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Magnetization of Needle Graphene Embedded in a Polystyrene Matrix

© A.N. Ionov, M.P. Volkov

Ioffe Institute, St. Petersburg, Russia
E-mail: ionov.tuch@mail.ioffe.ru

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In this work, we study the magnetization of two types of particles of a composite consisting of polystyrene and multilayer graphene chemically bonded to it, obtained by magnetic separation of the initial composite. For needle-shaped particles, a ferromagnetic type of magnetization was observed for the first time, with values of saturation magnetization that are large for graphene. For flat, macroscopic particles of the composite, a superposition of several contributions to the magnetization was observed.

Keywords: graphene, polystyrene, composite, magnetization, ferromagnetism, superconductivity.

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Recently, in the papers on structural engineering of various materials, it was shown that nanometer-sized materials acquire new promising properties for practical use, which were absent in bulk materials [1]. So, for example, if you reduce the size of graphite, which is known to be diamagnetic at macroscopic dimensions, to nanosize, then it begins to exhibit magnetic properties [2,3]. In this case, graphene magnetism is not associated with either d or f impurity or defect electrons, as is the case in traditional magnetic materials. In this paper, we report on the observation of ferromagnetic properties up to room temperature in samples of a graphene–polystyrene composite with an acicular shape. Initially, the composite consisted of a polystyrene matrix with embedded graphene flakes.

In this case, covalent bonds were specially created between graphene flakes and polystyrene. The technology for preparing such composites was described in detail in [4]. In the same paper, the results of complex studies of their morphology by X-ray diffraction and Raman spectroscopy were presented, a detailed analysis of impurities was carried out, and micrographs of the composite surface obtained using scanning electron microscopy were also presented. In [4,5] it was shown that the macroscopic particles of the composite exhibit dependences of the magnetic moment on the magnetic field, which are characteristic of granular high-temperature superconductors of the second type. The superconducting behavior of the magnetization hysteresis loop for macroscopic particles of the composite is confirmed by the fact that:

1) Josephson current-voltage characteristics are observed in the same temperature range, which distinguishes a superconductor from a normal metal [6,7];

2) study of the electron spin resonance in a composite with a hysteresis magnetization loop showed that the value of the g-factor did not depend on temperature and was in the range characteristic of a free carbon electron ($g = 2.0022$–2.0035), such behavior g-factor excludes the occurrence of an internal magnetic field in the composite [8];

3) when a magnetic impurity is introduced into polystyrene, the hysteresis loop of the composite is determined exclusively by the magnetic impurity of polystyrene, and the hysteresis loop associated with graphene is not observed, in contrast to the hysteresis of the composite, which had no magnetic impurity in polystyrene [9].

In the present paper it is experimentally shown that samples of a needle-shaped composite with transverse dimensions of no more than ten micrometers have an anomalously large magnetic moment with a behavior characteristic of a ferromagnet, namely, with the attraction of the needle-shaped composite to the pole of a permanent magnet.

A distinctive feature of our version of the composite was that the composite was preliminarily exposed to vibration at an acoustic frequency for several hours. As a result

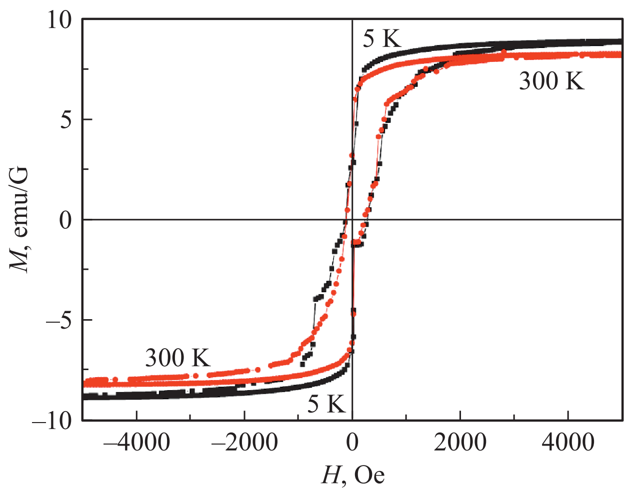

Figure 1. Magnetization vs. magnetic field for F-samples of graphene–polystyrene composite.

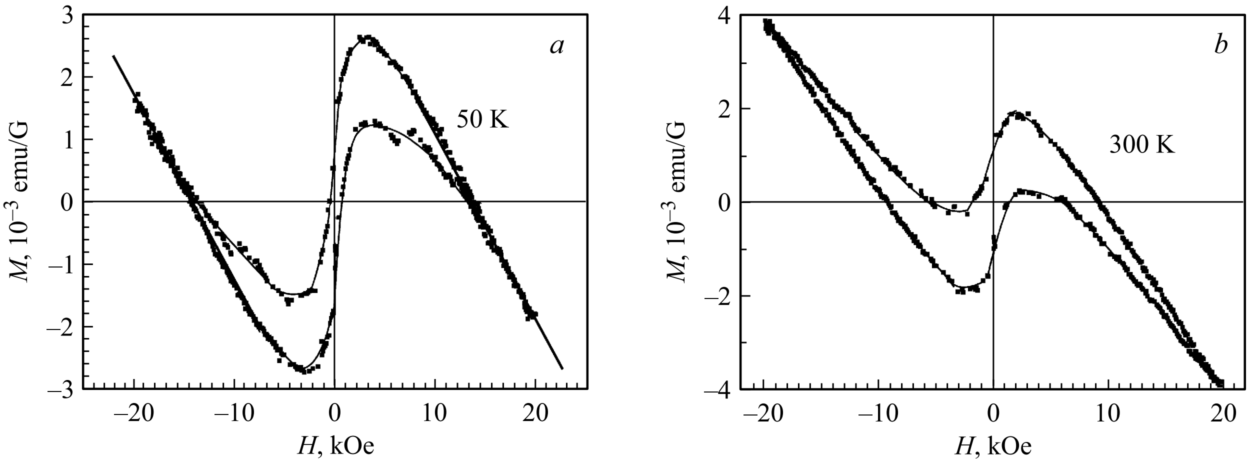

Figure 2. Magnetization vs. magnetic field for D-samples at $T = 50$ (a) and 300 K (b).

of this action, fragmentation of the composite occurred, in particular, with the formation of needle-shaped fragments $50-100\,\mu$m long and $5-10\,\mu$m wide, and larger flat fragments (plates with a length of the order of several hundred micrometers).

At room temperature, using strong permanent magnets, magnetic separation of the composite was carried out. In this case, it was found that the needle-like fragments of the composite (F-fragments) are strongly attracted to the pole of a permanent magnet. At the same time, planar fragments of the composite (D-fragments) weakly repelled from the magnet pole. As a result of magnetic separation, two groups of samples were obtained: F (ferromagnetic) and D (diamagnetic). Note that no magnetic impurities [4] were found in the obtained samples. The magnetization (M) of the F- and D-samples was measured using a vibrating magnetometer PPMS-9 (Quantum Design) in the temperature range from 5 to 300 K and magnetic fields from 0 to ± 20 kOe. Let us consider separately the magnetic properties of F- and D-samples. Fig. 1 shows the field dependences of the static magnetization of F samples at $T = 5$ and 300 K. As can be seen from Fig. 1, in low magnetic fields, a magnetization curve with ferromagnetic-type hysteresis is observed. The magnetization saturation occurred at $H_c \approx 2000$ Oe, and the shape of the magnetization curve was practically independent of temperature. The value of the saturation magnetization of about 9 emu/G significantly exceeds the values of graphene magnetization given in the literature [10,11].

The magnetic properties of needle-shaped composite samples have the following features:
— the dependence $M(H)$ has a hysteresis character in the entire studied interval;
— the shape of the $M(H)$ curves weakly depends on temperature;
— the absolute values of the saturation magnetization are by order of magnitude higher than the maximum values given in the literature for graphene.

Fig. 2, a, b shows the field dependences of the static magnetization for D composite samples at $T = 50$ and 300 K. As in the previous case, samples of the D composite also exhibit a magnetization curve with a ferromagnetic hysteresis. However, for D-samples there are also the following significant differences:
— magnetization M is by three orders of magnitude smaller than that of F-samples;
— the saturation of the hysteresis loop occurs at a much higher field than for F-samples;
— the diamagnetic slope in high fields is less than that of the composite with needle-like fragments;
— a slightly stronger temperature dependence of the maximum magnetization in the region of the ferromagnetic loop is observed;
— in the presence of a hysteresis loop of ferromagnetic type D-samples are repelled from the pole of a permanent magnet.

At first glance, the dependence $M(H)$ for D-samples can be considered as a superposition of a diamagnetic contribution from the polystyrene matrix and a small ferromagnetic contribution associated with the presence of small amounts of fragments of F-samples in the D-samples. When analyzing the magnetization of D samples, it is necessary to take into account the contribution of the polystyrene magnetization to the total magnetization of the samples. The fact is that in addition to a large diamagnetic component polystyrene also has a small paramagnetic contribution due to styrene, which is associated with the technology of its production. In our case, the second component is negligibly small for F-composite samples; however, for D-composite samples, it makes a significant contribution to their small magnetization. As was shown in [5], when this contribution is subtracted, the hysteresis loop of static magnetization will change significantly: the contribution to the magnetization from planar crystallites in D samples will decrease with increasing H in the region of positive magnetic fields and increase in the region of negative magnetic fields. This behavior of the magnetization hysteresis loop of the *D*-composite samples, as noted above, is characteristic of type II superconductors.

Thus, the type of its magnetization depends on the shape and size of the particles of the graphene–polystyrene polymer composite. In micron-sized needle-shaped composite samples, ferromagnetic magnetization is indeed observed with high values of saturation magnetization.

Our data on the presence of ferromagnetic properties in needle-shaped composite samples are consistent with the results of a study of small-angle magnetic-nuclear interference scattering of polarized neutrons, carried out on mixed samples of the same composite synthesized using a technology similar to the technology for obtaining our samples [12]. As was shown in [12], the presence of magnetic-nuclear interference scattering in relatively weak magnetic fields indicates the presence in the systems under study of magnetized regions on the order of 100 nm, which can be associated with needle-shaped composite samples.

Thus, we shown in paper that needle-shaped particles exhibit ferromagnetic magnetization, which depends weakly on temperature, with saturation magnetization values that are record high for graphene. The use of composite with magnetic properties together with composite with the effect of superconductivity can be used in spintronics as the next evolutionary step in the development of the electronics industry.

Conflict of interest

The authors declare that they have no conflict of interest.

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