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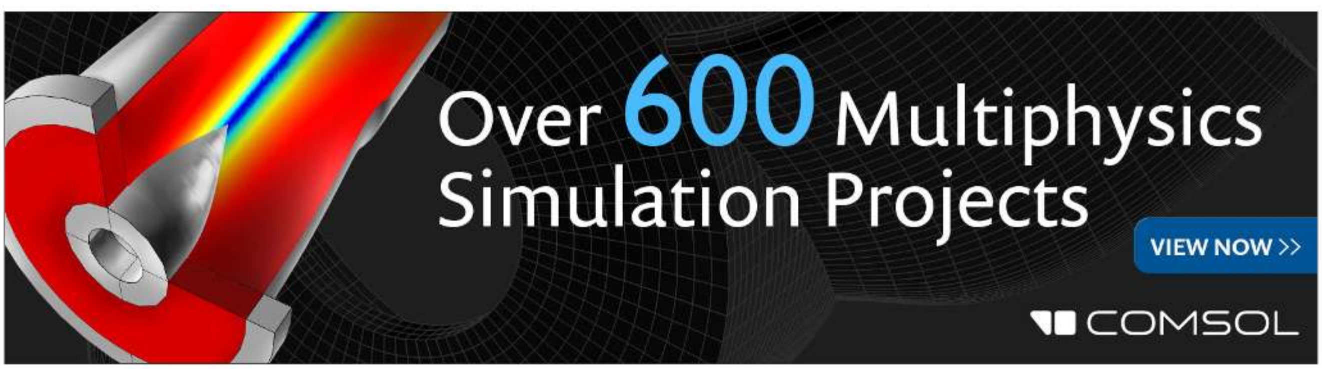

Anomalous magnetic behavior in nanocomposite materials of reduced graphene oxide-Ni/$NiFe_2O_4$

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Magnetic Reduced Graphene Oxide-Nickel/$NiFe_2O_4$ (RGO-Ni/NF) nanocomposite has been synthesized by one pot solvothermal method. Respective phase formations and their purities in the composite are confirmed by High Resolution Transmission Electron Microscope and X Ray Diffraction, respectively. For the RGO-Ni/NF composite material finite-size effects lead to the anomalous magnetic behavior, which is corroborated in temperature and field dependent magnetization curves. Here, we are reporting the behavior of higher magnetization values for Zero Field Cooled condition to that of Field Cooled for the RGO-Ni/NF nanocomposite. Also, the observed negative and positive moments in Hysteresis loops at relatively smaller applied fields (100 Oe and 200 Oe) are explained on the basis of surface spin disorder. © *2014 AIP Publishing LLC*.
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Ever since the discovery of graphene,[1] researchers have been exploring its potential application in organic flexible electronics, transistors, and optoelectronic devices.[2] Recently, magnetic tunnel junctions based on graphene are demonstrated for devices such as reprogrammable spin logic, tunnel transistor, and non-volatile magnetic memory.[3] Composite material of Graphene-Fe_3O_4 magnetic paper is developed for magnetic controlled switches as mechanical actuators.[4] Tunable dielectric constant values from negative to positive and a higher magneto-resistance of 46%–72% to that of pristine graphene is reported for the composite of Graphene-Fe/Fe_3O_4 by Zhu *et al*.[5] Graphene usage is also explored in the form of magnetic composites with nickel ferrite (NF) for applications; including as an anode material for Li-ion batteries,[6] microwave absorbing material,[7] and for photocatalysis in removal of organic dyes.[8]

There are numerous studies on magnetic properties of graphene[9–11] and nano sized nickel ferrite individually,[12,13] but studies related to their composite magnetic behavior are limited. Recently, quantum Monte Carlo simulations have shown an indirect coupling between magnetic impurities for a system comprising of magnetic nanoparticles decorated on the zigzag edge of graphene and have shown improved antiferromagnetic correlations in it.[9] Density Functional Theory (DFT) calculations for transition metal adsorbed on graphene surface have shown the possibility of charge transfer from the adsorbed transition metal to graphene surface and significantly changed its electronic density of states near the Fermi region.[14] The above theoretical calculations suggest that there will be a perturbation in graphene properties on addition of magnetic impurities.

On size reduction, magnetic properties of nanosized particles are dominated by finite-size effects because of competence between core and surface magnetic properties. Under-finite size effects, Kodama *et al*.[13,15] have proposed the surface spin disorder in NF nanoparticles. In ferrite nanoparticles, intra-sublattice exchange is weaker than the inter sublattice exchange leading to bulk ferrimagnetism and the superexchange interactions between magnetic cations occur through intermediary oxygen. When oxygen atom is released from the surface of the nanoparticle then the exchange bond breaks thus broken bonds are created. In case of organic-ferrite composites, the broken exchange bonds are bonded by organic species leading to the absence of superexchange.[16] Any type of these broken exchange bonds reduce the effective coordination of surface cations on the nanoparticle surface causing surface spin disorder or canted surface spin structures. These canted spin structures freeze into a spin-glass like phase around a temperature of 50 K for NF.[13,15] Keeping in mind the theories and models in anticipation of different kind of behavior, we have synthesized nanocomposite materials of Reduced Graphene Oxide-Nickel/Nickel Ferrite (RGO-Ni/NF) nanocomposite and in this report; we are presenting the anomalous behavior of "temperature and field dependent magnetization" at low field (about 100 Oe and 200 Oe).

With the experience of extensive study on graphene[17] and graphene based magnetic composites,[18] we have synthesized RGO-Ni/NF nanocomposite by one pot solvothermal synthesis by dispersing the appropriate quantities of precursor materials in ethylene glycol. Precursor materials include $FeCl_36H_2O$, $NiCl_26H_2O$, and previously prepared (modified Hummer's method) GO. The dispersed precursors are ultrasonicated for 2 h. Subsequently, sodium acetate and

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polyethylene glycol have been added in appropriate amount with continuous stirring for 30 min. The mixture has been transferred to a Teflon-lined stainless steel autoclave and thermally heated at 200 °C for 10 h. The resultant black product has washed with MilliQ water and ethanol several times by centrifugation and is dried at 45 °C in vacuum oven. Further, it was used for various characterizations.

Fig. 1 shows the X Ray Diffraction (XRD) micrograph for RGO-Ni/NF nanocomposite with all peaks corresponding to three phases. Peaks with symbol (**Δ**) indicate typical spinel structure of NF with Fd3m space group,[20] and peaks with symbol (**$**) represent Nickel (Ni) nanoparticles that belong to space group Fm3m.[21] Presence of RGO is confirmed from the peak (around $2\theta = 23°$ marked with the symbol (*).[20] Fig. 2(a) is a High Resolution Transmission Electron Microscope (HRTEM) image of RGO-Ni/NF, which shows the uniform distribution of magnetic phases over RGO. Because of strong adsorption, the RGO layers are crumpled (as shown in Figure 2(b)) around the magnetic nanoparticles of (Ni/NF). This may lead to some structural disorder associated with some strain at the surface of magnetic nanoparticles. Williamson-Hall plot (W-H plot) ($\beta \cos\theta = \varepsilon \sin\theta + 0.9\lambda/D$) is used to estimate the crystallite size and the strain (inset of Fig. 1) developed in the NF phase of the nanocomposite and the values are found to be 7.7 nm and 18×10^{-3}, respectively.

Crystallite size for Ni nanoparticles is estimated as 7 nm from Scherrer equation by using major peak (111)

$$D = 0.9\lambda/\beta\cos\theta,$$

where D = crystallite size, λ = wavelength of X-rays used, and θ = Bragg's angle.

We have very recently reported multiple magnetic interactions in graphene.[22] The temperature, magnetic field (externally applied), the spin density along the graphene edges, and the interactions among them are the deciding factors for the magnetism in graphene. The dominating factors could be paramagnetic centers/density of edge states and interactions among them. For an evidence ESR (Electron Spin Resonance) studies have shown that the localized spins in exfoliated graphene are responsible for observed magnetic properties.[22] The physical origin of magnetism can also be due to the localized states, which arise at the Fermi level of graphene due to the distortion in the lattice. Thus, the local moments exist by electron-electron interactions and these moments interact ferromagnetically.[23] Missing of atoms or voids can be the another type of source for the magnetism in graphene.[24] Fig. 3 shows the temperature dependent magnetization of RGO under different field starting from 100 Oe to 2000 Oe. This is the material that we have used in the nanocomposite of RGO-Ni/NF. The XPS data show the presence of carbon and oxygen only and there are no other peaks corresponding to any magnetic impurities, see the

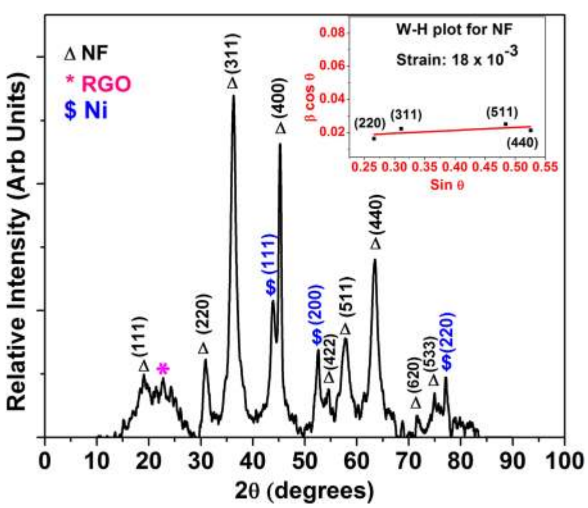

FIG. 1. XRD of RGO-Ni/NF nanocomposite.

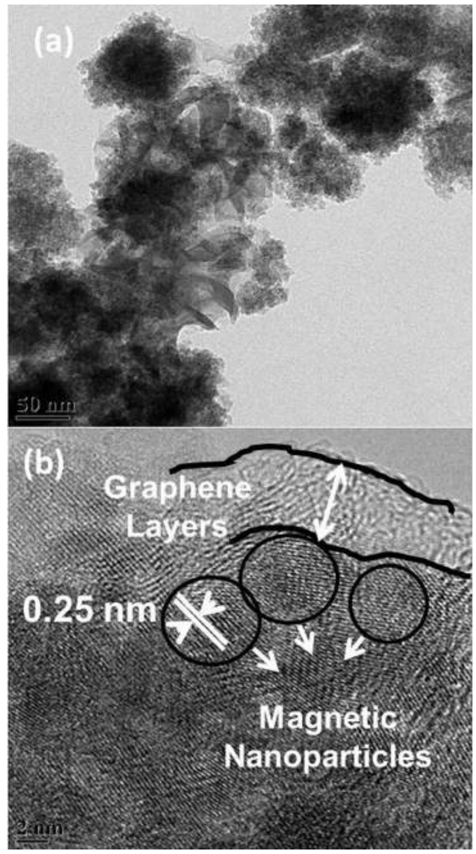

FIG. 2. HRTEM of RGO-Ni/NF nanocomposite at a scale of 50 nm (a) and 2 nm (b).

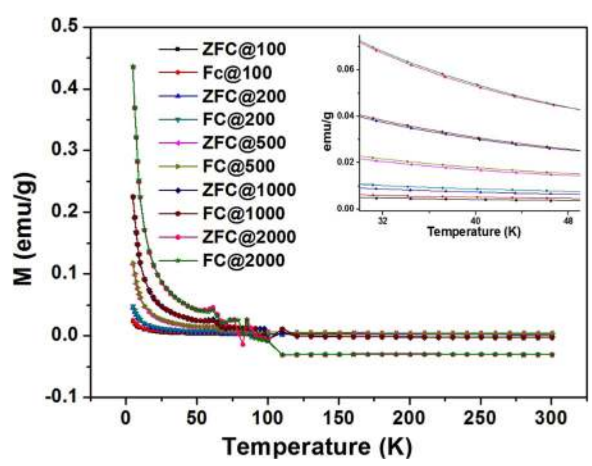

FIG. 3. ZFC-FC curves for RGO.

supplementary material S2 for graph.[34] Zero Field Cooled-Field Cooled (ZFC-FC) curves represent magnetic behavior of RGO and there is a divergence between them. This typical feature suggests the presence of ferromagnetic (FM) and antiferromagnetic (AFM) spin states on graphene[25] and in our previous studies, we have reported the typical ferromagnetic nature of RGO.[19,22] On increase in applied field value, FM correlation dominates AFM interaction and divergence between ZFC, FC curves decreases (inset of Fig. 3) under sub ambient temperatures. Recent theoretical calculations support this assumption.[9,25] At low field (100 Oe and 200 Oe), ZFC-FC curves show positive magnetic moment values up to the room temperature but at higher field (500 Oe and 2000 Oe) there is a transition to diamagnetic state showing negative magnetic moment. Since, the magnetic behavior resembles frustrated spin system, the transition temperature is not sharp, and it is evident from Fig. 3 which shows the transition temperature from 60 K to 100 K. Such type of similar behavior along with room temperature ferromagnetic nature for exfoliated graphene is earlier reported.[10] The TEM image of as prepared RGO is shown as S1, see the supplementary material for image.[34]

Bulk NF possesses inverse spinel structure. Site occupation in inverse spinel is out of 64 tetrahedral sites 8 are occupied by Fe^{+3} and out of 32 octahedral sites 16 (8 Ni^{+2}, 8 Fe^{+3}) are occupied equally by Ni^{+2}, Fe^{+3}. In case of nanoferrite, the distribution may change from inverse spinel to mixed spinel structure facilitating the Ni^{+2} nanoparticles to occupy tetrahedral sites. On tetrahedral sites, the orbital magnetic moment of Ni^{+2} is not quenched and lead to the magneto-crystalline anisotropy. This magneto-crystalline anisotropy causes canted spin structures for the core,[12] and it is also known that broken bonds cause surface spin canting for reduced dimensionality of nanoparticles.[13] Therefore, NF nanoparticles can have a core of ferrimagnetically interacting canted spins which is surrounded by shell of disordered spins, i.e., spin-glass like surface layer.[13,26] Previously reported Mossbauer studies also revealed the existence of canted surface spin structure of Fe^{+3} for NF nanoparticles.[12,27]

In RGO-Ni/NF nanocomposite RGO sheets are crumpled around the magnetic nanoparticles, and Ni/NF nanoparticles are uniformly adsorbed on graphene sheets (Fig. 2). Ni, NF nanoparticles in the composite are having average particle size around 7 nm and 7.7 nm, respectively. These are the typical sizes for these magnetic particles to possess superparamagnetism.[28,29] Ni nanoparticles can also possess surface spin disorder.[21] Fig. 4 represents the temperature dependent magnetization of RGO-Ni/NF nanocomposite (ZFC-FC) under different applied fields starting from a low field of 100 Oe to a maximum of 5000 Oe. These curves show the variation in blocking temperature from 110 K for 100 Oe to 30 K for 1000 Oe. Applied field above 1000 Oe can sufficiently overcome the blocking effects and results in overlapping of ZFC-FC curves. For field values around 100 Oe and 200 Oe, there is an anomaly in ZFC-FC behavior showing higher ZFC values to that of FC. To understand this peculiar behavior, we should consider the various possible magnetic interactions in the nanocomposite under low fields.

The coexistence of FM and AFM region for graphene are well reported,[10,22] and the pristine RGO prepared for the purpose of nanocomposite also shows signature of FM and AFM regions as we have discussed with the help of Fig. 3. In superparamagnetic nanoparticles (Ni and NF) individually, canting of core and surface spin structures have also been understood clearly.[12,13] Apparently, the composite comprising of these materials, under sufficiently low fields competes with various interactions of FM, AFM, and canted spin structures. These interactions on an average may turn into frustrated spin system giving signals in the form of anomalous behavior of temperature dependent magnetization curves, showing higher ZFC values to that of FC under 100 Oe and 200 Oe. This similar type higher ZFC to FC behavior has been previously reported by Chinnasamy *et al.* for nanocrystalline NF.[12] The frustrated spin behavior at low fields was also observed by the M-H loops, shown in Fig. 5.

Fig. 5 shows the field dependent magnetization behavior of RGO-Ni/NF nanocomposite under a maximum field of 100 Oe at different temperatures (M-H curves). Magnetization loops at all temperature show irregular (zigzag region in M-H curves) region of positive and negative moment with respect to the applied field and the extent of zigzag region is not same on both sides of field dependent magnetization curves.

In RGO-Ni/NF nanocomposite, it was observed that, there were interactions among the canted spins of core (due to magneto-crystalline anisotropy) and disordered spins of

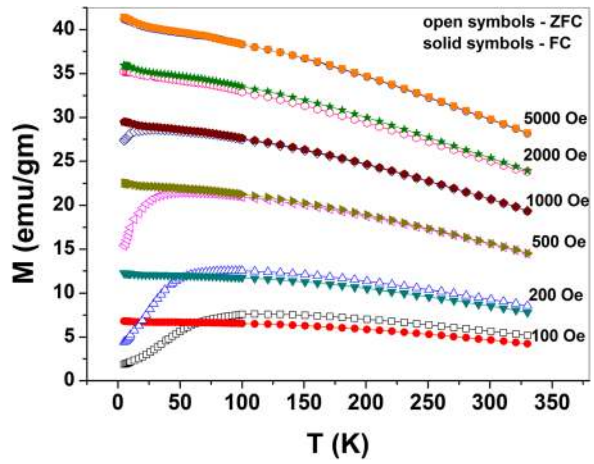

FIG. 4. ZFC-FC curves for RGO-Ni/NF nanocomposite.

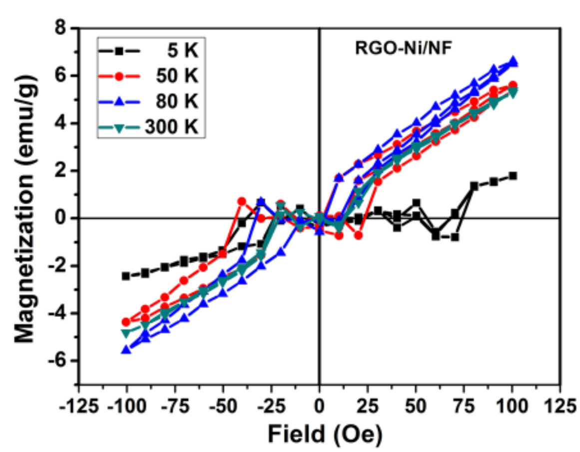

FIG. 5. M-H loops for RGO-Ni/NF nanocomposite at various temperatures.

surface of Ni, NF (due to broken bonds) nanoparticles in addition to FM and AFM interactions from RGO. We have earlier reported the FM and AFM correlations in graphene.[22] These interactions among various components of nanocomposite may result in complex stochastic spin behavior, i.e., at lower applied field values (100 Oe) at all temperatures there exist some value of field region where thermal energy for the spin of Ni, NF nanoparticles is not sufficient to overcome its intrinsic anisotropy to align with the applied field, and further there is an interaction with the FM and AFM regions arising from RGO with disordered surface spin of Ni/NF nanoparticles. Therefore, there exist some competences among various interactions with different stochastic spin configurations, which may lead to the negative and positive moment of RGO-Ni/NF nanocomposite under low applied fields. In all M-H loops, with increase in temperature the extent of zigzag region comes down and show typical superparamagnetic behavior with almost zero remanence. This may be due to a decrease in the number of stochastic spin configuration with increase in temperature by overcoming anisotropic energy of the RGO-Ni/NF system to some extent. Cyclic M-H loops drawn under various field sweeping values and the AC Magnetic Susceptibility(ACMS) measurements under 4 Oe supports this proposed explanation, see supplementary material S3 and S4 for ACMS and cyclic M-H curves.[34]

Graphene based devices are technologically important. Recently, water soluble and magnetic functionalized reduced graphene oxide for magnetic resonance imaging (MRI) applications has been introduced.[30] For spintronics applications, Wang *et al.*[31] proposed that the topological frustration or size effects can lead to the magnetic ordering in graphene related structures, and they have been introduced a rigorous classification schemes for the graphene to have large net spin or AFM correlations. In high density ultrafast spintronics, these topological schemes with AFM correlations are desired to create spin based fundamental logic gates like NOR and NAND. Hidden multiferroic ordering has been proposed for graphene nanoribbons with zigzag edges,[32] and the NF based composites have been reported for multiferroic applications.[33] In near future, the composites of graphene-Ni/NF may work for multiferroic applications. Therefore, in view of above applications which involve the spin structures, the present work of "anomalous magnetic properties of RGO-Ni/NF" has got importance and emphasizes to consider various possible interactions in graphene based magnetic composites for possible device applications.

In the summary, by using one pot solvothermal synthesis RGO-Ni/NF nanocomposite material have been synthesized. ZFC-FC measurements of the material show spin-glass like behavior with a peculiar phenomenon of ZFC magnetization values greater than the FC magnetization values. The observed anomalous behavior for field dependent and temperature dependent magnetization was effectively explained on the basis of possible canted spin structures.

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[34] See supplementary material at http://dx.doi.org/10.1063/1.4892476 for TEM of RGO, XPS of RGO, ACMS of RGO-Ni/NF, and Cyclic M-H loops of RGO-Ni/NF at the link.