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Edge ferromagnetism of graphene oxide

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ABSTRACT

Using SQUID magnetometry and ferromagnetic resonance we show that the intrinsic ferromagnetism in graphene oxide (GO) is related to the zigzag edges created by breaking GO layers in the process of exfoliation. The 1D magnetic order existing below 2 K is destroyed by spin fluctuations enhanced by spin-flip transitions of the magnetic moments of protons from hydroxyl groups. Dipole-dipole interactions between short ordered segments at zigzag edges result in superferromagnetism below 65 – 75 K and superparamagnetism at higher temperatures. The strong ferromagnetism is observed for GO flakes in vacuum while the weak residual ferromagnetism of GO paper is due to magnetic moments surviving in the closed pores.

1. Introduction

Theoretical considerations show that intrinsic magnetism can exists in graphene and related materials [1,2]. Magnetism of a pure graphene is best understood [3–6]. It is also known that covalent functionalization can induce magnetic moments [7,8]. Ferromagnetism of graphene oxide (GO) was proved experimentally by observation of magnetic hysteresis [9–15]. However, attempts to explain origin of this phenomenon are inconclusive due to the lack of the effective interactions between magnetic moments attributed either to hydroxyl groups [9–15] or the mixed sp^2-sp^3 hybridization [13,14]. First of all, the exchange interaction between randomly distributed magnetic moments attributed to surface defects in the monolayer GO should result in the antiferromagnetic ordering [3,16]. Then, the RKKY interactions, which can lead to magnetic ordering, are ineffective in the defected graphene-like regions, where spin decoherence of conduction electrons is enhanced. Although possibility of ferromagnetic ordering in zigzag graphene ribbons functionalized by an epoxy pair-chain has been shown theoretically [17], the edge ferromagnetism in GO is usually not considered because the edges of the graphite oxide layers became functionalized in the oxidation process. Such approach does not take into account that exfoliation results in GO flakes smaller than the original graphite layers. Exfoliation methods, including ultrasound irradiation, crack the GO layers along linear defects functionalized by epoxy groups which are often along zigzag directions [18]. Unfortunately, functional groups on a surface of GO layers preclude direct observation of the edges by such methods as HRTEM [19]. In the absence of direct methods for studying the edge states in GO, a challenge remains to find alternative methods. One of them seems to be ferromagnetic resonance with its peculiarities for one-dimensional systems.

In this paper, we present combined SQUID, ferromagnetic resonance (FMR) and electron paramagnetic resonance (EPR) measurements of GO and demonstrate ferromagnetism in this material purified from unwanted ferromagnetic inclusions. The studies of magnetic properties of GO are complemented by scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR) spectroscopy. Peculiarities of GO samples in the form of paper and monolayer flakes produced by cavitation and deposited on MgO powder are used to find a most probable source of the observed ferromagnetism.

2. Experimental

GO was produced from natural graphite using the modified Hummers method [20] and purified to the contamination level of 6 ppm for Mn^{2+} and 3 ppm for Fe^{3+} [21,22]. Most of GO flakes in suspension were monolayer [23].

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We used two types of GO samples. GO paper was obtained by drying the "as purchased" GO suspension. The second type of sample was sealed under vacuum and consisted of the isolated monolayer GO flakes deposited on the spectrally pure MgO powder. Concentration of GO flakes in MgO powder was 0.063 mg/g. GO monolayers were prepared by sonication under moderate ultrasound power for 1 – 60 min.

Morphology of GO flakes was characterized by scanning electron microscope (Quanta FEG 250 FEI) in high vacuum conditions using an accelerating voltage of 2 kV. The water dispersions of GO were drop casted on silicon wafer substrate and dried at room temperature.

FTIR measurements were carried out in the range 2000–850 cm^{-1} on a spectrometer FTIR 4000 with an ATR cell (Jasco).

Magnetic measurements were performed using a Bruker SQUID magnetometer. Hysteresis loops were recorded at 5 and 300 K in the magnetic field range of ± 0.5 T. Temperature dependences of magnetization were measured in the range of 2 – 300 K under zero-field cooling (ZFC) and field cooling (FC) at the magnetic field $\mu_0 H =$ 0.03 T.

A continuous wave X-band RADIOPAN SX spectrometer with a TM110 cylinder resonator and an Oxford ESR900 cryostat was used to measure magnetic properties of our samples by the FMR/EPR method in the temperature range of 4.2 – 300 K.

3. Results and discussion

$M(H)$ hysteresis loops of the GO paper at 5 K and 300 K shown in Fig. 1a are obtained by subtracting the linearly dependent diamagnetic and paramagnetic contributions and prove the presence of a weak ferromagnetism. The inset presents the recorded $M(H)$ dependences of the static magnetization. The negative slope of $M(H)$ dependences shows a dominant contribution of diamagnetism at low and high temperatures. The slope is stronger at 300 K than at 5 K indicating that the linear contribution originates from the superimposition of diamagnetic and paramagnetic components and the paramagnetic component is much weaker than the diamagnetic one. The negative slope of $M(H)$ confirms that a number of paramagnetic impurities in our samples is significantly lower than previously reported for GO samples [9–15] in which the magnetization increases with magnetic field. In addition, the observed hysteresis loops indicate that in order to avoid the effects of saturation, one should measure the $M(T)$ dependence in a magnetic field not greater than 0.03 mT.

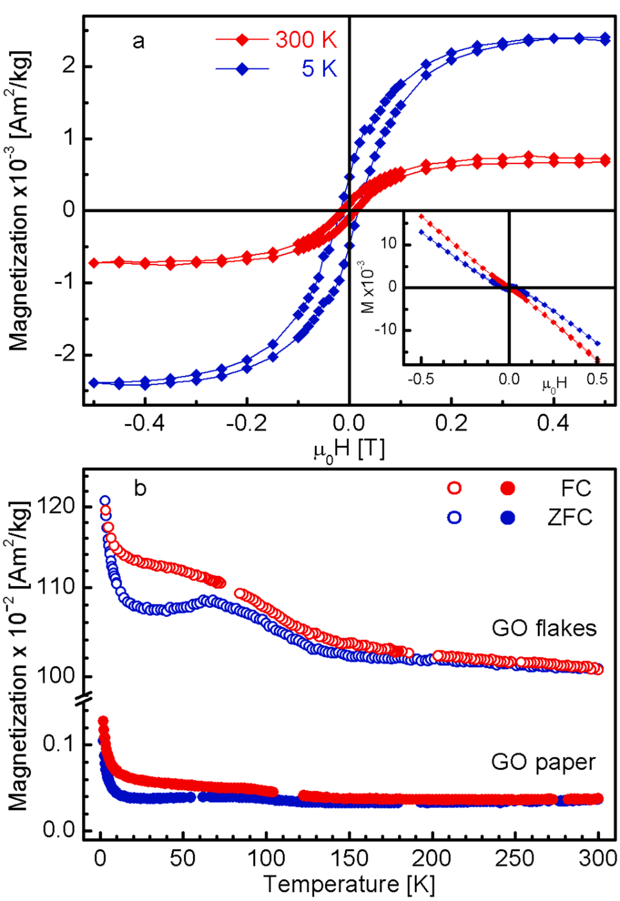

Fig. 1. (a) $M(H)$ hysteresis loops for GO paper at 5 K and 300 K. Inset shows $M(H)$ dependences before subtraction of the linear paramagnetic and diamagnetic contributions. (b) Temperature dependences of magnetization at the magnetic field $\mu_0 H = 0.03$ mT for GO paper and GO flakes deposited on MgO.

Fig. 1b depicts temperature dependences of the magnetization measured in the ZFC and FC regimes for the GO paper and the GO flakes which were sonicated for 10 min and deposited on MgO. At the used magnetic field and high temperatures (above blocking temperatures of 65 K and 75 K for GO flakes and GO paper, respectively), these dependences show peculiarities characteristic for small magnetic particles exhibiting superparamagnetic behavior. These peculiarities were not observable in GO when $M(T)$ dependences were measured at saturating magnetic fields [10,12,24]. Below the blocking temperature, thermal fluctuations influence neither the ordered magnetic moments nor the values of the FC magnetization which is expected to be constant. However, the strong temperature dependences is observed below 20 K and cannot be explained by paramagnetic impurities as the total diamagnetic and paramagnetic contribution to magnetization estimated at 5 K and 0.03 mT is -9×10^{-4} Am^2/kg. The observed $M(T)$ dependences suggest that the fully ordered ferromagnetic state exists below 2 K but is destroyed at higher temperatures. Regardless the ordering process, the measured mass magnetization of GO flakes is three orders higher than that of GO paper (Fig. 1b). Since dilution of GO could not increase the concentration of impurities and the purity of the MgO powder was confirmed by EPR, we conclude that the observed magnetism is an inherent property of GO.

Additional information about differences in magnetic properties of the GO flakes and the GO paper can be obtained from their FMR/EPR spectra, which are selectively sensitive to the type of magnetism (Fig. 2a). Intensities of these spectra are proportional to magnetic susceptibility and therefore to magnetization. The broad complex FMR signal at 215 mT is observed at 4 K in the spectrum of the GO paper cooled in the magnetic field of 700 mT (Fig. 2a), but it is hardly visible in the spectrum of the same sample cooled in zero magnetic field. It was estimated that the intensity of the EPR signal at 321 mT is less than 0.5 % of the FMR signal intensity. The weak narrow signal at 150 mT is attributed to 3 ppm of Fe^{3+} ions. The weak intensity of the EPR signals confirms that the paramagnetic contribution cannot explain the rapid

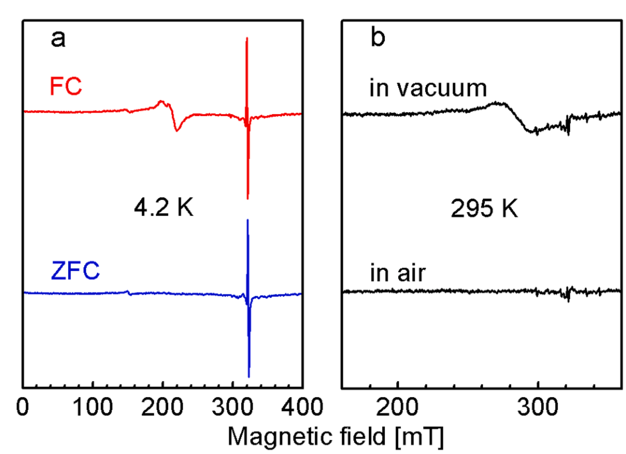

Fig. 2. (a) FMR/EPR spectra of GO paper recorded under the ZFC and FC regimes at 4 K. (b) Room-temperature spectra of GO flakes in vacuum and air.

increase of the magnetization with temperature lowering presented in Fig. 1b.

The room-temperature FMR/EPR spectra of GO flakes in vacuum and in air are shown in Fig. 2b. The six weak and narrow signals in the field range of 295–345 mT are due to traces of Mn^{2+} in MgO. The FMR signal observed for the sample in vacuum at 290 mT disappears after exposition of GO flakes to air. It seems that the magnetic moments which are capable to exchange coupling are sensitive to gasses in air.

The temperature evolution of the FMR signals of GO paper and flakes is shown in Fig. 3. The intensity of the FMR signal, which is maximum at 4.2 K, rapidly decreases with increasing temperature, then increases and again decreases (Fig. 3c). These dependences look like the $M(T)$ dependences shown in Fig. 2. Temperature-induced changes in the FMR signal intensity are accompanied by an increase of the resonant field of the FMR signal from 215 mT at 4 K to 290 mT at 295 K. The $M(T)$ and $I(T)$ dependences of both forms of GO are similar to the $I(T)$ dependences observed in graphene [25] and thermally reduced GO [26]. This similarity suggests that magnetism of GO is related to the edge ferromagnetism. Moreover, as it was already mentioned, the ultrasound exfoliation of graphite oxide can result in breaking the GO layers along zig-zag directions [18]. For these reasons we have studied an impact of cavitation on size and shape of GO flakes (Fig. 4a), their FMR (Fig. 4b) and FTIR (Fig. 4c) spectra.

SEM images show that the large flakes presented in the purchased GO suspension are broken to smaller ones. This process is observed in the first 10 min of sonication. Longer exposure to ultrasound has practically no effect on the size of flakes, but causes the destruction of the edges and the appearance of perforation inside the flakes. These observations are

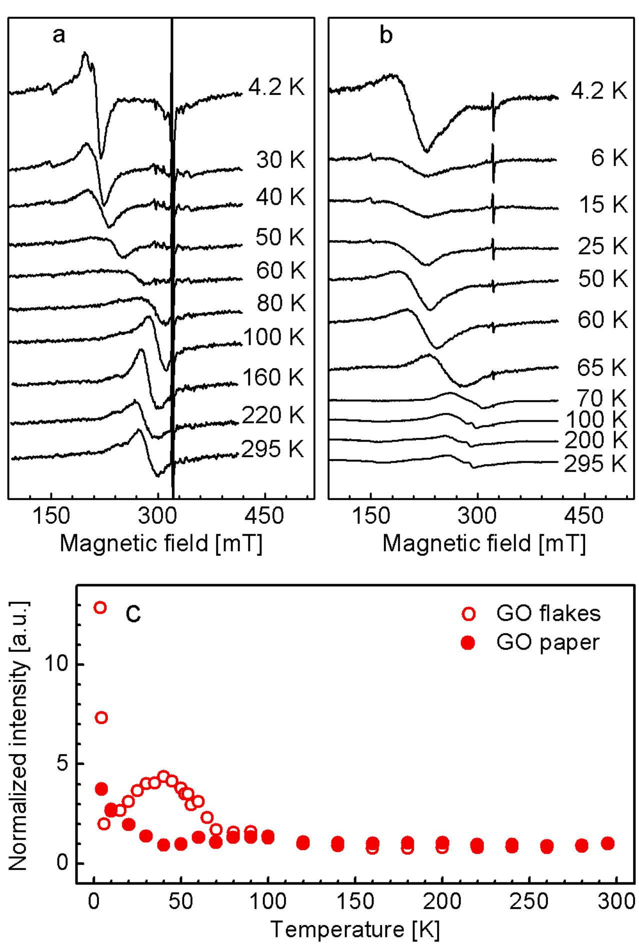

Fig. 3. The temperature evolution of FMR signals in GO paper (a), GO flakes (b) and normalized temperature dependences of the FMR signal intensity (c).

in agreement with early published results [27].

The FMR/EPR studies were performed for highly diluted samples containing about 0.02 mg of GO flakes. For this reason the FMR signal was not detected in the samples sonicated for times shorter than 5 min. The strongest signal was observed after 10 min of ultrasound irradiation. At the longer times of sonication the FMR signal decreases because ultrasound demages gradually the zigzag edges.

An impact of sonication on GO functionalization was monitored by FTIR spectroscopy. According to literature data [28], a band 1720 cm^{-1} is assigned to carbonyl functional groups C = O, bands 1221 cm^{-1} and 1370 cm^{-1} to bending mode of hydroxyl groups (C–OH), a band 1040 cm^{-1} to the epoxy stretching mode (C–O–C) and bands 968 cm^{-1} and 1615 cm^{-1} to the C = C vibrations of the graphene skeleton. Fig. 4c shows that the irradiation by the moderate power of ultrasound does not lead to GO reduction. Therefore the decrease in FMR signal with the cavitation time is not related to changes in the number of functional groups.

Our results not only confirm the presence of intrinsic ferromagnetism in GO, but point to the edge states as a source of this magnetism. The strong dependence of the FMR signal on cavitation time indicates correlation between ferromagnetism and the number of freshly opened edges. Since the rapid increase of magnetization and the FMR signal observed at low temperatures cannot be explained by paramagnetic impurities, ferromagnetism below 2 K is unquestionable. Weakening of the ferromagnetic order can be caused by spin fluctuations (spin waves), but only in one dimensional ferromagnets such fluctuations can fully destroy magnetic correlations. In graphene the 1D ordering of magnetic spins is expected for zigzag edges. There are, however, significant differences between effects observed in FMR of graphene flakes [25] and our results. Magnetic correlations at graphene edges were analyzed [5] and led to conclusion that the transverse fluctuations characterized by the high spin stiffness constant are the main factor limiting the spin correlation length. Our studies of the ferromagnetic correlations in the graphene flakes dispersed on MgO [25] and rGO flakes dispersed in paraffin [26] showed the rapid decrease of the FMR signal above 50 K and 40 K, respectively. The decrease of the FMR signal of GO is observed above 4 K (magnetization decreases above 2 K). Such strong shift in the $I(T)$ dependence cannot be explained by defects on zigzag edges, although they promote the longitudinal spin fluctuations. Since GO is rich in hydroxyl groups we suppose that decoherence of magnetic moments at zigzag edges can be enhanced by the spin-flips of proton magnetic moments resulting in spin stiffness lower than in pure graphene.

Another problem, which should be explained, is ferromagnetism of the GO paper. Since the zigzag edges are passivated by atmospheric oxygen and the GO paper is prepared by slow drying in air, it should not exhibit ferromagnetic properties. However, the residual ferromagnetism in GO paper can exist due to gelation of GO in the process of drying. Gelation can be describe as aggregation of flakes in such a way that it minimizes exposure of unfunctionalized and hydrophobic fragments of edges to water [29]. In the dry GO paper such edges in the closed pores are protected from the contact with air.

While the low-temperature ferromagnetism can be explained by ordering of the edge spins, the theory [5] predicts that this 1D ordering is destroyed by the spin fluctuations and graphene edges at finite temperatures are not actually ferromagnetic, but superparamagnetic ones. Superparamagnetism assumes no interaction between magnetic particles, however, small distances between short correlated fragments at GO edges should result in dipole–dipole interactions between these fragments. Below the blocking temperature these weak interactions lead to a superferromagnetic state. So, with increasing temperature the “true” magnetic order existing below 2 K is destroyed by the transverse spin fluctuations. As a result, superferromagnetism is observed up to 65 K and 75 K for GO flakes and GO paper, respectively. At higher temperatures superparamagnetism manifests itself.

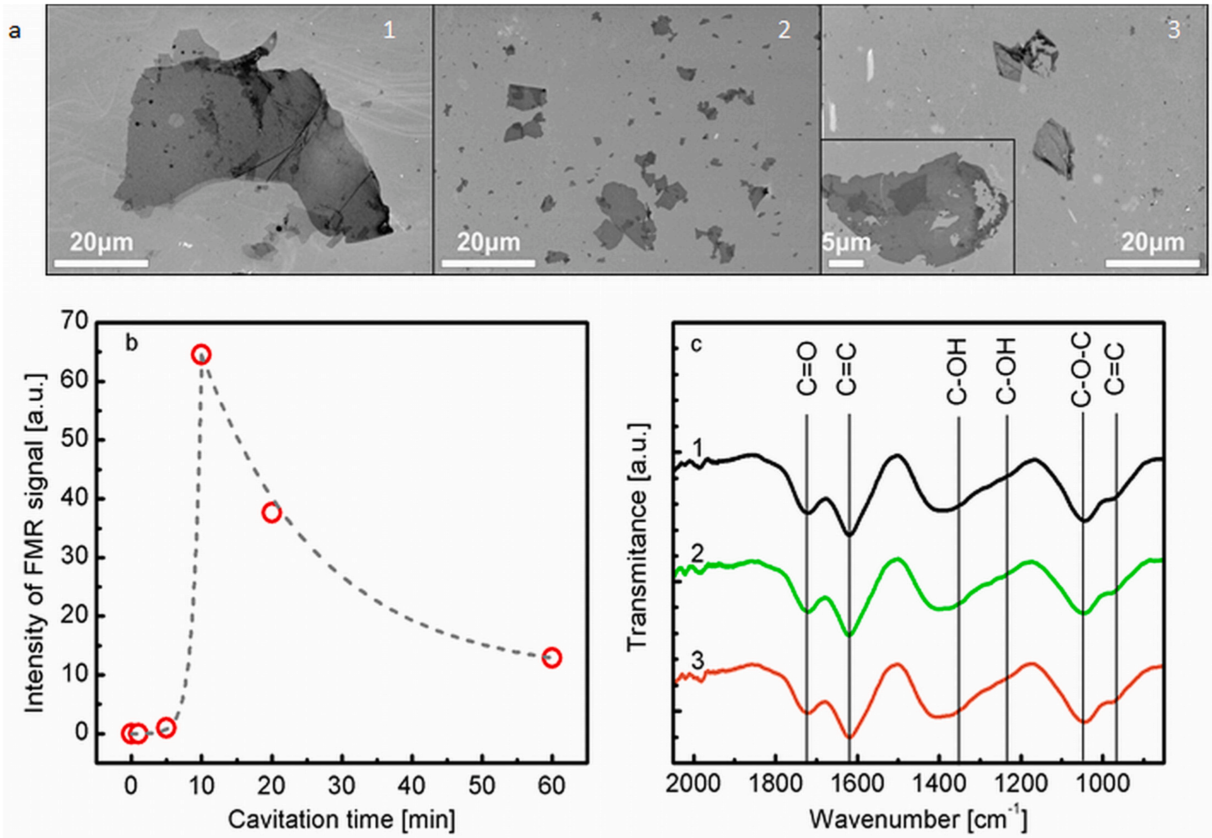

Fig. 4. An impact of cavitation on properties of GO flakes. (a) c SEM images before cavitation (1), after 10 min (2) and 60 min (3) of cavitation. (b) Intensity of the FMR signal as a function of the cavitation time. (c) FTIR spectra before cavitation (1), after 10 min (2) and 60 min (3) of cavitation.

4. Conclusion

We have experimentally shown that i) ferromagnetism in GO is observed in the temperature range of 2 – 300 K; ii) this ferromagnetism is intrinsic; iii) the mass magnetization of diluted GO flakes is higher than that of GO paper; iv) contact with air significantly diminishes ferromagnetic susceptibility of GO; v) the rapid decrease in magnetization of GO is observed above 2 K. The ferromagnetism of GO is explained by magnetic correlations at zigzag edges. Transverse spin fluctuations accompanied by spin-flips of the magnetic moments of protons from hydroxyl groups cause the rapid decrease in magnetization above 2 K. At higher temperatures superferromagnetic and superparamagnetic states exist. The residual ferromagnetism of GO paper survives in closed pores and has the same nature as that of isolated GO flakes in a vacuum.

CRediT authorship contribution statement

Roman Strzelczyk: Conceptualization, Investigation, Visualization, Writing – original draft. **Maria A. Augustyniak-Jabłokow:** Conceptualization, Validation, Supervision, Writing – original draft, Writing – review & editing. **Ryhor Fedaruk:** Validation, Writing – review & editing. **Łukasz Majchrzycki:** Investigation, Visualization, Resources. **Joanna Zwolińska:** Investigation. **Olga Kazakova:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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