Magnetization and electron spin resonance of a carbon/polymer composite

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Abstract. It has been shown that in multilayer graphene/polystyrene composite, the static magnetization curve looks the same as in a type-II superconductor. The electron spin resonance in the same composite was studied as a function on temperature and magnetic field. The observed g-factor of 2.003 was independent of temperature and was in the range (g = 2.0022-2.0035) characteristic of a free carbon electron. This behavior of the g-factor excludes the appearance of an internal magnetic field in the composite.

1. Introduction
The motivation for conducting magnetization studies in a composite based on multilayer graphene and chemically strongly bonded polystyrene was due to previously observed the current-voltage characteristic of the Josephson type [1,2]. The observation of a ferromagnetic-type hysteresis loop up to room temperature in some carbon materials has been the subject of many studies [3-6]. It has long been known that macroscopic graphite has a diamagnetic property, if there are no magnetic impurities. But this statement is not true for graphite, which has nanosizes. In this case a long-range ferromagnetic order may arise between the magnetic moments associated with dangling bonds at edge sites [7]. As for graphite with macroscopic dimensions, some researchers argue that a magnetic order can be created, if defects are introduced into graphite [8]. Based on an analysis of the behavior of the hysteresis loop on the same sample of the highly oriented pyrolytic graphite, it was suggested that the superconducting state coexists with ferromagnetism and that, with increasing temperature, a continuous transition from superconducting to ferromagnetic behavior is observed [9]. Moreover, there is an opinion that various magnetic properties can be obtained in a carbon sample: ferromagnetic, antiferromagnetic, superconductivity, discontinuous diamagnetic and discontinuous paramagnetic hysteresis depending on the orientation of the spins of its atoms [10]. But there is also point of view that the magnetic order is due to uncontrolled magnetic impurities [11].

In [12] was suggested that the hysteresis loops observed in macroscopic carbon samples during magnetization are not related to ferromagnetic ordering, but are related to type-II superconductivity. In a magnetic field, the type-II superconductor can have a mixed state when the sample simultaneously has regions with normal and superconducting properties. The effect is due to the fact that the penetration of a magnetic field into the type-II superconductor occurs in the form of quantized Abrikosov’s vortex filaments, where each filament has a non-superconducting core with a radius of the order of the coherence length of the superconductor. Around this normal cylinder in a region with a radius of the order of the penetration depth of the magnetic field, a vortex undamped current flows. Vortices are fixed.
mainly on defects with suppressed superconductivity (the so-called pinning centers). When the external magnetic field decreases to zero, not all vortices disappear in the sample; some of the vortices remain trapped at the pinning centers. In this case, the static magnetization exhibits a hysteresis loop.

In the paper, we report the results of studying the behavior of the $g$-factor by electron spin resonance method in the composite which has a hysteresis loop at magnetization up to $T \sim 500$ K. The result eliminates the appearance of an internal magnetic field in the composite. This means that the nature of the hysteresis loops is not related to the ferromagnetic effect.

2. Experimental details

As the first step from natural crystalline graphite was produced graphene oxide (GO) by modified Hummers method [13]. Conversion of graphene oxide to graphene (rGO) was produced by heating in a hydrogen or argon atmosphere. Reduced graphene (rGO) differs from graphene which was produced from graphite by mechanical exfoliation by scotch tape method [14]. In particular after reduction treatment, the oxygen content decreases significantly in rGO but does not completely disappear [15]. Prior to the synthesis rGO flakes with polystyrene the functionalization of them surfaces were made by 3 (trimethoxysilyl) propyl methacrylate (TMPMA) to improve the interaction of graphene and the polymer matrix [16,17]. Functionalized rGO can form covalent bonds with styrene under specified polymerization conditions, carried out by in situ polymerization in solution (toluene as the solvent) [18]. The graphene/polystyrene Composite was dispersed within a solvent by using sonication technique. The tolune was evaporated from the Composite at room temperature. As a result, the PS/TMPMA/rGO Composite was obtained, in which all three components should be linked together by covalent bonds. The Composite contained 1-3% (here and below, wt %) rGO assemblies with several microns long/wide and up to 200-nm thick, according to scanning electron microscopy (Zeiss EVO 50 instrument) [16].

Magnetic measurements of the samples were performed on the vibration magnetometer of the PPMS9 (Quantum Design) complex in the temperature range of 2–400 K and magnetic fields from 0 to 100 kOe.

3. Static magnetization

Figure 1 shows a typical field dependence of the static magnetization ($M_{\text{comp}}$) of the Composite at $T=300$ K. As seen the $M_{\text{comp}}$ consists from the superposition of diamagnetic component, more pronounced at high $H$ and hysteresis loop of ferromagnetic type at lower $H$. The $M_{\text{comp}}$, measured by a magnetometer includes three components: (i) the resulting magnetization of all carbon particles ($M_{\text{rGO}}$) in the Composite, (ii) the magnetization of the polystyrene and (3) the magnetization of the sample holder ($M_{\text{hold}}$). To determine the $M_{\text{rGO}}$, the magnetization of polystyrene and the $M_{\text{hold}}$ should be subtracted from the $M_{\text{comp}}$.

![Figure 1](image1.png)

Figure 1. The magnetization of the composite at $T = 300$ K. This dependence is characteristic of the entire investigated temperature range.

![Figure 2](image2.png)

Figure 2. Field dependence of the magnetization of the rGO particles after subtracting the diamagnetic and paramagnetic contributions of polystyrene from the $M_{\text{comp}}$ at $T = 300$ K.
It should be noted that the $M_{\text{hold}}(H, T)$ had a weak diamagnetic, temperature independent component and the magnetization of polystyrene consisted of the superposition of the diamagnetic and weak paramagnetic components [12].

Figure 2 shows the field dependence of the resulting magnetization for rGO particles at $T = 300\text{K}$, obtained after subtracting all the above contributions and taking into account the mass contribution of polystyrene to the composite. For convenient graphical illustration, the weight of the $M_{\text{comp}}$ was taken to be 1 g. The decrease in $M_{\text{rGO}}$ with increasing magnetic field to a value of $H \sim 5\text{kOe}$ is due to screening (Meissner) currents and indicates the superconducting properties of graphite particles, covalently coupled to polystyrene. The hysteresis loop looks like as in a granular type-II superconductor, where the hysteresis peaks are turned anticlockwise from the vertical axis in the bottom right/top left corners. With increasing temperature, thermal fluctuations significantly reduce the vortex pinning, and the hysteresis loops will be compressed, and at $T = 500\text{C}$ the hysteresis loop should not be observed (Fig.3).

![Figure 3](image_url)

**Figure 3.** With increasing temperature, the hysteresis loops will contract (indicated as $H_c$ in Figure. 2), and at $T = 500\text{C}$ the loop will apparently disappear.

However, the subtraction procedure, made above, may cause critics to doubt the reliability of the result about type-II superconductor because the small effect is concealed within large diamagnetic effect. And, possibly, the more correct background subtractions may turn the “superconducting” effect into ferromagnetism from noncontrolled magnetic impurities [19].

4. **Electron spin resonance**

Investigation of the electron spin resonance (ESR) can either confirm or exclude the presence of magnetic ordering in Composite. A diamagnetic contribution to the total magnetization is not detected by this method. Analysis of the line shape in the ESR spectrum depending on the temperature and magnetic field allows the ferromagnetic signal to be separated from paramagnetic contribution [20].

4.1 **Experimental setup**

The ESR in Composite samples was measured on an E-112 X-band spectrometer (Varian) using 10-GHz microwave radiation. The temperature dependence of ESR was studied using an ESR910 (Oxford Instruments) cryostat in a temperature range of 1.8–300 K stabilized to within ±0.1 K. The ESR measurements were performed in the interval of magnetic fields within 0 – 10 kOe at microwave radiation powers varied within 0.1 – 5 mW for controlling the ESR signal saturation. The spectrometer was equipped with TE103-type cavity having two magnetic field nodes. The $g$-factor was determined for a sample located in one of them. A standard sample, placed in the second node, had spin density of $2.58\times10^{15}$ spin/cm and a paramagnetic susceptibility of $\chi_{\text{st}} = 1.8\times10^{-10}$ emu at $T = 300\text{K}$. 
The paramagnetic susceptibility of samples was determined from ESR absorption of microwave radiation by a standard method based on the comparison of response signals from the sample and standard:

\[
\chi_{IP} \approx 1.8 \cdot 10^{-10} \frac{I_S}{I_{st}}
\]

where \(\chi_{IP}\) is the impurity paramagnetic susceptibility and \(I_S\) and \(I_{st}\) are the double integrals of ESR absorption lines of the sample and standard, respectively.

4.2 Experimental results

The ESR spectrum of the initial polystyrene free of rGO flakes did not show microwave absorption. Figure 1 presents the typical ESR spectra of the Composite with the rGO content not exceeding 3%, which were measured at various temperatures. The observed ESR line of microwave absorption corresponds to a \(g\)-factor of 2.0030 that falls in the interval characteristic of the free electron of carbon (\(g = 2.0022–2.0035\)) [21].

![Figure 1](image1.png)

**Figure 1.** ESR spectra of the initial polystyrene free of rGO flakes did not show microwave absorption.

The obtained ESR spectra of the Composites displayed no additional resonance lines, including those in the region of low fields, which could be indicative of the presence of nanoscale ferromagnetic impurities [22]. In the temperature interval studied, both position and shape of the resonance line remained constant: no such shift of the line toward lower magnetic fields was observed as the temperature decreased down to \(T = 2.7\) K, which was evidence of the absence of magnetic ordering [23]. ESR spectroscopy consists in its ability to detect only the paramagnetic part of magnetic susceptibility related to uncompensated electron spins. Figure 2 shows temperature dependences of the inverse paramagnetic susceptibility \((1/\chi_{IP})\) of two samples. As can be seen from these data, the magnetic susceptibility in the entire temperature interval studied obeys the Curie law:

\[
\chi_{IP} = \frac{C}{T - \Theta},
\]

with Curie–Weiss constant \(\Theta\) close to zero, which is indicative of the absence of any magnetic ordering. Here, \(C\) is the constant factor proportional to concentration \(N\) of spins,

\[
C = \frac{Ng^2\mu_s^2S(S+1)}{3k_B},
\]
where $\mu_B$ is the Bohr magneton, $S$ is the spin quantum number, and $k_B$ is the Bohr constant. As was pointed out above, the $g$-factor of composite samples studied amounted to 2.0030 and remained almost unchanged in the temperature interval studied. No increase in the $g$-factor with decreasing temperature, which could be interpreted as related to ferromagnetism due to the appearance of an internal magnetic field, was observed.

5. Conclusion
The study of ESR in a multilayer graphene/polymer composite showed that the hysteresis of the ferromagnetic type in the field dependence of the magnetization can be caused, rather, by superconductivity than by ferromagnetic ordering.

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References
[1] Ionov A N 2015 Technical Physics. Letter 41 651-3
[2] Ionov A N 2016 J. Low. Temp. Phys. 185 515-21
[3] Esquinazi P, Setzer A, Höhne R, Semmelhack C, Kopelevich Y, Spemann D, Butz T, Kohlstrunk B and Löhne R 2002 Phys. Rev. B 66 024429-10
[4] Makarova T 2004 Semiconductors 38 615-38
[5] Sai Qin, Pingping Sun, Qitao Di, Shuang Zhou, Caiping Yang and Qingyu Xu 2015 RSC Adv. 5 92899-904
[6] Sai Qin, Qingyu Xu 2017 Journal of Alloys and Compounds 692 332-38
[7] Joseph Joly V L et al 2010 Phys. Rev. B 81 245428
[8] Esquinazi P, Spemann D, Höhne R, Setzer A, Han K-H and But T 2003 Phys. Rev. Lett. 91 227201
[9] Moehlecke S, Kopelevich Y and Maple M B 2003 Brazilian Journal of Physics 33 762-65
[10] Numan Şarlı 2016 Diamond & Related Materials 64 103-9
[11] Vejpravova J, Pacakova B and Kalbac M 2016 Analyst 141 2639-56
[12] Ionov A N, Volkov M P and Nikolaeva M N 2019 JETP Letters 109 (3) 163–5
[13] Aleksenskii A E, Brunkov P N, Dideikin A T, Kirilenko D A, Kudashova Y V, Sakseev D A, Sevryuk V A and Shestakov M S 2013 Tech. Phys 58 1614-8
[14] Geim A K and Novoselov K S 2007 Nat. Mater 6 183-91
[15] Papageorgiou D G, Kinloch I A and Young R J 2017 Progress in Materials Science 90 75-127
[16] Nikolaeva M N, Bugrov A N, Anan’eva T D and Dideikin A T 2014 Russ. J. Appl. Chem. 87 1151-5
[17] Nikolaeva M N, Anan’eva T D, Bugrov A N, Dideikin A T and Ivankova E M 2017 Nanosystems: physics, chemistry, mathematics 8 266–71
[18] Yevlampieva N, Bugrov A, Anan’eva T, Antipov M, Ryumtsev E 2014 Am. J. Nano Res. and Appl. 2 1–8
[19] Forgan E M 2013 Papers in Physics 5 050008-3
[20] Augustyniak-Jablokowa M A, Maćkowiak M, Tadyszak K and Strzelczyk R 2015 Acta Phys. Polon. A 127 537
[21] Nair R R, Sepioni M, Tsai I-L, Lehtinen O, Keinonen J, Krasheninnikov A V , Thomson T, Geim A K and Grigorieva I V 2012 Nat. Phys. 8 199
[22] Garcia M A, Fernandez Pinel E, de la Venta J, Quesada A, Bouzas V, Fernández J F, Romero J J, Martín González M S and Costa-Krämer J L 2009 J. Appl. Phys. 105 013925
[23] Augustyniak-Jablokowa M A, Maćkowiak M, Tadyszak K and Strzelczyk R 2015 Acta Phys. Polon. A 127 537