

# TEMPERATURE DEPENDENCE OF FMR FIELD OF MAGNETIC NANOPARTICLES/POLYMER COMPOSITE

N. Guskos<sup>1,2</sup>, J. Typek<sup>2</sup>, T. Bodziony<sup>2</sup>, Z. Roslaniec<sup>3</sup>, U. Narkiewicz<sup>4</sup>,  
M. Kwiatkowska<sup>3</sup> and M. Maryniak<sup>1</sup>

<sup>1</sup>Solid State Physics Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784, Greece

<sup>2</sup>Institute of Physics, Szczecin University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland

<sup>3</sup>Institute of Materials Science and Engineering, Szczecin University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland

<sup>4</sup>Department of Chemical Engineering, Szczecin University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland

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**Abstract.** Two samples of the binary magnetic system of nanoparticles containing Fe<sub>3</sub>O<sub>4</sub>-35% of weight, Fe<sub>3</sub>C-29% of weight and C-36% of weight (carbon) in PTMO – block – PET polymer at low concentrations of 0.5% and 0.3% have been prepared. The temperature dependence of the FMR resonance field has been investigated. It has shown the evidence of the matrix critical points. In all temperature ranges, especially at high temperatures, the FMR spectra are dominated by the signal from the Fe<sub>3</sub>O<sub>4</sub> oxide. For both samples the fitting procedure has been done by using the Lorentzian lines. The influence of temperature on the FMR resonance line has an extraordinary character near the matrix critical points (mechanical or magnetic interactions). It is suggested that using the FMR method might be very fruitful in studying the critical points of the matrix or in investigations of the intermolecular interactions.

## 1. INTRODUCTION

Two magnetic materials have been used as a nanofiller in our ferromagnetic resonance (FMR) study of PTMO – block – PET polymer: magnetite (Fe<sub>3</sub>O<sub>4</sub>) and iron carbide (Fe<sub>3</sub>C). Magnetite is one of the most important compounds found in the nature. While it is playing a very important role in the bio-systems and technology, its magnetic and electrical properties are still intensively studied in different size-scales, from macroscopic to nanoparticles [1-8]. The other magnetic material in our binary system, iron carbide, is one of the most important components in metallurgy, with extraordinary me-

chanical and magnetic properties. The FMR study of iron carbide nanoparticle agglomerates in non-magnetic matrixes has shown very interesting behavior, e.g. the resonance absorption signal arises from nanoparticle agglomerates of iron carbide that strongly interacts, the influence of agglomerates concentration on the strength of magnetic interactions, *etc.* [8,9]. Polymers traditionally have been considered as excellent host matrices for the composite materials where many advanced polymer nanocomposite with magnetic particles dispersed in organic or inorganic matrices are of great interest due to their various applications [10]. Nanoscale size

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Corresponding author: N. Guskos, e-mail: ngouskos@phys.uoa.gr

magnetic materials have attracted a wide attention because of their extraordinary physical properties including the superparamagnetism or quantum tunneling of magnetization [11]. Recently, study by the FMR method of magnetic nanoparticles system dispersed in a nonmagnetic matrix has shown sharp anomalies in the temperature dependence of the resonance line near the critical points in mechanical and magnetic properties of the matrix as well as the agglomerates [12,13].

The aim of this report is preparation, characterization and investigation of the temperature dependence of FMR resonance line of magnetic nanoparticles binary system of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{C}$  dispersed in the PTMO – block – PET polymer. The magnetic mixture filler was used at low concentration of 0.5% (sample designated as I) and 0.3% (sample designated as II) to study the magnetic interaction between agglomerates.

## 2. EXPERIMENTAL

The procedure of obtaining the magnetic binary system of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{C}$  nanoparticles dispersed in PTMO – block – PET polymer has been described in details elsewhere [13]. In the first step the fusion of magnetite with a small amounts of  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  (3 wt.%) was accomplished to produce the base for obtaining material used in preparation of the sample. The obtained material after the fusion was cooled to room temperature, crushed, sieved (with a fraction of 1.2 – 1.5 mm taken) and it was reduced in hydrogen at temperatures in the 620-770K range. The nanocrystalline iron was obtained after reduction, while the promoter oxides remained in the oxidized state. The role of the additives ( $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ) was to stabilize a well developed nanocrystalline iron structure. To avoid oxidation, the sample after the reduction was passivated with nitrogen containing traces of water vapor. The mean size of iron crystallites was determined by using XRD method and the size has been estimated to be about 17 nm. The sample of nanocrystalline iron was carburised with  $\text{CO}/\text{CO}_2$  mixture (98 vol.%  $\text{CO}$ ) at 720K in a glass flow reactor. The carburising gas mixture was obtained in the Boudouard process ( $\text{C} + \text{CO}_2 = 2\text{CO}$ ), passing carbon dioxide through the bed of active carbon at 1370K. The analysis of the gas at the inlet and at the outlet of the carburisation reactor was performed using gas chromatography (Hewlett Packard, 4890D). The molecular sieves of 5 Å were used as column filling. The samples after the carburisation were characterized using the XRD (Philips X Pert,  $\text{CoK}_{\alpha 1}$ ), TOC (total carbon, Multi N/C, equipped with

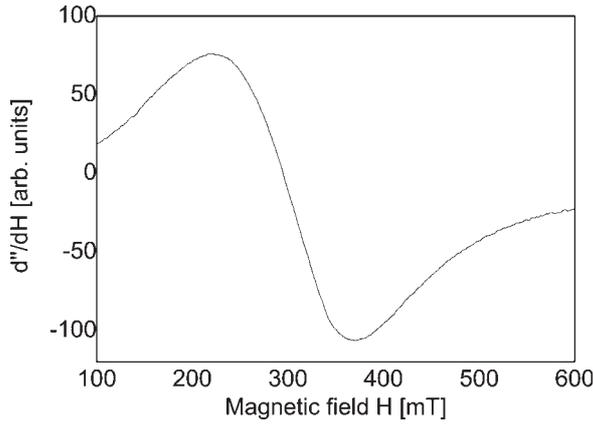
oven Eltra HFT-540, Analytik Jena) and SEM (DSM-962, Leo Zeiss Jena) methods. The specific surface area and the pore distribution were measured using a low temperature nitrogen adsorption (Micromeritics, ASAP).

In order to prepare the nanoparticles/polymer composite, the multiblock copoly(ether-ester) was applied as a composite matrix. It belongs to a group of ester block elastomers in which the hard phase is made by crystallizable polyester rigid segments (PET) settled down in a soft phase with characteristic low glass transition temperature (PTMO). The composite samples were obtained by introducing the filler into polymer matrix during its synthesis (*in situ*). The whole process was carried out in a steel polycondensation reactor with a horseshoe stirrer. In order to ensure the homogenous distribution of nanoparticles in polymer system, an appropriate amount of filler was first dispersed in liquid ethylene glycol by ultrasonication and high-speed stirring. The process of polymer synthesis was performed in the following sequence: at the first stage the transesterification of dimethyl terephthalate (DMT) with ethylene glycol proceeded in order to obtain dihydroxyethylene terephthalate, at the second stage the polycondensation of polyester (PET) as well as polyester and a,w-dihydroxy-polyoxytetramethylene (PTMEG) proceeded simultaneously. The progress in polymer chains growth was observed by the increase of stirrer torque. Obtained composite was extruded from the reactor in a form of filament directly to the cooling bath. All parameters of the process, i.e. temperature, pressure, stirrer torque, duration, etc. were determined experimentally and described previously [13].

Magnetic resonance absorption measurements were carried out with a conventional X-band ( $\nu=9.43$  GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation. The samples, each containing around 20 mg of the material, were placed into 4 mm diameter quartz tubes. Prior to the measurements, the sample has been magnetized by a steady magnetic field of 1.6 T to saturate any domain structure. The measurements were performed in the temperature range from room to helium temperature with  $\Delta T = \pm 1.0\text{K}$  stability using an Oxford cryogenic system.

## 3. RESULTS AND DISCUSSION

The samples have been characterized by using XRD and scanning electron microscopy (SEM) methods. The XRD pattern is dominated by lines from a binary system of magnetic nanoparticles in carbon.



**Fig. 1.** The FMR spectrum of sample I at room temperature.

The XRD and TOC measurements have shown that the samples after carburisation and before polymerization contained:  $\text{Fe}_3\text{O}_4$ -35% of weight,  $\text{Fe}_3\text{C}$ -29% of weight, and C-36% of weight. A SEM micrograph shows that the grains of the magnetic binary system in carbon were distributed almost homogeneously in the PTMO-block-PET polymer matrix. The two magnetic phases were contained in each grain with carbon being the nonmagnetic matrix before filling in the polymeric matrix. The radii of the grains were mostly below 100 nm (over 95% of their total number).

Fig. 1 presents the FMR spectra of 0.5% of the magnetic nanoparticles binary system  $\text{Fe}_3\text{O}_4$  with  $\text{Fe}_3\text{C}$  in the PTMO-block-PET polymer composite at room temperature (sample I). At high temperatures, an intense resonance line is observed with a slightly asymmetric lineshape. Previous FMR study of magnetic nanoparticle binary system of  $\text{Fe}_3\text{O}_4 + \text{Fe}_3\text{C}$  in a nonmagnetic matrix has shown that the resonance line could be fitted by two separate Lorentzian function [12,13]. Similar procedure has been applied successfully for the present case and the lineshape asymmetry observed at high temperatures was explained by assuming that the spectrum is the superposition of two separate Lorentzian-

shaped lines, including the tail of the resonance absorption at negative field due to the linearly polarized radio frequency field. Full analysis of the FMR spectra of samples I and II was presented in Ref. 13. The FMR parameters displayed very interesting temperature dependence. Especially the shift of the resonance field with temperature change is difficult to interpret and understanding of this phenomenon is far from complete [14-17].

Figs. 2 and 3 illustrate the temperature dependences of the FMR resonance field  $H_r$  of samples I and II. Strong shift towards lower magnetic fields with decreasing temperature is observed for both samples. If the ferromagnetic nanoparticles are not well separated the spin of a nanoparticle is subjected to the following total magnetic fields:

$$H_{\text{tot}} = H_{\text{dem}} + H_{\text{app}} + H_{\text{dip}} + H'_{\text{dip}}, \quad (1)$$

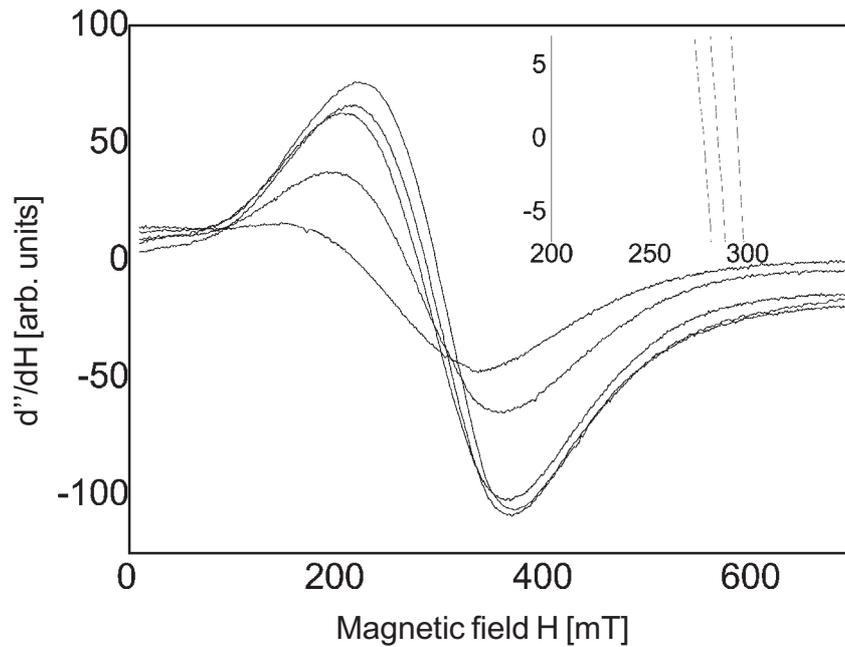
where the first term represents the demagnetization field ( $H_{\text{dem}}$ ), the second term the applied external magnetic field ( $H_{\text{app}}$ ), the third term the dipole field from the neighboring nanoparticles ( $H_{\text{dip}}$ ) and the last term the dipole-dipole interaction between aggregates ( $H'_{\text{dip}}$ ). The collective spins of agglomerates could recognize additional magnetic field, which broadens the FMR line and shifts it in the direction of lower magnetic fields. This could change the resonance condition:  $h\nu = g\mu_B(H_{\text{app}} - H_{\text{int}})$ , where  $\mu_B$  is Bohr magneton and  $H_{\text{int}}$  is an internal magnetic field produced by the magnetic interactions.

The nanoparticles are distributed in the polymer almost homogeneously because a few samples taken from different parts of a bulk polymer sheet have shown the same FMR spectra with the same values of the resonance field, linewidth and intensity. Thus in the exchange interaction only the neighboring nanoparticles are involved and the magnetic interaction between agglomerates should not play a significant role. This type of temperature dependence has been frequently observed in the FMR spectra of iron oxide nanoparticles and it suggests the presence of the superparamagnetic phenomenon [14-16].

Table 1 presents the values of the derivative of the resonance field with respect to temperature,

**Table 1.** Values of  $\Delta H/\Delta T$  (in Gs/K) in different temperature ranges for both investigated samples.

Sample designation	Temperature range				
	250-300 K	200-250 K	150-200 K	115-150 K	90-115 K
I	1.29	1.14	3.18	0.89	14.16
II	2.11	1.44	2.34	1.91	16.44



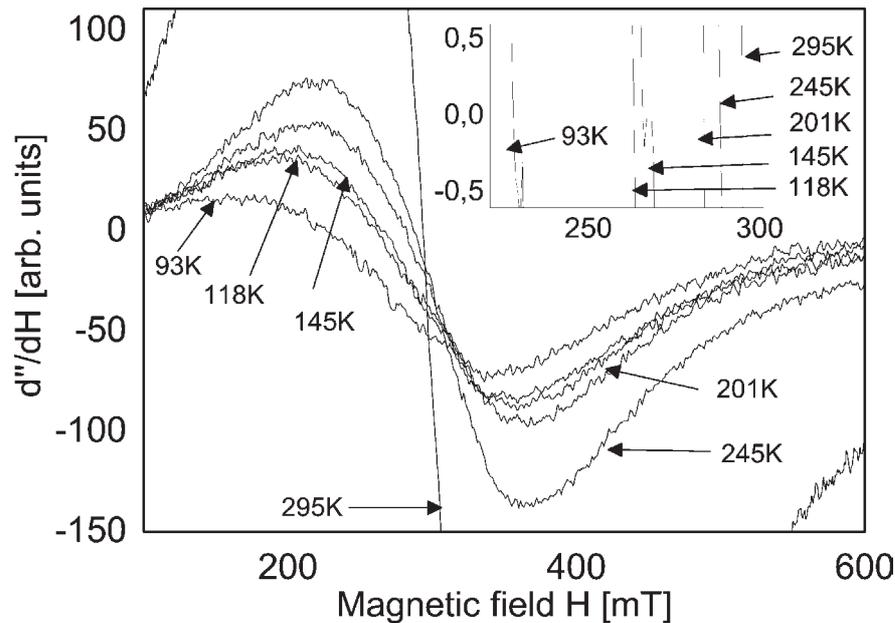
**Fig. 2.** The FMR spectra of sample I at different temperatures. The insert, presenting the central part of the spectra, illustrates temperature shift of resonance lines.

( $\Delta H/\Delta T$ ), for different ranges of temperatures. As it could be seen these values depend strongly on temperature and on the presence of matrix critical points. The nonmagnetic matrix, the PTMO – block – PET polymer, displays many mechanical phase transitions: the so called  $\alpha$ -,  $\beta$ -,  $\delta$ -,  $\gamma$ - and  $\varepsilon$ -relaxations [18,19]. The first one is the transition to a glass state (<250K), the second is connected with the freezing of rotation of the polyether chain (<200K), the next the freezing of the local rotation of the ether group (<160K), and the most intense relaxation is the freezing the rotation of the benzene rings ( $\gamma$ -relaxation) below 120K. The temperature derivative of the resonance field shows apparent correlation with the transition points of the matrix in both samples and for the sample with lower filler concentration the derivatives are greater (Table 1). The influence of polymer matrix relaxations on the position of the FMR line is suggesting the modification of the magnetic anisotropy of individual nanoparticles and to a lesser extent modification of their mutual interactions. Moreover, the magnetoelastic effect may be invoked to explain the appearance of stress exerted on the nanoparticles by the elastic deformation of the surrounding matrix accompanying the freezing of the copolymer. In different temperature ranges the appearing stress might have different magnitude and thus cause various FMR line shifts. Addition-

ally, a chemically inert interaction between the polymer matrix and the ferromagnetic nanoparticles could be changed slightly by increased concentration of magnetic nanoparticles and thus influence the value of the ( $\Delta H/\Delta T$ ) gradient. Thus the method of study of the temperature dependence of the FMR resonance field could be used for study of a wide range of extraordinary physical behavior of nonmagnetic matrices and the magnetic interaction between magnetic nanoparticles.

#### 4. CONCLUSIONS

The binary system of magnetic nanoparticles ( $\text{Fe}_3\text{O}_4+\text{Fe}_3\text{C}$ )/C in a nonmagnetic matrix of the PTMO-block-PET polymer has been used for the investigation of the FMR resonance field as a function of temperature. A very strong dependence of the position of resonance field on temperature has been observed. The value of  $\Delta H/\Delta T$  gradient depended strongly on the physical state of the matrix, especially on the freezing processes which govern the shifts of the FMR resonance line. Additionally, concentration of the magnetic nanoparticles has significant influence on the intensity of the observed phenomena. It is suggested that the method of the FMR spectroscopy might be a powerful technique to study various important physical properties of the



**Fig. 3.** The FMR spectra of sample II at different temperatures. The insert, presenting the central part of the spectra, illustrates temperature shift of resonance lines.

matrix as well as magnetic interaction between the magnetic nanoparticles.

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## REFERENCES

- [1] A. Chainani, T. Yokoya, T. Morimoto, T. Takahashi and S. Todo // *Phys. Rev. B* **51** (1995) 17976.
- [2] F. Walz // *J. Phys.: Condens. Matter* **14** (2002) R285.
- [3] F.J. Owens // *J. Phys. Chem. Solids* **64** (2003) 2289.
- [4] S. Hirano, T. Yogo, W. Sakamoto, S. Yamada, T. Nakamura, T. Yamamoto, H. Ukai, K. Banno, T. Nakafuku and Y. Ando // *J. Sol-Gel Sci. Technol.* **26** (2003) 35.
- [5] X.Y. Zhang and Y.J. Chen // *J. Magn. Magn. Mat.* **271** (2004) 184.
- [6] U. Narkiewicz, N. Guskos, W. Arabczyk, J. Typek, T. Bodzionny, W. Konicki, G. Gasiorek, I. Kucharewicz and E.A. Anagnostakis // *Carbon* **42** (2004) 1127.
- [7] N. Guskos, E.A. Anagnostakis, G. Gasiorek, J. Typek, T. Bodzionny, U. Narkiewicz, W. Arabczyk and W. Konicki // *Mol. Phys. Rep. (Poland)* **37** (2004) 58.
- [8] N. Guskos, J. Typek, U. Narkiewicz, M. Maryniak and K. Aidinis // *Rev. Adv. Mater. Sci.* **8** (2004) 10.
- [9] Y. Xiaotun, X. Lingge, N.S. Choon and C.S.O. Hardy // *Nanotechnology* **14** (2003) 624.
- [10] T. Tango, T. Hatsuta, K. Miyajima, M. Kishada, S. Tashiro and K. Wakabayashi // *J. Am. Ceram. Soc.* **85** (2002) 2188.
- [11] J.P. Wright, J.P. Attfield and P.G. Radaelli // *Phys. Rev. B* **66** (2002) 214422.
- [12] N. Guskos, E.A. Anagnostakis, V. Likodimos, T. Bodzionny, J. Typek, M. Maryniak, U. Narkiewicz, I. Kucharewicz and S. Waplak // *J. Appl. Phys.* **97** (2004) 024304.
- [13] T. Bodzionny, N. Guskos, J. Typek, Z. Roslaniec, U. Narkiewicz, M. Kwiatkowska and M. Maryniak // *Rev. Adv. Mater. Sci.* **8** (2004) 86.
- [14] F. Gazeau, V. Shilov, J.C. Bacri, E. Dubois, F. Gendron, R. Perzynski, Yu.L. Raikher and V.I. Stepanov // *J. Magn. Magn. Mater.* **202** (1999) 535.
- [15] R. Berger, J. Cliava, J.C. Bissey, and V. Baietto // *J. Appl. Phys.* **87** (2000) 7389.

- [16] R. Berger, J.C. Bissey, J. Cliava, H. Daubric and C. Estournes // *J. Magn. Magn. Mater* **234** (2001) 535.
- [17] Yu.A. Koskarov, D.A. Pankratov, S.P. Gubin, I.D. Kosobudsky, M. Beltran, Y. Khodorkovsky and A.M. Tishin // *J. Appl. Phys.* **89** (2001) 2293.
- [18] O Yano and Y. Wada // *J. Polymer Sci. A* **9** (1971) 669.
- [19] J. Majszczyk, J. Slonecki and A. Kozłowska // *Macromol. Chem. Phys.* **202** (2001) 1207.