Magnetic Measurements of Graphene and Defected Graphene Generated by Laser Ablation Method

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ABSTRACT— **In this paper, the magnetic properties of carbon based material, graphene is studied, which is generated by laser ablation in cryogenic media. Transmission electron microscopy (TEM) and alternating gradient force magnetometer (AGFM) are applied to investigate the graphene morphology and magnetic properties, respectively. The graphene synthesized by the laser ablation method exhibits diamagnetic behavior. However the magnetic transition from diamagnetic to paramagnetic effect is lucidly observed by functionalizing the graphene sample with silver atoms.**

KEYWORDS: Alternating gradient force magnetometer (AGFM), Diamagnetic, Ferromagnetic, Graphene, Paramagnetic, Transmission electron microscopy (TEM).

I. INTRODUCTION

Two-dimensional (2D) crystalline materials have recently been identified and analyzed. First material in this new class is graphene, a single atomic layer of carbon. This new material has a number of unique properties, which makes it interesting for both fundamental studies and future applications. The electronic properties of this 2D-material lead to, for instance, an unusual quantum Hall effect. It is a transparent conductor, which is one atom thin. It also gives rise to analogies with particle physics, including an exotic type of tunneling, which was predicted by the Swedish physicist Oscar Klein.

In addition graphene has a number of remarkable mechanical and electrical properties. It is substantially stronger than steel, and it is very stretchable. The thermal and electrical conductivity is very high and it can be used as a flexible conductor.

The Nobel Prize in Physics 2010 honors two scientists, who have made the decisive contributions to this development. They are Andre K. Geim and Konstantin S. Novoselov, both at the University of Manchester, UK. Graphene is the flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, accounting for the basic building block for graphitic materials of all other dimensionalities. It can be wrapped up into 0D fullerenes, rolled as 1D nanotube or stacked in the faces of 3D graphite. A carbon-carbon distance of 0.142 nm in graphene monolayer. It is the first truly two-dimensional crystalline material and it is representative of a whole class of 2D materials including for example single layers of Boron-Nitride. And molebdynum disulfide (MoS_2), which is reported after 2004. Theoretically, graphene (2D graphite) has been studied for sixty years [1-3] and widely used for describing properties of various carbon-based materials. Graphene has a number of properties, which makes it interesting for several different applications. It is an ultimately thin, mechanically very strong, transparent and flexible conductor. Its conductivity can be modified over a large range either by chemical doping or by an electric field. The mobility of graphene is very high, which makes the material very interesting for electronic high frequency applications. Recently it has become possible to fabricate large sheets of graphene. Using near-industrial methods, sheets with a width of 70 cm have been produced. Since graphene is a transparent conductor it can be used in applications such as touch screens, light panels and solar cells, where it can replace the rather fragile and expensive Indium-Tin-Oxide (ITO). Flexible electronics and gas sensors are other potential applications. The quantum Hall effect in graphene could also possibly contribute to an even more accurate resistance standard in metrology. New types of composite materials based on graphene with great strength and low weight could also become interesting for use in satellites and aircrafts.

Graphene is produced as a powder and as dispersion in a polymer matrix, or adhesive, elastomer, oil and aqueous and non-aqueous solutions. The dispersion is stated by the manufacturer to be suitable for advanced composites, paints and coatings, lubricants, oils and functional fluids, capacitors and batteries, thermal management applications, display materials and packaging, inks and 3D-printers' materials, and barriers and films. The presence of any magnetic order is very challenging in the carbon-based materials i.e. carbon nanotubes, fullerenes, activated-carbon-fibers, graphite and Nano graphite, which make these carbon materials suitable for magnetic applications. The origin of magnetism in materials lies in the orbital and spin motions of electrons and how the electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials respond to magnetic fields. The magnetic behavior of materials can be classified into different groups of diamagnetism, paramagnetism and ferromagnetism. Diamagnetism is a fundamental property of all matter, although it is usually very weak. It is due to the non-cooperative behavior of orbiting electrons when exposed to an applied magnetic field. Diamagnetic substances are composed of atoms, which have no net magnetic moments (ie., all the orbital shells are filled and there are no unpaired electrons). However, when exposed to a field, a negative magnetization is produced and thus the susceptibility is negative. In case of paramagnetic materials, some of the atoms or ions in the material have a net magnetic moment due to unpaired electrons in partially filled orbital's. However, the individual magnetic moments do not interact magnetically, and like diamagnetism, the magnetization is zero when the field is removed. In the presence of a field, there is now a partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility. Unlike paramagnetic materials, the atomic moments in ferromagnetic materials exhibit very strong interactions. These interactions are produced by electronic exchange forces and result in a parallel or antiparallel alignment of atomic moments. The elements Fe, Ni, and Co and many of their alloys are typical ferromagnetic materials. In case of Carbon structures the d and f shell electrons, which are responsible for the magnetic coupling in conventional ferromagnets are absent. Despite both theory and experiment suggest that a magnetic order exist in these carbon structures under particular circumstances. Graphene has magnetic properties due to its unique band structure. The magnetic response in the intrinsic non-magnetic graphene by the introduction of various defects appears. Defects in ideal graphene can be introduced by both vacancies and external doping.

Many experimental works have reported the existence of magnetism in carbon materials by electrons or ions irradiation. The common feature of these defects is that carbon atoms are removed from the graphene sheet, which gives quasilocalized states at the Fermi level. This may lead to the generation of novel spintronic devices where spin and charge can be correlated together [4]. Room-temperature ferromagnetism has been observed in both pristine and ion irradiated highly oriented pyrolytic graphite (HOPG) [2-4], reduced graphene oxide (RGO) flakes [5, 6], graphene nanoribbons [7] and hydrogenated graphene

[8,9]. Theoretical and experimental studies have demonstrated the coexistence of ferromagnetic effect along with antiferromagnetic one in the graphene-related materials attributing the presence of various defects, disordering and edge states [10-15]. On the other hand, some studies have recently demonstrated that no ferromagnetism was detected even at the temperature down to 2 K in graphene nanocrystals [16]. In contrast, graphene is a strong diamagnetic with a weak paramagnetic coupled component [16]. Further investigations have shown that missing C atoms, called vacancies, and additional atoms bonded to the lattice, the adatoms could lead to the generation of spin-half paramagnetism but still no ferromagnetism was detected down to liquid helium temperatures [17]. Therefore not only defects can produce magnetism, atom or molecule adsorptions also can lead to the occurrence of magnetic moments.

Yazyev *et al*. and Boukhvalov *et al.* [17] have studied the adsorption of hydrogen atoms on graphene. Their results confirmed that such adsorption will lead to magnetic moments on neighboring carbon atoms, and such spin-polarized states are mainly localized around the adsorptive hydrogen. Another feature is that the sp^2 carbon atoms will become sp^3 carbon, and make the graphene lose the symmetry. The room-temperature ferromagnetism in graphene was attributed to the presence of magnetic impurities such as micrometer-sized magnetic particles within graphene crystals [17]. However, most of the investigated graphene-related materials that exhibit dominant ferromagnetic properties were originated from GO. During the preparation of GO by the modified Hummers' method, graphitic flakes generally confront strong acid and oxidizer treatment followed by repeated centrifuging and washing. Afterwards, GO flakes will be re-dispersed in water by sonication and further assembled into macroscopic membranes by drop-casting or vacuum filtration, etc. The relationship among paramagnetism, diamagnetism and ferromagnetism in graphene materials has not been well understood yet. One of the theoretical approaches usually adopted in this field is the density functional theory (DFT). These calculations attribute the source of magnetism to localized electronic states that are spin polarized which occur at the level of the Fermi energy. In the case of nanostructured graphene, the edges of the honeycomb lattice introduce the magnetic moments in zigzag configuration, while zero magnetic moment looks like the armchair edges [18]. Magnetic moments also originate from localized states in the presence of point defects in the graphene lattice, like vacancies and adatoms [19, 20]. In the light of these findings, the introduction of defects in graphene became a tool to investigate the presence of relevant magnetic phenomena. The irradiation by ions of different atomic species is a useful experimental method to create defects in the carbon lattice, although not all of them are magnetic as is the case for interstitials and some types of multi-vacancies [21].

In this work, graphene is synthesized by laser ablation method and then defected by silver atoms to investigate the corresponding magnetic properties accordingly. Synthesizing other carbon nanostructures and studying their physical properties were carried out in our previous works [22, 23].

II. EXPERIMENTS

There are different methods to synthesize graphene. Most of the techniques for graphene fabrication suffer from several drawbacks such as high synthesis temperatures, high vacuum conditions, low yield and difficulty to control the size and long growth duration, which exhibit challenges for the material integration, cost. Here we used a simple and fast technique for the graphite exfoliation by laser in cryogenic liquid. The remarkable advantage of this method is the fabrication of graphene without need to high vacuum devices and additional chemical components [24]. Graphene is synthesized based on the pulsed laser ablation of graphite target inside the cryogenic liquid using the pulsed nanosecond Q-switched Nd:YAG laser at 1064 nm with 100 mJ pulsed energy and 10 nsec duration. The mechanism of the graphene formation is proposed based on the penetration of liquid nitrogen into the interlayer spacing of graphite and the subsequent expansion to gas phase during laser heating. Transmission electron microscopy (TEM) and alternating gradient force magnetometer (AGFM) are employed to study graphene morphology and magnetic properties.

III. Results and Discussion

For the TEM experiments the graphene sample were collected directly from the solution by dipping commercially available TEM copper grids with amorphous holey carbon support films. The flakes are typically several μm across and less than 100 nm thick; they consist of one or more graphitic *c*-planes. Figure 1 shows TEM image of the graphene sample synthesized by laser ablation method, where layers of graphite are visible.

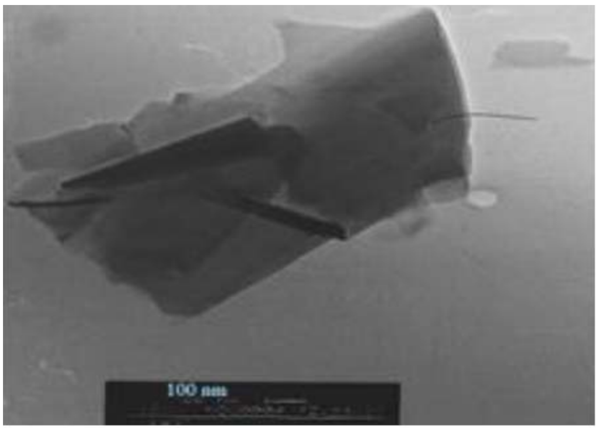

Fig. 1 TEM image of graphene synthesized by laser ablation method.

Diamagnetism, paramagnetism and ferromagnetism can coexist in graphene derivatives and magnetic transition among the three aspects can be achieved depending on edge states, vacancies, chemical doping and the attached functional groups [25]. Studies show that magnetization signals M were small (typically, less than ~0.1 emu/g, i.e., less than 0.1% of the magnetization of iron), a consensus is emerging that, despite the absence of d- or f- electrons, magnetism in carbon systems may exist under a variety of experimental conditions. Furthermore, it is shown theoretically that atomic scale defects in graphene-based materials, e.g. adatoms and vacancies, can carry a magnetic moment μ of about one Bohr magneton, μ_B. Also, extended defects such as edges can give rise to M. The possibility of long-range magnetic ordering has been predicted for randomly distributed point defects and grain boundaries, and bilayer graphene was suggested to exhibit spontaneous many-body ferromagnetism. All this leaves little doubt that magnetism in graphene-based systems can in principle exist, although the whole subject remains highly controversial, especially as concerns (i) the role of environment and magnetic contamination and (ii) the mechanism that could lead to the strong interaction required for ferromagnetism at room Temperature.

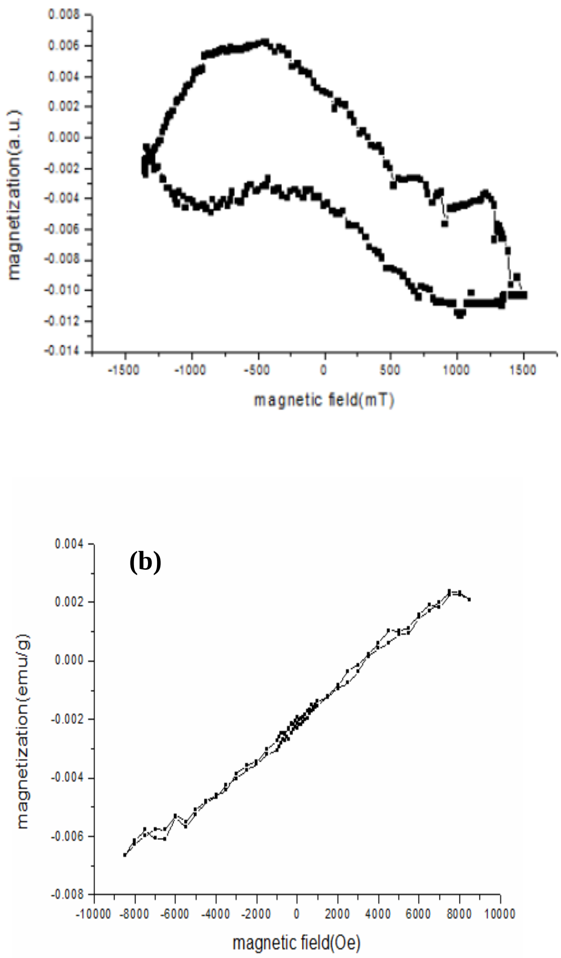

Fig. 2. Magnetization versus magnetic field of (a) graphene generated by laser ablation method and (b) graphene powders fabricated by chemical method.

Figure 2.a plots the graph of magnetization versus magnetic field for graphene sample prepared by laser ablation method. It is lucid to find diamagnetism behavior in the sample. Fig 2.b depicts similar magnetization for chemically synthesized graphene in comparison. This is consistent with other reports, which shows magnetism in the pristine graphene [26]. Beside the negative magnetization in this curve, there is a hysteresis loop that may be related to superconductivity of highly ordered pyrolytic graphite (HOPG) sample [27]. In order to improve the magnetism in graphene, it is possible to insert defects in graphene lattice.

Inducing the magnetism by defects can be described by Lieb's theorem of bipartite system such as graphene, derived from the tight binding Hubbard model. According to this theorem $S= \frac{1}{2} \mid N_A-N_B \mid$ give the total spin of lattice where NA and NB are the numbers of sites in sub-lattices A and B, respectively. For the perfect graphene ($N_A=N_B$), total magnetic moment is zero and for each point defect S=1/2 expected in the system [28]. Here, silver atoms were used to induce magnetism in graphene, which has one free electron in its valence band, therefore bonds to free $2p_z$ orbitals and changes hybridization of graphene from sp^2 to sp^3. This breaks the sublattice symmetry of the graphene lattice and thus total spin becomes non-zero with a net magnetic moment. Figure 3 illustrates the schematic of bonding of silver atom to graphene lattice.

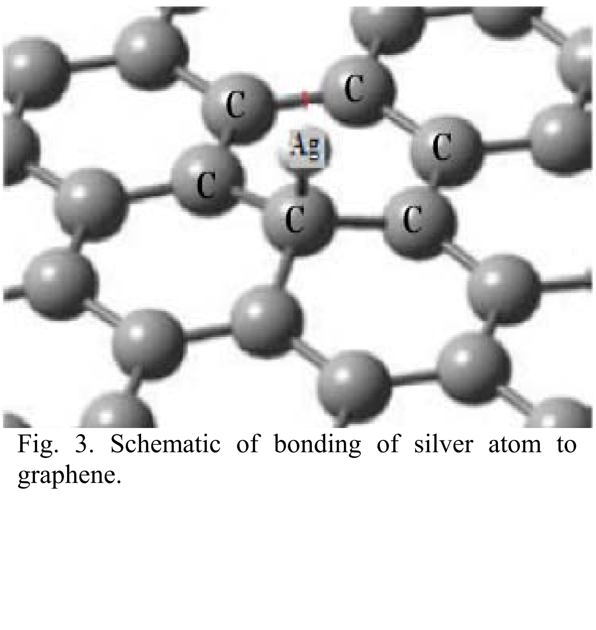

Fig. 3. Schematic of bonding of silver atom to graphene.

Figure 4 illustrates a graph of magnetization versus magnetic field for defective graphene. The susceptibility of a sample is approximately in the range of $10^{-7}$to demonstrate stronger paramagnetism in comparison of the data reported previously by other group [26]. There is a positive slope around zero which arises from an intrinsic magnetic moment caused by the defects [29].

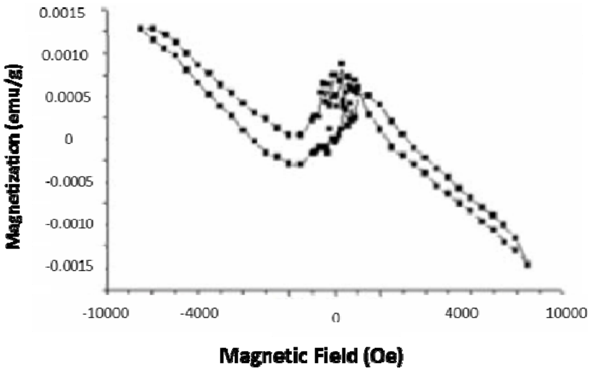

Fig. 4. Magnetic curve of hybrid graphene (G+Ag).

IV. CONCLUSION

The development of this new material, opens new exiting possibilities. As it was mentioned, graphene is the first crystalline 2D-material and it has unique properties, which makes it interesting both for fundamental science and future applications. One physical property that so far has been missing from this impressive list is magnetism. In its pristine state, graphene exhibits no signs of the conventional magnetism usually associated with such materials as iron or nickel. But recent researches on magnetic properties of graphene reveal magnetic behavior in graphene in some experimental conditions, which makes this 2-D carbon material promising candidate for spintronics applications.

Here, the magnetic properties of graphene synthesized by laser ablation and graphene functionalized with silver atoms are investigated. In order to compare the magnetism of graphene prepared by laser ablation and chemical method, magnetic measurements of these samples are also carried out. The results show that the graphene generated by laser ablation method is strongly diamagnetic and its structure resembles to possess high quality and close to low defect lattice however, the graphene generated by chemical methods is in the ferromagnetic state. Therefore, there are many defects in the system. In order to improve the magnetic properties of laser-fabricated graphene, hybridization with silver atoms was carried out. Metal on graphene growth is one of the current research interests, aiming at improving and manipulating the electronic and magnetic properties of graphene through metal atom adsorption or doping to meet various requirements in device applications. The results suggest that the graphene synthesized by laser ablation exhibits diamagnetic behavior. However, after functionalizing the same sample with silver atoms the transition from diamagnetism to paramagnetism is observed. Therefore comparing Figures 2.a and 4 we found that the hysteresis loop is shrinking in case of hybrid graphene (G+Ag). The net magnetic moment around zero fields and the corresponding susceptibility increment are strong evidence of this phenomenon.

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