ION IRRADIATION INDUCED MAGNETISM IN CARBON-BASED COMPOUNDS

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Introduction

Because of the biological compatibility, light weight and low cost, the possibility of having a room temperature carbon-based metal-ion free magnet attracts currently the interest of the scientific community. The search for magnetic ordering in carbon-based materials started, however, more than 15 years ago as Makarova [1] recently reviewed in detail. First claims on the existence of carbon-based ferromagnets with room temperature spontaneous magnetization were published beginning of the 90's [2-4]. Some of the reports of carbonaceous materials show a saturation magnetization at room temperature M_s ~ 10 emu/g [3], just a tenth of that for magnetite (Fe_3O_4)! Theoretical work [5-7] pointed out on the possibility of having ferromagnetic carbon with a large magnetization (larger than α-Fe !). Ferromagnetic loops up to 800 K were reported in photo-assisted polymerised fullerene C_{60} [8]. At room temperature the magnetic samples showed a saturation magnetization M_s ~ 0.15 emu/g, which would indicate a magnetic moment of about 0.1 μ_B per C_{60}. This result has been recently reproduced independently [9]. A ten times larger saturation magnetization was found in hydrofullerite $C_{60}H_{24}$, however the magnetization was not stable at room temperature after one year [10]. In spite of the above cited work this topic was not taken into account seriously by the main stream of scientists working on magnetism. We guess that poor reproducibility added to an insufficient characterization of the impurity concentration at every step of the sample preparation and measurement were the reasons that hindered a broad discussion on the magnetism in carbonaceous materials.

In the early work on magnetism in carbonaceous samples [2,3], the role of hydrogen was not clearly stressed. Recently published work using a STM and AFM indicates that hydrogen atoms cause long-range electronic effects in graphite, in the range of 20 to 25 lattice constants [11]. Furthermore, muon spin rotation and relaxation experiments in graphite indicate the formation of a local moment around a positive muon, which has virtually the same electronic structure as hydrogen [12]. These works added to the recently published theoretical result on the ferrimagnetism with 100% spin polarized band at the Fermi energy for a mixture of mono- and di-hydrogenated carbon edges in graphene layers [13], indicating clearly that hydrogen can have a much more drastic effect on the electronic properties of carbon samples than one ever thought before. The recently published evidence for magnetic ordering in graphite induced by proton irradiation [14,15], supports this view and opens a new research area in the magnetism

of carbonaceous samples. In this contribution we review some of the evidence for a magnetic ordering at room temperature produced by proton irradiation in highly oriented pyrolytic graphite (HOPG), amorphous carbon and in a fullerene film. We will restrict ourselves to report here only on the effects due to proton irradiation. The effects produced by He^+ irradiation on the magnetism of HOPG, though not negligible, are much weaker than those obtained with protons and deserve further study.

Experimental

In the last three years of our research in this topic we have measured the following samples: highly oriented pyrolytic graphite (HOPG) from different sources [16], commercial high-temperature annealed graphite powders of different purities, commercial fullerene powders, polymerized fullerene at different temperatures and pressures [17], fullerene films [9], diamond powder and crystals, carbon multiwalls nanotubes and carbon nanowalls. Some of the samples were irradiated with protons and characterized after irradiation. The magnetic characterization was done with a SQUID magnetometer and magnetic force microscope (MFM). Structural characterization was done by x-rays. Some of the irradiated samples were characterized with μ-Raman and XPS.

An important aspect of the experimental research and of primary importance to study weak magnetic signals in unconventional (from the magnetic point of view) materials is the characterization of the magnetic impurities in the samples. Without a sensitive and reliable method for this characterization it would not be possible to continue the research in this topic, since in several samples the measured magnetization is not much larger than the magnetization we would expect from the measured magnetic impurities [16]. For the impurity concentration measurements we use the method of ``Particle Induced X-ray Emission" (PIXE). Having a carbon matrix, this method reaches a sensitivity of ~0.1 ppm Fe and is therefore very convenient for all the elemental analysis prior and after the magnetic characterization with MFM and SQUID. The same accelerator LIPSION with a proton microbeam (of ~1 μm diameter) of 2.25 MeV energy (or a broad beam of ~ 0.8 mm diameter at 2 MeV) is used for the PIXE spectrum, and therefore it allows simultaneously proton irradiation and element analysis (using the same protons). Of course, the analysis is possible with fewer protons than are required to produce a detectable magnetic signal in graphite. To learn more about the contribution of magnetic impurities in carbon-based magnetic samples we refer to our recent publications [16-19].

Whereas the range of protons in graphite is known, the effective penetration depth of the protons that produced the magnetic ordering in graphite is unknown. Figure 1 shows the numerical results for the defect density as a function of the distance to the sample surface, obtained using Monte Carlo simulations (SRIM 2003 [20]) and performed with full damage cascades using a displacement energy of E_d = 35eV for the creation of Frenkel pairs in graphite. Since MFM is only sensitive to the near surface region (depths < 1 μm) and the SQUID measurements are bulk measurements, it is unclear what is the thickness of the magnetic layer. According to the numerical results one would speculate

that the largest magnetic region is situated at a depth of 46 μm from the sample surface, see Fig.1. However, a larger density of defects may diminish the effect of the protons on the magnetic ordering. On the other hand, a finite defect density would be produced at or near the surface, see Fig.1.

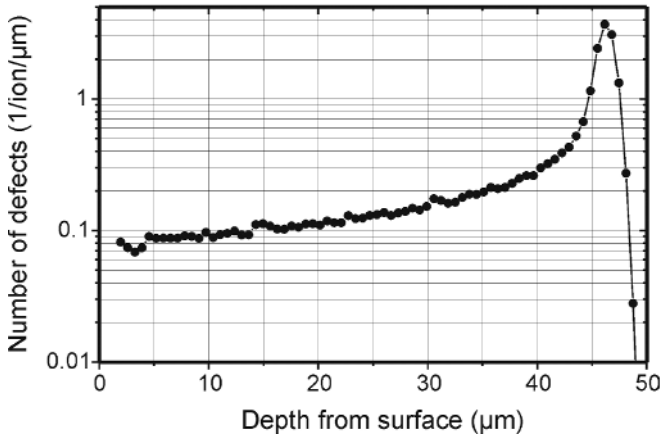

Figure 1. Number of defects per ion and 1 μm depth interval obtained for 2.25 MeV protons in HOPG, according to SRIM2003 [20] Monte Carlo simulations.

Usually, the samples were fixed on high purity Si substrates and fixed in a high-vacuum chamber of the LIPSION accelerator on an uncooled substrate holder. During the irradiation no control of the temperature of the sample was done. Our results indicate that at high enough proton currents self heating effects are important and influence clearly the induced magnetic properties. Future experiments will control the sample temperature during irradiation and try to characterize the self heating effect on the magnetism.

Results and Discussion

I. Magnetic spots produced with a proton microbeam

Topography (top) and MFM (bottom) images of a magnetic spot and its surroundings created in HOPG with a fluence 0.2 nC/μm^2 are shown in Fig.2(a). Here, the scan area was 20 $\times$ 20 μm^2 and the tip-to-sample distance was 50 nm for the MFM measurement. Figure 2(b) shows the line scans (black lines in Figs. 2(a)) of the topography (top) and MFM (bottom) images near the spot regions at different scan heights. As shown in Fig. 2(a), clear enhancement in both topography and MFM signals at the irradiated spot is found. The spot regions are clearly visible in the topography for all fluences between 0.1 and *75* nC/μm^2. Below 0.1 nC/μm^2 even though clear MFM signals are found, the topography reveals no significant change from the original surface [21]. The swelling peak in topography increases as the fluence increases under similar irradiation conditions. The peak height is ~ 5 nm (~ 60 nm) in topography for a fluence of 0.2 nC/μm^2 (2.2 nC/μm^2) and is reproducible after performing the MFM measurements at

different scan heights. As expected for a magnetic signal, the maximum phase shift decreases as the scan height increases from 50 nm to 200 nm (see Fig. 2(b)). This indicates that the MFM signals are not related to the topography. As shown in Fig. 2(b),

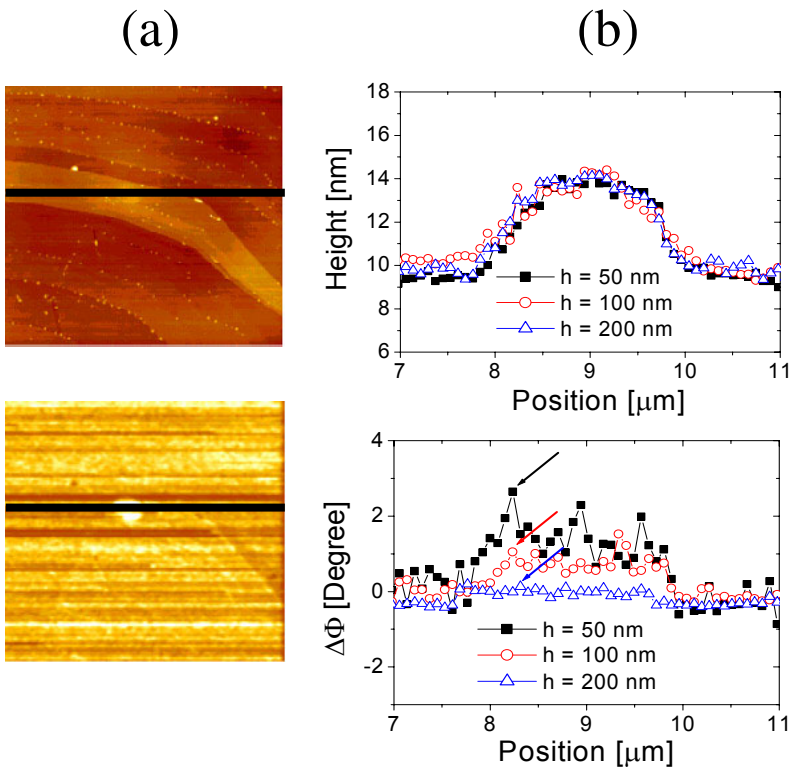

Figure 2. (a) Topography (top) and MFM (bottom) images measured at a distance h = 50 nm of a spot and its surroundings irradiated with a fluence of 0.2 nC/μm^2. The scan area was 20 × 20 μm^2. Horizontal black lines across the spot produce the line scans in (b) of topography (top) and MFM (bottom) images at different scan heights. The swelling height is ~ 5 nm and is independent of the scan height. The magnetic image, however, shows a decrease of the phase shift from 3° to ~ 0.2° after increasing the scan height from 50 nm to 200 nm.

a non-homogeneous magnetic structure within the spots appears, an indication for the existence of magnetic domains inside the irradiated spots. With the maximum phase shift value and its change with scan height, one can estimate the value of the magnetization M ~ 6 x 10^5 A/m at the spot surface using the point probe approximation of MFM [22]. This value is significant and indicates a large localized magnetic moment.

The obtained magnetic signals at the spots indicate non-simple fluence and proton current dependences. The behavior of the maximum phase shift measured by MFM with the fluence depends on the proton energy [23]. We speculate that high enough currents locally anneal the sample. This speculation is supported by the change of the magnetic structure observed at spots produced with high proton currents (I > 500pA).

II. Large area proton irradiation effects

In large area proton irradiated samples we observe a clear development of the ferromagnetic signal after irradiation [15]. The MFM pictures obtained at the irradiated areas show homogeneously distributed magnetic domains, as shown in the top of Fig.3(a). In this example, the maximum phase shift observed at these irradiated regions is of the order of $\Delta\phi \sim 0.15°$, see Fig.3(b). The space periodicity of the magnetic domains depends on the total charge and decreases with irradiation [15].

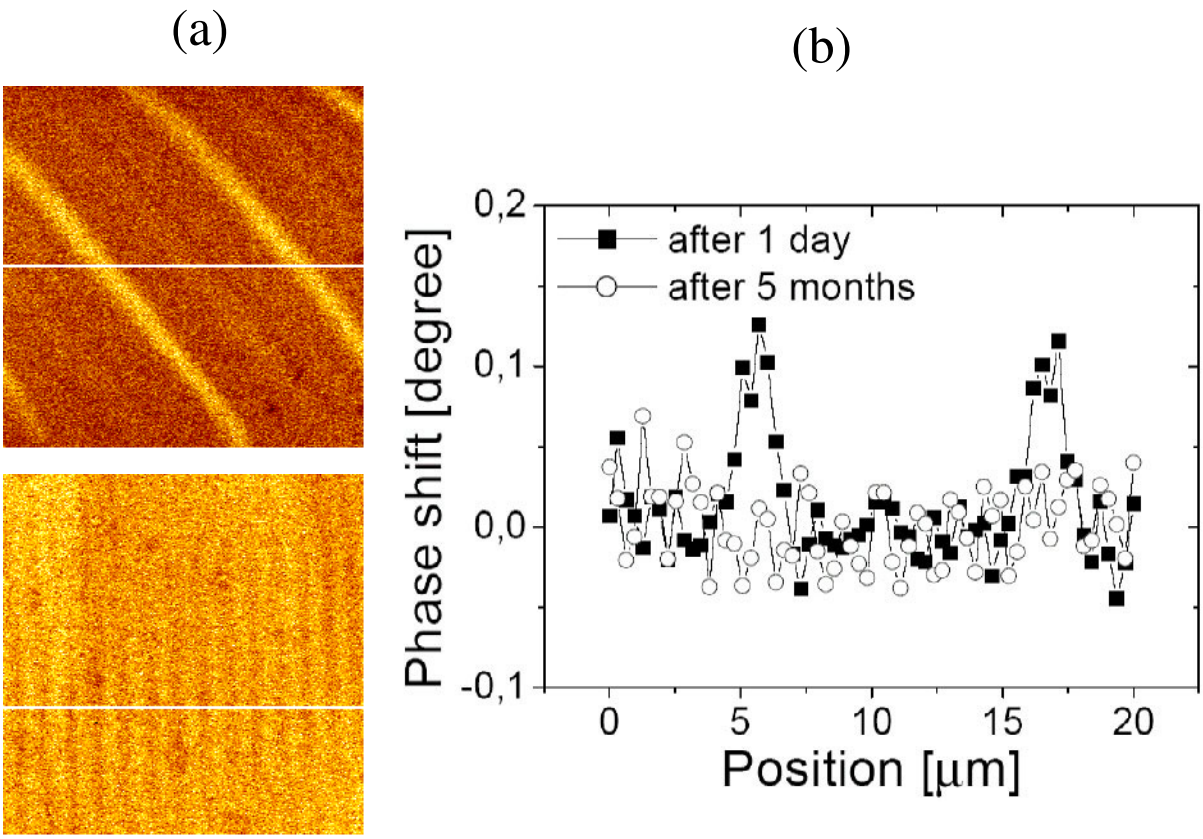

Figure 3. (a) MFM images (20 x 20 μm^2) obtained at the irradiated areas just one day after irradiation (top) and after 5 months (bottom). The tip-to-sample distance was 50nm. (b) Line scans (white lines in (a)) obtained from the MFM images in (a).

Taking into account previous reports on the behavior and diffusion of H in graphite [24] as well as aging effects in the magnetization of the fullerene $C_{60}H_{24}$ [10] one may expect to observe some time dependence in the magnetic response at the irradiated surface by MFM (or in the bulk magnetic moment by SQUID) if H is involved in the induced magnetism. In this contribution we report on aging effects at room temperature of the induced magnetic structures produced by proton irradiation on graphite after several months. After 5 months the magnetic domain pattern of Fig. 3(a) (top) changed as shown in the bottom of Fig. 3(a) and the magnitude of phase shift decreased, see Fig. 3(b). After 10 months these magnetic domain patterns are found only in small areas of the whole sample surface.

III. Irradiation of disordered carbon and fullerene films

Disordered carbon films (~0.5 μm thickness) deposited by Pulsed Laser Deposition on Si(100) substrates were measured with MFM and SQUID before and after proton irradiation. Whereas in the MFM image of the non-irradiated area no indications for magnetic structures were obtained, the images of the irradiated areas show magnetic domains, which change with the scan direction of the microscope due to the influence of the magnetic tip on the magnetic structure under investigation [23]. Further evidence for ferromagnetic behavior was obtained from the hysteresis loops measured with a SQUID magnetometer [23].

In a similar fullerene film used for light polymerization [9], we have selected a non-treated area for proton irradiation of 20 spots of ~2 μm diameter each. Before irradiation neither the topography (the white spots in topography are due to lose particles at the surface) nor the MFM images show any significant signal, see Fig. 4 top images. After irradiation a clear domain structure was observed but, in contrast to the swelling produced by the microbeam in HOPG surfaces, no clear change in the topography was measured, probably due to the polycrystallinity of the fullerene film.

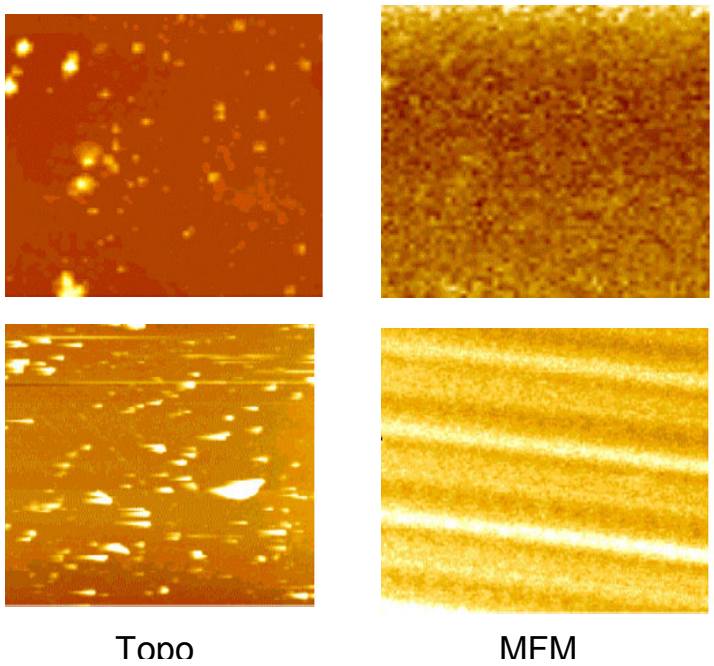

Figure 4. Top images: Topography (left) and MFM images (right) of a non-polymerized area of a fullerene film (~0.25 μm thickness) [9]. Bottom images: images obtained after proton irradiation of 20 spots of ~2 μm diameter each. All the images are obtained within an area of 10 x 10 μm^2. The film was kindly provided by T. Makarova and was characterized in Ref. [9].

Conclusions

Our studies indicate that proton irradiation trigger magnetic ordering at room temperature in carbonaceous samples and rule out impurities as the origin for the unconventional magnetism in a material without d or f electrons. In HOPG samples aging effects are observed at the surface of the irradiated samples 5 or more months after irradiation. These effects are probably related to H diffusion in graphite. Taking into account the results obtained in disordered and fullerene carbon films, we speculate that H may also play a role in the ferromagnetic ordering observed in polymerized fullerenes [25]. Taking into account that the thickness of the films is much smaller than the penetration depth of protons in carbonaceous samples, the results indicate that a finite density of protons should either be present a priori or be trapped in the first micrometer of the samples. Further experiments are needed to clearly understand the role of H and irradiation-produced defects in the magnetic ordering.

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