Research articles

Structural and magnetic properties of graphene-based Fe$_2$O$_3$-decorated composites

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ABSTRACT

We present studies of structural and magnetic properties of graphene + Fe$_2$O$_3$ composite samples with the magnetic oxide content changing from 0 to 50%. Our studies revealed that irrespective of the cleaning procedure the magnetic behavior of pure graphene samples changed from diamagnetic to paramagnetic for samples made with either acetone or ethanol, respectively. The paramagnetic samples contained a significant concentration of magnetic moments. For all our samples with Fe$_2$O$_3$ at $T < 110$ K we observed the superparamagnetic blocking. Moreover, due to the presence of Fe$_2$O$_3$ nanoparticles with diameter > 10 nm we observed a transition at $T = 495$ K and another at $T > 600$ K. The synthesis solvent changes modified the magnetic behavior of our samples resulting in higher effective magnetic moment for the ethanol related samples. The shape and the parameters characterizing the magnetic hysteresis loop change strongly with the change of preparation method and the amount of Fe$_2$O$_3$. Large exchange bias was observed for all our samples indicating the significance of antiferromagnetic surface spin-alignment of Fe$_2$O$_3$ nanoparticles. It is therefore possible to control the magnetic properties of graphene + Fe$_2$O$_3$ composites over a wide range of parameters.

1. Introduction

Low-dimensional structures made of carbon, such as nanotubes, fullerenes, graphene and others have been the subject of great interest since two decades [1]. In the recent years, graphene, allotropic form of carbon having a quasi-two dimensional lattice structure has been the subject of considerable interest due to remarkable properties it possesses i.e. high electron mobility due to Dirac-like band structure [2], high breaking strength which is 200 times greater than the value for steel [3], high thermal conductivity [4], very high specific surface area [5] and many others.

High specific surface area of graphene was the reason for the increasing interest in the recent years towards the decoration of graphene with magnetic nanoparticles [6]. Nanocomposite materials consisting of graphene with magnetic nanoparticles are considered to be of major interest in the recent years since they are capable of significantly improving functional properties of base materials. Transition metal oxides, and in particular iron oxides such as Fe$_2$O$_3$ [7] and Fe$_3$O$_4$ [8] are considered to be very important from the applicability point of view due to their biocompatibility in physiological environments and low toxicity. Graphene decorated with magnetic iron oxide will have a significant impact on magnetic properties of the resulting composite, making it very promising for a variety of fields of applications such as magnetic energy storage, biomedicine, catalysis, magnetic fluids, and environmental remediation [9,10].

The present paper is focused on the studies of structural and magnetic properties of several graphene + Fe$_2$O$_3$ composites with the average Fe$_2$O$_3$ content equal to 5%, 25%, and 50%. We study the effects of graphene decoration with different amounts of magnetic oxide on the resulting magnetic order of the composite. In particular we focus on finding limits at which the magnetic properties of the composite, such as parameters of the magnetization hysteresis loop, can be varied via changes in Fe$_2$O$_3$ content and the type of solvent used for sample synthesis.

2. Sample preparation

As a starting graphene material we used graphene oxide prepared by modified Hummers method from commercially available natural graphite. Commercially available graphite was ground with sodium chloride in order to start graphite exfoliation and reduce the size of flakes. In the next step NaCl was removed by washing and filtering graphitic flakes using warm water and porous filter paper. The filtrated graphite was mixed with concentrated sulfuric acid and stirred vigorously overnight at a constant temperature. Afterwards, the temperature of the mixture was lowered using an ice bath while potassium...
permanganate was carefully added. Afterwards, the mixture was continuously stirred for some time and finally the reaction was stopped by adding distilled water with hydrogen peroxide. The final solution was filtered and washed 10 times using diluted HCl and distilled water to eliminate byproducts. In order to reduce the width (lateral breaking) and thickness (further exfoliation) of graphene oxide, acetone or ethanol was added and the solution was then subjected to ultrasounds using a high frequency ultrasonic probe [11].

Sample were made of graphene flakes with the addition of different amounts of Fe₂O₃ (5, 25 or 50% wt.). Graphene-Fe₂O₃ hybrid materials were synthesized by applying a microwave solvothermal reactor. At first, a mixture of graphene oxide (prepared by the above described method) in ethanol or acetone was chosen and subjected to ultrasounds for 20 min. In the next step, iron nitrate and ammonia water were added to the solution and it was vigorously stirred. Consequently, the obtained solution was subjected to a pressure treatment using a microwave reactor. The microwave solvothermal reactor was operated at 4 MPa for 15 min. In this step we obtained nanocomposite material of graphene/n-Fe₂O₃ (n = 5, 25 and 50 wt% Fe₂O₃). Next, the obtained materials were filtered and washed with deionized water to remove salt residues. Finally, the materials were dried at 80 °C for 24 h in the air.

3. Structural characterization

The structural characterization of our graphene samples consisted of a series of different measurements used in order to verify the quality of the obtained composites.

We studied the structural quality of our graphene + Fe₂O₃ samples with x-ray diffraction method (XRD) using the Empyrean (PANalytical) X-ray diffractometer with Cu-Kα (λ = 1.54 Å). XRD characterization results were analyzed in the X’Pert HighScore program with ICDD PDF-4 + database and are presented in Fig. 1.

As we can see in Fig. 1 all the sharp peaks in the XRD patterns can be assigned to the rhombohedral Fe₂O₃ phase (ICDD 01-072-0469, space group R-3c, space group number 167, hkl inserted on the graph). The broad peaks at position about 26 and 43° 2Theta in the samples with 5% Fe₂O₃ can be assigned to graphene agglomerates.

Additionally, we studied sample morphology with the transmission electron microscope (TEM). The selected results of the TEM measurements are presented in Fig. 2.

As we can see in Fig. 2 the presented materials obtained in a microwave solvothermal reactor have two main structures. All the graphene – Fe₂O₃ samples exhibit a typically wrinkled, sheet-like structure of graphicitic material. We can also observe Fe₂O₃ nanoparticles with the average particle size of < 10 nm, which were rather uniformly distributed over graphene sheets. Differences can be seen in a sample with 50% of Fe₂O₃ (prepared in acetone) where crystallite size was much larger (> 100 nm).

4. Magnetic properties

Magnetic properties of our graphene samples containing different amounts of α-Fe₂O₃ were studied with two magnetometers allowing the measurements of dynamic magnetic susceptibility, χAC, and static magnetization, M. Magnetic susceptibility was measured with the mutual inductance method, while high-field static magnetization was measured using Weiss extraction method, both employed to the LakeShore 7229 AC susceptometer/DC magnetometer system. Measurements were done over the temperature range from T = 4.3 K up to 320 K. We extended the temperature range of our magnetization measurements with a vibrating sample magnetometer (VSM) system allowing measurements at high temperatures from 300 K up to 650 K, the maximum temperature at which the measurements can be done without the risk of samples annealing and/or oxidizing and as a result changing their magnetic properties.

4.1. Magnetic moments in pure graphene

At first, measurements of AC magnetic susceptibility, χAC, over the temperature range from T = 4.3 K up to 320 K were performed for all our samples. Prior to measurements the samples were packed into nonmagnetic containers and the air remaining in the containers was evacuated. During preliminary magnetic susceptibility measurements samples were put into the alternating magnetic field with the frequency, f, equal to 625 Hz and amplitude, HAC = 1 mT. As a result of these measurements, we obtained a series of temperature dependencies of both the real and the imaginary parts of AC magnetic susceptibility, Re(χAC) and Im(χAC), respectively. The measurements done for both undoped graphene samples and the samples containing Fe₂O₃ indicated a vanishing imaginary part of AC magnetic susceptibility.

We started our studies from the measurements of the temperature dependences of the magnetic susceptibility for two graphene samples prepared with no intentional doping with magnetic impurities. The results of the measurements in the form of the Re(χAC)(T) dependencies are presented in Fig. 3.

As we can see in Fig. 3 the pure graphene sample made with ethanol shows positive magnetic susceptibility at low temperatures, a signature typical of the presence of paramagnetic impurities. It is therefore possible, that the technological process leading to production of the graphene flakes has led to unintentional contamination of the samples with magnetic ions of unknown origin. This contribution however, is not strong and should be orders of magnitude lower than the magnetic susceptibility expected from our samples with Fe₂O₃. Moreover, these results allow us to estimate the amount of magnetic moments present in the pure graphene sample made with ethanol and allow subtraction of this component from the magnetic susceptibility measured for graphene + Fe₂O₃ samples. For the pure graphene sample made with acetone negative values of Re(χAC) are observed over the entire studied temperature range. The average magnetic susceptibility value calculated for the Re(χAC)(T) dependence will be used as the χdia value for the analysis of the data obtained for samples with Fe₂O₃ made with acetone.

The temperature dependence of the inverse of the real part of the magnetic susceptibility for the paramagnetic graphene sample can be described using the modified Curie-Weiss law with the following equation:

$$\text{Re}(\chi_{AC}) = \frac{C}{T - \theta} + \chi_{\text{dia}},$$

(1)

where θ is the Curie-Weiss temperature, and C is the Curie constant described with the following equation:
where $\theta$ is the paramagnetic Curie-Weiss temperature, $N_0$ is the number of atoms per gram, $g$ is the effective spin splitting factor (since we do not know the exact type of magnetic ions let us assume $J = S = \frac{1}{2}$), $\mu_B$ is the Bohr magnetron, $x_\theta$ is the content of the magnetic moments in the sample, $k_B$ is the Boltzmann constant, and $\chi_{dia}$ is the diamagnetic susceptibility of graphene flakes.

The Re($\chi_{AC}$)($T$) dependence for the paramagnetic sample shows dependence that can be described with the Curie-Weiss law. It allowed us to perform fitting of the experimental data to the Curie-Weiss law described with Eqs. (1) and (2). We fitted the results with the value of the diamagnetic contribution to AC magnetic susceptibility taken as the fitting parameter. The experimental Re($\chi_{AC}$)($T$) curve was fitted with three fitting parameters: the Curie constant, $C$, the Curie-Weiss temperature, $\theta$, and the diamagnetic component of the magnetic susceptibility $\chi_{dia}$. The fitted line is shown together with the experimental data ($\chi_{dia}$ term is subtracted from the data in order to show linear behavior of the paramagnetic moments) in the inset to Fig. 3. Fitting procedure showed that the magnetic susceptibility of our samples can be very well fitted with the Curie-Weiss law described with Eqs. (1) and (2). As a result of the fitting procedure we obtained the values of three parameters, $C$, $\theta$, and $\chi_{dia}$. The values of the fitted parameters are gathered in the inset to Fig. 3. An obvious conclusion is that the value of the Curie constant, $C$, has a significant value for the sample without magnetic ions. It leads to the statement that the method of preparation of graphene samples utilizing ethanol has led to introduction of a large quantity of paramagnetic impurities of unknown origin. The obtained $C$ values can be further used to calculate the amount of magnetic moments, $x_\theta$, present in the pure graphene sample, using Eq. (2). The calculated $x_\theta$ value equals about $0.021 \pm 0.002$. The obtained $x_\theta$ value (under assumption that the magnetic moment of this impurity equals $S = \frac{1}{2}$) is rather large indicating the presence of a large fraction of magnetic impurities present in the studied graphene flakes. However, for Mn$^{2+}$ ions with $J = S = 5/2$ the estimated $x_\theta$ value would be equal to about 0.001.

The presence of magnetic moments in graphene can be also due to the introduction of different defects to the lattice structure and is very important from the applicability point of view due to the addition of controllable magnetic properties to graphene. Several theoretical studies predicted that point defects in graphene, such as vacancies and adatoms, should carry a magnetic moment. On the other hand, there exist ample experimental evidence of defect-induced magnetic moments in graphene. Point defects in graphene (fluorine adatoms and vacancy type defects) carry magnetic moments with spin momentum, $S$, equal to $1/2$. It was therefore justified to calculate the amount of magnetic moments in our paramagnetic sample with the total magnetic momentum $J = S = 1/2$. It is also possible that the non-intentional doping with either transition metal or rare earth ions occurred during the preparation of the pure graphene sample when a significant amount of magnetic moments was introduced to the system. These atoms, however, were not detected with standard methods of determining the chemical content of the material.

Fig. 2. Selected images of graphene + Fe$_2$O$_3$ samples showing sample morphology.
The magnetic impurities were not present in the sample synthesized using acetone. It is a clear signature that the technological synthesis procedure utilizing ethanol is responsible for the creation of magnetic moments in the sample. Moreover, it should be stressed that these unintentional magnetic impurities were most probably also present in all the graphene samples with Fe₂O₃ made with ethanol.

For the paramagnetic sample made with ethanol the Curie-Weiss temperature, \( \theta \), obtained during the fitting procedure had a value different than 0. It is a signature that the magnetic moments present in this sample do interact with each other and cannot be treated as isolated magnetic moments. The Curie-Weiss temperature is negative which indicates the occurrence of short-range antiferromagnetic interactions between magnetic moments present in the paramagnetic sample. It is therefore possible that small clusters, such as pairs of magnetic moments or possibly more complex magnetic structures are present in this sample.

In addition to AC magnetic susceptibility measurements made for pure graphene samples we made DC magnetization measurements. We made a series of magnetization measurements as a function of the magnetic field done at several stabilized temperatures for pure graphene samples. Magnetization \( M(B) \) curves were measured at temperatures lower than \( T = 200 \) K and at constant magnetic fields up to \( B = 9 \) T. All results were corrected by subtracting the contribution of the sample holder from the total magnetic moment. \( M(B) \) curves were measured at low temperatures and up to high magnetic field values carry the most information about magnetic ions in the material. Magnetization \( M(B) \) curves obtained at different temperatures for pure graphene samples are presented in Fig. 4.

As we can clearly see in Fig. 4 the \( M(B) \) curve for the graphene sample made with acetone showed a diamagnetic, negative slope. The diamagnetic susceptibility for this sample, estimated from the slope of the \( M(B) \) curve, was equal to about \( \chi_{\text{dia}} = -2.6 \times 10^{-7} \) m³/kg. This result is different than the diamagnetic susceptibility value determined from AC susceptibility data. It can be understood when we take into account the complicated nature of the magnetic properties of graphene. Orbital magnetism is responsible for the strong diamagnetism of graphene flakes, with the magnetic susceptibility strongly dependent on the type of flakes, their geometrical parameters, and the level of disorder [18]. The observed susceptibility value is therefore justified. Another aspect requiring attention comes from the difference between the \( \chi_{\text{dia}} \) values estimated using magnetization and magnetic susceptibility data. The magnetic field dependence of the diamagnetic susceptibility for graphene is known and shows complex behavior [19]. A much larger \( \chi_{\text{dia}} \) value calculated from magnetization data is due to the fact that it was calculated at a different magnetic field region than that of AC magnetic susceptibility data.

The \( M(B) \) curves obtained for the paramagnetic graphene sample made with ethanol have shape typical for paramagnetic material. The \( M \) \( (B) \) curve measured at \( T = 4.5 \) K shows Brillouin-like behavior with magnetization saturation at \( B > 8 \) T, allowing us to estimate saturation magnetization, \( M_S \), for the paramagnetic sample. In order to do that \( M(B) \) curves have been fitted with the modified Brillouin function to properly estimate saturation magnetization of our samples and the role of short range magnetic interactions related to the magnetic impurities present in this paramagnetic graphene sample. We fitted our experimental data to the following expression [20]

\[
M = M_S B_0 \left( \frac{g \mu_B S B}{k_B (T + \theta_0)} \right) + \chi_{\text{dia}} B,
\]

with

\[
M_S = x_{\text{dia}} N_0 \mu_B g S S,
\]

where \( B_0 \) is the Brillouin function and \( x_{\text{dia}} \) is the effective magnetic moment content estimated from the saturation magnetization value. The term \( \chi_{\text{dia}} B \) represents the diamagnetic contribution originating from graphene flakes. The \( \chi_{\text{dia}} \) value was set as a fitting parameter for the purposes of proper estimation of \( M_S \). Experimental \( M(B) \) curves were fitted with three fitting parameters: \( M_S \), \( T_0 \) and \( \chi_{\text{dia}} \). The results of the fitting procedure are presented in Fig. 3 together with the experimental data. As we can see the experimental \( M(B) \) curve obtained at \( T = 4.5 \) K is well fitted with the theoretical curve. The fitting parameters, obtained during the fitting procedure, are gathered in Fig. 3. The obtained \( T_0 \) temperature value is positive and we estimate the error in \( T_0 \) to be about 20%. Positive \( T_0 \) in Eq. (3) corresponds to negative \( \theta \) in Eq. (1). The saturation magnetization, \( M_S \), estimated for the paramagnetic sample was used to calculate the amount of magnetically
active magnetic ions, \(x_{\text{m}}\), using Eq. (4) under assumption that \(S = 1/2\). The calculated \(x_{\text{m}}\) value equals 0.020 ± 0.002, a value very close to the \(x_0\) value obtained from the Curie-Weiss constant, \(C\), within the margin of estimation error of both above quantities. It is a clear signature that the analysis of magnetic susceptibility and magnetization curves gave reliable results. It is also a reliable proof that the conclusions drawn from the obtained \(x_0\) and \(x_{\text{m}}\) values are correct. The saturation magnetization value obtained for the paramagnetic graphene sample is an order of magnitude higher than \(M_{\text{s}}\) values reported in the literature for the intrinsic graphene paramagnetic contribution equal to about 0.1 A·m²/kg [16]. It is therefore evident that most magnetization comes from defect related magnetic moments.

4.2. \(\text{Fe}_2\text{O}_3\) nanocrystals in composite Graphene + 5% \(\text{Fe}_2\text{O}_3\) samples

We performed a series of AC magnetic susceptibility measurements for graphene samples containing 5% \(\text{Fe}_2\text{O}_3\). Initially, we measured temperature dependence of AC magnetic susceptibility with the sample placed in the alternating magnetic field with \(f = 625 \text{ Hz}\) and \(B_{\text{AC}} = 1 \text{ mT}\). As a result, we obtained temperature dependencies of both real and imaginary AC magnetic susceptibility, \(\text{Re}(\chi_{\text{AC}}(T))\) and \(\text{Im}(\chi_{\text{AC}}(T))\), for ethanol and acetone samples. The imaginary part of AC magnetic susceptibility was close to zero and almost temperature independent. Results of AC magnetic susceptibility measurements for both studied samples are presented in Fig. 5a.

As we can clearly see in Fig. 5a the presence of cusp in the \(\text{Re}(\chi_{\text{AC}}(T))\) dependencies is observed at temperatures either around 40 K or 105 K for the sample made with ethanol or acetone, respectively. The appearance of a cusp in the \(\text{Re}(\chi_{\text{AC}}(T))\) dependencies indicates that magnetic transition is observed. However, more detailed magnetometric measurements need to be done to determine the nature of the observed magnetic state.

To further study the type of the magnetic order present in graphene samples with 5% \(\text{Fe}_2\text{O}_3\), we made a series of measurements of \(\text{Re}(\chi_{\text{AC}}(T))\) dependencies measured at different frequencies of an alternating magnetic field \(f = 7, 80, 625,\) and 9980 Hz. Results are presented in Fig. 5b. The maxima of the \(\text{Re}(\chi_{\text{AC}}(T))\) dependence shift on the temperature scale with an increasing frequency (see an exemplary result in Fig. 5b). The frequency dependent data in the vicinity of maxima can be analyzed using the empirical parameter, \(R_{\text{M}}\) proposed by Mydosh [21] and expressed in the empirical form:

\[
R_{\text{M}} = \frac{\Delta T_y}{(T_y)\Delta \log(f)}.
\]

where \(T_y\) represents the freezing temperature at a frequency \(f\), \(\Delta T_y = T_y(f) - T_y(f_i)\), and \(\Delta \log(f) = \log(f) - \log(f_i)\). \(T_y(f)\) values are estimated from the position of the maximum in the \(\text{Re}(\chi_{\text{AC}}(T))\) dependence at the temperature scale measured at the frequency, \(f\). The calculated values of the \(R_{\text{M}}\) factor change between 0.05 and 0.07 between samples made with acetone or ethanol, respectively. \(R_{\text{M}}\) values are close to those reported for superparamagnetic systems, for which \(R_{\text{M}}\) values are typically > 0.1 [21]. It is therefore evident that both our samples with 5% of \(\text{Fe}_2\text{O}_3\) show superparamagnetic blocking at low temperatures. The values of \(R_{\text{M}}\) factor are slightly lower than 0.1 indicating the presence of inter-particle interactions in this system. Our antiferromagnetic nanoparticles have small magnetic moment and thus dipole-dipole interactions are generally weak and most probably it is due to the presence of exchange interactions between surface atoms of neighboring particles [22].

Further analysis of the superparamagnetic blocking present in both our graphene + 5% \(\alpha\text{-Fe}_2\text{O}_3\) samples originates from the Néel theory of superparamagnetism [23]. The magnetic moment of single-domain and identical magnetic nanoparticles that do not interact and have uniaxial anisotropy fluctuate between two easy axis directions and can be described with the Arrhenius law

\[
\tau = \tau_0 \exp \frac{\Delta E}{k_B T_f},
\]

where \(\tau\) is the relaxation time, \(\tau_0\) is the attempt frequency, and \(\Delta E\) is the energy barrier for the magnetic moment reversal in a single nanoparticle. For the AC magnetic susceptibility measurements \(\tau = 1/\omega\) and thus for the non-interacting nanoparticles \(\ln(\tau) \propto 1/T_f\) dependence should be linear. The \(\ln(\tau) \propto 1/T_f\) dependence is linear for both graphene + 5% \(\alpha\text{-Fe}_2\text{O}_3\) samples (see example in Fig. 5d). We made fit of the experimental \(\ln(\tau) \propto 1/T_f\) dependences for both samples to Eq. (6) with \(\tau_0\) and \(\Delta E\) as fitting parameters. The fitted line is presented in Fig. 5d. The attempt frequency, \(\tau_0\), for noninteracting nanoparticles should have values in the range from \(10^{-13} \text{ s}\) up to \(10^{-9} \text{ s}\) [24]. For our samples we obtained \(\tau_0\) values ranging from \(8 \times 10^{-22} \text{ s}\) to \(2 \times 10^{-15} \text{ s}\) for samples made with acetone or ethanol, respectively. Such a low \(\tau_0\) value is a clear signature of strong inter-particle interactions present in our samples.

The temperature of transition to the superparamagnetic state, \(T_B\), can be determined from the frequency shifting of the freezing temperature, \(T_T\). Approximation of the \(T_T(f)\) dependence to \(f \rightarrow 0\) Hz allows estimation of the superparamagnetic blocking temperature, \(T_B\), for both samples. \(T_T\) values are equal to 35.6 K and 89 K, for samples made with ethanol or acetone, respectively. Superparamagnetic blocking with the
blocking temperatures, $T_B$, changing from 40 to 105 K is known for $\alpha$-
Fe$_2$O$_3$ nanoparticles. Literature data shows that the lowest $T_B$ values for
$\alpha$-Fe$_2$O$_3$ nanoparticles were observed for particles with a diameter of
about 4 nm with $T_B$ of about 16 K for the particles embedded into the
silica matrix [25] and for particles with a diameter of about 5 nm with
$T_B$ of about 22 K for the particles embedded into the polymer matrix [26].
On the other hand literature data for $\alpha$-Fe$_2$O$_3$ nanoparticles with a
diameter of about 3 nm embedded in the alumina matrix shows $T_B$
around 120 K [27]. It is therefore evident that $T_B$ is not a simple
function of nanoparticle size but can be also matrix dependent. $T_B$
values obtained for our samples with 5% $\alpha$-Fe$_2$O$_3$ with particle size of
about 10 nm are close to the values reported in literature.

The studies of magnetic phase transitions present in our samples
were supplemented by the measurements of magnetization as a func-
tion of temperature from 300 K to 600 K. Measurements were done with
VSM and AGM magnetometers. $M(T)$ measurements at $B = 50$ mT were
done with the sample being heated from 300 K to 650 K followed by the
measurement with the sample being cooled down to 300 K (for the FC
curve sample was cooled to 4.5 K). $M(T)$ measurements are presented in
Fig. 5a. As we can see in the studied temperature range magnetization
does show magnetic transition at $T \approx 475$ K. At $T > 300$ K magneti-
zation does not show paramagnetic decay. It is a signature of anti-
ferromagnetic order at higher temperatures with the transition tem-
perature higher than 800 K. Moreover, we observe anomaly in the ZFC
$M(T)$ curve at a temperature close to 490 K. This anomaly we interpret
as the presence of Morin transition in our samples related to the mini-
mal fraction of Fe$_2$O$_3$ nanoparticles with diameters different than the
majority of nanoparticles in this sample. Giant shifts of the Morin
transition temperature were reported in the literature [28]. The second
effect observed for the FC $M(T)$ curve at about 650 K is related to the
fact that we measure magnetization inside the antiferromagnetic high-
temperature phase known for $\alpha$-Fe$_2$O$_3$ to be present with transition at
around 850 K [29].

In addition to the magnetic susceptibility studies we also performed a
series of magnetization as a function of magnetic field measurements.
$M(B)$ measurements were done in the temperature range from $T = 4.5$ K
up to 200 K and magnetic field $B < 9$ T. Magnetization curves mea-
asured at low temperatures carry most information about magnetic in-
teractions between magnetic moments in the sample. Due to this we
focused on data analysis of the $M(B)$ curves obtained at $T = 4.5$ K.

Results for two graphene samples with 5% of Fe$_2$O$_3$ are presented in
Fig. 6a.

As we can see in Fig. 6a the shape of $M(B)$ curves differs between
both samples with 5% Fe$_2$O$_3$. For the acetone sample the $M(B)$ curve
shows saturation at high magnetic field $B > 8$ T while for the ethanol
sample saturation of the $M(B)$ curve was not observed. Moreover, $M$
values observed for the sample made with ethanol are almost three
times higher than the corresponding values for the sample made with
the use of acetone. The above two differences should be attributed to
the magnetic moments present in undoped graphene samples made
with ethanol. This paramagnetic contribution is at least partially re-
 sponsible for higher $M$ values and the lack of the saturation of the $M(B)$
curve for the ethanol sample.

We performed measurements of magnetization hysteresis curves for
all graphene samples with Fe$_2$O$_3$ at temperatures below 600 K.
Magnetization hysteresis curves obtained at $T = 4.5$ K are presented in
Fig. 6b. The irreversible behavior of the magnetization $M(B)$ curves was
observed for both graphene samples with 5% of Fe$_2$O$_3$. Fig. 6b shows
large differences in the magnetization hysteresis curves of samples
made with ethanol or acetone, respectively. The hysteresis loop for the
ethanol sample shows an elliptical shape while the hysteresis loop for
the acetone sample has a rectangular shape. It is therefore possible that
the distribution of shapes and/or sizes of magnetic clusters present in
this sample was broad. Another factor influencing the shape of the $M(B)$
loop for the ethanol sample comes from the presence of the para-
magnetic component in overall magnetization. The temperature de-
pendencies of the parameters characterizing magnetization hysteresis
loops change drastically as a function of temperature and synthesis
solvent. The coercive field, $B_C$, and remnant magnetization, $M_R$, esti-
ma ted from the magnetization hysteresis loops, as a function of tem-
perature are presented in Fig. 6c and 6d, respectively. A major decrease
of both $B_C$ and $M_R$ occurred at temperatures close to the reorienta-
tion transition temperature. It is therefore probable that this process is re-
sponsible for major changes in the domain structure of our samples.

Another very important feature of the observed magnetization hysteresis
loops is related to the presence of exchange bias in our samples. The
obtained $M(B)$ results (Fig. 6a–c, d) clearly show that magnetization
hysteresis curves are biased for the sample being cooled in the absence
of the applied magnetic field. The exchange bias is most probably due
to the presence of a small residual field in the sample during cooling in
the magnetometer. In order to study this biasing we made a series of $M(B)$ hysteresis curve measurements with the sample being cooled in the presence of DC magnetic field with $B = \pm 3.3 T$. The selected, representative exchange bias measurement results are presented in Fig. 6f and g. From $M(B)$ measurements done at several temperatures we estimated the exchange field, $B_{ex}$ plotted for both currently studied samples in Fig. 6d. As we can see the samples show well defined exchange bias with bias field diminishing at about 100 K. The exchange bias has a significant value for both samples reaching 32 mT at $T = 4.5 K$ for the sample made with the use of ethanol. The presence of exchange bias effect is known for Fe$_2$O$_3$ nanoparticles and is related to the presence of antiferromagnetic alignment of the surface spins [30].

4.3. Magnetic order in graphene with 25% and 50% Fe$_2$O$_3$

Finally, the magnetic properties of graphene samples containing 25% and 50% Fe$_2$O$_3$ were studied with different magnetometric techniques. Initially, we measured the temperature dependencies of AC magnetic susceptibility for four different graphene samples with 25% and 50% Fe$_2$O$_3$ made with ethanol or acetone. Measurements were done with samples put into the alternating magnetic field with frequency $f = 625 Hz$ and amplitude $B_{AC} = 1 mT$ over the temperature range from $T = 4.5 K$ up to 320 K. The results of our measurements, in the form of the temperature dependencies of the AC magnetic susceptibility are presented in Fig. 7.

As we can see in Fig. 7 the $R(\chi_{AC}(T))$ curves for samples made with ethanol show higher $R(\chi_{AC}(T))$ values than the corresponding curves for the samples made with acetone. It is therefore probable that again the preparation procedure of the samples using ethanol introduced a significant concentration of magnetic moments to the system which increased magnetic susceptibility with respect to the samples made with the use of the acetone. We observe a decrease of the $R(\chi_{AC}(T))$ curves for all our samples at temperatures lower than 120 K. This effect was observed earlier for samples with 5% Fe$_2$O$_3$ and is superparamagnetic blocking of Fe$_2$O$_3$ nanoparticles [25–27]. At temperatures higher than 120 K the $R(\chi_{AC}(T))$ curves show a slow increase towards higher values, observed up to about 320 K, the maximum temperature at which the Lakeshore 7229 Magnetometer system can perform measurements. In order to determine the nature of the magnetic order present in our samples we were forced to extend the temperature range at which the magnetic properties of graphene + Fe$_2$O$_3$ samples were studied. In order to do that we used a VSM magnetometer equipped with a high temperature oven. This allowed us to extend the temperature range of magnetization studies up to 650 K. The results of the $M(T)$ measurements are gathered on the right side of Fig. 7. As we can see in Fig. 7 the presence of three different magnetic transitions are observed for these samples. At temperatures from about 470 K up to 550 K the second magnetic transition is observed. This transition, in similarity to previous samples, is related to the Morin transition of Fe$_2$O$_3$ nanoparticles with a diameter increasing slightly above 10 nm. At $T > 550 K$ an increase of $M(T)$ curves is observed. Shift of the Morin transition is known in the literature [28]. In contrast to the samples with 5% Fe$_2$O$_3$ this increase in the $M(T)$ dominates over magnetization observed at low temperatures. It is therefore evident that the Morin transition in the Fe$_2$O$_3$ nanoparticles with sizes well over 10 nm dominates the $M(T)$ dependence for our samples with 25% and 50% Fe$_2$O$_3$, with the effect increasing with the concentration of Fe$_2$O$_3$.

Magnetic properties of graphene + Fe$_2$O$_3$ samples were also studied with magnetization as a function of magnetic field measurements. We measured magnetization as a function of the magnetic field at several stabilized temperatures $T < 200 K$ and magnetic field $B < 9 T$. Since low temperature $M(B)$ results carry most information about magnetic properties of the system we present $M(B)$ measurements obtained at $T = 4.5 K$ in Fig. 8.

As we can see in Fig. 8 the magnetization $M(B)$ curves at $T = 4.5 K$ show different behavior for the samples made with the use of either ethanol or acetone. Both sets of $M(B)$ curves show nonsaturating behavior up to $B = 9 T$. Magnetization increases slowly for samples made with ethanol and reaches higher values than those of acetone samples. It is therefore evident that the sample synthesis procedure has got significant influence on the magnetic properties of the samples. The same differences can be observed in magnetization hysteresis curves (Fig. 8b). The parameter characterizing magnetization hysteresis curves shows large variation with the change of sample parameters. For all samples except for the sample with 25% Fe$_2$O$_3$ (acetone) we observe usually decreasing $B_C(T)$ and $M_C(T)$ dependencies. However, for the sample with 50% Fe$_2$O$_3$ the opposite $B_C(T)$ and $M_C(T)$ dependencies are observed. Anomalous behavior of the $B_C(T)$ dependence with maximum at $T \approx T_b$ is known for Fe$_2$O$_3$ nanoparticles [27]. This effect is related to strong surface magnetic anisotropy which at $T < T_b$ leads to freezing of the surface magnetic moments at the easy axis direction. Anomalous $B_C(T)$ and $M_C(T)$ dependencies were also observed in other systems such as BiFeO$_3$ and are due to magneto-caloric effects reducing surface anisotropy [31].

We also performed measurements of exchange bias in magnetization hysteresis loops. $M(B)$ measurements were done after cooling samples in DC magnetic field $B = \pm 3.3 T$. As a result of the exchange bias measurements we estimated the temperature dependence of the exchange field, $B_{ex}$ shown in Fig. 8d. An increase of Fe$_2$O$_3$ content in the graphene + Fe$_2$O$_3$ composite led to an increase in the coercive field and the value of the exchange field. It is a very important feature of the studied samples indicating a broad range of values the properties of these composites can be tuned.

5. Summary

Summarizing, we report experimental studies of the magnetic properties of several graphene samples with changeable amounts of Fe$_2$O$_3$. Our study showed that pure graphene samples made with ethanol or acetone were either paramagnetic or diamagnetic, respectively. The magnetic properties of graphene strongly depend on the type of the solvent used during the preparation procedure. For all our samples with Fe$_2$O$_3$ we observed spin reorientation process at $T < 110 K$ followed by two high temperature magnetic transitions at $T \approx 495 K$ and at $T > 650 K$. The high temperature transitions are
related to α-Fe₂O₃ nanoparticles with diameters exceeding 10 nm. The parameters of the magnetization hysteresis curve change significantly as a function of both synthesis type and the amount of Fe₂O₃ in the composite. Large exchange bias was observed in our samples indicating an increasing significance of antiferromagnetic surface spins of α-Fe₂O₃ nanoparticles.

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References


Fig. 8. Selected results of the magnetization measurements obtained for graphene samples with 25% or 50% Fe₂O₃ obtained with ethanol or acetone including: (a) magnetization M(B) curves obtained at T = 4.5 K, (b) magnetization hysteresis curves obtained at T = 4.5 K, (c) remnant magnetization, M₀, as a function of temperature, and (d) coercive field, Bᵥ, as a function of temperature.