

PRESSURE STUDY OF FMR SPECTRA OF γ -Fe₂O₃ NANOPARTICLES IN COPOLYMER MATRIX

N. Guskos^{1,2}, A. Krupska³ and J. Typek²

¹Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784, Greece

²Institute of Physics, West Pomeranian University of Technology, Al. Piastow 48, 70-311 Szczecin, Poland

³Institute of Molecular Physics, Polish Academy of Science, ul. M. Smoluchowskiego 17, 60-179 Poznan, Poland

Received: February 16, 2012

Abstract. Pressure dependence of the ferromagnetic resonance (FMR) spectra of two samples consisting of γ -Fe₂O₃ nanoparticles embedded in nonmagnetic polymer matrix has been investigated. Magnetic nanoparticles used in this study differ in agglomerations sizes. Significant variations of the FMR parameters were observed as a function of an applied external pressure for both samples. It has been demonstrated that pressure has a different effect on small and large nanoparticles agglomerates due to a crucial role of the surface spins.

1. INTRODUCTION

Magnetic iron oxide nanoparticles are the most frequently used materials in theoretical and experimental study of the superparamagnetic processes, e.g. [1-9]. Nanosize iron oxides have very interesting physical properties used in application of a new generation of functional materials. Ferromagnetic resonance (FMR) spectra of small amounts of ferrimagnetic iron oxide γ -Fe₂O₃ embedded in a multiblock copolymer matrix have shown that the resonance field shifts towards smaller magnetic fields with decrease in temperature [10,11]. The temperature dependence of the FMR spectra have revealed the critical points connected with α , β , γ , and δ relaxations which have an essential influence on the mechanical properties of the used matrices. The viscosity and temperature of the viscoelastic magnetic materials could play an important role in the reorientation processes of the correlated spin system [12]. Additionally, it has been suggested that the different thermal expansion properties of a matrix and magnetic nanoparticles system could produce an internal stress on the

correlated spin system which in turn - through the orbital moments of electrons - influences the resultant magnetic moment of a nanoparticle [13]. This would modify the resonance condition of the FMR because of creation of an internal magnetic field in the matrix.

The aim of this report is to presents the results of an external hydrostatic pressure effect on the FMR spectra arising from a small amount of magnetic nanoparticles embedded in a polymer matrix. Two samples will be studied with the same concentration of magnetic nanoparticles in an agglomerated state, but with different agglomerates sizes. The pressure dependence of the FMR parameters at constant temperature will be compared with the previous temperature study of the same samples [10].

2. EXPERIMENTAL

The procedure for obtaining nanocomposites with small amounts of iron oxides was described previously [10,11]. The nanocomposites, both containing 0.1 wt.% of the γ -Fe₂O₃ nanofiller, were

Corresponding author: J. Typek; e-mail: typjan@zut.edu.pl

obtained by *in situ* polycondensation in the molten state, where nanoparticles are introduced into the polymer during its synthesis. As a nonmagnetic polymer matrix the multiblock poly(ether-ester) copolymer based on polyoxytetramethylene and poly(ethylene terephthalate) (50:50 wt.%) was used. Two forms of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (with an average size of 4 nm) were used to prepare the polymer composite: one as a solid powder (sample designated as 1) and the other as a suspension, where nanoparticles were diluted in trichloromethane to prevent phase separation (sample designated as 2). In sample 1 an average size of agglomerates was 10 μm , in sample 2 in the range 10-20 nm.

FMR experiment was performed on a RADIOPAN SE/X spectrometer. FMR measurements at a frequency of 9.4 GHz under high hydrostatic pressure were carried out using a special appliance connected to a standard spectrometer [14]. This equipment, made at the Institute of Molecular Physics in Poznan, Poland, is a modified version of the apparatus used previously [15]. The cylinder corundum resonator TE_{112} mode was coupled to a microwave coaxial line and placed inside a chamber made of hardened beryllium bronze. The coupling between the resonator and the microwave line was adjusted by moving the coaxial line antenna. The diameter of corundum resonator was 11 mm and its length is 12 mm. Surfaces of this resonator were coated with a thin layer of vacuum-deposited silver and then electrolytically reinforced by a thin layer of copper. The pressure seal between the resonator and the high pressure plug was based on the unsupported area principle. The apparatus enables to perform high-pressure FMR experiment up to 600 MPa (and higher) in the 80-400K temperature range. The pressure of the transferring liquid (petroleum ether) was supplied to the pressure chamber via a capillary. A heat exchanger placed on the pressure chamber and a heater connected to a controller enabled to keep a desired temperature within the chamber. 80 Hz magnetic field modulation was provided by modulation coils mounted outside the pressure chamber. The sample was placed into the 2 mm diameter hole of corundum resonator. The pressure measurements were carried out at constant temperature of 82K and 92K.

3. RESULTS AND DISCUSSION

The FMR parameters (resonance field B_r , peak-to-peak linewidth ΔB_{pp} , integrated intensity I) have been calculated by using procedure described by Koksharov *et al.* [3]. At room temperature the values

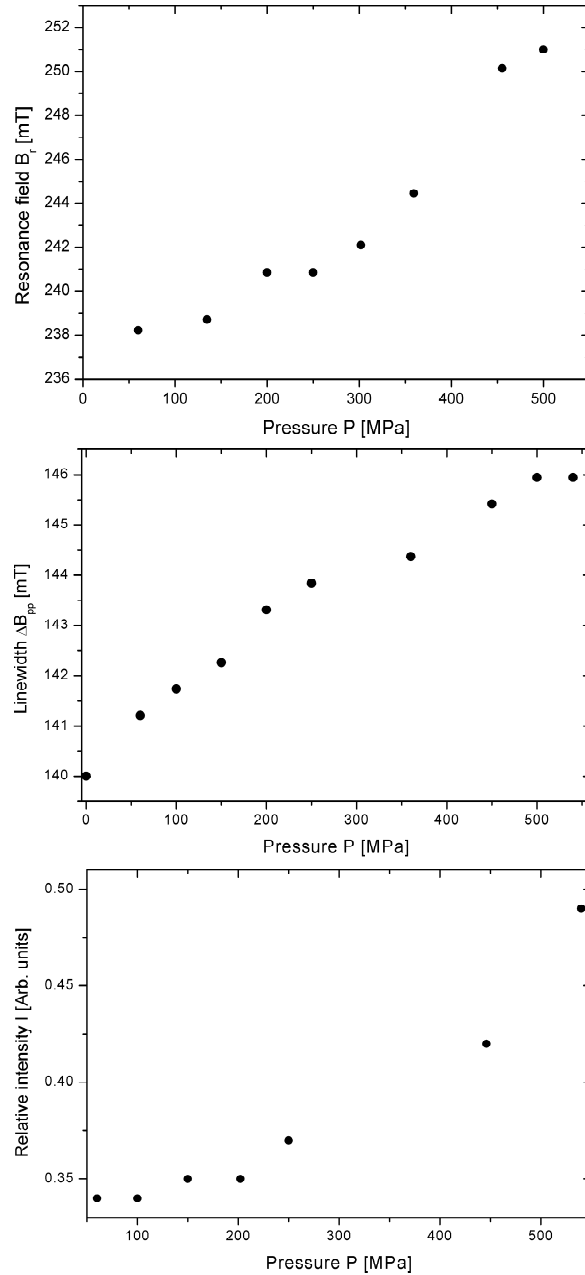


Fig. 1. Pressure dependence of the FMR parameters of sample 1 at $T=82\text{K}$; a) resonance field B_r , b) linewidth ΔB_{pp} , and c) integrated intensity I .

of the resonance field and the linewidth of the FMR resonance line of two investigated samples were the same as obtained in an earlier study [16]. Figs. 1 and 2 present the pressure dependence of the FMR parameters for both samples. The FMR integrated intensity I was calculated as the product of the line amplitude A_{pp} and the square of the peak-to-peak linewidth ΔB_{pp} , $I = A_{pp} \cdot \Delta B_{pp}^2$.

In both samples the resonance field shifts towards stronger magnetic fields (Figs. 1a and 2a)

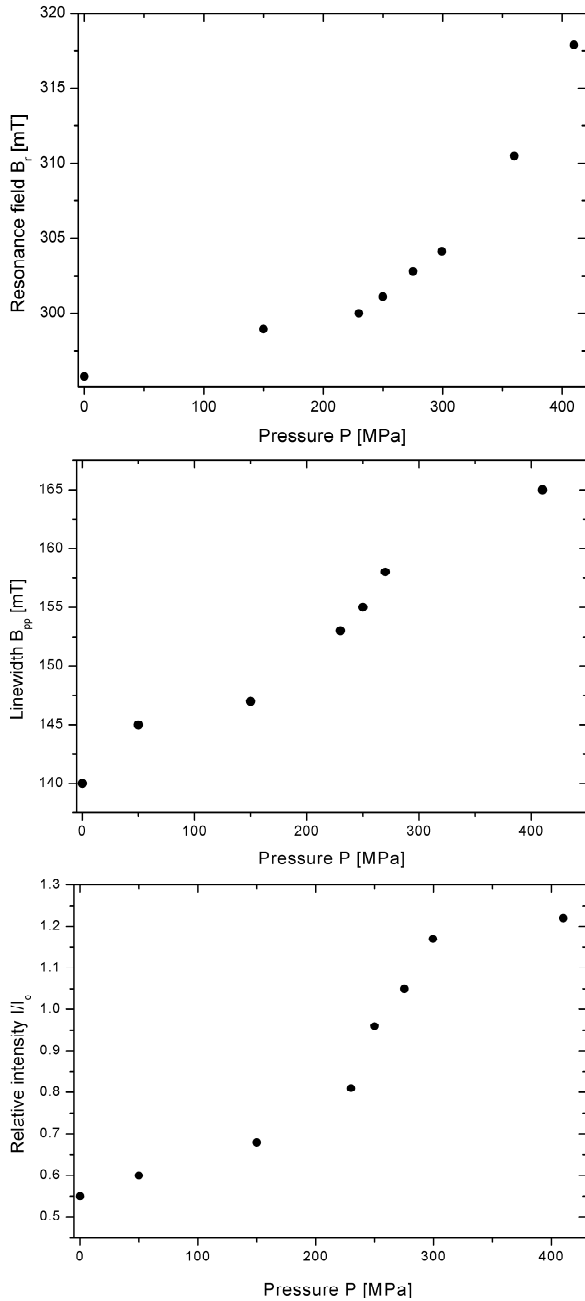


Fig. 2. Pressure dependence of the FMR parameters of sample 2 at $T=92\text{K}$; a) resonance field B_r , b) linewidth ΔB_{pp} , and c) integrated intensity I_c .

with the increase in pressure. A similar behavior of the resonance field was recorded for the same FMR spectra with increase in temperature in the high temperature range [10,11]. The linewidth increases with an increase in applied pressure for both samples (Fig. 1b and 2b), but for sample 2 in which magnetic agglomerates are smaller, that increase is significantly bigger. The integrated intensity of FMR line increases with increase in an applied

external pressure for both samples (Figs. 1c and 2c).

The temperature gradient of the resonance field, $\delta B_r/\delta T$, has a maximum for both samples: at about 82K for sample 1 and close to 50K for sample 2 [10,11]. As the pressure dependence of the resonance field below 100K is different for sample 1 and 2, the pressure measurements were carried out for sample 1 at 82K, which corresponds to temperature of the maximum of the temperature gradient $\delta B_r/\delta T$. Unfortunately, in our pressure study we were limited to temperatures above 80K, and hence for sample 2 we could not examine the pressure dependence of the FMR spectrum at temperature where a maximum of $\delta B_r/\delta T$ occurs [10]. The variation of $\delta B_r/\delta T$ could reflect an increase of magnetic anisotropy or even interparticles interactions that might be connected with the reorientation processes in the correlated spin system. An elastic stress could also strengthen the interactions by reducing an average interparticle distance [17].

It was suggested that an internal stress between the matrix and the agglomerated magnetic nanoparticles could have significant influence on the correlated spin system [13]. An increase of the external pressure shifts the FMR resonance lines towards larger magnetic fields as does the increase of temperature. The pressure gradient of the resonance field has value $\delta B_r/\delta T \sim 2.8 \cdot 10^{-2}$ mT/MPa for sample 1 and $\delta B_r/\delta T \sim 4.4 \cdot 10^{-2}$ mT/MPa for sample 2. The temperature gradient of the resonance field has the following values: $\delta B_r/\delta T \sim 2 \cdot 10^{-2}$ mT/K above 100K and $\delta B_r/\delta T \sim 0.8$ mT/K below 90K for sample 1, $\delta B_r/\delta T \sim 7 \cdot 10^{-2}$ mT/K above 100K, and $\delta B_r/\delta T \sim 8$ mT/K below 90K for sample 2. In the high temperatures range the temperature and pressure gradients of the resonance line shifts have comparable values, but for sample with smaller agglomerates (sample 2) the obtained value of the pressure gradient is two times greater. This could be related to smaller value of the saturation magnetization M_s for sample 2 as the resonance field B_r is expected to vary with applied external pressure p according to the formula [18]:

$$B_r \approx \frac{\lambda_s}{M_s} p,$$

where λ_s is the magnetostriction constant. The saturation magnetization in nanoparticles is usually much reduced in comparison to bulk material and this behaviour is mainly related to the presence of surface anisotropy and disorder. The surface layer

of a nanoparticle could be in a paramagnetic state due to the interaction with the matrix [19]. As in sample 2 the aggregates are much smaller and the surface effect is much more pronounced leading to decrease in saturation magnetization.

Strong influence of the agglomerates sizes on the FMR spectrum could be also observed in the pressure dependence of the linewidth. At 92K the linewidth of both samples increases with the temperature increase with the following values of temperature gradients: $\delta\Delta B_{pp}/\delta T$: -0.70 mT/K and -0.15 mT/K for samples 1 and 2, respectively [10]. An increase of pressure has an opposite effect on linewidth as changes of temperatures have – the pressure gradients $\delta\Delta B_{pp}/\delta P$ are positive and have the following values: +0.012 mT/MPa and +0.050 mT/MPa for samples 1 and 2, respectively. Thus the effect of pressure is bigger on smaller agglomerates in sample 2.

The observed FMR line is the sum of many individual component lines reflecting the different orientation of each nanoparticle relative to the external magnetic field. Thus the unresolved component lines determine the observed linewidth that would depend directly on the magnetocrystalline anisotropy field of the nanoparticles system [20]. The magnetocrystalline anisotropy field H_{mc} could be calculated as [20]

$$H_{mc} = \frac{K_1}{M_s},$$

where K_1 is the first-order uniaxial anisotropy constant. This field, and in consequence the resulting linewidth, would increase as the applied pressure decreases the saturation magnetization. As the pressure gradient $\delta\Delta B_{pp}/\delta P$ is roughly 4 times bigger for sample 2 it follows that M_s change is bigger for the smaller aggregates than for the large ones.

Figs. 1c and 2c present the pressure dependence of the FMR integrated intensity. To determine the change of the integrated intensity with an increase of applied pressure, the $\delta I/\delta P$ gradients will be calculated. The calculated values of these gradients are the following: $\delta I/\delta P \sim 7 \cdot 10^{-2}$ 1/MPa for sample 1 and $\delta I/\delta P \sim 30 \cdot 10^{-2}$ 1/MPa for sample 2. Although the order of magnitude of these pressure gradients is the same for both samples, that one containing smaller aggregates is more sensitive to applied pressure changes. The spins placed on aggregates surfaces seems to play a significant role in the integrated intensity increase with pressure.

4. CONCLUSIONS

The influence of an external pressure on the FMR spectra of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles embedded in a nonmagnetic polymer matrix has been investigated for two samples with the same concentration of magnetic nanoparticles but differing in sizes of nanoparticles agglomerates. Pressure dependence of the FMR parameters showed that the shift of the resonance line and the FMR integrated intensity change due to the applied external pressure are similar to what was observed previously for these parameters as temperature was varied. An opposite effect of temperature and pressure was observed for the linewidth changes. For sample with smaller agglomerates the values of calculated $\delta B_r/\delta P$, $\delta\Delta B_{pp}/\delta P$ and $\delta I/\delta P$ pressure gradients were larger. These observations indicate on the crucial role of the surface spins in formation of the FMR spectrum.

REFERENCES

- [1] L.J.L. Dormann, D. Fiorani and E. Tronc // *Adv. Chem. Phys.* **98** (1997) 283.
- [2] B. Martínez, X. Obradors, Ll. Balcells, A. Rouanet and C. Monty // *Phys. Rev. Lett.* **80** (1998) 181
- [3] R. H. Kodama and A. E. Berkowitz // *Phys. Rev. B* **59** (1999) 6321.
- [4] Yu.A. Koksharov, S.P. Gubin, I.D. Kosobudsky, M. Beltran, Y. Khodorkovsky and A. M. Tishin // *J. Appl. Phys.* **88** (2000) 1587.
- [5] P. Dutta, A. Manivannan, M. S. Seehra, N. Shah and G. P. Huffman // *Phys. Rev. B* **70** (2004) 174428.
- [6] N. Guskos, J. Typek, U. Narkiewicz, M. Maryniak and K. Aidinis // *Rev. Adv. Mater. Sci.* **8** (2004) 10.
- [7] M. Maryniak, N. Guskos, J. Typek, I. Kucharewicz, U. Narkiewicz, Z. Roslaniec, M. Kwiatkowska, W. Arabczyk and K. Adinis // *Rev. Adv. Mater. Sci.* **12** (2006) 200.
- [8] N. Guskos, J. Typek, M. Maryniak, A. Guskos, Z. Roslaniec, D. Petridis and E. Sanderek // *Rev. Adv. Mater. Sci.* **14** (2007) 157.
- [9] S.N. Ivicheva, Yu.F. Kargin, E.A. Ovchenkov, Yu.A. Koksharov and G.Yu. Yurkov // *Phys. Solid State* **53** (2011) 1114.
- [10] N. Guskos, V. Likodimos, S. Glenis, J. Typek, M. Maryniak, Z. Roslaniec, M. Baran, R. Szymczak, D. Petridis and M. Kwiatkowska // *J. Appl. Phys.* **99** (2006) 084307.

- [11] N. Guskos, V. Likodimos, S. Glenis, M. Maryniak, M. Baran, R. Szymczak, Z. Roslaniec, M. Kwiatkowska and D. Petridis // *J. Nanosci. Nanotech* **8** (2008) 2127.
- [12] M.R. Dudek, N. Guskos, E. Senderek and Z. Roslaniec // *J. Alloy. Compd.* **504** (2010) 289.
- [13] N. Guskos, J. Typek and M. Maryniak // *Phys. Stat. Sol. (b)* **244** (2007) 859.
- [14] J. Stankowski, A. Gałęzewski, M. Krupski, S. Waplak and H. Gierszal // *Rev. Sci. Instrum.* **47** (1976) 128.
- [15] M. Krupski // *Rev. Sci. Instrum.* **67** (1996) 2894.
- [16] N. Guskos, J. Typek, M. Maryniak, Z. Roslaniec, D. Petridis and M. Kwiatkowska // *Mater. Sci.-Poland* **23** (2005) 972.
- [17] J. Dai, J.-Q. Wang, C. Sangregorio, J. Fang and E. Carpenter // *J. Appl. Phys.* **87** (2000) 7397.
- [18] A. Chevalier, E. Le Guen, A.-C. Tarot, B. Grisart, D. Souriou, P. Queffelec, A. Thakur and J.-L. Mattei // *IEEE T. Magn.* **47** (2011) 4132.
- [19] C. Caizer // *Physica B* **327** (2003) 27.
- [20] A. Helminiak, W. Arabczyk, G. Zolnierkiewicz, N. Guskos and J. Typek // *Rev. Adv. Mater. Sci.* **29** (2011) 166.