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# Magnetoresistance studies of MeV ranged $^{1}H^{+}$ and $^{12}C^{+}$ ion irradiated HOPG flakes

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## ABSTRACT

2 MeV protons and 1 MeV carbon ions are bombarded on highly oriented pyrolytic graphite (HOPG) samples and their electronic transport measurements are carried out in the presence of magnetic field. The Magneto-Resistance (MR) measurements show measurable hysteresis in the resistance value after ion beam irradiation for the in-plane magnetic field direction as well as for the out-of-plane field direction. The MR depends on the thickness of the flake and the method of its separation from the bulk HOPG. The results substantiate that the ferromagnetic coupling between the magnetic moments at the vacancy defect sites in HOPG sensitively depends on the average defect separation. The average defect separation range of 1.7–0.5 nm allows only a part of the 40 μm thick proton beam irradiated sample to go for ferromagnetic ordering. Similar conclusions are drawn from carbon ion irradiated HOPG flake. The irradiation increases the resistance of the flake as well.

## 1. Introduction

Magnetism in different forms of carbon has been a very interesting research area for quite some time [1,2]. The mechanism of appearance of magnetic moments in the s–p systems and their interaction has been studied theoretically and experimentally using a number of tools [3–6]. It has been shown that graphite can exhibit ferromagnetic ordering upon optimum irradiation by Ion beams [7–9]. Highly Oriented Pyrolytic Graphite (HOPG) has given us a good opportunity and challenge in revealing the magnetic characteristics in various conditions. Due to fascinating transport properties of graphite and its dependence on various geometrical factors like sample thickness, width etc., it has been extensively investigated [10–12]. The magnetism seems to appear due to various kinds of defects, crystallite boundaries and so on [13,14]. As a result, varied experimental findings have been reported in different studies depending on the subtle experimental parameters [10,15].

From several studies using ion beam irradiation, it is believed that the vacancy defects created by the energetic ions going in HOPG creates magnetic moments due to unfilled p orbitals, and if the separation between such defects falls in a narrow favorable window, the moments so created can order ferromagnetically [16,17]. Another possible mechanism for magnetism in ion-irradiated HOPG, that has been suggested, is the cracking of adsorbed hydrogen molecules on surface by the irradiation and subsequent chemisorptions [18]. In any ion irradiation experiment, the defect density itself has a distribution in the collision cascade along the ion beam direction and hence the magnetization exhibited sensitively depends on the thickness of the sample, ion energy and ion fluence. The regions across the sample depth with very small defect density may not contribute towards magnetic ordering due to large separation between the magnetic moments and those with too large defect density can partially amorphize the crystal itself and may not induce ferromagnetic interaction [7].

The magnetic ordering in such ion irradiated HOPG samples has been largely investigated using SQUID (Superconducting Quantum Interference Device) and VSM (Vibration Sample Magnetometer). Magento-Resistance (MR), defined as $[R(B)/R(0)-1]\times 100$, where conduction electrons interact with the magnetic defects, is another sensitive method to look at the magnetic ordering, which has not been utilized extensively. Zhang et al. [19] have studied powdered graphite of several particle sizes and have found negative MR in the sample with average particle size of 30.2 nm, while for samples with larger particle sizes ($>1$ μm) MR is positive. Various length scales viz: de Broglie wavelength, mean free path and 2D Fermi wavelength

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are of the order of few micrometer for graphite due to electrons behaving like mass-less Dirac fermions (in the basal plane) and low charge carriers density of Graphite [11]. Therefore sample size plays a crucial role in exploring transport properties of thin graphite flakes [10,15]. Low temperature MR studies of unirradiated HOPG and Kish graphite have been performed by Kaburagi et al. [20] depicting the importance of structural perfections of graphite. HOPG is found to show anisotropic MR which is large and positive when the field is applied perpendicular to the basal planes (out-of-plane) and is almost negligible when it is parallel (in-plane) to the basal plane [16,21]. Kopelvich et al. have measured the out-of- plane MR and have found that the MR is positive for fields up to a critical value $B_0$, beyond which it becomes negative [22]. Kempa et al. have found positive MR for out-of-plane magnetic field, at least up to 10 T [23]. Barzola-Quiquia et al. used characteristics of MR to show the existence of granular superconductivity and magnetic order in HOPG flakes [24]. Granular superconductivity was also observed by Dusari et al. in HOPG samples with special constrictions made on the sample [15]. The study by Esquinazi et al. [16] showed that when HOPG sample was irradiated with 2 MeV protons with 100 pC/$\mu$m$^2$ of fluence, a negative MR for in-plane field appeared. The MR curve also showed hysteresis with the magnetic field sweep, establishing the ferromagnetic ordering. It seems that in HOPG the MR results sensitively depend on sample shape, dimensions and defect structure inside. More data on different types of sample would be useful to understand the actual behavior of MR in this graphite structure.

In the present work we investigate MR of two samples of HOPG, having thicknesses around 40 $\mu$m and 10 $\mu$m, each prepared in a different way. The samples were also irradiated with 2 MeV $^1H^+$ and 1 MeV $^{12}C^+$ ions and their subsequent effect on MR is investigated for both in-plane and out-of-plane orientations. The thickness of the first sample is chosen to be close to the range of the proton beam in it while that of the other sample is several times larger than the range of 1 MeV $^{12}C^+$ ion in it.

## 2. Experimental

HOPG samples of grade one quality (angular spread less than 1°) with impurities less than 10 ppm, procured from SPI supplies were used. For transport measurements, two samples were prepared, ‘S1’ by scalping a thin flake from the bulk HOPG using a non magnetic tool and ‘S2’ by peeling off a thin layer from the bulk using a scotch tape and then adhering it onto $SiO_2$/Si substrates by GE varnish. The thickness of S1 was about 40 $\mu$m as measured from the SEM image. Thickness of S2 could not be measured directly but is estimated from the resistance measurement on the present sample and the order 0.5–2.0 $\mu\Omega$ m of resistivity reported for HOPG samples [23]. The value obtained is around 10 $\mu$m (taking resistivity to be 1.5 $\mu\Omega$ m) which is likely to be an overestimate as because of the small size and mechanical stresses during peeling off, resistivity could go up and the thickness would be less than this. The relevant point is that it is several times thicker than the range of 1 MeV $^{12}C^+$ ions (1.4 $\mu$m) with which it is irradiated. For four probe measurement, 100 nm silver parallel stripes were made on the samples S1 and S2 by masked thermal evaporation. The schematic of the four probe measurement geometry is shown in Fig. 1.

Ion-beam-irradiation experiments were performed at Ion Beam Complex for Science, Engineering and Technology at IIT Kanpur, with a 1.7 MV Tandetron particle accelerator (from High Voltage Engineering, Europa, B.V.) micro-beam line. Quadrupole triplet electromagnetic lens capable of focusing low-mass ions ($Z \leq 6$), is utilized for the micro-beam line. Protons were extracted from hydrogen plasma, whereas carbon ions were extracted from an Source of Negative Ions by Cesium Sputtering (SNICS) source using high-purity graphite powder as the target. The current of the focused micro ion beam in the range of 1–20 nA at the sample was used for irradiations. An electromagnetic scanner was utilized to scan the ion beam over the HOPG sample in a 1.0 mm × 1.0 mm area for the desired ion-fluences. The same process was repeated to scan the remaining 1.0 mm × 1.0 mm portion of the sample. The scan was repeated to irradiate the graphite stripe between the two voltage stripes, covering the whole width of the sample.

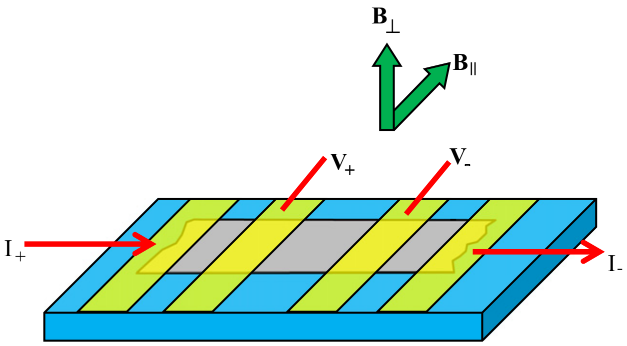

**Fig. 1.** Schematic diagram of the HOPG sample (Gray) with four metallic silver stripes (yellow) on $SiO_2$/Si substrate prepared for four probe transport measurement in in-plane and out-of-plane applied magnetic field. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Low temperature transport measurement in the presence of magnetic field (up to 5 kG) was performed with the help of Keithley source meter and 4.2 K closed cycle refrigerator, with a 0.5° precision rotation capability of the external magnet. As shown in Fig. 1, the applied magnetic field is perpendicular to the direction of current for both the in-plane and out-of-plane geometries. To study the effect of the ion-fluence, low temperature MR measurements were performed on the sample, before and after irradiation in similar conditions.

## 3. Results and discussion

### 3.1. MR of unirradiated samples

As discussed in the experimental section, the Magneto-Resistance(MR), defined as $[R(B)/R(0)-1] \times 100$, of the two samples S1 and S2 were measured using four probes with $B$ field parallel to the basal planes (in-plane) at 20 K. The results are shown in Figs. 2(a) and (b) for fields up to 4.5 kG. Both the samples show positive MR, the magnitude being much larger for the sample S2 (thickness $\sim$10 $\mu$m), as compared to the case of sample S1 (thickness $\sim$40 $\mu$m). The value of MR at 4 kG is 0.8% for S1 and 12% for S2. The MR shows no hysteresis in S2 as the field is swept between positive and negative maximum values. For the sample S1, a very small hysteresis is seen in the field range between $-2$ kG and 2 kG. This curve is asymmetric in positive and negative sweeps and shows separation for only small values of the magnetic fields ($-2$ kG to $+2$ kG). Similar asymmetry has also been observed in earlier studies of MR in HOPG [16,17]. The reason of such a behavior is not well understood.

The positive MR in unirradiated HOPG sample with $B$ parallel to the basal plane is in contrast with the results of Esquinazi et al. [16], where they report almost no MR in unirradiated HOPG film of thickness 10 $\mu$m with similar field orientations. However different natures of MR in HOPG have been reported in literature. For 1 mm thick HOPG, Kopelvich et al. found positive MR [22] with $B$ parallel to the basal plane, which increases with temperature. The MR is