Research Article

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Magnetic properties of TiO$_2$/graphitic carbon nanocomposites

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Abstract: TiO$_2$ is the most promising oxide semiconductor extensively used as photocatalyst in solar energy conversion into hydrogen and electric energy as well as in degradation of contaminants in water. To increase its efficiency, carbon dopants are applied. A series of TiO$_2$/graphitic carbon nanocomposites with enhanced photocatalytic performance was synthesized at different temperatures in the 300 – 850°C range in the presence of benzene vapours. To investigate the magnetic properties of these nanocomposites, the dc magnetic susceptibility and electron paramagnetic resonance (EPR) measurements were carried out. Magnetometry revealed the presence of three very different components: a temperature independent and easily recognized in the high-temperature range, another one in 20 – 100 K range displaying a slow increase with temperature decrease and saturation at low temperatures, and the third one observed at $T < 20$ K showing a sharp increase with decreasing temperature. Five types of EPR spectra were detected in the investigated samples and attributed to various paramagnetic centres. The role of TiO$_2$ phase composition, nanocrystalline sizes, carbon content in its different forms in establishing static and dynamic magnetic response of our samples will be discussed.

Keywords: Titanium dioxide; graphitic carbon; magnetic properties; electron paramagnetic resonance

1 Introduction

Titanium dioxide (TiO$_2$), a wide band-gap semiconductor, is a very interesting material from the point of view of pure science and technology [1–3]. The main reason is due to its various applications, especially in heterogeneous catalysis. TiO$_2$ as a stable, nontoxic, low cost and efficient photocatalyst can be used for solar energy conversion into hydrogen and electric energy, and in contaminated environment for the degradation and mineralization of toxic organic compounds [4–6]. Remarkable efforts put in the synthesis and modifications of TiO$_2$ in form of nanomaterial have brought new properties and applications with improved performance [7–10]. Since 1970s researchers have begun to dope TiO$_2$ with metallic ions including iron and nickel, or non-metallic ions such as nitrogen and carbon to enhance its visible-light-responsive photocatalytic ability [11]. On the other hand TiO$_2$ doped with transition metals (Fe, Ni, Co, Mn, Cr) - as an example of diluted magnetic semiconductor - seems to be a promising material in the development of spintronic devices [12–16].

Recently, a series of TiO$_2$/graphitic carbon nanocomposites with enhanced photocatalytic performance was synthesized [17]. The new materials were obtained at different temperatures (300 – 850°C) in the presence of benzene vapours. The presence of graphitic carbon was confirmed by Raman analysis which showed that graphitization process started already at 400°C. The obtained pho-
tocatalysts were tested under UV irradiation during acetic acid and methylene blue decomposition and it was found that photocatalytic activity increases with the temperature modification up to 600°C and correlates positively with carbon concentration. It has been also shown that the crystallite size, type of the crystal structure (anatase or rutile), specific surface area and adsorption degree have a strong influence on the photocatalytic activity of these nanocomposites.

Electron paramagnetic resonance (EPR) is a spectroscopic technique often used to study the structure and interactions of paramagnetic entities (molecules or ions with unpaired electrons) such as free radicals, transition metal ions and defects in solids like electrons trapped in lattice vacancies. These paramagnetic defects may be of significant importance for the catalytic properties of TiO₂. Magnetometric study complements EPR investigations and allows to elaborate a more comprehensive picture of magnetic centers and magnetic interactions.

In the present work, dc magnetometry and EPR spectroscopy have been used to investigate the magnetic properties of a series of TiO₂/graphitic carbon nanocomposites obtained at different temperatures (300 – 850°C) in the presence of benzene vapours. In Section 2 a short review of magnetic properties of TiO₂ and TiO₂/carbon nanocomposites will be presented. The obtained experimental results of TiO₂/graphitic carbon nanocomposites will be given in Section 4. They will be carefully analysed and the underlying magnetic entities responsible for the magnetic response will be recognized. The role of TiO₂ phase composition, nanocrystalline sizes, carbon content in its different forms in establishing the obtained outcomes will be discussed.

2 Short review of magnetic properties of TiO₂ and TiO₂/carbon nanocomposites

EPR has been commonly used in the study of structural modification of titanium dioxide, in metal ion substitutions (V⁶⁺, Fe³⁺, Cu²⁺, Mn⁴⁺, etc.) and in the determination of different kinds of structural defects [18-43]. Among often encountered EPR active defects in TiO₂ is titanium vacancy V₆⁺, an intrinsic defect of the acceptor type, producing spectrum located at g = 1.960 – 1.990. Another possible vacancy is oxygen vacancy V₀, donor type of defect, showing line at g = 2.003. Studies of oxygen vacancy formation in bulk TiO₂ suggest that surface vacancies are more stable than bulk vacancies and that vacancies can migrate from the bulk to the surface of the oxide. F-center, which is an oxygen vacancy with a trapped electron, displays an EPR spectrum at g = 2.0034. Ti³⁺ defects can be located in the bulk or on TiO₂ surface. They can be distinguished by the differences of their EPR parameters. The values of the g-factors for surface Ti³⁺ particles are significantly lower than those usually found in bulk TiO₂. For bulk Ti³⁺ usually the spectrum described by g₁ = 1.992 – 1.988 and gₚ₀ = 1.962 – 1.960 is observed. When a host Ti⁴⁺ ion is changed to Ti³⁺ ion, the local electrostatic balance is broken, and an V₀ should be introduced because of charge compensation. Moreover, many types of oxygen radical species like O²⁻ or O⁻ producing anisotropic signals with components of the g tensor close to 2.00 has been investigated.

Experimental and theoretical research devoted to carbon-doped or carbon-modified TiO₂ materials indicates that doping with carbon is an efficient method to increase its visible-light absorption threshold. EPR technique was very useful in identification of many kinds of paramagnetic centers involving carbon and existing in bulk or on the surface of TiO₂ nanoparticles [26, 27, 44-61]. Investigations of carbon-doped TiO₂ revealed differences in EPR spectra of surface- and volume-doped samples [26]. The latter signal showed an asymmetric shape with g-factor values of g₁ = 2.0043, g₂ = 2.0027, g₃ = 1.9801, the former displayed an isotropic line at g = 2.0030 (linewidth about 4 G) with constant parameters in 5 – 300 K temperature range. EPR spectrum of the volume-doped sample was assigned to a CO₂ radical [26]. In carbon-doped titania Li et al. registered two kinds of Ti³⁺ EPR centers at low temperature [46]. The signals at g₁ = 1.9709, gₚ₀ = 1.9482 was assigned to surface, and the signal at g = 1.9190 to vacancy-stabilized Ti³⁺ in the lattice sites in the subsurface layer. A strong symmetric EPR line at RT (but not in pure anatase titania) was attributed to the electron trapped on the oxygen vacancy (F center) [46]. A similar line was reported by Reyes-Garcia et al. in their C-doped TiO₂ synthesized by sol-gel and hydrothermal methods [27]. A very strong signal at g = 2.002 was attributed to free electrons in the conduction band [27]. Minnekhanov et al. studied carbon-doped TiO₂ samples of two types: bulk-modified and surface-modified [33]. The latter samples displayed an isotropic and strong signal at g = 2.0030 that could be attributed to the carbon dangling bonds in amorphous carbon particles or (less probable) to F-center. The former samples showed asymmetric spectrum with g₁ = 2.0042, g₂ = 2.0027, g₃ = 1.9801 assigned to CO₂ radical located in the interstitial sites of TiO₂ lattice [33].
Carbon incorporated in TiO$_2$ nanocomposites could exist in different forms: graphite, grapheme, multi-shell nanographites, carbon nano-onions etc. In crystalline graphite EPR spectrum arises from mobile charge carriers [44]. At RT g-factor varies from 2.0026 to 2.0495 as the magnetic field is shifted from perpendicular to parallel to the c axis and the Dysonian line has a linewidth of a few gauss. Investigation of quasi-two dimensional graphites showed that the increase of the density of the electrically active structure defects or of a boron impurity leads to a shift of the Fermi level into the interior of the valence band and to a sharp decrease of g-factor anisotropy [45]. EPR study of anthracite (metamorphosed graphitizeable coal, with a high carbon content of 91–98 wt%) showed that the EPR signal of the thin bulk sample represented a single Lorentzian line ($g = 2.0030$ at RT), while the spectrum of the powder samples was composed of two Lorentzian lines having identical g-factors and different linewidths [56]. This signal was mainly due to the conduction electrons existing in two states - one corresponding to the interacting conduction electrons, which form a conduction band and show Pauli paramagnetism, the other to conduction electrons isolated in some regions and not interacting with the others [56].

An interesting attempt was made by Ottaviani et al. to find correspondence between EPR spectra and the surface of graphitized and activated micro- and meso-porous carbons [57, 58]. The variation of the EPR lineshape as a function of the surface area has allowed them to identify the three main carbon structures at different porosities, classified as graphitized, activated and highly polar zones. The EPR signal from the graphitized zone, where the carbon atoms are mainly organized in a hydrophobic graphite structure, presents a single, narrow line with $g$-factor close to 2.0 and linewidth below 40 G. With the activated zone, which is partially oxygenated and at high surface area due to micropores available for the adsorption of dangerous pollutants, an EPR broader signal (between 200 and 900 G) and with similar $g$-factor could be associated. Finally, a very broad EPR signal (linewidth above few kG) at $g$-factor of about 4.3 which is characteristic of ionic paramagnetic centres such as isolated Fe$^{3+}$ ions in rhombic symmetry was attributed to highly polar zone because of charged sites in activated carbons.

Recently, much attention has turned towards novel fullerene related materials, carbon nanocapsules or carbon onions that consist of concentric fullerene-like shells (astralen). EPR spectrum of astralen consists of two clearly distinguished components: a very broad signal and an asymmetric narrow line centered close to $g = 2.0$ [48, 53]. The latter could be successfully simulated as the superposition of two Lorentzian lines with different linewidths, with $g$-factors equal to $g_1 = 2.0034$ and $g_2 = 2.007$. Shames et al. have noticed that EPR spectra of pure graphite powder demonstrate the same general features as found in astralen samples, i.e. superposition of the very broad line and the narrow asymmetric line in the region of $g = 2.0$ [48]. The very broad line was attributed to spins of delocalized (conduction) $\pi$-electrons while the narrow components to localized and quasi-localized spins on defects near the corners of the astralen polyedral [48]. Another detailed EPR study of defective carbon nano-onions demonstrated high sensitivity of EPR spectrum to the ambient air and microwave power [53]. They have discovered that combination of microwave-pumping, low cryostat temperature and intrinsic properties of the air leads to the formation of magnetic complexes located at the nanographene edges. A peculiar temperature dependence of EPR signal was attributed to the magnetic interaction between nano-graphene having the edge-state spins ($S = 1/2$) and molecular oxygen with $S = 1$ allowing formation of the antiferromagnetic dimer at low temperatures [53].

As combining TiO$_2$ with graphene or with graphene related materials is an attractive strategy for enhancing the TiO$_2$ photocatalytic activity through charge separation at the TiO$_2$/grapheme hetero-interface, many EPR studies were devoted to characterization of such systems [47–55, 59–61]. The EPR spectra typically exhibit a single and asymmetric signal at $g$-value of 2.0035, characteristic of carbon-centered radicals and related to the localized spins generated at the edge of the $\pi$-electron system. Often the edge states couple to itinerant electrons giving rise to exchange-narrowed EPR spectra and antiferromagnetic ordering at low temperatures. EPR signal of the ideal graphene can originate only from the zig-zag edge states, but the real graphene is more or less disordered, part of defects are paramagnetic, and those, with energy close to the Fermi level can dope electrons to the conduction band. It was evidenced that functionalization of graphene induces both localized paramagnetic centers and conduction electrons and preserves edge magnetism.

### 3 Experiment

The photocatalysts were obtained by carbon modification of the crude titanium dioxide containing 2.1 wt% of residual sulphur. Before modification, the crude TiO$_2$ has been pre-treated to reach pH 6.8. As a carbon source a benzene (99.5%) was used. Starting TiO$_2$ was placed in a quartz crucible, and put inside a quartz tube in the central part of
horizontal furnace. The calcination of photocatalysts was conducted in 300 – 850°C temperature range. The preparation process was executed in four steps. In the first step argon was passed through the quartz tube to remove air. Next, the furnace was heated up to a desired temperature in argon flow. Then, the photocatalyst was calcined at appropriate temperature in argon flow with benzene vapours. Finally, the furnace was slowly cooled down to room temperature in argon atmosphere. The details of the preparation process could be found elsewhere [17]. The obtained samples will be designated B-xxx, where B stands for benzene and the number xxx is the calcination temperature expressed in °C.

In Table 1 the phase composition, main crystallite sizes and the intensities of graphitic carbon line in Raman spectrum of the obtained samples is presented. The former two parameters were determined from XRD measurements. Raman spectra were registered using Raman Microscope with the excitation wavelength of 785 nm.

Dc magnetic susceptibility measurements were carried out using MPMS-7 SQUID magnetometer in 2 – 290 K temperature range in the field cooling (FC) mode. EPR spectra were recorded using a standard X-band (ν = 9.4 GHz) spectrometer (Bruker E 500) with magnetic field modulation of 100 kHz. The microwave power was in 0.4 – 2.0 mW range in no saturation regime. The measurements were performed in 4 to 290 K temperature range using Oxford helium-flow cryostat. All samples were loaded into quartz EPR tubes under ambient conditions and no special precautions were taken in their handling.

4 Results and discussion

Figure 1 presents temperature dependence of dc magnetic susceptibility, defined as $\chi = M/H$, where $M$ is magnetization and $H$ an external magnetic field, for all investigated samples measured in FC mode in an external magnetic field $H = 100$ Oe. The vertical axis is in logarithmic scale for better separation of $\chi(T)$ curves and to see them more clearly. The general form of all $\chi(T)$ curves is the same for all samples: they could be seen as composed of at least three very different components:

$$\chi(T) = \chi_1 + \chi_2(T) + \chi_3(T)$$

Figure 1: Temperature dependence of dc magnetic susceptibility of all investigated samples measured in FC mode in an external magnetic field $H = 100$ Oe.
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Figure 2: Temperature-independent component $\chi_1$ of dc magnetic susceptibility in all investigated samples measured in FC mode in $H = 100$ Oe.

Figure 3: Temperature dependence of $\chi_2$ magnetic susceptibility for B-700 sample in FC mode in magnetic field $H = 100$ Oe. Vertical arrow defines the saturation susceptibility $\chi_2(0)$ at low temperatures of the $\chi_2$ component. Inset shows the values of $\chi_2(0)$ in all investigated samples.

The first component on the right hand-site, $\chi_1$, is temperature independent and is easily recognized in Figure 1 in the high-temperature range ($T > 120$ K). The second component can be seen in 20 – 100 K range as slowly increasing with decreasing temperature and saturating at low temperatures. The third component, observed at $T < 20$ K, displays a sharp increase with decreasing temperature.

Value of the temperature independent susceptibility term $\chi_1$ changes from sample to sample in the $(1.3 \div 45) \cdot 10^{-7}$ emu/(g · Oe) range and no obvious dependence on sample calcination temperature could be perceived (see Figure 2). Apparently, other factors besides calcination temperature (e.g., phase content, nanoparticles sizes, defect structure, oxygen deficiency, etc.) play more important role in this dependence. Three possible sources of this term should be considered: ferromagnetic (FM) component with a Curie temperature considerably higher than RT, Van Vleck paramagnetism and Pauli paramagnetism of free electrons. As the samples showed no FM at RT in magnetisation studies, the first possibility should be discarded. Static susceptibility of bulk anatase and rutile TiO$_2$ in the 4 - 300 K temperature range has been investigated by Chauvet et al. [62]. Both crystals displayed temperature independent susceptibility at temperatures above 100 K and rutile showed a few times bigger value than anatase, but anatase susceptibility might be increased a few times by oxygen deficiency. The susceptibility of both types of samples was dominated by the Van Vleck paramagnetism [62]. Spin susceptibility determined from the EPR measurements of anatase has been explained by contributions from the electrons localized on the unionized donor level (Curie-like component) and from the electrons activated into the conduction band (Pauli-like component).

The second component $\chi_2$ is presented for the case of B-700 sample in Figure 3. It starts to show below ~100 K and saturates at low temperatures. The vertical arrow in Figure 3 defines the saturation susceptibility $\chi_2(0)$ at low temperatures of the $\chi_2$ component. This saturation susceptibility is different for our different samples. Inset in Figure 3 shows the values of $\chi_2(0)$ for all investigated samples. It seems that oxygen molecules could play an important role in formation of this component of susceptibility, which is similar in form to $\chi(T)$ in superparamagnetism measured in FC mode. Using analogy with model proposed by Shames et al. [53], formation of FM clusters involving ambient molecules and spins of graphene edges might explain the appearance of $\chi_2$ component. As the temperature decreases, oxygen molecule and other ambient gas species such as nitrogen and water molecule co-adsorbed on planes and edges of the nano-graphene sheets. When oxygen molecules approach edges and defect sites on the graphene planes, the electron transfer from the graphene plane’s $\pi$-reservoir to the oxygen molecule takes place. It turns some dioxygen molecules to negatively charged oxygen ions having $S = 1/2$. Spins of negatively charged oxygen ions form spin clusters with the edge spins. These clusters disintegrate by desorption of oxygen molecules from the graphene planes above ~100 K.

To determine the role of carbon in formation of magnetic response of our samples, the changes of carbon content and changes in $\chi_1$ and $\chi_2$ components are compared. Comparison is made in relation to the neighbouring sample (with calcination temperature higher by 50°C) and the results are presented in Figure 4. The increase of carbon
Figure 4: Carbon content change (upper row) and changes of values of two susceptibility components (middle and bottom row) in comparison to a neighbouring sample (with annealing temperature bigger by 50 K). Increase of carbon content and susceptibilities from sample to sample are indicated by + sign and blue colour, decrease of carbon content and susceptibilities by − sign and red colour. It is obvious that positive correlation is observed only for samples annealed at temperatures higher than 600°C (e.a. samples B-650, B-700, B-750, B-800, B-850). In these samples an increase or decrease of carbon content brings proportional increase or decrease of $\chi_1$ and $\chi_2$ components. Furthermore, in these samples the rutile phase starts to play the dominant role and an average crystalline size greatly increases.

Below ~20 K the third component $\chi_3$ of dc susceptibility dominates the magnetic response of our samples (Figures 1 and 3). A strong increase of susceptibility with temperature decrease indicates the presence of certain paramagnetic entities. The magnetic susceptibility $\chi_3$ in low temperature range could be described by the Curie-Weiss law:

$$\chi(T) = \frac{C_{mol}}{T - T_{CW}} \tag{2}$$

where $C_{mol}$ is the molar Curie constant, and $T_{CW}$ is the Curie-Weiss temperature. Knowledge of the molar Curie constant $C_{mol}$ allows to calculate the effective magnetic moment (in units of Bohr magnetons):

$$\mu_{eff} = \sqrt{\frac{3k_B C_{mol}}{N_A \mu_B}} = 2.828 \sqrt{C_{mol}} \tag{3}$$

where $k_B$ is Boltzmann constant, $N_A$ is Avogadro constant, and $\mu_B$ Bohr magneton. In Figure 5 values of the Curie-Weiss constant (top panel) and the effective magnetic moment (bottom panel) of the low-temperature component $\chi_3$ in the investigated samples are presented. The Curie-Weiss constant for all samples is negative (in $-1$ to $-5$ K range) what points to antiferromagnetic (AFM) interaction between paramagnetic centres. The effective magnetic moment (in Bohr magnetons) calculated for a single TiO$_2$ molecular unit is in 0.08 to 0.15 $\mu_B$ range, what is equivalent to one magnetic moment of $S = 1/2$ spin (1.73 $\mu_B$) spreading over 22 to 12 TiO$_2$ units. It is interesting to note that there is a positive correlation between $T_{CW}$ and $\mu_{eff}$ for samples calcined at temperature below 600°C (the stronger the AFM interaction the bigger the effective moment) and negative correlation for samples calcined at temperatures above 650°C (the stronger the AFM interaction the smaller the effective moment). This suggests an important role of kind of crystallographic polymorph (anatase or rutile) in establishing magnetic properties as this particular calcined temperature limits the presence of each polymorph.

In Figure 6 (top panel) the EPR spectra of all investigated samples, registered in the whole magnetic field range and both susceptibilities from sample to sample are indicated by + sign and blue colour, decrease of carbon content and susceptibilities by − sign and red colour. It is obvious that positive correlation is observed only for samples annealed at temperatures higher than 600°C (e.a. samples B-650, B-700, B-750, B-800, B-850). In these samples an increase or decrease of carbon content brings proportional increase or decrease of $\chi_1$ and $\chi_2$ components. Furthermore, in these samples the rutile phase starts to play the dominant role and an average crystalline size greatly increases.

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sweep range, are presented. Although the mass of each sample was different, the EPR spectra were calibrated to the same unit mass to make comparison possible. The spectra were rather complicated indicating a few different spin systems are involved in formation of the EPR response. To make the analysis of the EPR spectra more transparent, specific components were recognised due to their appearance and thermal behaviour. Table 2 lists various identified EPR spectral components observed in the investigated samples. Five main components were recognized. They are as follows: the very broad (designated as VB) component, the narrow (N) component, the broad high-temperature range (BHT) component, the broad low-temperature range (BLT) component, and the broad low-magnetic field (BLF) component. Moreover, the N component will be further decomposed on additional three (or two) subcomponents.

The VB component is seen only at high temperatures as a very broad background line that has a linewidth in excess of the magnetic field sweep of our spectrometer (14 kG). A very similar EPR line was reported for astralen nanoparticles and conducting graphite samples [48]. This line was attributed to the conduction electrons, i.e. it is a CESR line. It is well known that in many metals CESR lines may be so broad that they are not observable. Observation of very broad CESR lines is not uncommon for carbon-based and nano-sized systems [48]. Because in this circumstance the spectral parameters of this line were not possible to determine, the intensity of this component was estimated by calculation a magnetic field gradient of the line amplitude, i.e. the slope of this VB line. The value of this parameter for all samples at RT is shown in lower panel in Figure 6. In this respect all samples could be divided into two groups: samples calcined at 650° or at lower temperatures have relatively weak VB component, while those calcined at 700° or higher have that component much more intense. The slope of the VB component correlates very strongly with the content of rutile phase in our samples (see Table 1). It suggests that the concentration of conduction electrons is much higher in rutile than in anatase polymorph. This conclusion is in agreement with results of theoretical consideration of electron conductivity in rutile and anatase TiO$_2$ nanoparticles studied by using multiscale simulations [63].

The narrow (N) component is the easiest to recognize feature in EPR spectra in all our samples. In Figure 7 EPR spectra registered at RT of the N component in all studied samples are presented. The spectra are rescaled to a unit mass. Due to very strong EPR signals, B-800 and B-850 samples are shown separately in insert with greatly enlarged vertical scale. The N component is a narrow, slightly asymmetrical line that could be characterised by typical EPR parameters: effective $g$-factor, peak-to-peak linewidth $\Delta B_{pp}$, and integrated intensity $I_{int}$. The effective $g$-factor, $g_{eff}$, can be calculated from the magnetic resonance condition:

$$h\nu = g_{eff}\mu_B B_r$$

where $h$ is Planck constant, $\nu$ is the microwave frequency, $\mu_B$ is Bohr magneton and $B_r$ magnetic resonance field. The integrated intensity, which is proportional to the magnetic susceptibility on microwave frequency of a spin system producing EPR spectrum, is defined as

$$I_{int} = A \cdot \Delta B_{pp}^2$$
where $A$ is signal amplitude. How these parameters depend on temperature in samples B-800 and B-850 could be seen in Figures 8 and 9, respectively. Comparison of these plots shows a marked difference in thermal behaviour of the spectral parameters in these two samples. The effective $g$-factor in B-800 sample decreases with temperature decrease down to ~20 K and increases sharply on further cooling. In contrast, in sample B-850 there is practically no temperature dependence of $g$-factor above ~40 K but it significantly decreases with temperature decrease below that temperature. Also, the peak-to-peak linewidth varies with temperature differently in B-800 and B-850 samples. In sample B-800 it stays constant above ~200 K, increases on cooling and reaches a local maximum at ~110 K, then decreases and reaches a minimum at ~20 K, but sharply increases again on further cooling. Such complicated $\Delta B_{pp}(T)$ dependence might only be explained by assuming that the N component in fact encompasses a few independent subcomponents originating from different paramagnetic entities.

Figure 10 presents temperature dependence of the product of integrated intensity and temperature of the N component in all investigated samples. That product is proportional to the square of the effective magnetic moment of the spin entities producing EPR spectrum:

$$T \cdot I_{int} \sim \mu_{eff}^2$$  (6)

Although each sample presents its individual behaviour seen in Figure 10, the following general picture could be inferred from the plots. In the high-temperature range ($T > 40$ K) there is a smaller or bigger decrease of the mag-
Magnetic moment with temperature decrease what indicates that the effective AFM interaction is prevailing in that thermal range. Below ~40 K the magnetic moment increases with temperature decrease down to ~10 K what points out on the dominating FM interaction. In the low-temperature range, below ~10 K there is yet another decrease of magnetic moment. Consequently, the temperature behaviour of magnetic moment indicates the presence of a few independent magnetic centres, with different thermal behaviour, that govern the appearance of the N component.

It would be interesting to relate the dc magnetic susceptibility (obtained from magnetometry) with the integrated intensity $I_{int}$ which is its equivalent in EPR spectroscopy. This comparison (both values measured at RT, EPR only of the N component) is displayed for all studied samples in Figure 11. The changes of both $\chi$ and $I_{int}$ parameters stepping from a particular sample to the neighbouring sample (with higher calcined temperature) are correlated rather well for samples from B-300 to B-600 (low calcined temperature), but there is no correlation for samples from B-650 to B-850 with high calcined temperature. The former group of samples is characterized by dominating anatase form of TiO$_2$ and relatively small average crystallite sizes (below 30 nm), while in the latter rutile phase prevails and nanocrystallites are much bigger. A simple explanation of a good correlation between $\chi$ and $I_{int}$ in B-300 to B-600 samples is to suppose that the N component is the most intense EPR component in EPR spectra in these samples. It will be shown later that this is indeed the case. Moreover, the analysis of different components participating in formation of EPR spectrum of the N component will be given after presentation of other EPR components.

In Figure 12 the EPR spectra of five samples (B-650, B-700, B-750, B-800, B-850) registered at RT are shown. Apart of a narrow central line (N component) a broad Lorentzian-like EPR line (BHT component) is also visible. The resonance field of these two components is similar. The intensity of BHT component increases with the sample calcination temperature while a reverse trend is observed for the linewidth. The BHT component is only visible in these five samples and only in the high-temperature range (above ~150 K). Figure 13 shows, as an example, the EPR spectra of BHT component in B-800 sample registered at few different temperatures. In Figure 14 the temperature dependence of the linewidth, integrated intensity, and signal amplitude of the BHT component in this sample is displayed. The resonance field of BHT component is temperature independent, but the linewidth strongly decreases with the increase of temperature. The integrated intensity
of BHT component is the strongest among all other EPR components what is illustrated in Figure 15 where comparison with strong N component is shown. Besides, this figure substantiates a former supposition about the N component being the strongest in B-300 to B-600 samples. An EPR line with a similar spectral characteristic as our BHT was often observed in multi-shell nanographite samples [48–50, 53]. The line was attributed to \( \pi \)-electronic edge state spins. The nonbonding \( \pi \)-electron states arise in the vicinity of the Fermi level in a flat nanographene sheet with the zigzag-type edge. These states give rise to the localized spins responsible for the specific magnetic properties of this material. The broadening of the BHT line in an oxygen atmosphere is considered to be due to the magnetic (dipole–dipole and exchange) interaction between the paramagnetic triplet spins of oxygen molecules and the spins localized at the open edges of a nanographite particle. Because the broadening is stronger on temperature decrease, it follows that this interaction increases due to contraction of average distances between oxygen molecules and \( \pi \)-electrons and changes in the aggregative state of oxygen adsorbed on/within the nanographite particles. It means that during the cooling more and more oxygen molecules approach the edge-localized spins and adsorb on nanoparticles and within their hollows [50].

Figure 16 presents the EPR spectra of B-800 sample registered at different low temperatures. The narrow N and broad asymmetric BLT components are clearly visible. The BLT component asymmetric line spreads from 3400 to 3475 G what is equivalent to 1.9787 and 1.9434 \( g \)-factors (\( g_\perp \) and \( g_\parallel \), respectively). Its amplitude quickly diminishes with increasing temperature and the line is only visible below \(~40\) K. Regarding the values of \( g \)-factors this component is unambiguously related to Ti(III) in rutile allotrope and is located at interstitial sites [64, 65]. These interstitial sites could be formed either by substoichiometric preparation or by extreme reductive conditions [66]. The short spin-lattice relaxation time of Ti(III) species generally hinders their detection at higher temperatures. The BLT component is detected only in rutile allotrope in our sample what is evidenced in Figure 17. Figure 17 displays the EPR spectra of B-700, B-750, B-800, and B-850 samples taken at \( T = 4\) K that shows the narrow N line (~3375 G) and the broad asymmetric BLT component (3400 – 3500 G). The EPR intensity of the BLT component is strictly correlated with the amount of rutile phase in these sample (see Table 1). Additionally, a weak line close to 3540 G (\( g = 1.93 \)) is visible in EPR spectrum of B-700 sample. It could be attributed to the surface sites in anatase phase. Its traces could be also visible in other three samples (B-750, B-800, and B-850) where...
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Figure 17: EPR spectra of B-700, B-750, B-800, and B-850 samples taken at $T = 4$ K showing the narrow N and the broad asymmetric BLT components.

Figure 18: EPR spectrum of BLF components at RT in B-550 sample. The anatase content is low. This line is broader because of the surface heterogeneity. Such a line could be formed by reductive annealing [66].

In Figure 18 the EPR spectrum of B-550 sample registered at RT is shown with two broad low-field (BLF) lines clearly evident. Effective $g$-factors for these lines are $g_1 = 3.90$ and $g_2 = 2.26$. Such type of spectrum is only recorded for that particular sample. The lines are broad and asymmetrical and their intensity decreases with decreasing temperature. At helium temperature they were not visible in EPR spectrum of B-550 sample. These specific spectral features exclude attribution of BLF lines to isolated paramagnetic ions (most probably high-spin Fe$^{3+}$). A feasible explanation of origin of these lines might be the clusters of strongly interacting paramagnetic metal ions with an antiferromagnetic ground state. At RT the EPR signal is due to transitions to magnetic excited states, while at low temperatures only nonmagnetic ground state is occupied. These metal ions (e.g. iron ions) might be found in a very small amount in our sample as unintentional admixture and probably could be not detected by other spectroscopic methods.

Because the N component line is asymmetric, it could be generated by a few different paramagnetic centres. To gain information about these centres the line was decomposed on simple Gaussian and Lorentzian lineshape lines. It was found that at most three subcomponents were adequate to obtain satisfactory fitting to the experimental N component line. An example of such fitting is shown in Figure 19 for B-400 sample registered at $T = 290$ K. The three subcomponents, one Lorentzian and two Gaussian, designated as $N_{1\text{L}}$, $N_{1\text{G}}$, and $N_{2\text{G}}$, are displayed. The $g$-factors of subcomponents of the N component line in all investigated samples are shown in Figure 20. For samples calcined at temperature $650^\circ$C and lower three subcomponents were needed, for samples calcined at $700^\circ$C and higher two subcomponents were sufficient for successful fitting of experimental spectra. The size of used symbols in this figure is proportional to the square root of the integrated intensity of a specific subcomponent. The values of $g$-factors of the subcomponents for all studied samples are in $2.0030 - 2.0060$ range and the linewidths are below 15 G at RT.

To make attribution of specific paramagnetic centres to the observed EPR subcomponents more reliable, a literature search has been carried out for similar EPR spectra of various carbon containing nanomaterials, titanium oxide nanoparticles, and TiO$_2$/carbon nanocomposites. The results are presented in Table 3. The search is limited to EPR...
Table 3: EPR lines in various carbon nanomaterials, TiO$_2$ nanoparticles, and carbon/TiO$_2$ nanocomposites with $g$-factor in 2.000 – 2.010 range and linewidth in 0.5 – 15 G range.

| Material                                              | Ref  | $g$-factor  | Linewidth [G] | Thermal behaviour type                                                                 | Paramagnetic centre responsible for EPR spectrum                                                                 |
|-------------------------------------------------------|------|-------------|---------------|----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| High-surface-area anatase titania nanoparticles        | 23   | 2.0034 (RT) | 4.2 (RT)      |                                                                                        | F-centre on the surface of nanoparticle                                                                        |
| Carbon doped TiO$_2$ nanoparticles                     | 26   | 2.0030 (at RT) | 4.7 (at RT) |                                                                                        | Carbon radicals on surface of TiO$_2$                                                                           |
| Carbon doped TiO$_2$ nanoparticles                      | 27   | (a) 2.0020 | (b) 2.0050 |                                                                                        | (a) Free electrons in conduction band (b) F centre                                                                 |
| Carbon doped TiO$_2$ nanoparticles                      | 33   | 2.0030 | 3.7                                                       |                                                                                        | Carbon dangling bonds on the surface                                                                            |
| Carbon nano-onions                                     | 48   | 2.0022 | 7.2                                                       |                                                                                        | Localized spins associated with a presence of the sp$^3$-like defects                                          |
| Multi-shell nanographite                               | 49   | 2.0022 | 5                                                         | Curie-Weiss + Pauli                                                              | Distant spins localized on the opposite zigzag edges/sides of the nanographite particle mediate by conduction\pi-carriers propagating in the interiors of graphene sheets |
| Multi-shell nanographites                              | 50   | 2.0022 | 5                                                         | Curie-Weiss                                                              | Localized spins of the sp$^3$-like defects originating from the cross links between the graphitic shells.     |
| Microporous activated carbon                           | 51   | 2.0028 (at RT) | 7 (at RT) |                                                                                        | Delocalized $\pi$ conduction electrons at the surface                                                         |
| Nanosized graphite                                     | 52   | 2.0035 | 2.1                                                       | Curie-Weiss + Pauli                                                              | Localised edge states coupled to itinerant electrons                                                          |
| Graphene oxide                                         | 54   | (a) 2.0030 | (b) 2.0056 |                                                                                        | Carbon inherited radical-like defects in graphene planes distinguishing by different electron spin–lattice relaxation rates |
| Anthracite powder                                      | 56   | (a) 2.0030 | (b) 2.0056 |                                                                                        | Two lines with different linwidths due to conduction electrons isolated in some regions (not interacting with each other) with different relaxations by scattering on different grain surfaces |
| Carbon nano-onions                                     | 60   | 2.0022 (at RT) | 3.9 (at RT) | Curie-Weiss                                                              | Superoxide ion-radicals interacting with some neighbouring $\pi$-electronic edge $S = 1/2$ spins creating exchange coupled zigzag edge-O$_2$ complexes having $S = 1$. |
| TiO$_2$/graphene nanocomposite                         | 61   | 2.0033 | 3.2                                                       |                                                                                        | Carbon-centred radicals related to the localized spins generated at the edge of the $\pi$-electron system     |
| Graphene single layer                                  | 67   | 2.00245 (RT) | 0.6 (RT) | Curie-Weiss                                                              | Electrons trapped on the carbon vacancy (a) spins localized at the “pure” carbon, (b) spins strongly interacting with molecules adsorbed at the carbon surface electron trapped on an oxygen vacancy. |
| Graphene oxide                                         | 68   | (a) 2.0027 | (b) 2.0031 |                                                                                        | Single electron trapped oxygen vacancies or F$^+$ centres                                                |
| Polycrystalline TiO$_2$                                | 69   | 2.0030 | 3.9                                                       |                                                                                        | Dangling bonds in the sp$^3$ diamond core.                                                                        |
| Slightly reduced TiO$_2$                              | 70   | 2.0030 | 3.9                                                       |                                                                                        | Strong coupling between localized paramagnetic spins and conduction electrons                               |
| Rutile TiO$_2$ microstructure                          | 71   | 2.002 | 7.8                                                       |                                                                                        | Edge states narrowed by exchange interaction with mobile electrons                                            |
| Detonation nanodiamond powder                         | 72   | 2.0028 (at RT) | 7.8 (at RT) |                                                                                        |                                                                                                               |
| Reduced graphene oxide                                 | 73   | 2.003 | 3 (at RT) | Curie + Pauli                                                              | Strong coupling between localized paramagnetic spins and conduction electrons                               |
| Milled graphite                                        | 75   | 2.0033 (at 200 K) | 2.8 (at 200 K) | Complex                                                               |                                                                                                               |
lines with \( g \)-factor in 2.000 - 2.010 range and linewidth below 15 G to find spectra as similar as possible to our subcomponents. As could be seen in Table 3 there are several different kinds of defect paramagnetic centres or itinerant electrons that might be responsible for such EPR spectra (they are given in the last column in Table 3). Frequently the knowledge of the temperature dependence of the line intensity could help to establish the nature of a paramagnetic centre. Typical expected \( I_{int}(T) \) dependences include the Curie, Curie-Weiss or Pauli type behaviour (the second last column in Table 3).

In Figure 21 the temperature dependence of the \( g \)-factor, linewidth, and integrated intensity of the three sub-components of the N component in B-400 sample, is presented. The \( g \)-factor of \( \text{N}_{1L} \) and \( \text{N}_{2G} \) subcomponents do not display any significant variations with temperature in contrast to \( \text{N}_{3G} \) line which exhibits a decrease of \( g \)-factor with decreasing temperature below ~50 K. The latter sub-component shows also the biggest variation of linewidth with its sharp increase after cooling the sample below ~10 K. Figure 22 shows the temperature dependence of the reciprocal integrated intensity of the three subcomponents of the N component in B-400 sample. All three subcomponents demonstrate Curie-type behaviour (linear dependence in this coordinate system) only in low temperature range (\( T < 60 \) K). Besides, this figure shows a remarkable difference in thermal behaviour of \( \text{N}_{1L} \) and two Gaussian subcomponents (\( \text{N}_{2G} \) and \( \text{N}_{3G} \)) in the intermediate temperature range (\( 70 < T < 250 \) K). This difference suggests rather dissimilar paramagnetic centres involved in formation of Lorentzian and Gaussian subcomponent lines.

Based on the similarity of \( g \)-factor and linewidth of \( \text{N}_{1L} \) line to those reported in the literature (see Table 3), this subcomponent could be assigned to oxygen vacancy with trapped electron (\( \text{F}^+ \)-centre) in \( \text{TiO}_2 \) nanoparticle. This line appears both in anatase and rutile phase of \( \text{TiO}_2 \) and is the strongest in B-850 sample. It was shown by the use of density functional approach that the \( \text{F}^+ \)-centres with anisotropic \( g \)-values (\( g_x = g_y = 2.003 \) and \( g_z = 2.004 \)) belong to the surface of nanoparticle, while \( \text{F}^+ \)-centres with isotropic \( g \)-values (\( g = 2.003 \)) belong to a core of nanoparticle [74]. Our method of the N component decomposition do not allow to draw unambiguous conclusion about location of \( \text{F}^+ \)-centres in our samples, but anal-
ysis of temperature dependence of spectral parameters of N$_{1L}$ line (Figures 21 and 22) suggests that both locations are realised. Anisotropic g-factors might reveal itself by broadening of the line (in case of small anisotropy) and the linewidth of N$_{1L}$ decreases going from sample B-750 to B-850 indicating bigger share of the core F$^+$-centres in larger TiO$_2$ nanocrystallites.

The other two subcomponents (N$_{2G}$ and N$_{3G}$) are probably connected with centres involving carbon atoms (nanographites and graphene-based materials). The N$_{2G}$ line is the most intense among the three subcomponents and thus it must be responsible for the correlation between the temperature independent dc susceptibility component $\chi_1$ and the EPR integrated intensity of the N component in B-300 to B-550 samples. There are two important differences: its linewidth is bigger (an average ~12 G) than N$_{2G}$ line and it is only present in B-300 to B-650 samples. In these samples anatase is the dominating phase of TiO$_2$, but perhaps more important in that case is the fact that an average size of nanocrystallites is smaller than in other samples calcined at 700$^\circ$C and higher. Therefore, it would be reasonable to assume that the paramagnetic centres producing N$_{3G}$ line are the same as in case of N$_{2G}$, but now the localized spins are closer to each other (smaller nanoparticles) and therefore the magnetic dipole-dipole interaction is stronger, resulting in broader linewidth. In larger nanoparticles (B-700 to B-850), due to weak magnetic interaction between nanoparticles, only N$_{2G}$ line would be visible.

5 Conclusions

Magnetic susceptibility versus temperature curves were composed of three very different components: a temperature independent and easily recognized in the high-temperature range ($T > 120$ K) component, another one seen in 20 – 100 K range displaying a slow increase with temperature decrease and saturation at low temperatures, and the third one observed at $T < 20$ K showing a sharp increase with decreasing temperature. The first contribution represents the Pauli paramagnetism of free electrons, the second is due to FM component and the third to low-temperature paramagnetism with small negative Curie-Weiss temperature and a small effective magnetic moment. Five types of EPR spectra were detected in the investigated samples of which the first two types were presented in all investigated samples: a very broad component (VB) with linewidth bigger than the sweep field of the spectrometer arising from conduction electrons; a narrow line (N component) that could be decomposed on two or three Gaussian\Lorentzian components; a broad line (BHT) appearing only in the high-temperature range in samples calcined in 650 - 850$^\circ$C interval; a broad line (BLT) appearing only in the low-temperature range in samples calcined in 700 - 850$^\circ$C interval; a low field lines (BLF) in samples calcined at 550$^\circ$C. The N component was decomposed on a line attributed to F$^+$-centre and one or two lines from localized paramagnetic centres strongly coupled to conduction electrons. The BHT spectrum was ascribed to $\pi$-electronic edge state spins, the BLT component to Ti(III) in rutile allotrope, and the BLF to clusters of paramagnetic admixture ions with AFM ground state. In general, magnetism of our samples is of rather inhomogeneous type, where various kinds of defects play a very important role.

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