature T_b. The magnetic uniaxial anisotropy energy creates two potential wells and the magnetic moment is subjected to thermal fluctua-
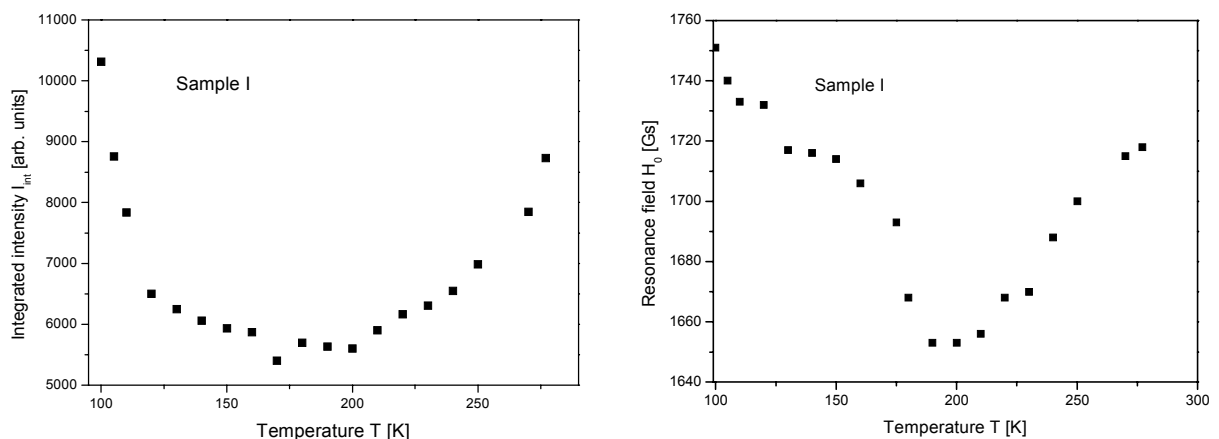

Fig. 3. Temperature dependence of the integrated intensity (a) and the resonance field H_0, (b) for sample I.
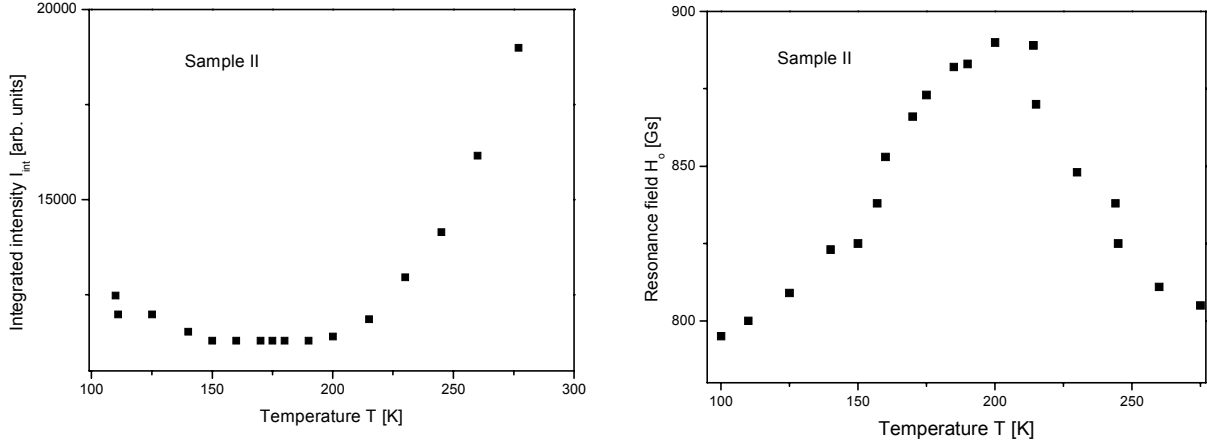
Fig. 4. Temperature dependence of the integrated intensity (a) and the resonance field H_o, (b) for sample II.

tions. Above blocking temperature the magnetic moment surmounts the potential barrier and maintains the thermalequilibrium distribution of orientations (superparamagnetism regime), while below T_b the magnetic moment is blocked in one of the potential wells.

The thermal behavior of the magnetic field H_0 is very interesting because the temperature dependence of that parameter shows opposite effect for both samples. Starting from RT the value of H_0 decreases with temperature decrease, reaching a minimum at 200K. For sample I, the temperature gradient of H_R, $\Delta H_R/\Delta T$ has a value 0.10(1) mT/K for $T>200$K and $\Delta H_R/\Delta T=-0.11(1)$ mT/K for $T<200$K. For sample II the temperature gradient of H_R is -0.13(1) mT/K for $T>200$K and $\Delta H_R/\Delta T=0.10(1)$ mT/K for $T<200$ K. It is assumed that with increasing concentration of nanoparticles the main magnetic interaction is arising from the dipole interaction between agglomerates [27]. The shift of the magnetic field H_0 towards lower magnetic field is due the increase of an internal magnetic field. Appearance of that field would modify the resonance condition:

$$h\nu = g\mu_B (H_{app} - H_{int}),\qquad(1)$$

where h is the Planck constant, ν is the resonance frequency, μ_B is the Bohr magneton, H_{app} is the external magnetic field, H_{int} is the internal magnetic field. The internal magnetic field H_{int} is produced as a result of magnetic interactions between dipoles existing inside and outside agglomerates, and could be described by the following expression:

$$H_{int} = H_{dem} + H_{dip} + H'_{dip},\qquad(2)$$

where H_{dem} is the demagnetization field, H_{dip} is the magnetic field from interacting dipoles inside agglomerates and H'_{dip} is the magnetic field from dipole interaction between agglomerates. The third term could play an essential role in systems with relatively high concentration of magnetic nanoparticles [27]. The analytical calculation using advanced theory for the resonance condition is very complicated and it is unfortunately very difficult to obtain exact results [28,29]. Dipole–dipole interaction is long-ranged and anisotropic, which makes it awkward to treat both analytically and numerically. Randomness in particle positions and anisotropy directions yields frustration and magnetic disorder leading to glassy dynamics for strongly interacting systems.

Now an attempt will be made to propose a mechanism responsible for the behavior of the magnetic field H_0 at two different concentrations of magnetic cobalt nanoparticles. This additional magnetic field arising from nanoparticles and agglomerated dipoles is very important because it not only changes the resonance condition but also essentially broadens the FMR lines. For a sample with a lower concentration of nanoparticles the first two terms in Eq. (2) are dominating. To estimate the magnetic field produced by magnetic interaction we used the following relation:

$$H_{dip} = \sum_i^n \frac{3\cos^2\Theta - 1}{r_i^3}\mu_i,\qquad(3)$$

where Θ_i is the angle between i - magnetic momentum and **z** direction, r_i is the distance between magnetic center and magnetic dipole, and μ_i is magnetic momentum of i-th nanoparticle/agglomerate. At room temperature, the values of the internal magnetic field produced by agglomerates were calculated as: 24.7mT for sample I and 115.8 mT for sample II.

The opposite thermal behavior of the magnetic field H_0 for sample II suggests that the geometrical factor in Eq. (3) is very important and strongly depends on the concentration of agglomerates in the matrix. At lower concentrations, the magnetic dipoles are more easily oriented in the direction of the magnetic field and the term $(3\cos^2\Theta_i)_{av}$ is lower than 1. With increasing concentration the dipole interaction becomes stronger and the anisotropic interaction could be more intense. At lower temperatures, the integrated intensity of the FMR spectra increases strongly for sample I while for sample II it increases very slowly reaching a broader plateau. Below the temperature of 200K, the demagnetization processes in the freezing lattice could be more important than the dipole interaction. Thus the dipole interaction plays an essential influence in samples with higher concentration of magnetic cobalt.

4. CONCLUSIONS

Two investigated samples showed unusual behavior regarding temperature dependence of their FMR spectra. The reorientational processes of the magnetic nanoparticle dipoles were strongly influenced by their concentration. For higher concentration of cobalt nanoparticles the dipole interaction could produce a more anisotropic magnetic configuration. In both samples the integrated intensities of the FMR spectra has a minimum at about 200K. At the same temperature the thermal dependence of magnetic field displayed maximum/minimum values. The geometrical factor in the expression describing dipole interaction is of great importance and could be changed significantly by changing concentration of the magnetic nanoparticles. This study could be very useful in the characterization of different materials in which magnetic nanoparticles are embedded. The FMR investigations of different magnetic nanoparticles/agglomerates at low concentration in different matrixes could prove a very effective and economical way for the characterization of materials.

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