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TEMPERATURE DEPENDENCE OF EPR/FMR SPECTRA OF CARBON COATED NICKEL NANOPARTICLES AND TEMPO SPIN PROBE DISPERSED IN PARAFFIN

MARCIN SOBOŃ[1], IGNACY-ERYK LIPIŃSKI[2], URSZULA NARKIEWICZ[3], MARIUSZ PODSIADŁY[3]

[1]The Faculty of Management and Economics of Services of Szczecin University, Cukrowa 8, 71-004 Szczecin, Poland
[2]Institute of Physics, West Pomeranian University of Technology, Szczecin , Al. Piastów 48, 70-311 Szczecin, Poland
[3]Institute of Chemical and Environment Engineering, West Pomeranian University of Technology, Szczecin, Pułaskiego 10, 70-332 Szczecin, Poland

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Electron Paramagnetic Resonance and Ferromagnetic Resonance (EPR/FMR) measurements of the agglomerated nickel magnetic nanoparticles coated with carbon and TEMPO spin probe dispersed in low concentration in paraffin matrix were carried out. Temperature dependence of the EPR/FMR spectra has been recorded in the temperature range from 5K - 325K. Very intense EPR spectra of TEMPO spin probe and a broad FMR line of nickel have been recorded in the whole temperatures range. A strong temperature dependence of the EPR lines position was observed in both cases. EPR resonance lines of spin probe are shifted essentially towards the direction of low magnetic fields with the temperature increase. After thermal annealing the "soft" matrix field with low concentration of magnetic nanoparticles could provide new arrangement of dipole-dipole interaction which influence on the internal magnetic field.

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 (Kodama, 1999, Ebels, Duvail, Wigen, L. Piraux, Buda, Ounadjela, 2001, Guskos, Anagnostakis, Likodimos, Bodziony, Typek, Maryniak, Narkiewicz, I. Kucharewicz, Waplak, 2005). Their remarkable magnetic properties (Guskos, Typek, Narkiewicz, Maryniak, Aidinis, 2004) have been exploited in many applications in engineering, technology and medicine (Tang, Santare and Advani, 2003, Shmidt and Malwitz, 2003, Qian, Liu, Wei, Wang, Li, 2004, Thostanson, Li and Chou, 2005). The macroscopic physical properties of nanostructure magnetic systems and their application are strongly dependent on the type and strength of magnetic coupling (Guskos *et al.*, 2005, Guskos *et al.*, 2004). The soft matrix type has played a very important role. For a low concentration of magnetic nanoparticles embedded in a polymer matrix it has been proved that the size of agglomerates influenced essentially the FMR spectra (Zolnierkiewicz, Guskos, Typek, Blonska-Tabero, 2006). The temperature dependence of the EPR spectra revealed the presence of critical points of the matrix (Guskos *et al.*, 2004).

Magnetic interactions could be very effectively investigated using the ferromagnetic resonance (FMR) technique. This method allows characterization of different critical processes (phase transitions, crossovers) of the matrices filled with magnetic nanoparticles. The temperature dependence of the FMR spectra of magnetic nanoparticles and agglomerates in different matrices can 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 temperature dependence of FMR spectra for paraffin samples with TEMPO spin probe. The samples contained cobalt nanoparticles coated with carbon and embedded at low concentration of 0.5% in paraffin matrix. The obtained temperature dependence of the EPR spectral parameters will be used for magnetic characterization of the investigated samples.

EXPERIMENTAL

The samples of Co(C), Fe_3C(C) and Ni(C) nanomaterials were prepared by carburisation of nanocrystalline Co, Fe and Ni with ethylene. At first, to obtain nanocrystalline metals, the solution containing cobalt (II) (Sample 1), iron (III) (Sample 2) or nickel (II)

(Sample 3) nitrates were used. Small amounts of calcium and aluminium nitrates were added to such solutions. To precipitate metal hydroxides, a solution of 25% NH_3.aq was added to obtain the solution with pH equal to 8. The obtained deposits was washed with water, filtered and next dried at 70°C.

The next preparation step was calcinations at 500°C for one hour to obtain the precursors of nanocrystalline metals – Co_3O_4, Fe_2O_3 and NiO (with small amount of structural promoters – CaO and Al_2O_3). The structural promoters stabilised the nanocrystalline cobalt, iron or nickel structure at elevated temperatures. The chemical composition of samples was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY 238 Ultrace, Jobin Yvon). Samples of cobalt precursor containing 0.2% CaO, 1.5% Al_2O_3, iron precursor containing 1.1% CaO, 2.1% Al_2O_3, and nickel precursor containing 0.8% CaO, 3.6% Al_2O_3 were obtained.

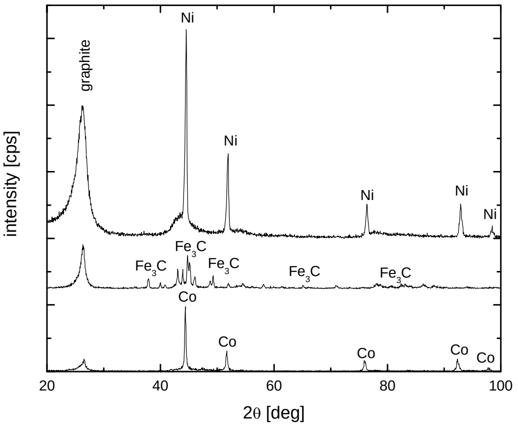

Fig.1. XRD patterns after carburization at 700°C for samples with: 1 – Co(C), 2 – Fe_3C(C), 3 – Ni(C).

Samples with m = 1g of this metal oxides were put into quartz crucible and placed into a high-temperature oven. The samples were next reduced (on order to transform metal oxides into metallic cobalt, iron or nickel) under pure (99,999%) hydrogen flow (20 dm^3/h). The reduction process was carried out in the temperature range of 25 – 500°C, with the heating rate of 15°C/min. The temperature of 500°C was kept during 1 h. Next, hydrogen was replaced by ethylene (99,9%, 20 dm^3/h). The carburisation process was carried out during one hour, next the oven was cooled to 300°C under flow of argon.

The mean carbon content in the prepared samples was about 10,7 gC/gCo (for Sample 1), 5.4 gC/gFe (for Sample 2) and 12.3 gC/gNi (for Sample 3).

Samples, consisting of magnetic nanoparticles dispersed at a low concentration in a paraffin matrix, were placed in 5 mm diameter quartz tubes. The measurements were performed at room temperature using a standard EPR X-band spectrometer (Bruker E500, ν=9.5 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. Before proper measurements 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 angular dependence.

For the purpose of the required insertion of the TEMPO marker (the content in samples amounted 0.015%), the paraffin was dissolved with the turpentine with the ratio 50%/50%. Three series of measurements were performed. The first series was carried out in the range from room to 325K temperature, the second in the temperature range from 100K to 290K and the last series in the range 5K to 130K.

Samples containing the paraffin with a TEMPO marker were placed in quartz tubes with the diameter about 5mm and investigated by the same equipment.

RESULTS AND DISCUSSION

The results of FMR measurements for carbon nanocapsules in paraffin matrices are shown in Fig. 2.

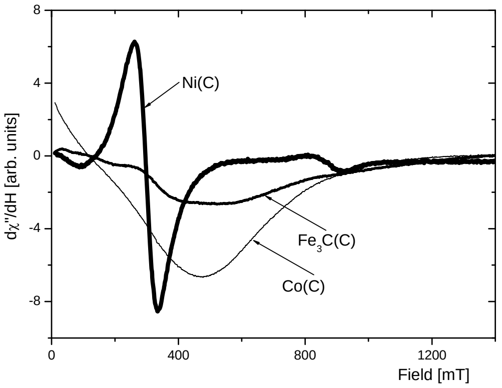

Fig.2. FMR spectra for Ni, Co, Fe carbon nanostructure recorded at room temperature.

Sample with nickel, in spite of similar structure like the remaining ones, presents very different spectrum from these samples investigated so far. Moreover, temperature dependence measurements and the

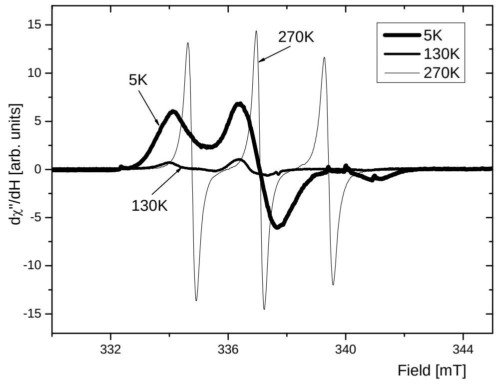

Fig. 3. EPR spectra of paraffin samples with TEMPO marker.

comparison of their results with already realized, i.e. for iron and the cobalt, could perhaps explain this difference.

Analyzing the above spectra (Fig. 2), one can draw the conclusion that the contribution of the matrix is rather not clear. It is therefore necessary to recognize the properties of the matrix itself in order to determine its contribution to local surrounding of the centre. Therefore, we carried out additional EPR measurements for samples containing used matrices doped with very low concentration of spin probe TEMPO.

This paper reports the EPR results only for the temperature range 160 - 290K, because the rest of obtained data considering their quantity and diversity have not been yet properly analyzed and interpreted. An exemplary spectra obtained in the range below 160K with reference to spectra at 270K is show in Fig. 3.

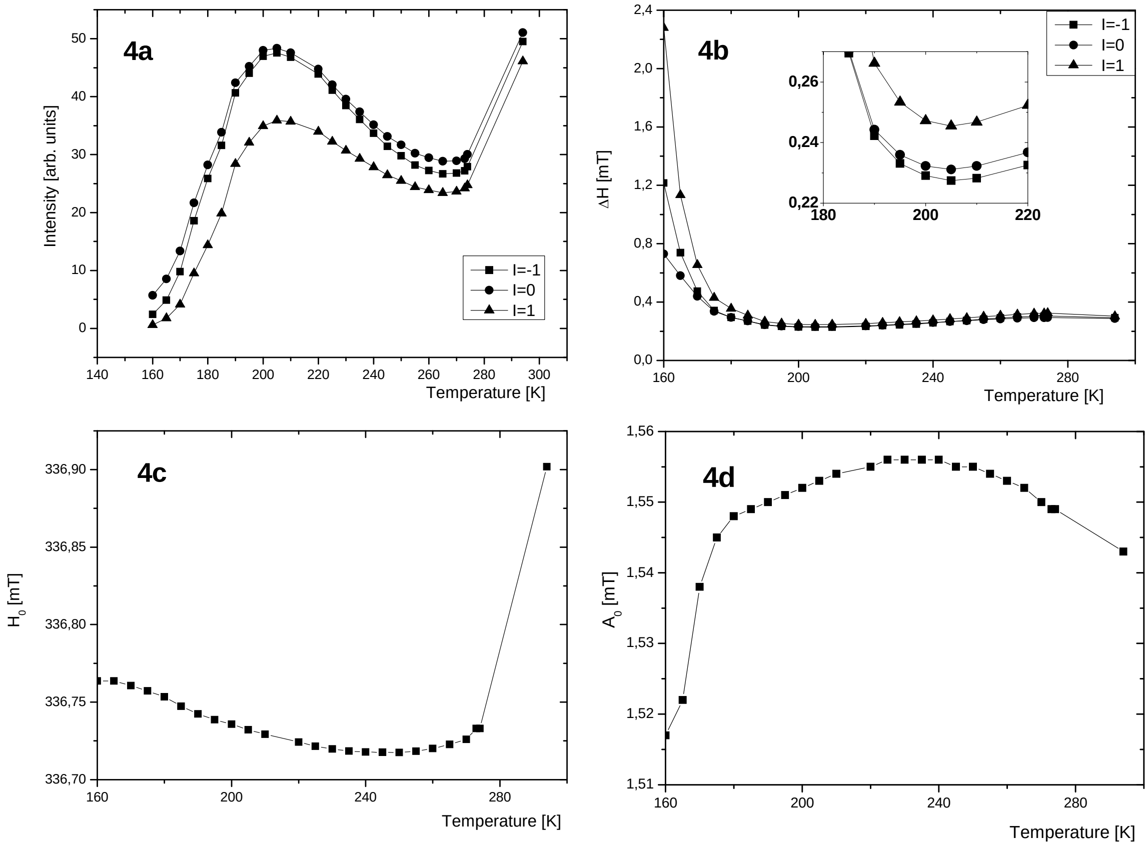

Fig. 4. The temperature dependence of: a) intensity for paraffin samples with TEMPO marker for each of three lines, b) line width (ΔH) at half of the maximum intensity for each three lines of paraffin samples with TEMPO marker, c) the resonance magnetic field H_0 for paraffin samples with TEMPO marker for central line I=0, d) hyperfine splitting for paraffin samples with TEMPO marker.

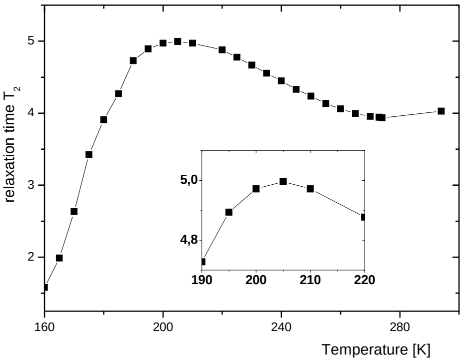

Fig. 5. Temperature dependence of spin-spin relaxation time T_2 for paraffin samples with TEMPO marker.

Spectra obtained in the range 160-290K were fitted by functions of the form:

$$W(H) = dL_{-1(\Delta H_{-1},H_{0-1})}(H) + dL_{0(\Delta H_0,H_{00})}(H) + dL_{1(\Delta H_1,H_{01})}(H) + w_0 \qquad (1)$$

where: dL (H) – the derivative of the Lorentz function:

$$dL(H) = \frac{2A}{\pi} \cdot \frac{\Delta H \cdot (8H - 8H_0)}{(4 \cdot (H - H_0)^2 + \Delta H^2)^2} \qquad (2)$$

ΔH – is line width (width at half maximum intensity), H_0 – is the magnetic resonance field, A-is the area under resonance line.

The fitting to function (1) was realized by software ORIGIN. For better precision, we replaced parameters of resonance fields for the high field lines with values of their differences between resonance field for the central line, that is to say, with values of hyperfine splitting (H_{0-1}=H_{00}-A_0, H_{01}= H_{00}+A_0) denoted here as A_0.

The adjustment allowed better specification of the changes in such parameters like: line intensity (Fig.4a), line width parameter ΔH (Fig.4b), the resonance field H_0 (Fig.4c) and the value of hyperfine splitting constant A_0 (Fig.4d). As a consequence we also were able to determine the spin-spin relaxation time T_2 according to the following relation:

$$T_2 = \frac{2}{\Delta H \sqrt{3}} \qquad (3)$$

in the same temperature range, what can be seen in Fig.5.

It is interesting to compare the maximum of this dependence at 205K of temperature with those found by EPR for the line width at half of the maximum intensity (ΔH) and the intensity of the resonance line. With decreasing temperature we observed a sharp increase of ΔH and decrease of the line intensity. With increasing temperature we obtained similar dependence, however, running much more smoothly. The sharp increase of ΔH and the decrease of the line intensity was observed with temperature decrease. When temperature was increasing, similar dependence was observed, but running much more smoothly.

CONCLUSIONS

In our investigations particular emphasis has been directed to the spectroscopic technique which can be a useful tool in study of nanostructure materials. Preliminary analysis of the obtained spectra does not allow full interpretation of the changes of all parameters but only to show that these changes take place in these systems. Changes of such parameters as ΔH, the value of resonance magnetic field and the value of hyperfine splitting constant A_0 both below 160K and above 274K were also detected. These changes correspond to variation observed for spin-spin relaxation time T_2 at about 205K. That is, some local extreme in appropriate values of considered functions appears. Moreover, we would like to indicate on important role played by paraffin as a matrix. It was showed that in our case application of paraffin as a matrix does not contribute to any changes in the resonance spectrum.

Unfortunately, for the first (RT (room temperature) to 325K) and third measurement series (5K-130K), up till now it was not able to fit the function with the error sufficiently small for precise determination of the interesting parameters. We hope that our further efforts deliver not only new experimental data contributing to a better characterization of physical properties such complex systems but contribute to the development of nature of critical phenomena.

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