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Low Concentration Effect of Fe_3O_4 and Fe_3C Magnetic Nanoparticles in Non-Magnetic Matrix on the FMR Spectra

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PTMO–block–PET polymer filled with a low concentration (0.1 wt.%) of binary magnetic system: magnetite (Fe_3O_4) and iron carbide (Fe_3C) with carbon (C) was prepared. Characterization of the sample was done by using X-ray diffraction and scanning electron microscopy methods. Temperature dependence of the FMR spectra was carried out in the 10–300 K temperature range. The extraordinary temperature dependence behaviour of FMR spectra was recorded. The FMR spectra were fitted by two Lorentzian lines originating from magnetite and iron carbide. The anomalous behaviour of FMR spectra below 100 K could be explained by the skin effect or by the freezing of the matrix benzene rings at about 115 K. The temperature dependence of the g parameter below 75.5 K (opposite shift of the resonance field to usually observed) was interpreted as a result of strong antiferromagnetic interaction of some portion of agglomerates.

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1. Introduction

Magnetite (Fe_3O_4) is a well-known oxide from 8 century B.C. where its magnetic properties (“magic”) gave the name of one of the more important chapter of

physics [1]. It is still intensively studied due to its interesting (not only magnetic properties) electrical properties in different size-scales, from macroscopic to nanoscopic [2–5]. Iron carbide is one of the more important compound in metallurgy and its influence on magnetic properties of metallurgic processes is not fully understood. The magnetic resonance studies of iron carbide nanoparticle agglomerates in a carbon matrix have shown its extraordinary properties [1, 6, 7]. Nanocomposite materials with magnetic particles dispersed in organic or inorganic matrices are of great interest due to their various applications [8, 9]. Recently, the binary magnetic systems containing iron carbide and iron oxide in non-magnetic matrices have shown a very interesting behaviour of the temperature dependence of FMR spectra [10–12]. The observed FMR signal of iron carbide and magnetite strongly depended on concentration of magnetic nanoparticles in a non-magnetic matrix.

The aim of this report is to study the temperature dependence of the FMR spectra of PTMO–block–PET polymer (synthesizing multiblock poly(ether–ester) copolymers based on polyoxytetramethylene and poly(ethylene terephthalate)) filled with a low concentration (0.1 wt.%) of binary magnetic system (Fe_3O_4 and Fe_3C) with C.

2. Experimental

The details of preparation of the binary magnetic system of the magnetite and iron carbide was described in Refs. [10, 12]. The samples after the carburization were characterized using the X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. A composite used in our experiment consisted of a PTMO–block–PET polymer filled with a very low concentration (0.1 wt.%) of nanoparticle mixture: Fe_3O_4 — 35 wt.%, Fe_3C — 29 wt.%, and C — 36 wt.%.

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 in 4 mm diameter quartz tubes. Prior to the measurements, the sample was magnetized 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 $\Delta T = \pm 1.0$ K stability using an Oxford cryogenic system.

3. Results and discussion

The XRD measurements have shown that the pattern is dominated by magnetite and iron carbide [10]. Figure 1 presents a SEM picture of the PTMO–block–PET polymer filled with a low concentration (0.1 wt.%) of binary magnetic system magnetite and iron carbide with carbon. The above binary system has

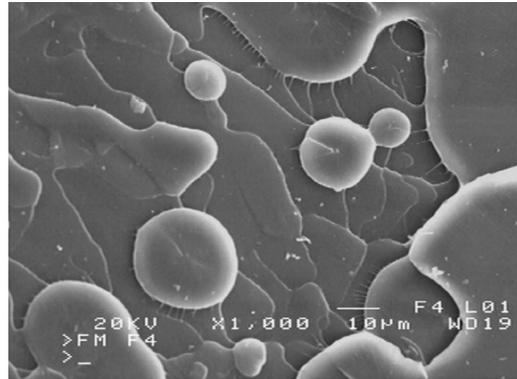


Fig. 1. The SEM micrograph of magnetic binary system with carbon in the polymer matrix.

formed ball-like shape agglomerate of nanoparticles with sizes in the 10–20 μm range.

The temperature dependence of the FMR spectra is given in Fig. 2. An intense and slightly asymmetric shape of FMR resonance line is recorded. The line shape asymmetry 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 polarized radio-frequency field (Fig. 3). The first, rather narrow line has g -factor value of $g = 2.356(2)$ and the peak-to-peak line widths $\Delta B_{\text{pp}} = 154(1)$ mT (dotted line). The other broad component (dashed line) is centered at near zero resonance magnetic field and has the peak-to-peak line width $\Delta B_{\text{pp}} = 393(1)$ mT at $T = 95.8$ K. It is suggested

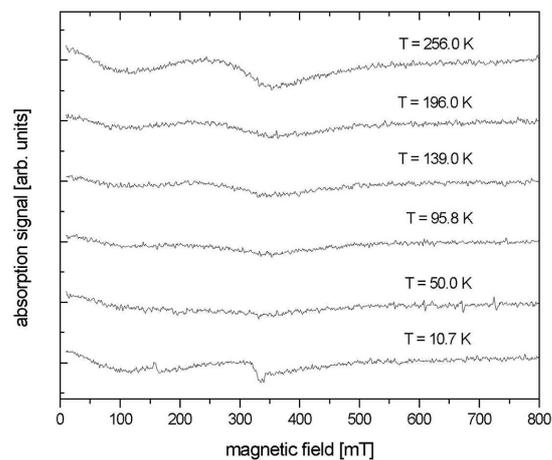


Fig. 2. The examples of FMR spectra of the sample at different temperatures.

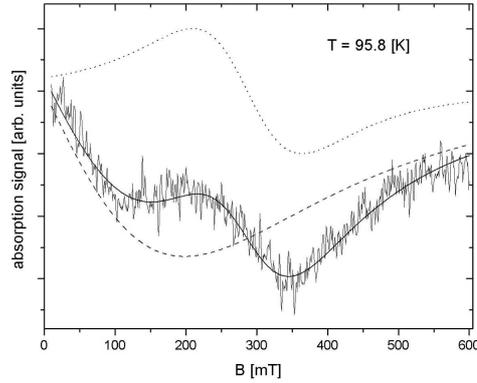


Fig. 3. The FMR spectrum for $T = 95.8$ K with fitting curves. The continuous line shows the best fit of the resonance spectrum by superposition of two Lorentzian shape lines. The dashed line and the dotted line show the broad and narrow Lorentzian lines originating from iron carbide and magnetite, respectively.

that the narrow line of the FMR spectra arises from magnetite while the broad line is coming from the iron carbide. The results of the fitting show that the FMR spectrum in the whole temperature range is dominated by iron carbide line, which is opposite to the results obtained for the samples with higher concentration of the same binary magnetic system (0.5 and 0.3 wt.%) [10, 12]. Figures 4 and 5 present the temperature dependence of the g parameter, peak-to-peak line width 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. Figure 4 gives the FMR parameters for iron carbide, and Fig. 5 for magnetite. The resonance field of FMR line originating from iron carbide is near zero, thus the g parameter for this line will be not discussed in this pa-

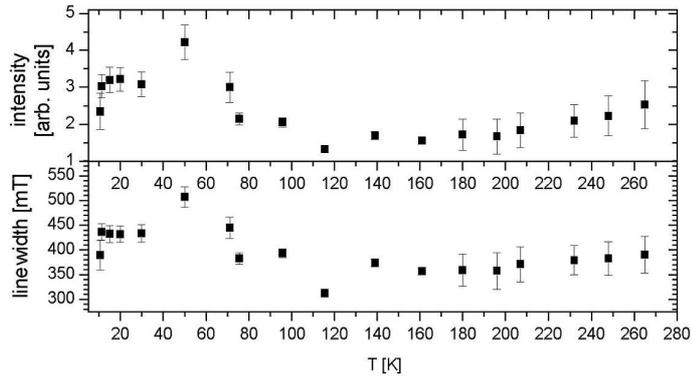


Fig. 4. Temperature dependence of the FMR intensity and peak-to-peak line width for the broad component originating from iron carbide.

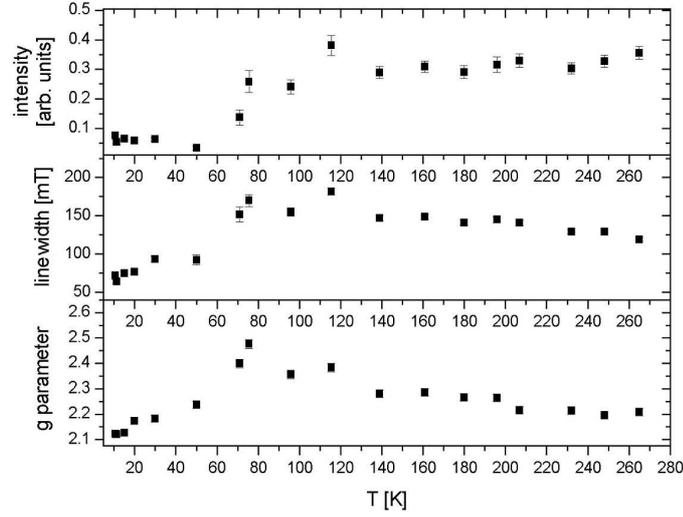


Fig. 5. Temperature dependence of the FMR intensity, peak-to-peak line width, and g parameter for the narrow component originating from magnetite.

per. The temperature dependence of the intensity and peak-to-peak line width originating from iron carbide is decreasing approximately linearly with decreasing temperature down to 115 K and starts to increase at lower temperatures. In the case of magnetite, the intensity decreases very slowly approximately linearly with temperature in the range from room temperature to 75.5 K. At this temperature an abrupt decrease in intensity and maximum of the line width with the value of g parameter is observed.

The ferromagnetic nanoparticles formed agglomerates. The whole magnetic field acting on the magnetic nanoparticle consisted of the following terms: the demagnetization field, the applied external magnetic field, the dipole field from the neighbouring nanoparticles, and the dipole–dipole field acting between aggregates. One component is dominating and it could influence essentially the line width of the FMR line and could shift it mainly towards lower magnetic fields. The essential change of the FMR spectra at lower temperatures for the magnetite could be explained by a sharp Verwey transition ($T_V \approx 125$ K for a bulk sample), where the structure distorts from the cubic to monoclinic symmetry and the electrical conductivity jumps about two orders of magnitude [3]. Additionally, there is a possibility of the influence of an abrupt FMR spectrum change by the “freezing” phenomenon where at 115 K some segments of the matrix (benzene rings) stopped their movements.

4. Conclusion

The strong influence of concentration on the FMR spectra is observed in the binary magnetic nanoparticles system dispersed in non-magnetic matrix. The

shift of the resonance field and integrated intensities decrease more faster with decreasing temperature for the samples with higher concentration of magnetic nanoparticles. The antiferromagnetic coupling of agglomerates could cause decrease in the internal magnetic field which in turn shifts the resonance field in opposite directions. It is hoped that the collecting of more experimental data could make the method useful for studying magnetic nanoparticles concentration phenomenon.

Acknowledgments

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