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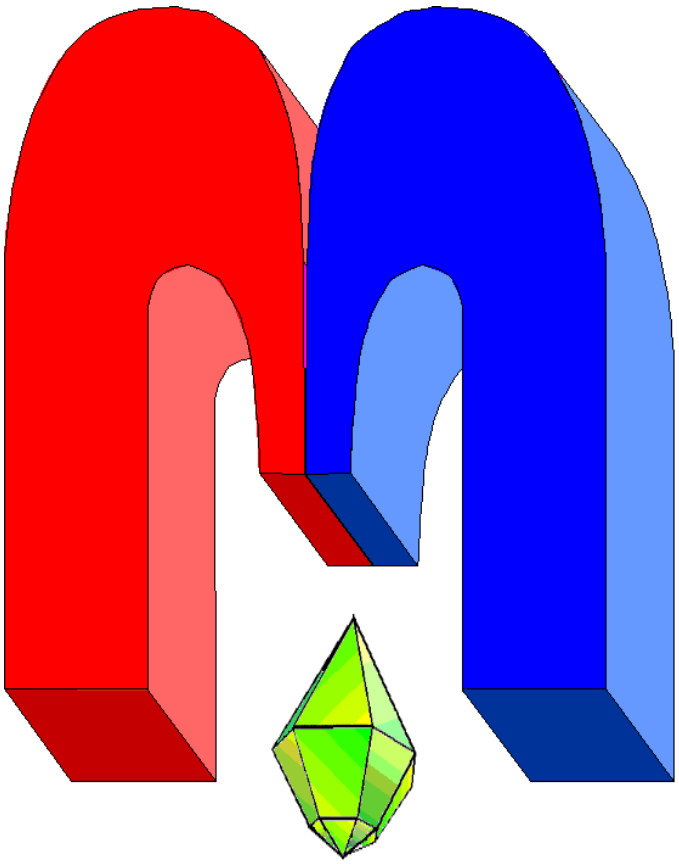

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† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Room temperature ferromagnetism of graphite: Impurity induced vs intrinsic origin†

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In this study, we report an experimental attempt to resolve whether ferromagnetism of graphite nanoflakes is an intrinsic phenomenon or it solely originates from impurities. A comparative study of either a nominally undoped or intentionally contaminated with NiO or Gd_2O_3 samples was performed. We show, first, that a detectable by X-ray diffraction contamination may occur via the agate mortar/pestle working surfaces if prior to sample dispersion it was used for grinding of hard oxides. Second, we find a systematic trend in a development of a FM component of all three samples under vacuum annealing at 400 or 800°C. Third, we notice that the samples notably contaminated with NiO or Gd_2O_3 do not reveal any drastic enhancement in ferromagnetism with respect to the sample free from intentional doping, contrary to an expectation related to nickel and gadolinium oxides reduction to metallic ferromagnetic at room temperature state. As a result, we conclude that ferromagnetism of graphite nanoflakes is probably an intrinsic phenomenon that could be stimulated slightly by NiO or Gd_2O_3 impurities, though an impact of the agate (SiO_2) contamination itself may also play a role.

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Keywords: graphite, nanoflakes, ferromagnetism, impurities, annealing

1. Introduction

Recently, ferromagnetism in twisted graphene layers, also known as moiré graphene, has emerged as a fascinating area of research. Twisted graphene refers to two graphene sheets that are rotated relative to each other at a specific angle, creating a moiré pattern. Surprisingly, it has been observed that when the twisted angle reaches a "magic" value, the system can exhibit unexpected ferromagnetic behavior. For example, authors in [1,2] claim that the moiré patterns and lattice distortions in twisted graphene layers can affect the electronic wavefunctions and orbital states of electrons. Modifications of the electronic structure can lead to an appearance of magnetic moments. Moments can interact and form ferromagnetic regions in a sample. These results suggest that an ensemble of graphene or graphite nanoflakes may reveal an intrinsic (as opposed to impurity-induced) ferromagnetic behavior. Indeed, ferromagnetic response has already been found and reported for graphite powders [3,4], however, its assignment to a graphite itself is debated [5].

Ferromagnetism, traditionally associated with metals and alloys, has long been considered an elusive property of carbon-based materials such as pyrolytic graphite. Highly oriented pyrolytic graphite (HOPG) is generally considered to be the strongest diamagnet among other types of carbon; it has no spontaneous magnetization and does not exhibit pronounced magnetic properties. However, studies conducted in the last two decades have shown that graphite can exhibit ferromagnetism, paramagnetism and even superconducting like behavior, when it has a morphology of small flakes with thicknesses of the order of units and tens of nanometers [3, 6–18]. Early investigations of carbon-based ferromagnetism were primarily focused at carbon nanotubes, nanofibers, fullerenes and graphene [8–12]. However, the realization that pyrolytic

†This paper is dedicated to Professor Boris I. Kochelaev on the occasion of his 90th birthday.

graphite, a highly ordered form of graphite, could exhibit ferromagnetic behavior opened up new possibilities.

The origin of graphite ferromagnetism is still a subject of debate and research, and several hypotheses have been proposed. One hypothesis is that the ferromagnetism in graphite arises from tiny amounts of uncontrolled magnetic impurities [5]. Another hypothesis can be referred to as defect-induced-magnetism (DIM) in the sample. So far, a large number of theoretical works has been published on DIM associated with the presence of sp^2 dangling orbitals at carbon vacancies and edge states, that induce localized magnetic moments [6, 12, 16]. Finally, it has also been suggested that ferromagnetism in graphite may be due to a formation of magnetic domains in material, similar to what happens in typical ferromagnetic metals. Exact mechanism for this domain formation is not yet developed, but it is thought to be related to complex interactions between carbon atoms in the lattice structure of the material [3, 12, 14]. Recently, it has also been shown that low temperature annealing energes as a crucial step for tailoring the magnetic behavior of pyrolytic graphite and graphene [19–21]. Mild annealing under specific environmental conditions can induce structural and open edge rearrangements [22], modify defects, and may affect the overall magnetic properties of a sample.

A nature of the annealing-induced ferromagnetism of graphite remains a matter of a debate, whether it is an intrinsic phenomenon or extrincis originating, e.g., from some impurities. In this work, we make another attempt to resolve this issue. The idea behind a study is that if one is unable to get rid for sure of hardly detected impurities, one *vice versa* can contaminate samples controllably and study a result of such doping.

In this work, fine graphite flakes were obtained by a long grinding process from the bulk HOPG. Prior to graphite grinding, the agate mortar used in the process was intentionally contaminated by grinding micrometer-grain powders of Gd_2O_3 or NiO oxides. The presence of the impurities in samples was detected by x-ray diffraction (XRD) and quantified with atomic absorption spectroscopy (AAS). If the oxides are reduced to elementary Gd or Ni, these impurities would provide a sample with extrinsic ferromagnetism as their Curie temperatures are close to the room temperature (293 K for Gd and 627 K for Ni). Ferromagnetism development with the annealing will be reported and discussed for either the HOPG powder for which maximum effort was paid to avoid any contamination, or HOPG intentionally doped with transition or rare-earth metal oxides that under annealing in vacuum in a presence of carbon may reduce to metallic ferromagnetic at room temperature state.

2. Experimental details

Highly oriented pyrolytic graphite (HOPG) wafer was received from the Advanced Technical Centre (Moscow, Russia). The Gd_2O_3 (99.95%) and NiO (99.98%) powders with the mean grain size of 10 μm were used in the experiment (from Sigma-Aldrich, USA). Splitting and dispersion of the bulk crystalline HOPG was carried out by grinding in agate mortar for 30 hours in a sealed Plexiglas glovebox under extra-pure nitrogen (99.995%) atmosphere. The glovebox is equipped with the gas treatment system to maintain the pressure and the purity of the gas.

Initially, we have produced thin graphite flakes from the bulk HOPG using the brand new and carefully cleaned with pure isopropyl alcohol mortar and pestle without adding any impurity. We refer to this sample in the further as "undoped HOPG sample". Then, we intentionally ground the Gd_2O_3 or NiO powders in a separate agate mortar for 3-4 hours aiming at a pollution of agate tools working surfaces with potentially magnetic impurities. Prior to grinding of either the Gd_2O_3 or NiO, the surfaces of the mortar and pestle were carefully cleaned employing the 20-μm

grade corundum abrasive. After the grinding of Gd_2O_3 or NiO, the mortar and the pestle were meticulously cleaned with lint-free paper soaked in isopropyl alcohol. Thereafter, we employed another piece of the same crystalline HOPG wafer for an extended grinding down to nano-size graphite flakes under the same atmosphere and following identical grinding procedure as for the undoped sample. In this way, we have obtained a set of three samples: undoped, Gd_2O_3 and NiO doped graphite flakes.

Further, one third of each as-prepared sample was annealed in the vacuum (base pressure 1.5×10^{-5} mbar) for 24 hours at 400°C while another one third - at 800°C following the same protocol. During the annealing, the sample was kept in a quartz tube that prior to sample thermal treatments had been pre-annealed under vacuum at 900°C. The tube was evacuated with the Agilent TPS-Compact oil-free system; the pressure during the annealing was monitored with the Varian FRG-700 universal full range gauge.

The morphology of the prepared samples was investigated with scanning electron microscopy (SEM, MERLIN by Carl Zeiss, Germany) combined with the energy-dispersive (EDX) AZTEC X-MAX spectrometer (Oxford Instruments) and by transmission electron microscopy (TEM) using the Hitachi 7700 setup operating at 100 kV with the facility for selected area electron diffraction (SAED) analysis.

In order to check whether our approach to doping the graphite flakes with NiO or Gd_2O_3 impurities has worked out, we studied two doped as-prepared samples with powder X-ray diffraction (XRD). As the qualitative and quantitative detection of low-content impurities in graphite flakes has always been a challenge, we performed the highly sensitive atomic-absorption spectroscopy (AAS) to confirm the occurrence of the added impurities in the prepared graphite samples. AAS indeed confirmed the presence of added impurity in the prepared graphite flakes with a concentration of 230 ppm for NiO and 380 ppm for Gd_2O_3, respectively. These quantities are close to our estimates of CoO impurity in HOPG powder obtained in the same way, though the doping occurred unintentionally and provided the sample both with ferromagnetism and exchange bias [23]. Other elements that potentially might induce ferromagnetism such as Fe and Co had concentrations below 1 ppm before and after annealing.

Magnetization measurements were carried out with the vibrating sample magnetometry (VSM) option of the Physical Property Measurement System PPMS-9 (Quantum Design, USA). For measurements, finely ground graphite samples were put into the gelatin capsules, sample mass ranged up to 20 mg.

3. Results and discussion

Morphology and flake size distributions of the prepared samples were characterized with scanning and transmission electron microscopies. Figure 1(a) and (b) displays the initial SEM and TEM micrographs of the prepared graphite flakes. HOPG particles manifest a pronounced clustering into stacks. Flake lateral size according to SEM results varied within 0.1 to 10 μm (Fig. 1(c)), while its thickness lied in the range of $10 - 50$ nm (Fig. 1(d)). The samples, both before and after annealing, contained multi-oriented and twisted graphite layers with a huge number of open edge terminations. The SAED pattern on the multilayer region of the aggregate (inset to Fig. 1(b)) reveals sets of maxima of the same order indicating that graphite flakes are randomly mutually oriented in the basal plane.

Graphite is a naturally occurring form of carbon that consists of parallel layers of hexagonally arranged carbon atoms, called graphene layers. These layers are held together by weak van

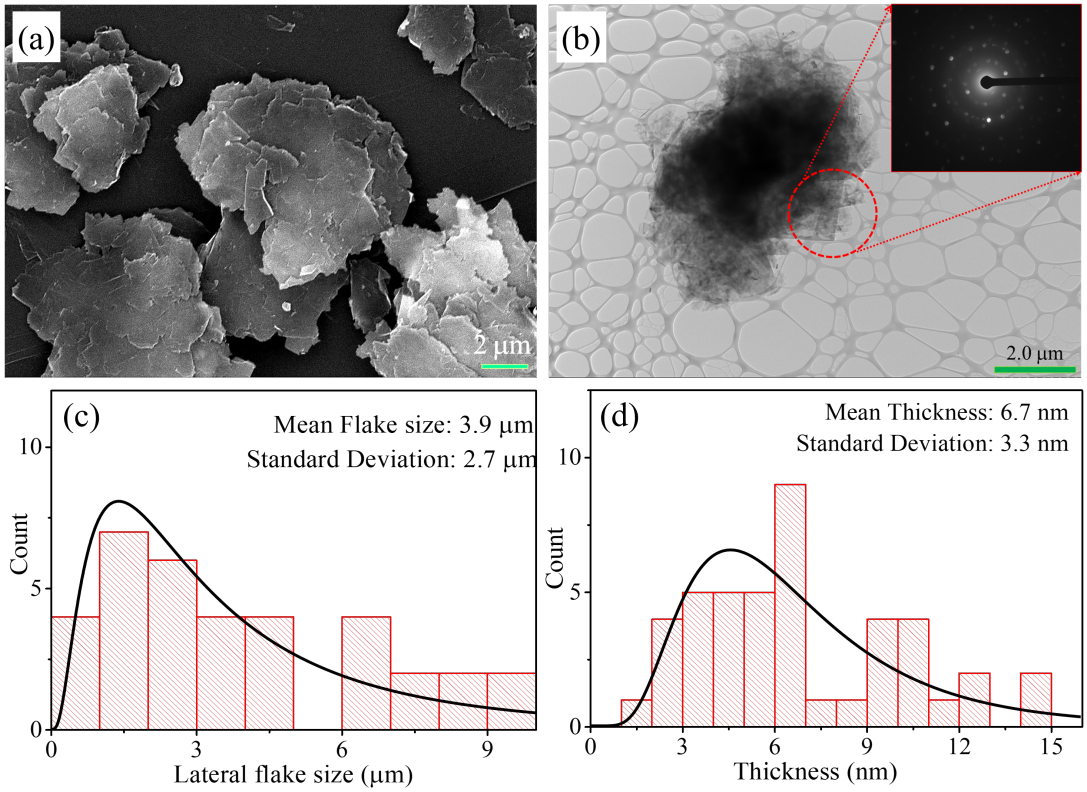

Figure 1. The initial SEM (a) and TEM (b) micrographs of the prepared fine graphite powders; the pattern of the SAED on the marked area is shown in the inset to panel (b). The lateral size and thickness distributions are given in panels (c) and (d), respectively; lines are the fits of the data with log-normal distribution function.

der Waals forces, allowing for easy sliding and separation of layers. When subjected to X-ray diffraction (XRD), graphite exhibits several characteristic peaks that can be attributed to the arrangement of its graphite layers. The XRD pattern of pyrolytic graphite typically consists of several peaks, with the most prominent ones being (002), (004), (006), (100), (101), (102), (110) and (112). Powder XRD is a powerful tool for detection of different crystalline components present in the sample: examining the positions, intensities, and shapes of the integral XRD pattern, it is possible to gain an insight to occurrence of impurity phases and structural modifications. Indeed, powder XRD data on NiO (Fig. 2(a)) and Gd_2O_3 (Fig. 2(b)) contaminated samples manifested weak though detectable patterns of these intentionally added impurities. The respective maxima are marked with red and blue indices in Fig. 2. Thus, NiO impurity reveals itself via (111), (200) and (220) peaks at their proper positions. Gadolinium oxide Gd_2O_3 occurrence is detected via (222), (400), (440) and (622) maxima. Moreover, we find that the gadolinium oxide experiences a mechanically-activated reduction to the elementary Gd-metal state. It should be noted that a search for the impurity manifestations in the XRD data was simplified by a fact that those impurities were either well known or expected.

In Fig. 3, the magnetization hysteresis loops of the prepared graphite samples are presented for either the nominally undoped (Fig. 3(a)) or intentionally contaminated with the transition metal NiO (Fig. 3(b)) and rare-earth metal Gd_2O_3 (Fig. 3(c)) oxides. The $M(B)$ curves at $T = 300\,\mathrm{K}$ in the field range of $-1\mathrm{T} < B < +1\mathrm{T}$ are presented with the subtracted linear in field contribution. The raw data, prior to the subtraction, is shown in the insets for each panel of Fig. 3. The linear contribution in fact is a superposition of two linear at room temperature terms with opposite slopes, diamagnetic (negative slope) and paramagnetic (positive slope).

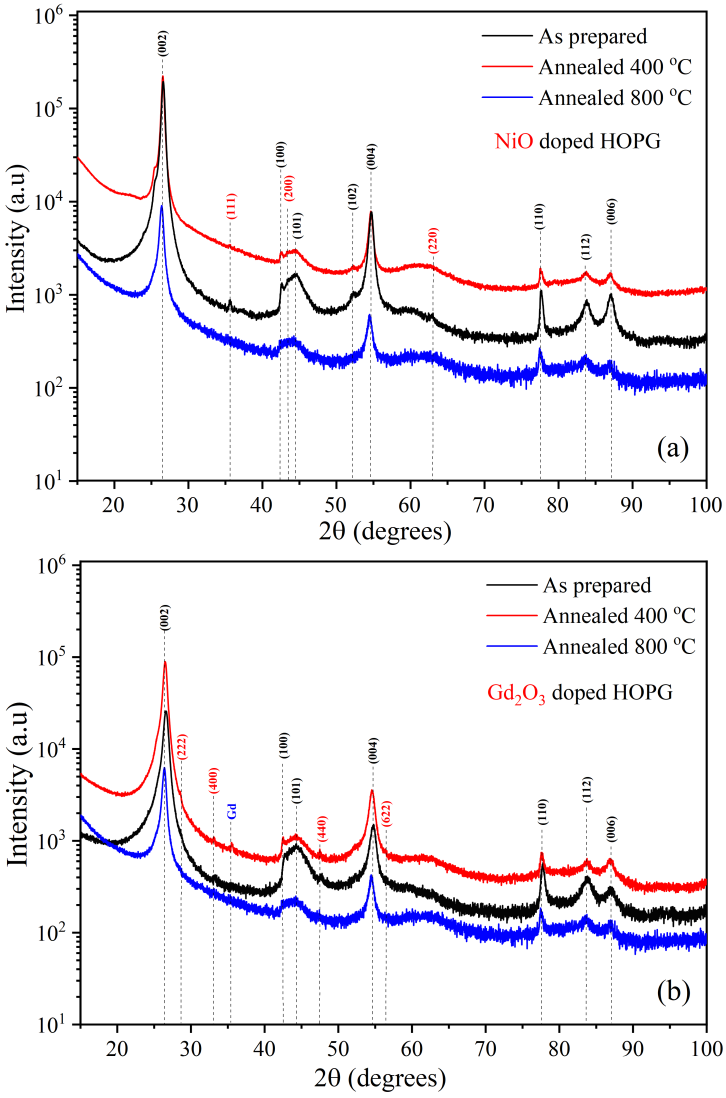

Figure 2. Powder X-ray diffraction patterns of the as prepared (black curve), annealed at 400°C (red) and 800°C (blue) samples of NiO doped (a) and Gd_2O_3 doped HOPG (b).

An integral quantity characterizing the linear contribution to the magnetization curve is its slope, or susceptibility, χ_{lin}. Its variation with doping and annealing is presented in Fig. 4. We find that annealing of any sample doesn't result in any strong modification of χ_{lin}. Prior to the heat treatment, the prepared samples had typical magnetic susceptibilities consistent with values reported in the literature for HOPG [3, 6, 7, 13, 15, 24]. The susceptibility χ_{lin} for all our samples before and after annealing are of the same order (10^{-6} emu$\cdot$g$^{-1}\cdot$Oe^{-1}). Contamination with NiO or Gd_2O_3 reduces the diamagnetic response, the latter - to a higher extent. This takes place evidently due to a paramagnetic signal of the impurities that is linear and has a positive slope. Oxide dopants NiO and Gd_2O_3 at room temperature are in different magnetic states: Gd_2O_3 is paramagnetic ($T_N = 17.2$ K) while NiO is antiferromagnetic ($T_N = 523$ K). Thus all Gd^{3+} ions possessing spin $S = \frac{7}{2}$ contribute to paramagnetic response of HOPG/Gd_2O_3 samples while only a small part of Ni^{2+} ions ($S = \frac{3}{2}$), most probably, from particles surface, decoupled from the antiferromagnetic core due to the structural disorder, lead to a weaker suppression of the diamagnetic response of HOPG/NiO sample.

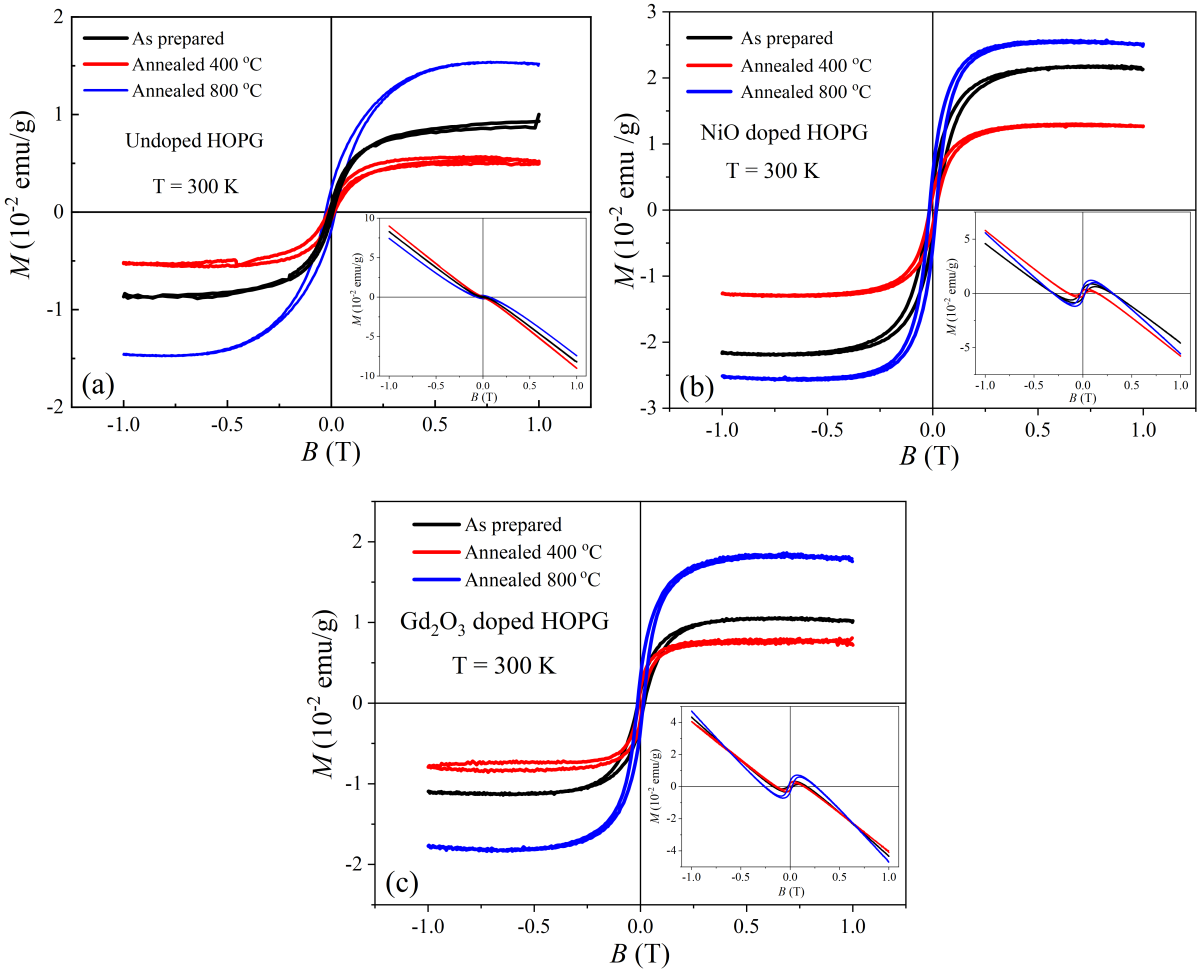

Figure 3. Magnetization curves at room temperature with the subtracted linear diamagnetic term for the undoped (a), NiO doped (b) and Gd_2O_3 doped (c) graphite flakes, before (black lines) and after the annealing at 400°C (red) and 800°C (blue). The as-measured signals are shown in the insets of each panel.

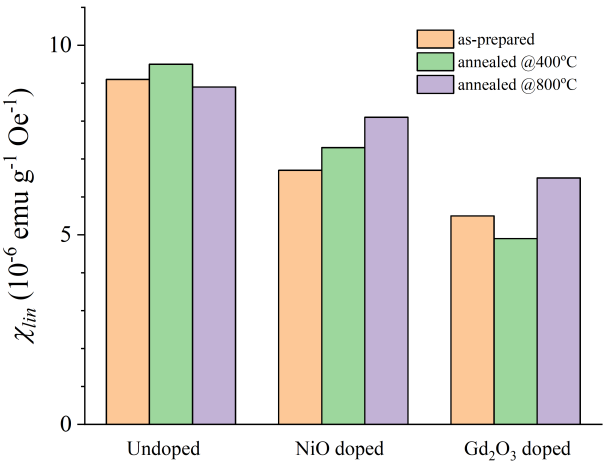

Figure 4. A histogram illustrating an evolution of the magnetic susceptibility characterizing the linear term of magnetization curves under annealing at 400°C and 800°C of the nominally undoped as well as NiO and Gd_2O_3 doped HOPG powders.

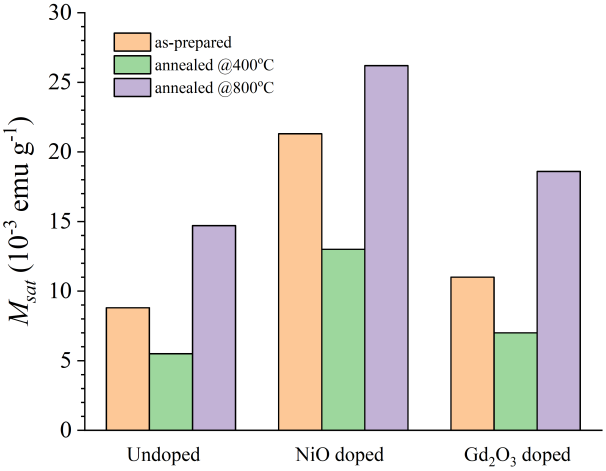

Figure 5. A histogram illustrating an evolution of the saturation magnetization under annealing at 400°C and 800°C of the nominally undoped as well as NiO and Gd_2O_3 doped HOPG powders.

As far as the nonlinear ferromagnetic response is concerned, all studied samples manifest qualitatively and quantitatively similar behavior (Fig. 3): hysteresis loops are smooth and round with the coercive field of 10 to 20 mT, and remnant magnetization one quater to one third of the saturation magnetization M_s. This nonlinear component saturates for most samples at ~ 0.5 T. Values of M_s for the whole series of samples are presented in Fig. 5. For each as-prepared sample, the evolution of M_s with thermal treatment is qualitatively the same: M_s drops by $30-40\,\%$ after annealing in vacuum at 400°C, and increases more than twice after annealing at 800°C. In this sense, the behavior of all three samples looks systematic. However, an influence of NiO or Gd_2O_3, in our opinion, can hardly be identified. Definitely, these impurities neither induce new magnetic responses nor enhance it drastically for doped samples compared with the nominally undoped one.

This result may have two general reasons: either the observed ferromagnetic response of HOPG powders is an intrinsic property of graphite nanoflakes (including various edge defects, terminations etc.) or it originates from an uncontrolled (and undetected) impurity whose influence on a magnetism of graphite is much stronger that an influence of nickel or cobalt oxides as well as the metallic Gd or Ni forming in samples from the oxides due to a reduction in a presence of carbon. We can claim for sure that ferromagnetic response appears after a grinding procedure as the bulk HOPG has not manifested any nonlinear magnetization responses prior to its processing. This does not exclude unintentional doping with the material of the mortar and pestle (agate, SiO_2). However, the usage of a new mortar and pestle pair (that had never been used for processing of potentially ferromagnetic materials) for grinding of the undoped sample and near-identical responses of this sample and the other two supports rather an intrinsic origin of the ferromagnetism of graphite than its induction by the impurities.

The saturation magnetization values differ noticeably, by $2-2.5$ times, for samples annealed at 400°C and 800°C. Assuming the room temperature of the graphite powder is its intrinsic property, we first recall that open hysteresis loop appeared after grinding the bulk HOPG to fine flakes. There are two factors that affect the ferromagnetic response. The first factor is the grinding process that primarily introduce defects mechanically to the HOPG structure. These defects can create localized magnetic moments and lead to the onset of ferromagnetic behavior. The second factor is the annealing of fine graphite powders at mild temperatures in a controlled environment that further modified magnetic behavior. A mild annealing process can promote

defects healing, recrystallization of flakes, and structural reorganization, leading to changes in the magnetic properties. Thus, annealing at 400°C can lead to the reduction or elimination of defects in the HOPG structure. As defects heal out, the density of magnetic moments associated with these defects decreases, resulting in a decrease in the saturation magnetization. Under annealing at elevated temperature of 800°C, the mobility of defects increases, and this may lead to an increased density of defects possessing magnetic moments. As the defects migrate and interact, the magnetic moments associated with the defects can align and contribute to a higher saturation magnetization. The alignment of magnetic moments can enhance the overall ferromagnetic response of the sample. Under annealing at very high temperatures ferromagnetic response vanishes as reported in [22]. In our opinion, annealing promotes the reorganization of the graphite lattice, which can affect the electronic and magnetic structure. Structural rearrangements can lead to changes in the density and arrangement of magnetic moments, influencing the saturation magnetization.

Thus, the conducted structural studies and magnetization measurements testify in favor of the fact that ferromagnetism of graphite nano-powders arising at their moderate annealing is a property of graphite and is not related to small impurities of ferromagnetic materials. The X-ray diffraction (XRD) analysis was conducted in the study to examine the related major peaks of the considered impurities (Gd_2O_3 or NiO) is an essential piece of evidence. The fact that the impurity-related peaks were detected in the XRD spectra while the magnetic properties remained consistent implies that the impurities introduced into the graphite structure are not the primary drivers of ferromagnetism. Instead, the data indicates that the impurities are largely inert in terms of contributing to the observed magnetic behavior.

Understanding that ferromagnetic behavior is inherent to graphite has important implications for potential applications. Intrinsic ferromagnetism in graphite flakes can be advantageous in various fields, including data storage, sensors, and spintronics. It offers opportunities for the development of novel materials and devices that harness these unique magnetic properties.

4. Conclusion

One of the key findings in our experimental observations is the remarkable consistency in the magnetization parameters across a series of fine graphite powder samples. Ferromagnetic response parameters including magnetic susceptibility, saturation magnetization and coercivity, are nearly identical, regardless of whether the graphite was or was not contaminated with Gd_2O_3 or NiO oxides during the grinding process. This uniformity strongly suggests that the origin of ferromagnetism in these samples is an intrinsic property of the graphite itself and does not solely originate from the addition of potentially ferromagnetic impurities.

Our results are in favor of the hypothesis that ferromagnetism of graphite nanoflakes is intrinsic to the graphite itself rather than related to the impurities. This implies that some aspect of the fine pyrolytic graphite nanoparticles, possibly related to their nanoscale structural defects, can be responsible for the magnetic behavior. Further research should aim at elucidating a specific mechanism or an origin of the intrinsic ferromagnetism within the graphite structure.

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