Rev.Adv.Mater.Sci. 8 (2004) 86-91

FERROMAGNETIC RESONANCE STUDY OF Fe_3O_4 AND Fe_3C MAGNETIC NANOPARTICLE MIXTURE FILLING THE PTMO – BLOCK – PET POLYMER

T. Bodziony[1], **N. Guskos**[1,2], **J. Typek**[1], **Z. Roslaniec**[3], **U. Narkiewicz**[4],
M. Kwiatkowska[3] **and M. Maryniak**[1]

[1]Institute of Physics, Technical University of Szczecin, Al. Piastow 17, 70-310 Szczecin, Poland
[2]Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784, Greece
[3]Institute of Material Engineering, Technical University of Szczecin, Al. Piastow 17, 70-310 Szczecin, Poland
[4]Department of Chemical Engineering, Technical University of Szczecin, Al. Piastow 17, 70-310 Szczecin, Poland

Received: October 14, 2004

Abstract. PTMO – block – PET polymer filled with a low concentration (0.5 wt.%) of nanoparticle mixture: Fe_3O_4-35 wt.% (magnetite), Fe_3C-29 wt.% (iron carbide or cementite) and C-36 wt.% (carbon), was synthesized. The sample has been characterised by using XRD and SEM method. Ferromagnetic resonance (FMR) investigations of the sample were carried out in the 30 - 300K temperature range. A slightly asymmetric FMR line has been recorded at higher temperatures, while a broad FMR line at lower temperatures was registered. A strong, extraordinary temperature dependence of FMR spectrum was observed. The resonance field shifted toward lower magnetic fields, a decrease in intensity and an increase of the linewidth with decreasing temperature was detected. This low-temperature line is very anisotropic and its low-field shoulder spreads to negative magnetic fields. With decreasing temperature, the linewidth of this line decreases slightly, in contrast to the behaviour of the high-temperature line. The intensity of the low-temperature line is weakly dependent on temperature. The FMR spectrum has been fitted by two Lorentzian lines: one centred at g = 2.259(2) with the linewidth ΔB = 146(1) mT, and the other at near zero applied magnetic field with the linewidth ΔB = 307(1) mT, at room temperature. It is believed that the FMR spectrum at higher temperatures is dominated by magnetite signal, while at lower temperatures it is dominated by iron carbide. The temperature dependence of FMR spectrum of magnetite at higher temperatures suggests the presence of thermal fluctuations and the interparticle interaction similar to the superparamagnetic resonance. The observed change of the FMR spectrum at 90K could be explained by Verwey transition and the skin effect.

1. INTRODUCTION

Magnetite, one of the best-known oxides, is still intensively studied due to its interesting magnetic and electrical properties in different size-scales, from macroscopic to nanoscopic. The microwave resonance absorption technique has been used to study the ferromagnetic crystalline anisotropy characteristics and the g-factors of the magnetite from an early period, after discovery of the magnetic resonance methods [1]. Recently, ferromagnetic resonance (FMR) of magnetic field oriented magnetite nanoparticles in frozen ferrofluid has been registered and the phase transition of the magnetic symmetry has been observed in the bulk state which occurs at much lower temperatures than for the substance in the bulk form [2]. The anisotropy field was directly deduced from the low temperature peak-to-peak linewidth analysis and the particle magnetic moment was estimated after subtraction of the intrinsic linewidth contribution [3]. One of the important compounds in metallurgy is iron carbide. The magnetic

---

Corresponding author: J. Typek, e-mail: typjan@ps.pl

resonance studies of iron carbide nanoparticle agglomerates in a carbon matrix have shown a very interesting behaviour [4,5]. The resonance absorption signal arises from agglomerates of iron carbide and strong magnetic interactions were observed which strongly depend on concentration of magnetic nanoparticles in a nonmagnetic matrix. Nanocomposite materials with magnetic particles dispersed in organic or inorganic matrices are of great interest due to their various applications [6]. Nanometer-sized magnetic materials have attracted attention of many researchers because magnetic nanoparticles exhibit such unusual chemical and physical properties as superparamagnetism and quantum tunnelling of magnetisation [7]. Besides, it is very interesting to study binary magnetic systems containing iron carbide and iron oxide in nonmagnetic matrices, especially magnetite which exhibits an extraordinary behaviour near T_c = 125K (Verway transition [8]) by using magnetic resonance methods.

In this work, we report the characterisation and the temperature dependence of ferromagnetic resonance spectra of magnetic nanoparticles (binary system of magnetite with iron carbide) dispersed in PTMO – block – PET polymer at low concentration of 0.5 wt.%.

2. EXPERIMENTAL

The basic material used for sample preparation was the nanocrystalline iron obtained by the fusion of magnetite with small amounts of Al_2O_3 and CaO (3 wt.%). The lava after the fusion was cooled to room temperature, crushed, sieved (with a fraction of 1.2 – 1.5 mm taken) and reduced in hydrogen at temperatures of 350-500 °C. After the reduction the nanocrystalline iron was obtained, while the promoter oxides remained in the oxidised state. The role of the additives (CaO, Al_2O_3) was to stabilise a well-developed nanocrystalline iron structure. To avoid oxidation, the sample after the reduction was passivated with a nitrogen containing traces of water vapour. The mean size of iron crystallites determined by using XRD method was 17 nm. The sample of nanocrystalline iron was carburised with CO/CO_2 mixture (98 vol.% CO) at 450 °C in a glass flow reactor. The carburising gas mixture was obtained in the Boudouard process ($C + CO_2 = 2\ CO$), passing carbon dioxide through the bed of active carbon at 1100 °C. The analysis of the gas at the inlet and at the outlet of the carburisation reactor was performed using gas chromatography (Hewlett Packard, 4890D), in which molecular sieves of 5 A were used as column filling. The samples after the carburisation were characterised using the XRD (Philips X Pert, Co$K\alpha_1$), 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).

A composite used in our experiment consisted of a PTMO – block – PET polymer filled with low concentration (0.5 wt.%) of nanoparticle mixture: Fe_3O_4-35 wt.%, Fe_3C-29 wt.%. and C-36 wt.%. The composite was carefully mixed manually, poured out into the mould and hardened thermally.

The nanocomposite samples were obtained by introducing the fillers into the reaction mixture and synthesising multiblock poly(ether-ester) copolymers based on polyoxytetramethylene and poly(ethylene tesephtkalate) (PET). An appropriate amount of filler was dispersed in 1.4–etanodiol (ED) by ultrasonication applying a Sonoplus-Homogernisator HD2200. The synthesis of multiblock copoly(ether-ester) was a two stage process carried out in an acid resistant steel reactor. The process of transesterification of dimethyl terephthalate (DMT) with etanodiol (ED) was the first stage processed. The reaction was carried out between in temperatures of 150-190 °C, under atmospheric pressure, until 90% conversion was measured by the amount of distilled methanol in relation to the theoretical amount. In the next stage the transesterification of di(2-hydroxytetramethylene) terephthalate with α, ω-dihydroxy-polyoxytetramethylene (PTMEG) was performed, and the polycondensation were carried out between 190-225 °C and at pressure decreased step by step down to 0.1 hPa. The progress of reaction was determined on the basis of the amount of distilled ED and on the increase in torque of the strirrer. The polymer was extruded from the reactor by compressed nitrogen.

Magnetic resonance absorption measurements were carried out with a conventional X-band (ν = 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 magnetised by a steady magnetic field of 1.4 T to saturate any domain structure. The measurements were performed in the temperature range from room to helium temperature with ΔT = ±1.0K stability using an Oxford cryogenic system.

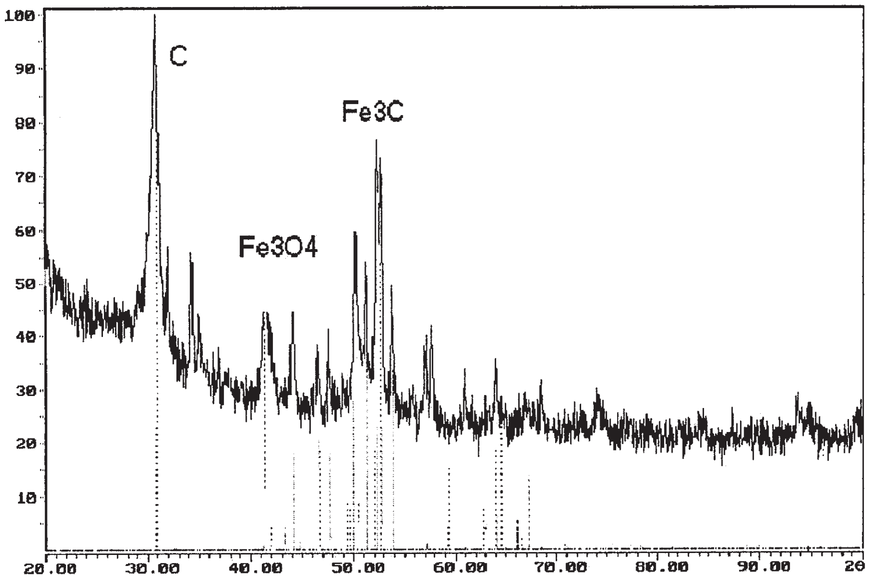

Fig. 1. The XRD pattern from a binary system of magnetic nanoparticles in carbon.

3. RESULTS AND DISCUSSION

The sample has been characterised by using XRD and scanning electron microscopy (SEM) method. Fig. 1 presents the XRD pattern from a binary system of magnetic nanoparticles in carbon. According to the XRD and TOC methods, the sample after decarburisation and before polymerisation contained: Fe_3O_4-35 wt.%, Fe_3C-29 wt.% and C–36 wt.%. A SEM micrograph (Fig. 2) shows that the grains of magnetic binary system in carbon are distributed almost homogeneously in the polymer matrix. The two magnetic phases are contained in one grain with carbon being the environment. Over 95% of all grains had the radius below 100 nm.

Fig. 2. The SEM micrograph of magnetic binary system in carbon in the polymer matrix.

Fig. 3 summarises the temperature dependencies of the FMR spectra of the polymer composite. At higher temperatures an intense and narrow resonance line is recorded with a slightly asymmetric lineshape. Extraordinary behaviour of the FMR spectrum is registered in its temperature dependence. The intensity of the FMR spectrum strongly decreases, the linewidth increases and the resonance field shifts towards lower magnetic fields with the temperature decrease. A visible change of the FMR spectrum occurs at temperature around 90K. At still lower temperatures, below 90K, another broad FMR

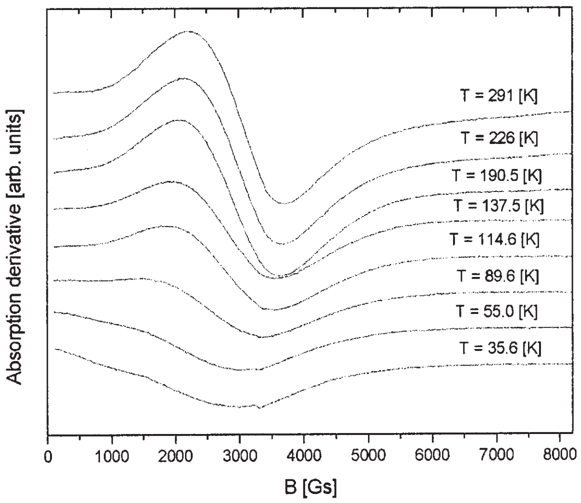

Fig. 3. The FMR spectra of the investigated sample at different temperatures.

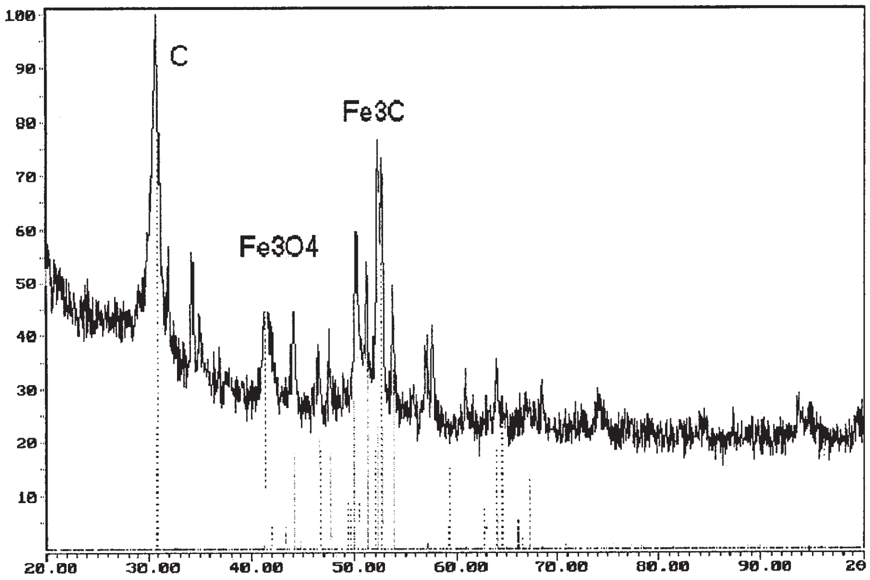

Fig. 1. The XRD pattern from a binary system of magnetic nanoparticles in carbon.

3. RESULTS AND DISCUSSION

The sample has been characterised by using XRD and scanning electron microscopy (SEM) method. Fig. 1 presents the XRD pattern from a binary system of magnetic nanoparticles in carbon. According to the XRD and TOC methods, the sample after carburisation and before polymerisation contained: Fe_3O_4-35 wt.%, Fe_3C-29 wt.% and C–36 wt.%. A SEM micrograph (Fig. 2) shows that the grains of magnetic binary system in carbon are distributed almost homogeneously in the polymer matrix. The two magnetic phases are contained in one grain with carbon being the environment. Over 95% of all grains had the radius below 100 nm.

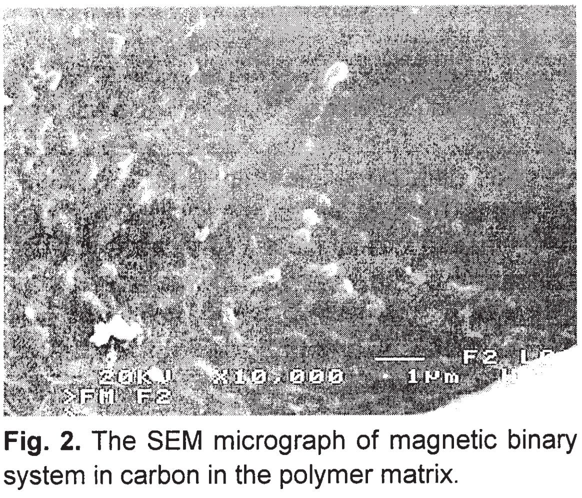

Fig. 2. The SEM micrograph of magnetic binary system in carbon in the polymer matrix.

Fig. 3 summarises the temperature dependencies of the FMR spectra of the polymer composite. At higher temperatures an intense and narrow resonance line is recorded with a slightly asymmetric lineshape. Extraordinary behaviour of the FMR spectrum is registered in its temperature dependence. The intensity of the FMR spectrum strongly decreases, the linewidth increases and the resonance field shifts towards lower magnetic fields with the temperature decrease. A visible change of the FMR spectrum occurs at temperature around 90K. At still lower temperatures, below 90K, another broad FMR

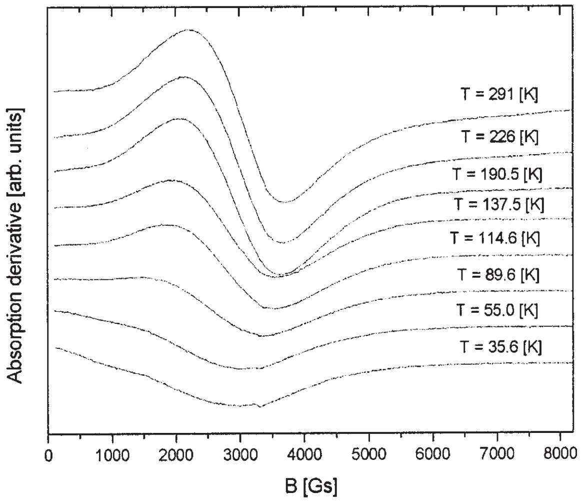

Fig. 3. The FMR spectra of the investigated sample at different temperatures.

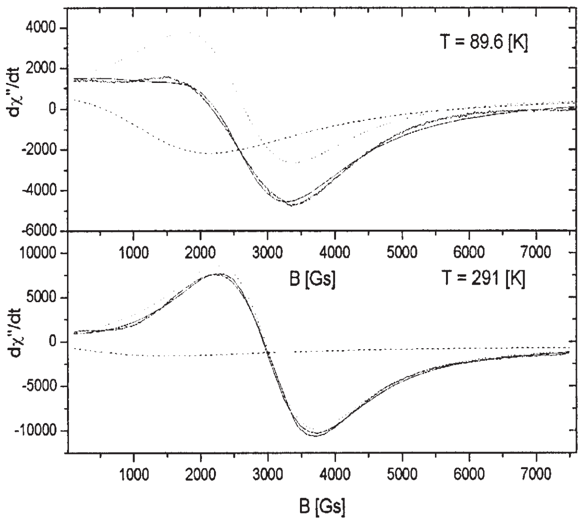

Fig. 4. An example of FMR spectrum for $T = 89.6$K and T = 291K. The continuos line shows the best fit of the resonance spectrum by using two Lorenztian shape lines. The dotted line and the dashed line shows the first (narrow) and the second Lorentzian line (broad) originating from magnetite and iron carbide, respectively.

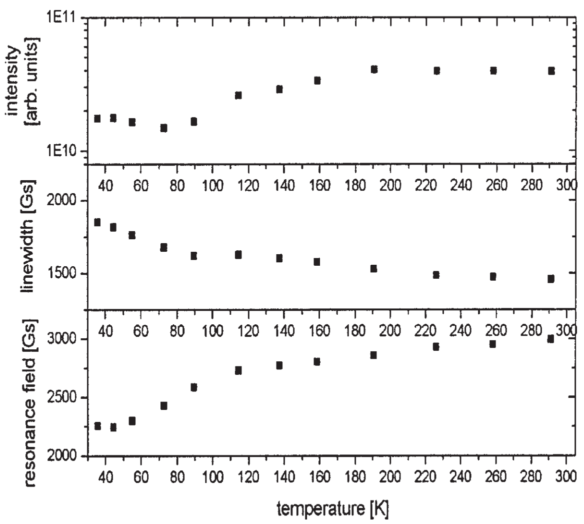

Fig. 5. Temperature dependence of the FMR intensity, peak-to-peak linewidth and a resonance field for the narrow component originating from magnetite.

line has began to dominate the spectrum. The lineshape asymmetry observed at higher temperatures can be explained by assuming that the spectrum is a superposition of two separate Lorentzian-shaped lines, including the tail of the resonance absorption at negative fields due to the linearly polarised radio frequency field, as shown in Fig. 4. Thus the FMR spectrum at room temperature is decomposed on two lines with the following g-factors and the peak-to-peak linewidths: the first line with $g = 2.259(2)$ and $\Delta B_{pp} = 146(1)$ mT, (dashed line in Fig. 4) and the other component (doted line) centred at near zero resonance magnetic field with the linewidth $\Delta B_{pp} = 307(1)$ mT. At temperature T=89.6K (Fig. 5a) the first line (dashed line) is centred at $g = 2.622(2)$, with the linewidth $\Delta B_{pp} = 161(1)$ mT, the second line (doted line) is centred at $g = 6.203(2)$ with the linewith $\Delta B_{pp} = 256(1)$ mT. The narrow component of the FMR spectrum arises probably from magnetite while the broad component is derived from the iron carbide. The integrated intensity of magnetite line I_m is about 4.3 times greater then the iron carbide line I_c at room temperature, while the ratio I_m/I_c decreases to 0.67 at 89.6K.

Figs. 5 and 6 show the temperature dependence of the resonance field B_r, peak-to-peak linewidth ΔB_{pp} and the integrated intensity derived by double integration of the absorption derivative spectra obtained by the fitting procedure of two separate Lorentzian lines: the first which arising from magnetite (Fig. 5), and the second arising from iron carbide (Fig. 6). The results of the fitting confirm that the FMR spectrum at room temperature is dominated by magnetite, while at lower temperatures (below 90K) the iron carbide dominates the spectrum. As could be seen in Fig. 5, in a high temperature range, 100K < T < 300K, this type of temperature dependence has been frequently observed in the FMR spectra of iron oxide nanoparticles and suggests the presence of the superparamagnetic phenomenon. The gradual suppression of the averaging effect of thermal fluctuations and the interparticle interaction or the emergence of the spin-glass like freezing with temperature decrease for magnetite nanoparticles could influence strongly the FMR spectrum [9-11] at higher temperatures when FMR line is dominated by the signal form magnetite.

The magnetite undergoes a sharp first-order transition at $T_v \sim 125$K for a bulk sample (Verwey transition), where the structure distorts from the cubic to monoclinic symmetry and the electrical conductivity jumps about two order of magnitude. The Verwey transition, although known for over seven decades, is still being investigated both theoreti-

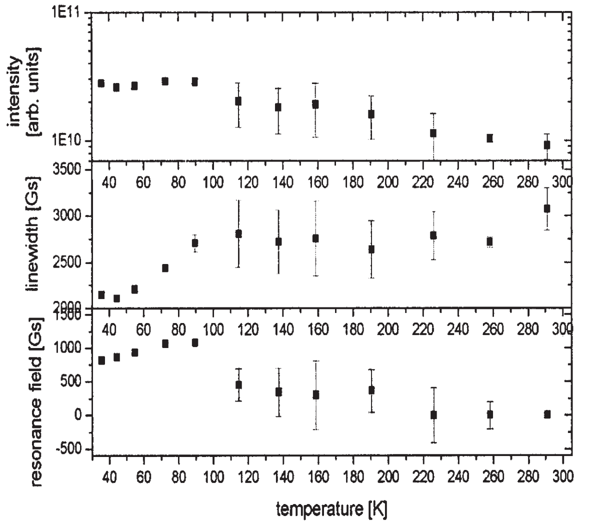

Fig. 6. Temperature dependence of the FMR intensity, peak-to-peak linewidth and a resonance field for the broad component originating from iron carbide.

cally [8] and experimentally [12]. Recently, the FMR study of the Verwey transition in nanoscale size of a binary system of magnetite-iron carbide in resin has shown an essential decrease of that temperature [13].

If the ferromagnetic nanoparticles are not well separated the spin of a nanoparticle is subjected to the following total magnetic field [4]:

$$\vec{B}_{tot} = \vec{B}_{dem} + \vec{B}_{dip} + \vec{B}_{app},$$

where the first term represents the demagnetisation field, the second term the applied external magnetic field, the third term the dipole field from the neighbouring nanoparticles and the last term the dipole-dipole interaction between aggregates. The collective spins of agglomerates could recognise additional magnetic field, which broadens the FMR line and shifts it in the direction of lower magnetic fields.

The nanoparticles are distributed in polymer almost homogeneously because four studied samples taken from different parts of the polymer have been used for FMR measurements and have shown the same spectrum, with the same values of resonance field, linewidth and intensity. Thus in the exchange interaction only the neighbouring nanoparticles are involved and the interaction from agglomerates should not be significant. The influence of environment on the FMR spectrum is clearly visible below 90K, where the signal from the iron carbide is dominating. In comparison to the binary magnetic system in resin matrix the resonance line from the binary magnetic system in polymer is significantly narrower (around three times), shifted to the higher fields and its intensity starts to decrease around the transition temperature $T \sim 90$K. This behaviour could be caused by an almost homogenous distribution of magnetic nanoparticles in the polymer matrix what results in a small exchange interaction and the dipole-dipole interaction between aggregates.

Another factor, which could influence the behaviour of FMR spectrum, is the skin depth. The computed skin depth for Fe_3O_4 in resin matrix has showed that the penetration of the microwave field is increasing about 15 times, while the temperature decreases from 300K to 125K [13]. Similar effect is expected for a binary system embedded in a polymer matrix. It might be assumed that the inner layer of a nanoparticle is made of iron carbide surrounded by magnetite and the outer layer is formed by carbon. Complex inner structure of a nanoparticle and the reduced possibility of forming large nanoparticle aggregates suggest that the microwave penetration depth for a polymer sample should be much shorter than for a resin sample. Thus the skin effect might be considered to be responsible for the observed different temperature shift of the FMR spectrum for a binary magnetic system dispersed in resin and polymer matrices. Another possible explanation of the abrupt FMR spectrum change might involve the dynamical spin fluctuations. This complex subject should be put into detailed scrutiny and will be considered in the future investigations.

4. CONCLUSIONS

The binary system of two magnetic components (iron carbide and magnetite) with carbon in a nonmagnetic matrix of the PTMO-block-PET polymer has been synthesised by the carburisation of nanocrystalline iron with carbon monoxide. The FMR measurements have shown that the spectrum at higher temperature is dominated by magnetite signal while at lower temperatures it is transformed to the FMR spectrum of iron carbide. The temperature dependence of FMR spectrum of magnetite at higher temperature suggests the presence of thermal fluctuations and interparticle interaction similar to the superparamagnetic resonance.

The change of the FMR spectrum at 90K could be explained by Verwey transition.

ACKNOWLEDGEMENTS

This work was partially supported by grant PBZ-KBN-095/TO8/2003.

REFERENCES

[1] L. R. Bickford // *Phys. Rev.* **78** (1950) 449.

[2] F. J. Owens // *J. Phys. Chem. Solids* **64** (2003) 2289.

[3] E. De Biasi, C. A. Ramos and R. D. Zysler // *J. Mag. Mag. Mat.* **262** (2003) 235.

[4] U. Narkiewicz, N. Guskos, W. Arabczyk, J. Typek, T. Bodzionny, W. Konicki, G. Gasiorek, I. Kucharewicz and E. A. Anagnostakis // *Carbon* **42** (2004) 1127.

[5] N. Guskos, E.A. Anagnostakis, G. Gasiorek, J. Typek, T. Bodziony, U. Narkiewicz, W. Arabczyk and W.Konicki // *Mol.Phys.Rep.* (Poland) **37** (2004) 58.

[6] Y. Xiaotun, X. Lingge, N. S. Choon and C. S. O. Hardy // *Nanotechnology* **14** (2003) 624.

[7] T. Tango, T. Hatsuta, K. Miyajima, M. Kishada, S. Tashiro and K. Wakabayashi // *J. Am. Ceram. Soc.* **85** (2002) 2188.

[8] F. Walz // *J. Phys.: Condens. Matter* **14** (2002) R285.

[9] F. Gazeau, J. C. Bacri, F. Gendron, R. Perzynski, Yu. L. Raikher, V. I. Stepanov and E. Dubois // *J. Magn. Magn. Matter* **186** (1998) 175; 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.

[10] R. Berger, J. Cliava, J. C. Bissey and V. Baietto // *J.Appl. Phys.* **87** (2000) 7389; R. Berger, J. C. Bissey, J. Cliava, H. Daubric and C. Estournes // *J. Magn. Magn. Mater* **234** (2001) 535.

[11] Yu. A. Koskarov, S. P. Gubin, I. D. Kosobudsky, M. Beltran, Y. Khodorkovsky and A. M. Tishin // *J. Appl. Phys.* **88** (2000) 1587; 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

[12] J. P. Wright, J. P. Attfield and P. G. Radaelli // *Phys. Rev. B* **66** (2002) 214422.

[13] N.Guskos, E.A. Anagnostakis, V. Likodimos, T.Bodziony, J.Typek, M. Maryniak, U.Narkiewicz, I.Kucharewicz and S. Waplak, submitted for publication to J. Appl. Phys.