Looking for ferromagnetic signals in proton-irradiated graphite

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1 Introduction

Pure graphite, the stable crystalline allotrope of carbon at room temperature and ambient pressure, is known to exhibit a strong and anisotropic "textbook" diamagnetism, due to its delocalized π electrons. Nevertheless, in the last two decades several researchers have reported more or less clear evidences of ferromagnetic behaviour in carbon at room temperature. We might mention the work by japanese groups [Mur91, Mur92], who observed it in amorphous carbon (relatively rich in hydrogen). The origin of this ferromagnetic behaviour could be theroretically justified as arising from the mixture of sp^2 and sp^3 bonding in carbon structure [Ovc88]. More recently, new findings of this kind have appeared in the literature, as the presence of ferromagnetic signals in some polymerized fullerenes reported by Makarova et al. [Mak01], or that found in proton-irradiated Highly-Oriented Pyrolitic Graphite (HOPG) by the group led by Esquinazi [Esq03, Han03]. In the latter experimental work, the analysis of possible magnetic impurities has been much more rigorous as to overcome the natural skepticism arose by the former experiments. Moreover, several theoretical works seem to support the importance of disorder [Voz04] and/or of vacancy-hydrogen complexes [Leh04] for the appearence of magnetic moments in graphite.

The interest in the possibility of producing organic materials with magnetic properties is obvious. Therefore, we have undertaken a joint research line to study this subject, by making use of the 5 MV tandem ion-accelerator hosted by the CMAM in the Universidad Autónoma de Madrid. At the same time of the ion implantation, the PIXE technique allows to determine in situ the amount of magnetic impurities in the sample, a crucial issue given the weakness of the reported ferromagnetic signals. The possible existence of the latter have been studied through SQUID magnetometry, Magnetic Force Microscopy (MFM) and magneto-optic Kerr effect (MOKE).

2 Experimental

High purity HOPG was used (NTI-Europe, ZYA quality, $0.4 \pm 0.1°$ rocking curve). Proton and/or carbon irradiations were conducted in a 5 MV tandem ion-accelerator (HVEE, using a Cockroft-Walton power supply system). Particle Induced X-ray Emission (PIXE) measurements allowed us to assess the amount of local concentration of heavier impurities. In some cases, we employed a fine square mesh of copper (G2000HS, SPI, with a pitch of 12.5 μm, with separating copper bars of 5 μm and squared holes of 7.5 μm each side) as a mask onto the irradiation area. Measurements of the total magnetic moment of the samples were performed with a SQUID magnetometer from Quantum Design. Possible ferromagnetic behaviour at the surface of the irradiated samples was studied by means of a Magnetic Force Microscope (MFM) from Nanotec Electronica S.L., operating under externally applied magnetic field [Ase00] at ambient temperature. In all experiments, a double-step procedure was employed: First, a simple topographic scan is taken by mantaining a constant amplitude of oscillation of the cantilever, very close to the surface. Afterwards, long-range interactions are measured in a second scan with no feedback, following the topography of the sample and measuring the frequency shift that is proportional to the magnetic force gradient. This second scan is performed by retracing the tip tens of nm from the sample in order to avoid the topographic interaction. We have also conducted magneto-optic measurements by using a high resolution vectorial Kerr set-up [Cam05].

3 Results and discussion

First of all, we cut HOPG samples with a typical surface area of $5 \times 3.3\,\mathrm{mm}^2$ and 0.2–0.3 mm thick, using clean diamond wire. We conducted ion-beam irradiation of H^+ protons of 3 MeV energy, in high vacuum. Montecarlo SRIM simulations indicate a corresponding implantation depth of $75.3 \pm 1.3\,\mu$m for the H^+ ions. Spot size was here always about 1 mm^2. In Fig. 1, we show the measured magnetization of the samples, with magnetic fields applied parallel to graphene planes, after subtracting the linear (negative) diamagnetic background, expected for bulk, pure graphite. Total irradiated doses ranged $40 - 1000\,\mu$C. As can be seen, in all cases a (weak) ferromagnetic curve is observed, with the sample of intermediate irradiation dose, $200\,\mu$C exhibiting the higher ferromagnetic signal. Nevertheless, we found somewhat surprisingly that also a non-irradiated HOPG sample exhibit some ferromagnetic signal,

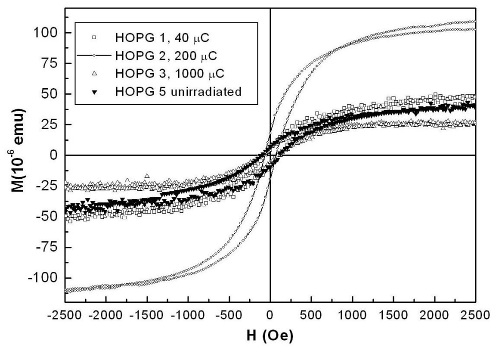

Fig. 1. SQUID measurements of the total magnetic moment of differently irradiated HOPG samples. See legend for ion-doses implanted. A linear diamagnetic background has been subtracted in all curves to show up the ferromagnetic contribution

comparable with the samples of lesser magnetization. We discard the possibility of all this behaviour being due to magnetic impurities, since our PIXE experiments performed on some of these samples always gave concentrations below 10 ± 4ppm of Fe element, and indetectable for other magnetic impurities. We believe that these observations simply confirm the findings of ferromagnetic behaviour in many non-irradiated HOPG samples, with different kinds of preparation quality, structural vacancies or disorder, as found by Esquinazi and co-workers [Esq02]. However, our first experiments using MFM

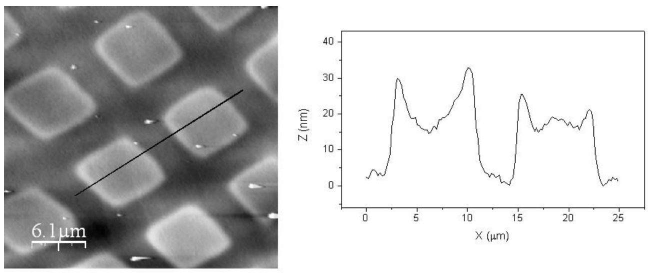

Fig. 2. Topographic profile of a HOPG sample irradiated with a copper mask with a dose of 150 μC of C^{4+} carbon ions of 25 MeV, and 225 μC of H^+ protons of 1.25 MeV (see text for details)

on these proton-irradiated samples, as on other ones irradiated in air with ion-beam spots smaller than 100 μm, provided no clear evidence of magnetic behaviour at the surface of proton-irradiated regions, in contrast to earlier

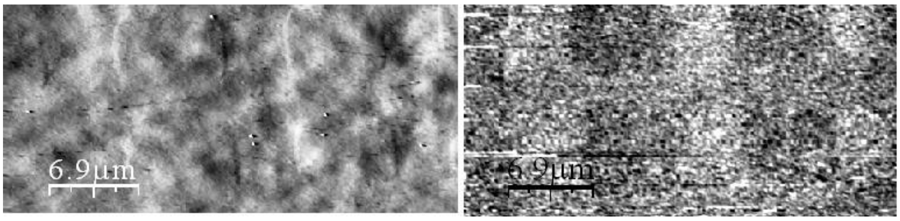

Fig. 3. Topographic image (left picture) and corresponding magnetic-contrast image (right picture) taken after applying an external magnetic field of 3 kOe to the same sample shown in Fig.2

reports [Esq03, Han03]. MOKE experiments performed in the same samples also gave negative results, always a pure linear diamagnetic curve was obtained. This is not too surprising, since the found ferromagnetic contributions superimposed on a large diamagnetic signal are very weak. Moreover, it is not clear what should be its relative strength at the superficial regions probed by these techniques.

In order to improve the layout of the samples surface to have a better contrast for MFM studies, we decided to use a grid or mask of copper. Thus, we put several grids of a fine copper mesh on one 1 cm^2 HOPG sample to be irradiated. The squared holes were of 7.5 μm $\times$ 7.5 μm with copper separating bars of 5 μm and 20 μm thick. In the experiments shown here, all studied sample regions were first irradiated with a dose of 150 μC of C^{4+} carbon ions impinging on the sample with an energy of 25 MeV, the spot size being around 1 mm^2. Hence the carbon ions were to stop at the middle of the depth of the copper separating bars. Through the holes of the grid however, these carbon ions will penetrate the HOPG sample with a calculated implantation range of 20.3 μm. In one region of the sample, a second irradiation was then conducted. A dose of 225 μC of H^+ protons was implanted, with an energy of 1.25 MeV chosen, so that the protons also stop at mid depth of the copper separating bars, whereas through the holes the penetration into the HOPG sample would be of about 20.0 μm. The surface topography of the latter sample after both consecutive ion irradiations and removing of the mask is shown in Fig. 2, where the topographic modifications induced by the irradiations are seen to clearly follow the pattern of the copper grid. Fig. 3 shows a clear magnetic-contrast pattern in the ion-irradiated spots. In contrast to this case, in the region of the sample were only the first carbon irradiation was performed, no magnetic features were observed, as can be seen in Fig. 4. MFM probes with different magnetic moment [Ase06] have been used in order to enhance the tip-sample interaction. This seems to support the relevant role played by H^+ ions in promoting ferromagnetism in carbon.

(a)

(b)

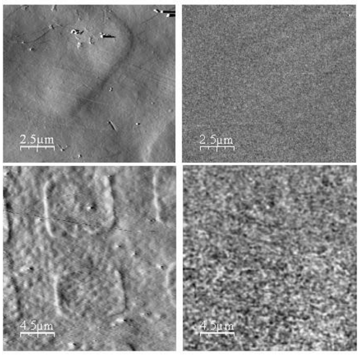

Fig. 4. Topographic images (left picture) and corresponding magnetic-contrast images (right picture) taken on a HOPG sample irradiated through a copper mask, with a dose of 150 μC of C^{4+} carbon ions of 25 MeV by using (a) a Mesp-LM MFM probe and (b) a MESP MFM probe from Veeco

4 Summary and conclusions

We have presented some representative experimental results found in proton- and carbon-irradiated HOPG samples, aiming to confirm or disregard the existence of ferromagnetic behaviour in pure carbon. To address that, we have combined macroscopic, bulk magnetic measurements (SQUID) with microscopic ones (MFM, MOKE). In brief, we have confirmed the existence of ferromagnetic features, both at macroscopic and microscopic scales. Nevertheless, the produced effects are still so weak, and the variables involved so many and unknown, that much more systematic studies are needed.

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