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# INFLUENCE OF CONCENTRATION OF FREE RADICALS/MAGNETIC AGGLOMERATES ON MAGNETIC RESONANCE SPECTRUM IN ORGANIC MATRIX

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**Abstract.** A sample containing an extended free radical network derived from the condensation of cyanuric chloride with p-phenylenediamine was used for obtaining different concentrations of magnetic centers (free radicals and magnetic agglomerates). The temperature dependent magnetic resonance spectra were measured in the 4–290K temperature range. At room temperature the magnetic resonance measurements showed that the EPR spectrum was the sum of two lines attributed to two different magnetic centers: a narrow line at $H_r$ = 3373.57(3) Gs ($g_{eff}$ = 2.0032(1)) with linewidth $\Delta H_{pp}$ = 8.31(2) Gs (due to free radicals) and a broad line centered at $H_r$ = 3198(5) Gs ($g_{eff}$ = 2.234(1)) with linewidth $\Delta H_{pp}$ = 1000(5) Gs (arising from magnetic iron oxide agglomerates). The sample was prepared in such a way that the narrow line was more intense. The integrated intensities decreased with decreasing temperatures in both spectra in the high temperature range. This type of behavior was similar to that of magnetic nanoparticles in non-magnetic matrixes. The resonance field of the broad line shifted to smaller magnetic fields upon lowering the temperature with gradient $\delta H_r/\Delta T$ = 1.5(1) Gs/K, while the narrow line shifted towards higher magnetic fields with $\delta H_r/\Delta T$ = 0.020(1) Gs/K. The broader line linewidth increased with the decreasing temperature while this change was only minor for the narrow line (especially at higher temperatures). The magnetic iron oxide clusters produced an internal magnetic field which acted on free radicals and its strength depended essentially on the relative concentration of clusters. This field could force free radicals to form a magnetic ordered state.

## 1. INTRODUCTION

A large number of papers devoted to magnetic ordering processes related to conduction electrons and free radicals in carbon or other organic matrixes have been published recently, e.g. [1-7]. The magnetic resonance methods – electron paramagnetic resonance (EPR) and ferromagnetic resonance (FMR) are very useful for studying magnetic ordering in these materials because they provide important information of this process on the microscopic level. Graphite oxide-like carbonic materials derived from a molecular precursor have shown magnetic ordering processes that are influenced by free radicals [6]. Organic networks derived from an assembly of organic molecules have served as a base for the coexistence of two different magnetic centers, one being free radicals and the other magnetic agglomerates, such as iron oxides [8]. The magnetic study of these materials could be useful for better understanding of magnetic interactions of conduction electrons in a carbon matrix in which the spins of free radicals have shown some similarity with the

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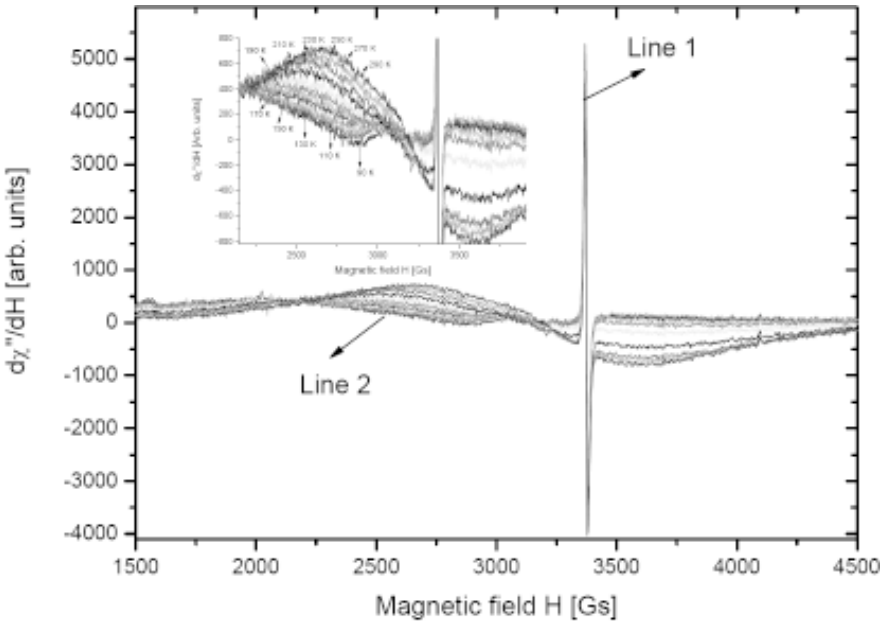


**Fig. 1.** Magnetic resonance spectra of graphite oxide-like carbonic at different temperatures.

behavior of the EPR spectra [8,9]. An experimental study of the evolution from the nano/micro-size (magnetic nanoparticles or agglomerates) to atomic-size scales (magnetic ions and conduction electrons) could lead to a better understanding of magnetic interactions that are similar to those studied in spintronic systems. The introduction of magnetic nanoparticles in a micro-silica/cement matrix together with DPPH free radicals has shown that a much stronger magnetic field acts on the DPPH in comparison with the case of isolated magnetic ions [9]. It is expected that the same effect could be observed in the present sample.

The aim of this report is to investigate the FMR/EPR spectra of a layered organic material derived from covalently bridging 1,3,5-triazine units with 1,4-phenylenediamine and a reconstructed derivative obtained from oxidation of the amine groups of the organic network. Two main magnetic resonance centers are produced in this material, one being the magnetic nanoparticle cluster of iron oxide and the other - the DPPH free radicals. As the concentration of free radicals is larger than in the samples studied in [8], a comparison of EPR/FMR spectra is possible and conclusions could be drawn concerning the role of this parameter.

## 2. EXPERIMENTAL

Cyanuric chloride was recrystallized from hexane. The layered network was prepared by condensation of cyanuric chloride with bridging para phenylenediamine, as described in details [6,8]. In comparison to the previously studied samples the present solid contained a larger concentration of free radicals, as a consequence of using a larger amount of ferro nitrate as the oxidant to generate free radicals.

The EPR/FMR spectra were recorded using a standard Bruker E 500 X-band spectrometer ($\nu$ = 9.4 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with an NMR magnetometer. The measurements were performed in the temperature range from 4 to 290K using an Oxford flow cryostat.

## 3. RESULTS AND DISCUSSION

Fig. 1 presents the resonance spectra of a graphite oxide-like carbonic material with free radicals and iron oxide registered in the 4-290K temperature range. The measurements showed a coexistence of two spectra arising from two different magnetic centers. At room temperature, the narrow line centered at $g_{eff}$ = 2.0032(1) ($H_r$ = 3373.57(3) Gs) with linewidth $\Delta H_{pp}$ = 8.31(2) Gs (line designated as 1) is assigned to free radicals, while the broader line centered at $g_{eff}$ = 2.2536(2) ($H_r$ = 3198(5) Gs) with linewidth $\Delta H_{pp}$ = 1000(2) Gs is ascribed to the iron oxide clusters (line designated as 2). The $g_{eff}$ and linewidth values for the latter component are very similar to what was observed for small concentra-

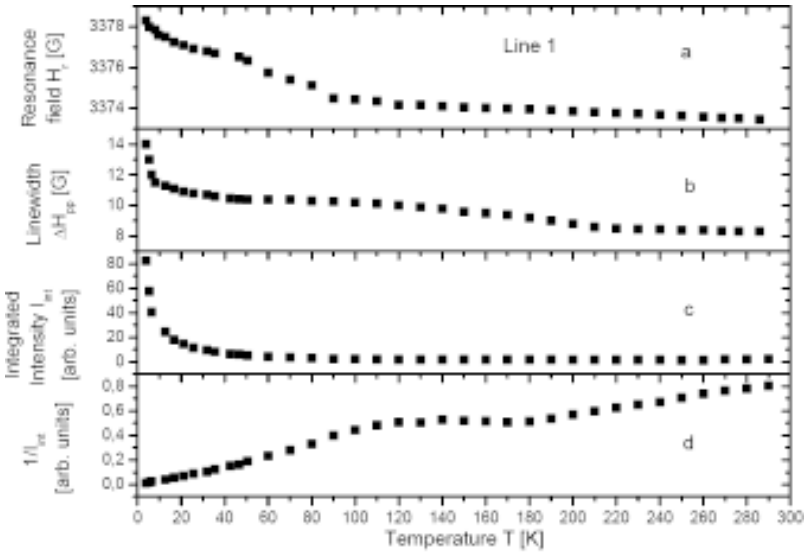


**Fig. 2.** Temperature dependence of the EPR parameters of the DPPH free radical line (line 1); (a) resonance field, (b) linewidth, (c) integrated intensity, (d) reciprocal integrated intensity.

tion of magnetite centers embedded in non-magnetic matrices [10].

The broad FMR line was more intense at high temperatures while the narrow EPR line was more intense at low temperatures (Fig. 1). The amplitudes of these lines at room temperature are reversed in comparison to what was registered for a similar system in [8]. Thus, it would be possible to study an interaction of magnetic clusters (or agglomerates) with free radicals when the concentration of free radicals were increased. It is expected to examine the so called "hen and chicken" phenomenon in which the internal magnetic field produced by clusters could order the spins of the neighboring free radicals and influence the concentration of the magnetic centers [8].

Figs. 2 and 3 show the temperature dependence of the calculated magnetic resonance parameters: resonance field $H_r$ and peak-to-peak linewidth $\Delta H_{pp}$ for both magnetic centers. The EPR integrated intensity ($I_{int}=A_0 \cdot \Delta H_{pp}^2$, where $A_0$ is the signal amplitude) is calculated only for line 1. The resonance field shifts to higher magnetic fields with the decreasing temperature for line 1, while an opposite effect is observed for a more intense line 2 (Figs. 2a and 3a). Line 1 shifts to higher magnetic fields with the following temperature gradients: for high temperatures the value is $\delta H_r/\Delta T_{290\text{-}90} = 0.005(1)$ Gs/K (0.006(1) Gs/K was registered in [8]) while for low temperatures $\delta H_r/\Delta T_{90\text{-}46} = 0.048(1)$ Gs/K, (0.035(1) Gs/K in [8]) and $\delta H_r/\Delta T_{4\text{-}20} = 0.076(1)$ Gs/K, (0.035(1) Gs/K in [8]). Thus, an essential difference in the values of the temperature gradient $\delta H_r/\Delta T$ is observed at low temperatures in samples with a different concentration of free radicals. The greater $\delta H_r/\Delta T$ gradient value in the current sample could be associated with the presence of some more intense freezing processes of the matrix and connected with the sizes of magnetic clusters [11].

The temperature dependence of the resonance field $H_r$ and linewidth $\Delta H_{pp}$ of the broad component (line 2) is very similar to those reported in other nanoparticle systems in that $H_r$ decreases ($g$-factor increases) and $\Delta H_{pp}$ increases with the decreasing temperature. The resonance field shifts in the direction of lower magnetic fields with the gradient $\delta H_r/\Delta T = 1.4(1)$ Gs/K (1.4(1) Gs/K was measured in [8]) at high temperatures, from 290 to 230K, and $\delta H_r/\Delta T = 3.0$ (1) Gs/K, (9.8(1) Gs/K in [8]) in the 150 to 90K temperature range. Thus, a similar value of $\delta H_r/\Delta T$ is observed at high temperatures while a more than three times smaller value is registered at lower temperatures in comparison to the previously studied sample [8]. The presence of three temperature ranges in the thermal behaviour of spectral parameters in line 2 is especially visible in Fig. 4. It shows a double logarithmic plot of the resonance field shift $\delta H_r$ vs. linewidth $\Delta H_{pp}$. The resonance field shift is defined as $\delta H_r = H_\infty - H_r$, where $H_\infty$ is the resonance field at high temperature. Three different temperature ranges could be recognized: 290-230K, 230-160K, and 160-90K. They are characterized by

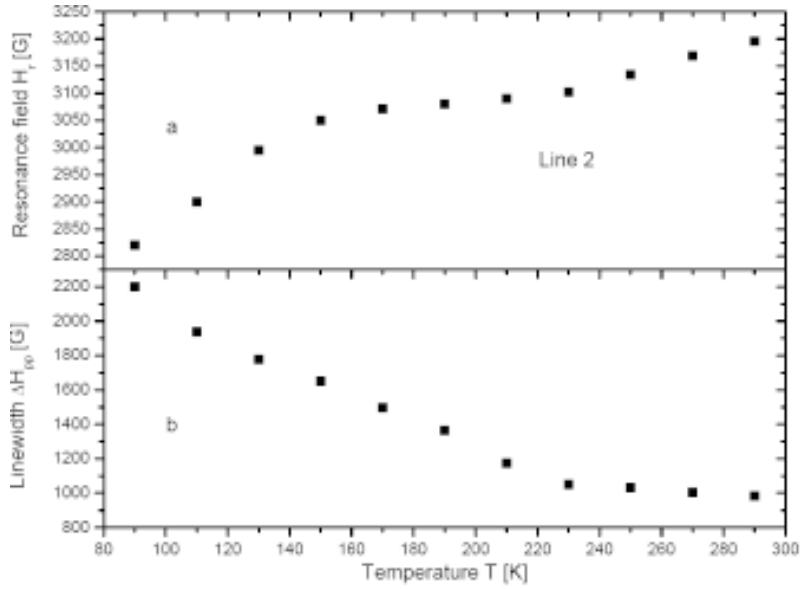


**Fig. 3.** Temperature dependence of the FMR parameters of the iron oxide line (line 2); (a) resonance field $H_r$ and (b) linewidth $\Delta H_{pp}$.

different slopes of $\ln(\delta H_r)/\ln(\Delta H_{pp})$. In the 90-230K range the linewidth decreases with the increasing temperature which is an indication of a superparamagnetic regime of the iron oxide nanoparticle spin system. In that regime thermal fluctuations average out random magnetic fields produced by nanoparticles leading to the narrowing of the resonance line. Thus, a characteristic blocking temperature $T_B$ for a magnetic system of iron oxide nanoparticles must be below 90K.

The integrated intensity of both lines increases with the decreasing temperature and the intensity of line 1 is almost constant in a high temperatures range (above 200K). The amplitude of line 2 decreases strongly with the decreasing temperature, while an opposite effect is observed for the narrow line. The broadening of the magnetic resonance line 2 is over two times larger than of line 1. The isolated paramagnetic centers feel an average internal magnetic field which is much weaker. The integrated intensities of both lines decrease with decreasing temperatures at high temperatures while an opposite trend is observed at low temperatures (Fig. 2c and 3c). The reciprocal intensity for line 1 shows a plateau at 160-120K and the Curie-Weiss type of behavior is registered for lower temperatures. The positive sign of the Curie-Weiss temperature, $\Theta_{CW}$=1.0(2)K, (Fig. 2c) indicates the existence of ferromagnetic interactions. Line 2 shows a sharp change in the integrated intensity at about 150K

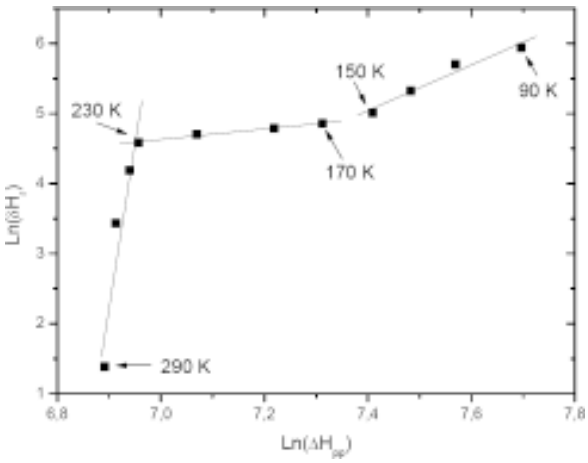


**Fig. 4.** Double logarithmic plot of the resonance field shift $\delta H_r$ *vs*. linewidth $\Delta H_{pp}$ for line 2. Three different temperature ranges could be recognized. Solid lines are the regression lines in appropriate temperature ranges.

that could be associated with the reorientation processes.

Large-size clusters (agglomerates) of $\gamma$-$Fe_2O_3$ could produce stronger average internal magnetic fields and generate stronger dipole-dipole magnetic interactions in comparison to smaller clusters. Similar magnetic behavior was observed for magnetic nanoparticles embedded in nonmagnetic matrixes for which a very intense FMR signal was registered [11]. This indicates that a low concentration of magnetic nanoparticles could generate a significant internal magnetic field in which a large amount of spins

could be subjected to an average magnetic field of a very low value. Similar arguments hold for the magnetic and electronic properties of multiwall carbon nanotubes that depend on a low concentration of magnetic impurities forming a magnetically ordered state [7]. The observed magnetic ordering process by free radicals could be produced by using a small amount of doped magnetic nanoparticles [9] and it could be connected with the so called "hen and chicken" effect. The orientation processes in spintronics (leading to a magnetic ordered state) play an important role and the above phenomenon could produce this state at a high temperature. The change of the relative concentration between a magnetic cluster and the localized magnetic moments could strongly influence the reorientation processes of free radicals and thus could be used to manipulate the spin system.

## 4. CONCLUSIONS

A covalent layered network was prepared by condensation of cyanuric chloridewith bridging para phenylenediamine with different relative concentration of magnetic clusters (aggregates) to free radicals (localized magnetic momentum). In the case of iron nitrate oxidant the EPR spectra indicated a generation of free radicals and $\gamma$-$Fe_2O_3$ nanoparticles. The magnetic ordering processes of spin electrons of free radicals were connected with the magnetic agglomerates which could generate a strong magnetic dipole-dipole interaction. The strength of this interaction depended essentially on the relative concentration of both magnetic components. It is proposed to use this dependence as a measure to manipulate the orientation processes in the spin system.

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## REFERENCES

[1] P. Esquinazi, A. Setzer, R. Hohne, C. Semmelhack, Y. Kopelevich, D. Spemann, T. Butz, B. Kohlstrunk and M. Losche // *Phys. Rev. B* **66** (2002) 024429.
[2] P. Esquinazi, D. Spemann, R. Hohne, A. Setzer, K.–H. Han and T. Butz // *Phys. Rev. Lett.* **91** (2003) 227201.
[3] V. Likodimos, S. Glenis, N. Guskos and C.L.Lin // *Phys. Rev. B* **68** (2003) 045417.
[4] D.L. Huber, R.R. Urbano, M.S. Sercheli and C. Rettori // *Phys. Rev. B* **70** (2004) 125417.
[5] K.W. Lee and C.E. Lee // *Phys. Rev. Lett.* **97** (2006) 137206.
[6] A.B. Bourlinos, E.P. Giannelis, Y. Sanakis, A. Bakandritzos, M. Karakassides, M. Gjoka and D. Petridis // *Carbon* **44** (2006) 1906.
[7] V. Likodimos, S. Glenis, N. Guskos and C.L. Lin // *Phys. Rev. B* **76** (2007) 075420.
[8] N. Guskos, G. Zolnierkiewicz, J. Typek, A. Guskos and D. Petridis // *J. Non-Cryst. Solids* **354** (2008) 4211.
[9] N. Guskos, G. Zolnierkiewicz, A. Guskos, J. Typek, J. Blyszko, W. Kiernozycki, U. Narkiewicz and M. Podsiadly // *J. Non-Cryst. Solids* **354** (2008) 4510.
[10] N. Guskos, J. Typek, M. Maryniak, Z. Roslaniec, D. Petridis and M. Kwiatkowska // *Materials Science-Poland* **23** (2005) 972.
[11] 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.