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Localized centers and correlated magnetic spin systems in titanium oxides nanocomposites

N. Guskos [a,b,*]
[a] Department of Solid State Physics, Faculty of Physics, University of Athens, 15 784 Zografou, Athens, Greece
[b] Department of Physics, Faculty Mechanical Engineering and Mechatronic, West Pomeranian University of Technology, Al. Piastów 17, 70-310 Szczecin, Poland
* Corresponding e-mail address: ngouskos@phys.uoa.gr

ABSTRACT

Purpose: The aim of this review is recapitulating the FMR/EPR study of localized magnetic centers and clusters in co modified nanocomposites titanium dioxide by nitrogen and group of transitions magnetic metals.

Design/methodology/approach: In some cases, modified in this way, titanium dioxides improve their photocatalytic properties where localized magnetic moments and spin-correlated systems play a very important role in their physical properties that are important in their applications.

Findings: The modified titanium dioxides without introducing ions from the group of transition metals may have EPR spectra of free radicals and titanium ions at a lower oxidation state, which are responsible for the increase in photocatalytic activity. Modifying the additional magnetic ions from the group of transition metals there are additional very intense FMR spectra which are strongly temperature dependent. Static measurements (DC), magnetization as a function of temperature indicate the formation of magnetic orderings, superparamagnetic and paramagnetic state.

Research limitations/implications: Modified nano-titanium dioxide composite prognosis applications in catalysis, photovoltaic or in spintronics.

Originality/value: A large amount of work appears annually associated with the modified titanium dioxide by the various elements and especially from the group of transition metals and noble gases. Against this background, very little work appears on their dynamic and static magnetic properties that may impact on their ability applications.

Keywords: Titanium dioxide; Nanocomposites; Localized magnetic centers; Magnetic clusters

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MATERIALS

1. Introduction

At the turn of the century 70s and 80s there was a huge amount of work in research using EPR method, both theoretical and experimental associated with a low concentration of localized magnetic centers in non-magnetic single crystals. Particular attention for their potential in the application of laser. Hence, attention was of great importance on the impact on the energy levels of magnetic ions doped. Also a lot of work appeared with magnetic resonance systems by examining correlated spin in single crystals. After mastering the technology of magnetic nanoparticles at the turn of the century began to appear a lot of work associated with putting them in low concentrations to polymers and nanocomposites. It turned out that substantially improved physical properties, which is essential in the formation of a new generation of functional materials. Particularly important are the studies magnetic dynamic and static interaction. In previous papers is shown works with dynamic magnetic investigation on polymers and nanocomposites of titanium (TiC and TiN) using EPR/FMR (electron paramagnetic resonance /ferromagnetic resonance) method [1,2]. As shown in Materials Engineering is a useful method to study physical processes at the atomic level. For thirty years intensively studied titanium dioxide is due to its catalytic and photovoltaic properties. After modification of noble gases and metals of transition group exhibit improved catalytic properties e.g. [3-14]. Recently magnetic ordering was observed at room temperature in the modified titanium dioxide [15-23]. Being a semiconductor it gives you a new opportunity to use in spintronics. One of the most effective methods of research centers located magnetic and correlated spin systems is the use of EPR/FMR (electron paramagnetic resonance/ferromagnetic resonance) [6,14, 24-47]. The temperature dependence of the EPR/FMR spectra have shown that the dynamical processes play important role on the interactions between localized magnetic centers and correlated spin system with their surroundings.

The aim of this work is to present the current state of knowledge about magnetic interactions in titanium dioxide and its modification with noble gases and ions transition group. I would like to point out that thousands of works appears annually modified titanium dioxides. Magnetic centers and modification of titanium dioxides significantly alter their physical properties that significantly affect their application possibilities. Therefore they must organize their electronic properties associated with electrical conductivity and magnetism.

2. Findings review and interpretation

Preparation and characterization of the results presented nanocomposites tested titanium dioxides described in the previous works [4,6,14,23,42-47].

The electron paramagnetic resonance/ferromagnetic resonance (EPR/FMR) absorption signal derivative measurements are carried out by a conventional X-band (f = 9.43 GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation, with the sample placed at the centre of the TE102 resonance cavity-at the local microwave magnetic component maximum and in the electric component nodal plane. Sample magnetization by a steady magnetic field of 1.6 T prior to FMR measurements is secured for saturation of any existing domain structure. Ambient temperature lowering is, before reregistering the FMR spectrum, regulated within an Oxford Instrument liquid helium flow cryostat for any region of the whole available range from RT down to 4.2 K.

Modified by noble gases, iron group metals or rare earth ions nanocomposites titanium dioxide changes significant their physico/chemical properties, which further increases their ability applications e.g. in catalysis, photovoltaics, in buildings materials, in water purification, in sunscreens or in spintronics. As pointed out above in among thousands of works, occur every year, relatively little work is the study of dynamic and static associated with magnetism and electric conductivity. Localized magnetic centers and magnetic agglomerates play an important role in their modifications of physical properties.

The nanocomposite modified titanium dioxide by noble gas atoms localized magnetic centers mainly derived from free radicals and complexes of lower oxidation level of titanium ions. They have a lot of work for modified titanium oxide at different temperatures of thermal treatment [25,26,38,42-44,47]. Generally, the titanium dioxide obtained in processing temperatures below 700°C is composed of rutile phase and anastase for example the processing temperature of 300°C are a 93% Anastase and 7% rutile. Sizes nanocrystallites were 12-18 nm.

Figure 1 shows the EPR spectra for the titanium dioxide modified with nitrogen. The resonant line is centered at g = 2.0033-8(1) with linewidth ΔH_{pp} = 7-10(1) G and comes from free radicals. During the processing temperature below 400°C, titanium dioxide is a spectrum dominated by free radicals (Fig. 1a and b). Fitting of resonance line at low temperatures are made by Lorentz function. At high temperatures if the electron conductivity significantly increased by Dysson function should be fitting.

Integrated intensity strongly depends on the temperature in the processing. Integrated intensity is related to the amount of free radicals which, in the photocatalytic process play an important role. You can increase the amount of these magnetic centers by irradiation with ultraviolet light in the course of EPR measurements at lower temperatures. All parameters of resonance line strongly depend on the temperature [43]. This is due to the complexity of localized magnetic moments in sublattice with their surroundings. At high temperatures there is still additional impact associated with the conduction electrons. Nanocomposites prepared at temperatures of 500°C-600°C showed additional spectrum EPR from trivalent titanium ions complexes (Fig. 1c and 1d). At higher processing temperatures there is only a very intensive EPR spectrum derived from the complexes of trivalent titanium ions and resonance lines are centered at g_{eff} = 1.948(1), g_{eff} = 1.959(3) and g_{eff} = 1.949(3) (Fig. 1e) [4]. The intensity of the resonance lines derived from the complexes of the trivalent titanium ions decreases rapidly with increasing temperature than that of free radicals. This is related to the relaxation process, i.e., the transfer of excitation energy to the spin system and the lattice. Hence, also to observe that the EPR spectrum of trivalent titanium ions often must go down to lower temperatures. The best performance was obtained for photocatalytic nanocomposite modified titanium dioxide EPR spectra occurred at appropriate concentrations of free radicals and ions of titanium at a lower oxidation state i.e. treated at temperatures of 500-600°C. The fact is that when the heat treatment of titanium dioxide nanocomposites can be prepared at higher temperatures than more than an order of magnitude number of defects associated with titanium ions could be increasing which adversely affect the photocatalytic performance. On the other hand, in some cases may enhance the properties of electrical conductivity.

Figures 2-4 show EPR spectra/FMR for modified nanocomposites *n*M, N-TO_2 (M=Fe, Ni and Co; *n*=1%, 5% and 10%), at different temperatures. From the Figs 2-4 shows that at high temperatures we have a very intense and broad resonances lines shifted toward lower magnetic fields. They are characteristic of nano-sizes magnetic agglomerates [1,2]. The intensity of these lines and the width depends strongly on the content of the output magnetic metal. A good fit is achieved by using a function Callen (Eq. 1) [48,49].

Localized magnetic centers usually dominates at low temperature spin-spin relaxation and higher spin-lattice. In the case of nano-size magnetic agglomerates at high temperatures both of the relaxation processes may coexist. In the case of nanocomposites titanium dioxide resonances are wider and shifted in the magnetic field than nickel. It shows that we strongly correlated spin systems and similar behavior is observed when the polymer nanocomposites fills the low concentration of magnetic nanoparticles [1,2,50,51].

Additionally, the lower temperatures observed EPR spectrum derived from trivalent ion complexes of titanium with different concentrations (Figs 2-4). At least amount introduced initially of metallic ions (*n* = 1%) is the largest concentration of trivalent titanium ions (by more than the order) for nanocomposites of titanium dioxide with Ni and Co. For other nanocomposites is reflected in very low temperatures in small quantities. The nanocomposite 5Fe, N-TiO_2 integral intensity at room temperature is the highest of samples *n* = 1% than *n* = 10%. This is due to the skin effect which is associated with the conduction electrons (the highest electrical conductivity). The presence of trivalent titanium ions, electron conductivity together with free radicals can be responsible for the improvement of the photocatalytic properties under visible light of the co-modified (Fe,N)-TiO_2 nanocomposite [45]. In the case of nanocomposites nickel titanium dioxide best performance was obtained for *n* = 5% as for iron [47]. It seems that to large concentration of nickel (more than 5 wt% in our case) hinders obtaining a good photocatalyst. The FMR spectra of co-modified *n*Co,N-TiO_2 nanocomposites have shown the occurrence of strongly coupled spin systems of two types. Relaxation processes and magnetic anisotropies quite significantly depended on cobalt concentration. The increase in concentration of correlated systems differently affects the resonance fields and dipole-dipole interactions. It has been suggested that the presence of two magnetic sublattices adversely affect the not good photocatalytic performance [46].

$$I(H) \propto \frac{H_0^2\left[\left(H_0^2+\Delta_B^2\right)\left(H^2\Delta_B+2H_0|H|\delta_B\right)+H_0^2\left(H_0^2+\delta_B^2\right)\Delta_B\right]}{\left[\left(H-H_0\right)^2H_0^2+\left(|H|\Delta_B+H_0\delta_B\right)^2\right]\left[\left(H+H_0\right)^2H_0^2+\left(|H|\Delta_B+H_0\delta_B\right)^2\right]} \quad (1)$$

where:

H_0 - the true resonance field,

Δ_B - the true linewidth connected with relaxation of the Landau-Lifshitz type (may be identified with the longitudinal (spin-lattice) relaxation),

δ_B - a true linewidth connected with relaxation of the Bloch-Bloembergen type (the transverse (spin-spin) relaxation).

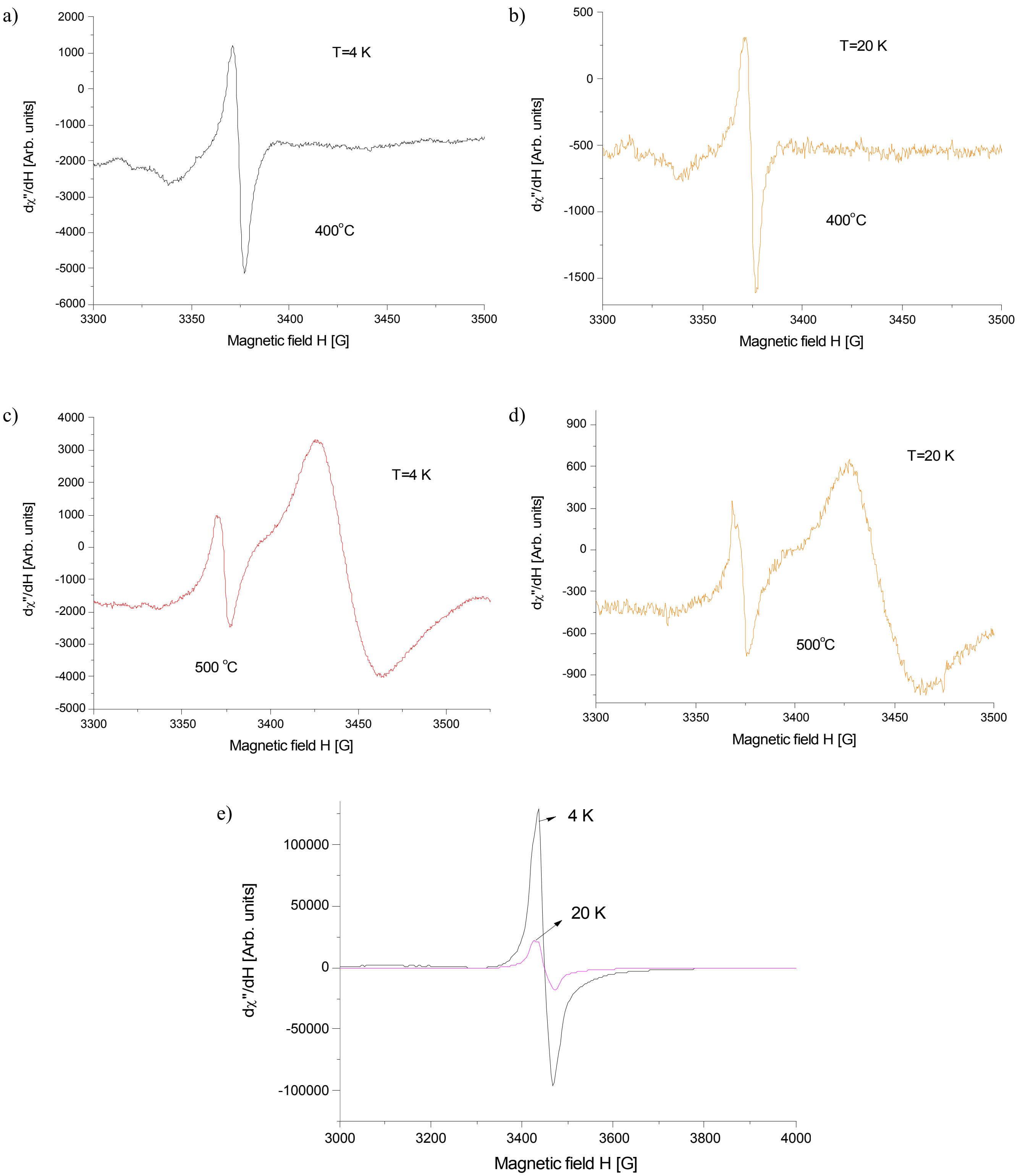

Fig. 1. The EPR spectra of nanocrystalline TiO_2 at different thermal annealing: a) 400°C at T = 4 K, b) 400°C at T = 20 K, c) 500°C at 4 K, d) 500°C at 20 K and e) 850°C at 4 K and 20 K

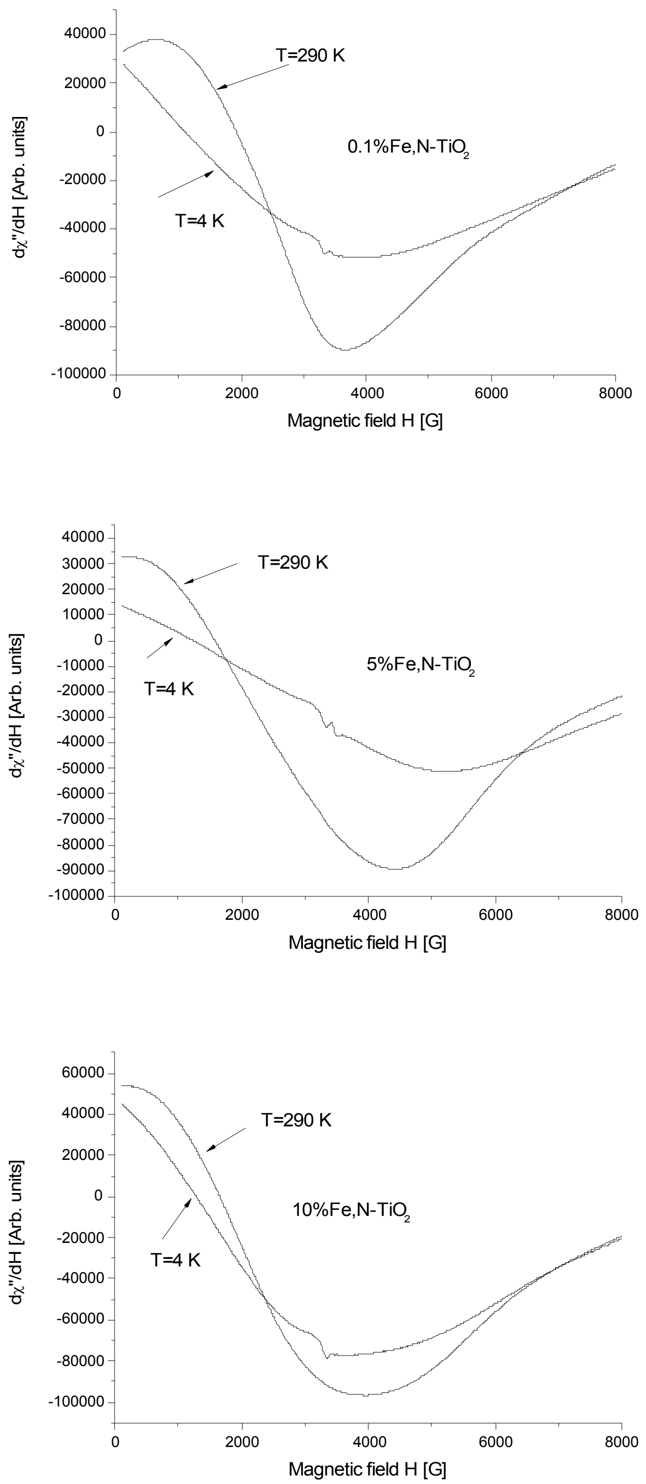

Fig. 2. The FMR spectra of modified nanocomposites nFe,N-TiO_2 with n = 1%, 5% and 10%

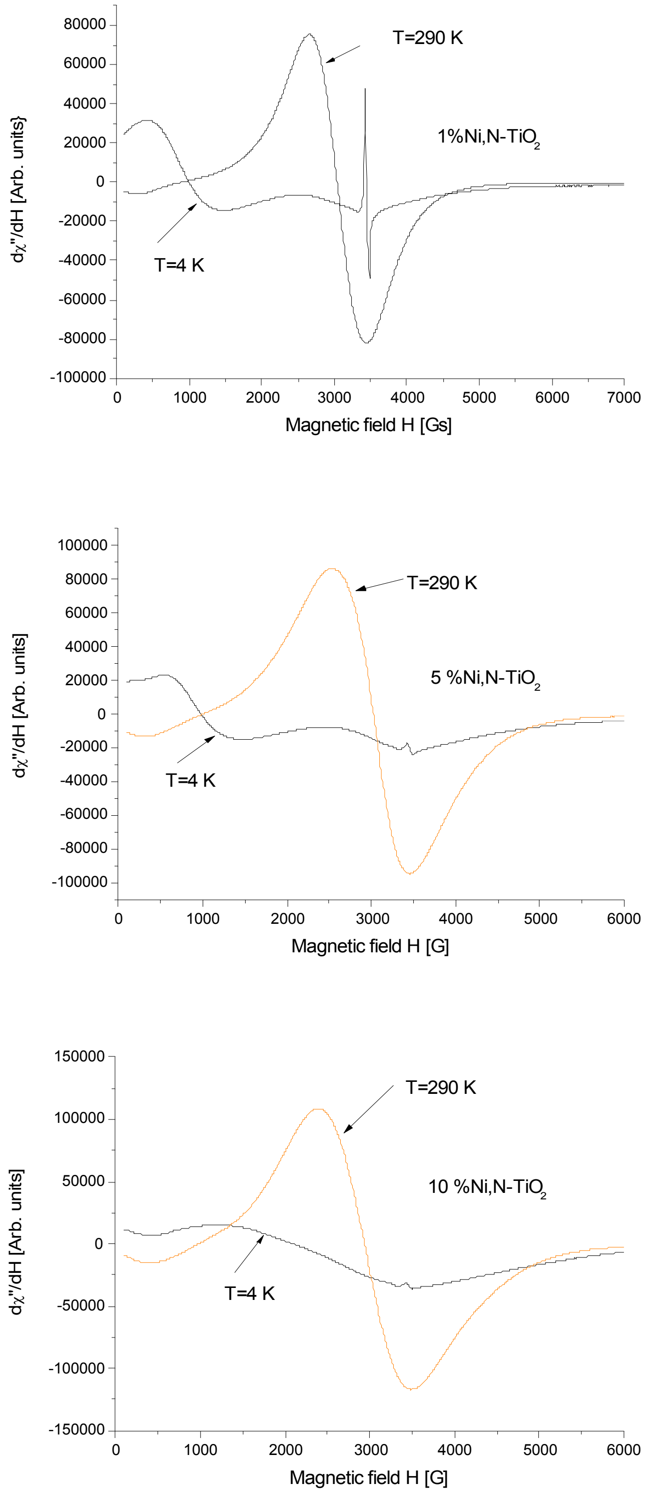

Fig. 3. The FMR spectra of modified nanocomposites nNi,N-TiO_2 with n = 1%, 5% and 10%

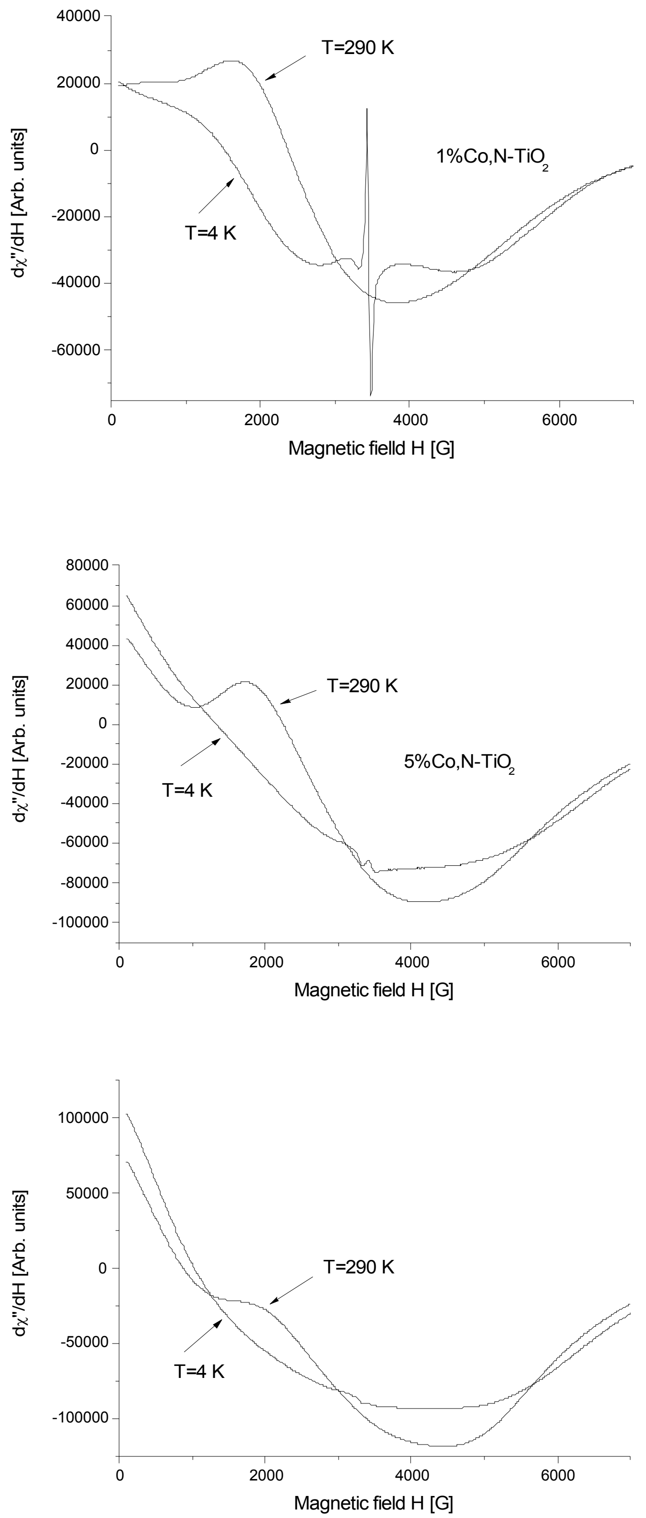

Fig. 4. The FMR spectra of modified nanocomposites nCo,N- TiO_2 with n = 1%, 5% and 10%

3. Conclusions

From these studies it shows that the photocatalytic processes significantly affect magnetic interactions by both the localized magnetic centers as the correlated spin systems. In the case of modification of titanium dioxide nanocomposites by noble gases is an important respective proportions located magnetic centers produced by free radicals and ions of titanium in a lower oxidation state in the photocatalytic process. This is achieved by suitable thermal treatment. When modifying titanium dioxide nanocomposites by noble gases and metals from transition group than they are an important of right amount magnetic metals and type. For iron is the highest but in the case of cobalt is the worst. This situations can cause formation of more complex magnetic structure by cobalt. In the case of nanocomposite 5Fe,N-TiO_2 where he achieved the best performance photocatalytic it could affect the magnetic interaction between the amount of iron, free radicals, defects associated with trivalent titanium ions and increase electrical conductivity.

Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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