Concentration dependence of free radicals/magnetic agglomerates on the EPR/FMR spectra

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Abstract

The sample of extended free radical network derived from condensation of cyanuric chloride with p-phenylenediamine have been used for obtained different concentration of magnetic centres (free radicals and magnetic agglomerates). The iron nitrate was used as oxidant and the temperature dependent magnetic resonance spectra were measured in the region 290 – 90 K. The magnetic resonance measurements have shown the coexistence of two spectra arising from two different magnetic centers **(Fig. 1)**: one narrow line the resonance field lying at H_r=3374.48(3) Gs (g_{eff}=2.0031(1)) with linewidth ΔH=8.31(2) Gs (free radical) and another broad line centered at H_r=2995(5) Gs (g_{eff}=2.254(1)) with linewidth ΔH_{pp}=1263(5) Gs (magnetic iron-oxide agglomerates) at room temperature. The sample has prepared in such way that the broader line was more intense for the one sample. The temperature dependence of the magnetic resonance lines has shown intense changes. The integrated intensities decreased with decreasing temperatures in both spectra in the high temperature region. This type of behavior is similar to that of magnetic nanoparticles in nonmagnetic matrixes. The resonance field of the broad line shifts to lower magnetic fields upon lowering the temperature with the gradient $\Delta H_r/\Delta T$=1.5(1) Gs/K , while the narrow line shifts towards higher magnetic fields with $\Delta H_r/\Delta T$=0.020(1) Gs/K. The linewidth of the broader line increases with decreasing temperature while the narrow line remains almost constant. The magnetic iron-oxide clusters could produce an internal magnetic field which acts on free radicals. This field could compel free radicals to form a magnetic ordered state at high temperatures.

Introduction

Recently it has appeared a lot of works on magnetic ordering processes connected with electron conductivity and free radicals in carbon or organic matrixes e.g. [1-7]. The magnetic resonance method is very useful for studying in these materials magnetic ordering processes because is given important information on the microscopic level. Graphite oxide-like carbonic materials derived from a molecular precursor have been shown magnetic ordering processes organizing by free radicals [6]. Organic networks derived from the assembly of organic molecules was as base for coexistence two different magnetic centers, one from free radicals and other from strong magnetic agglomerates like oxide irons [8]. The same or different kind are important supramolecular architectures with certain functionalities in the solid state. A such class of covalent layered organic materials results from the quaternization of cyanuric chloride with bridging 4,4-bipyridine units (1). The use of diamines as bridging spacers can give access to a wider class of triazine-based derivatives by varying the type of bridging diamine. Moreover, the local chemical environment of the targeted substance can be manipulated by redox or ion exchange reactions affording new reconstructed materials. One interesting phenomenon in these materials is formation of magnetically ordered state by free radicals [1]. The magnetic study of these materials could be helpful for better understanding of magnetic interactions of conducting electrons in the carbon matrix where the spins of free radicals is shown some similarity with behavior of the EPR spectra [2,3]. Going from the nano/atomic-size (interaction of magnetic nanoparticles) to electron-size scales (interaction magnetic ions with conduction electrons) could lead to a better understanding of magnetic interactions related to the spintronics phenomena where the directed processes could be the same important as ordering state of spins. Introduction of magnetic nanoparticles in micro-silica/cement matrix together with DPPH free radicals could induce interaction on the magnetic state of free radical with stronger magnetic fields than in the case of isolated magnetic ions and it is expected for the above compound the same behaviors [4,5].

In the context of these principals , we describe here the synthesis and FMR/EPR response of a layered organic material derived from covalently bridging the 1,3,5-triazine units with 1,4-phenylenediamine and a reconstructed derivative obtained from the oxidation of the amine groups of the organic network. The main two magnetic resonance centers are formed inside the material, one from magnetic clusters (oxide iron - nanoparticles) and the second from free radicals (ionic size - level).

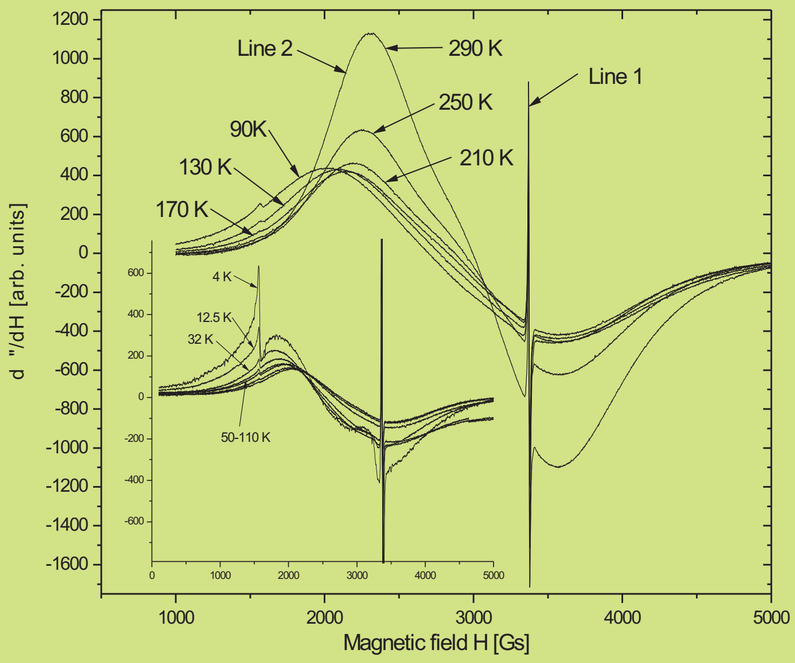

Figure 1 Temperature dependence of the FMR/EPR spectra of a graphite oxide-like carbonic.

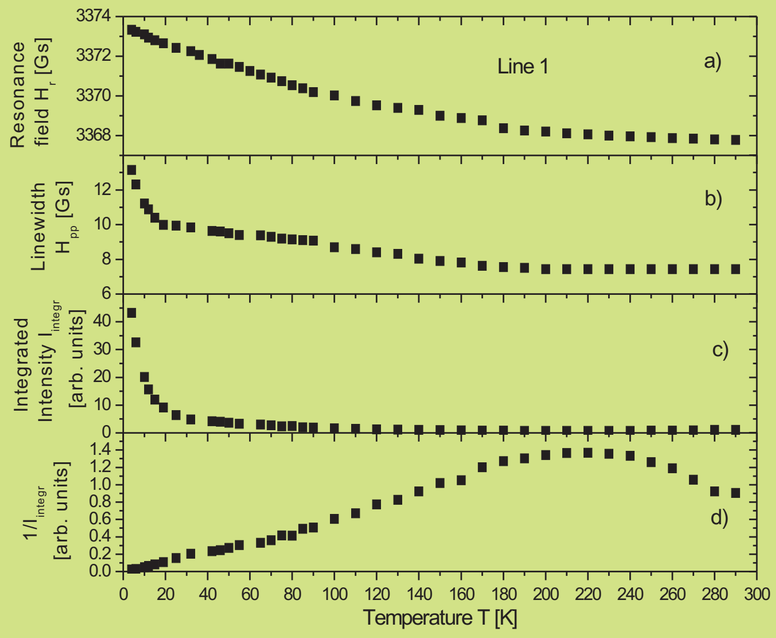

Figure 2 Temperature dependence of the EPR parameters of free radical DPPH; (a) resonance field, (b) linewidth, (c) the integrated intensity, (d) the reciprocal integrated intensity.

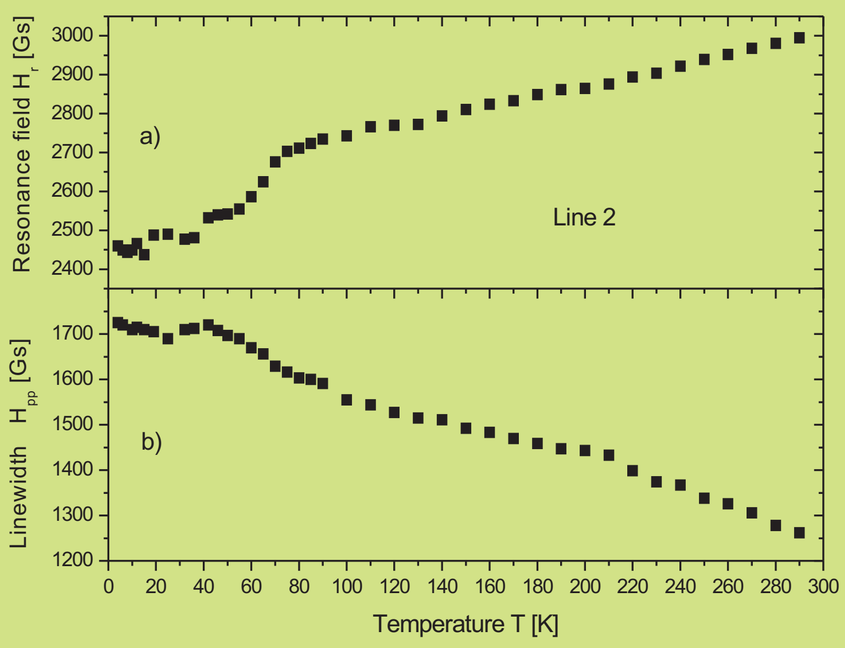

Figure 3 Temperature dependence of the EPR parameters of iron oxide; (a) resonance field and (b) linewidth.

Experimental

Cyanuric chloride was recrystallized from hexane. The layered network was prepared by condensation of cyanuric chloride with bridging para phenylenediamine in the following way. Fine slurry of cyanuric chloride was prepared by adding a solution of 1.11g (6.00mmol) of cyanuric chloride in 20ml of acetone to a well stirred ice-water (30ml). A solution of 0.972g (9.00mmol) of 1,4= phenylenediamine in 20 ml of acetone and 0.756g $NaHCO_3$ in 10 ml water were then added and the mixture was refluxed for one hour. The white solid was filtered off, washed with and the wet precipitate was divided into two parts. To one part, dispersed into 30ml of water, were added under stirring 0.456g (2mmol) of ammonium persulfate in 10ml of water. A dark blue precipitate was formed. Stirring was continued for 24h to ensure complete oxidation, and then the solid was isolated by centrifugation, washed with water and air dried. In a similar way, the other half was oxidized using 0.820g (2.00 mmol) of ferric nitrate. After addition of the ferric nitrate, the mixture was stirred for 48h. Finally, a third sample was prepared by a similar procedure but using 2.10g (5.00mmol) of ferric nitrate and stirring the mixture for 48h.

The EPR/FMR (electron paramagnetic resonance/ferromagnetic resonance) spectra were recorded using a standard X-band spectrometer type Bruker E 500 (9.455 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The measurements were performed in the temperature range 4 to 290 K using an Oxford flow cryostat and a standard hot air flow system.

Conclusions

A covalent layered network was prepared by condensation of cyanuric chloridewith bridging para phenylenediamine. Oxidation of the solid in water-alcohol dispersion with ferric nitrate or ammonium persulfate gave a blue product that signals the formation of an extended free radical system. In the case of iron nitrate oxidant the EPR spectra indicate the generation of free radicals and γ-Fe_2O_3 nanoparticles. The magnetic ordering processes of spin electrons of free radicals are connected with the existing strong magnetic agglomerates which could generate a strong magnetic dipole-dipole interaction.

ACKNOWLEDGMENTS

This work was partially supported by the European Union - European Social Fund, by grant ΓΓΕΤ 165ε, and by Poland Governments Science Budget 2007-2008 under a research project.

Results and discussion

Figures 1 presents the temperature dependence of magnetic resonance spectra of graphite oxide-like carbonic material with free radicals and iron oxide in the temperature region 290 – 4 K. The measurements show the coexistence of two spectra arising from two different magnetic centers. At room temperature the narrow line centered at g_{eff}=2.0038(1) with linewidth ΔH=7.42(2) Gs (line designated as 1) is assigned to free radicals, while the broader line centered at g_{eff}=2.2536(2) with linewidth ΔH=1298(2) Gs is attributed to iron oxide clusters (line designated as 2) . For the latter, the values of the g_{eff} and linewidths are very similar behavior to what has been observed for magnetite centers at low concentration in a non-magnetic matrix [6].

The broad FMR line was more intense at high temperatures while the narrow line was more intense at low temperatures **(Fig. 1)**. The aim here is to study the interaction of magnetic clusters (or agglomerates) with free radicals. It is expected to observe the so called “hen and chicken” phenomenon in which the internal magnetic field produced by clusters orders the spins of neighboring free radicals [5]. A **figure 2 and 3** is showing the temperature dependence of the position of resonance line (H_r – resonance field) and linewidth (ΔH) for both free magnetic centers. The EPR integrated intensity ($I_{inter}=I_o*\Delta H^2$) is given only for line 1. The resonance field shifts to higher magnetic fields with decreasing temperature for line 1 while the opposite effect is observed for a more intense line 2 **(Fig. 2a and 3a)**. Line 1 shifts to higher magnetic field with different temperature gradients: for high temperatures the value is $\Delta H_r/\Delta T$=0.006(1) Gs/K and for low temperatures $\Delta H_r/\Delta T$=0.035(1) Gs/K. The greater value of the $\Delta H_r/\Delta T$ gradient could be associated with freezing processes of the matrix and connected with size of clusters [7]. The resonance field of broader line (line 2) shifts in the direction of lower magnetic fields with the gradient $\Delta H_r/\Delta T$=1.4(1) Gs/K at high temperatures (from 290 to 75 K) and $\Delta H_r/\Delta T$=9.8(1) Gs/K in 75 to 50 K temperature range. Below 50 K a spin-glass like state is observed **(Fig. 3b)**.

The intensity of both lines increases with decreasing temperatures and the intensity of line 1 is almost constant in the high temperatures region (above 200 K). The broadening processes of the magnetic resonance line 2 is more intense (over two order) than for 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 at low temperatures an opposite trend is observed **(Fig. 2c and 3c)**. The reciprocal intensity for line 1 shows a maximum at 200 K and for lower temperatures the Curie-Weiss type of behavior is registered. The positive sign of the Curie-Weiss temperature **(Fig. 2c)** indicates the existence of ferromagnetic interactions. Line 2 is shows a sharp change in the integrated intensity at about 50 K that could be connected with the formation of a spin glass state after the freezing processes which do not exists for the system of free radicals spins.

The greater in size clusters of γ-Fe_2O_3 (agglomerates) can produce stronger average internal magnetic fields and generate stronger dipole-dipole magnetic interactions. A similar magnetic process was observed for low concentrations of magnetic nanoparticles embedded in nonmagnetic matrixes where the FMR signal was very intense [7]. This indicates that low concentration of magnetic nanoparticles could generate an essential internal magnetic field in which a great deal of the spin systems could feel an average very low value of magnetic field. Similar arguments hold for the magnetic and electronic properties of multiwall carbon nanotubes that depend on low concentration of magnetic impurities that could form magnetically ordered state [8]. The observed magnetic ordering process by free radicals could be formed using doped magnetic nanoparticles low concentration [1] and it could be connected with phenomena so called “hen and chicken”. On the “spintronic” could be important the directed processes (one of them is ordering state) and the above phenomena could form this state at higher temperature.

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