Ferromagnetism induced by heavy-ion irradiation in fullerene films

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Magnetic measurements using a superconducting quantum interference device and magnetic force microscopy were performed on fullerene films irradiated with 250 keV Ar and 92 MeV Si ions, to compare the effects of electronic excitation and collisional cascade on the magnetization. A ferromagnetic behavior increasing with ion fluence is observed. The magnetization is attributed to (i) the formation of an amorphous carbon network and (ii) the incorporation of oxygen in the irradiated films.

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Nanostructured carbon phases are increasingly attracting the attention of the scientific community, not only for their unusual physical properties but also for their potential applications in many types of electronic or biomedical devices.[1,2] The changes in the spatial arrangement of carbon atoms modify the electronic properties of carbon phases, which may be semiconductors, metals, or insulators.[3–6] An unexpected result of recent studies is that local rearrangements induced by treatments under high pressure and high temperature or by irradiation induces a permanent magnetization in some allotropes of carbon, which are intrinsically diamagnetic. The magnetism in different types of carbon is of great interest due to the possible bio medical applications because of light weight (density being about one fourth of that of conventional magnetic metals) and their biocompatibility. In the last few years, the possible existence of ferromagnetism in materials consisting solely of carbon has been studied experimentally and theoretically. A weak magnetic response has been reported for fullerenes after treatment under high-pressure and high-temperature conditions, inducing the formation of rhombohedraly polymerized C_{60} molecules.[7] A ferromagnetic behavior has also been evidenced in pyrolytic carbon and bulk graphite.[8–11] Other experiments indicate the occurrence of ferromagnetism in a semiconducting nanostructured carbon foam with a low mass density.[12,13] Some theoretical calculations were used to interpret the ferromagnetic behavior of carbon systems.[14] According to these calculations, the phenomenon might find its origin in the localization of unpaired electrons on certain topological defects at boundaries between coherent domains (zigzag or armchair edges between graphene layers in the case of graphite).[15] The magnetism in carbon based materials is found to persist above room temperature (>500 K),[7] which is very important for future application.

The ion irradiation of carbon materials induces drastic changes in their chemical and physical properties. It has been reported that irradiation of fullerene films with swift heavy ions (heavy ions with energy ~1 MeV/nucleon or more), results in the breaking of fullerene molecules, a polymerization at low fluences ($\sim 10^{11}$ ions/cm^2), and to a transformation into amorphous carbon at high fluence.[16–19] A detailed study on irradiation of fullerene films by various ions of energy 100–300 keV revealed that the polymerization occurs at low fluence ($\sim 10^{13}$ ions/cm^2) and complete amorphization occurs at high fluence.[19] A relationship between the ion irradiation induced disorder of carbon materials and their magnetization was reported by Esquinazi *et al.*,[20] who observed a stable magnetic ordering at room temperature in HOPG samples irradiated with protons. Talapatra *et al.*[21] recently reported that nanostructured diamond implanted with 100 keV *C* or *N* ions becomes ferromagnetic and they found that *N* implanted samples showed a higher saturation magnetization. Thus a weak ferromagnetism in different forms of carbon is established but its origin remains an open question. In the present work, we report the ferromagnetism in ion irradiated fullerene films. Magnetometery measurements and magnetic force microscopy are employed to demonstrate the magnetization.

Fullerene thin films (200 nm, 500 nm) were deposited on Si (100) substrates in a vacuum of $<1\times10^{-6}$ torr by resistive heating in a Ta boat of commercially available 99.9% pure C_{60}. The thickness of the films were measured by a quartz crystal thickness monitor. The samples (200 nm) were irradiated with a 92 MeV Si ion beam provided by the IUAC Pelletron, at fluences of 1×10^{12}, 3×10^{12}, and 1×10^{13} ions/cm^2. The Si ions deposit ~2.3 keV/nm in inelastic collisions (electronic energy loss S_e) with electrons, ~2.4 eV/nm in elastic collisions (nuclear energy loss S_n) with nuclei as estimated by TRIM simulations (transport and range of ions in matter).[22] The range (~33 μm) of ions being larger than the film thickness, they get buried in Si substrate. Since the threshold for track creation in fullerene film is around 2 keV/nm,[23] it is expected that the changes produced in the fullerene film are dominantly due to the electronic energy loss and the nuclear energy loss has insignificant effect. A sample (500 nm) was also irradiated with 250 keV Ar ions at a fluence of 5×10^{16} ions/cm^2 using low energy ion beam facility at IUAC. The electronic and nuclear energy losses for Ar ions were, $S_e\sim0.6$ keV/nm, $S_n\sim300$ eV/nm, respectively. The range ($R_p\sim260$ nm) of the ions being smaller than the film thickness, the incident ions get buried in the fullerene films. In this case, the S_e is below the threshold for track creation, the changes produced in the fullerene film will be dominantly due to the nuclear energy loss leading to cascade collision. The purpose of low energy Ar irradiation was to compare the effects of dense electronic excitations and collision cascades on the magnetization.

The magnetization of the films was studied by means of

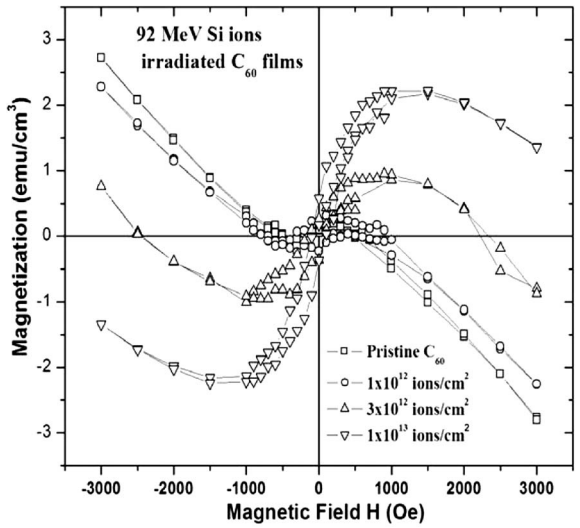

FIG. 1. Magnetization measurement on 92 MeV Si ion irradiated C_{60} film at indicated fluences at 15 K.

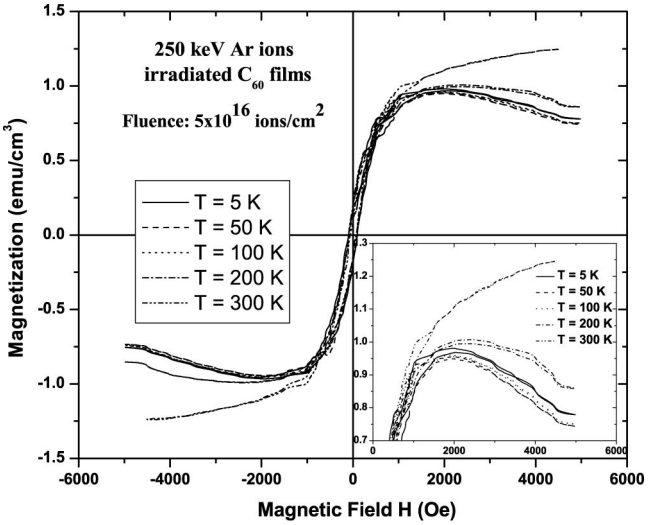

FIG. 2. Magnetization measurement on 250 keV Ar ion irradiated C_{60} film at fluence of 5×10^{16} ions/cm^2 at 5, 50, 100, 200, and 300 K temperature. The enlarged part of the first quadrant is shown in inset for better clarity.

magnetometry measurements at different temperatures, with a superconducting quantum interference device (SQUID) equipment. The temperature was fixed at 15 K for investigating the effect of Si ions at different fluences. The magnetization of the sample irradiated with Ar ions was measured at five temperatures of 5, 50, 100, 200, and 300 K. The topography and magnetic force gradients images were simultaneously recorded using a Nanoscope IIIa scanning probe microscope from Digital Instruments. The microscope was operated in the "tapping/lift" mode, to separate short-range topographic effects from the long-range magnetic signal. The scanning probes were batch-fabricated Si cantilevers with pyramidal tips coated with a magnetic Co-Cr alloy film. Before acquiring images, the scanning probe was put in the magnetic field of a permanent magnet. All the magnetic force microscopy (MFM) images reported here were collected with the tip magnetized perpendicular to the sample surface. X-ray fluorescence analyses were performed to check the presence of magnetic impurities in as-deposited (pristine) and irradiated films, with x-ray excitation at Punjab University, Chandigarh, and with proton excitation (PIXE) at C2RMF, Paris. These analyses showed that the studied films contained less than 20 ppm of magnetic metals. The composition of the samples was also analyzed by Rutherford Backscattering Spectrometry. The oxygen content in the pristine and irradiated films were measured by $^{16}O(d,p)^{17}O$ nuclear reaction. The film thickness deduced from these measurements was found to be in good agreement with that given by quartz thickness monitor. The films contained oxygen of 1 at. % increasing to 10 at. % with Si ion fluence. The Ar ion irradiated fullerene film had about 5 at. % of oxygen. The increase in oxygen is attributed to dangling bonds created during irradiation, which on exposure to air, pick up oxygen.

Figure 1 shows the curves of magnetization versus applied field recorded for the pristine C_{60} film and Si ion irradiated films at different fluence at 15 K. These hystereses are not corrected for the diamagnetic signal of the Si substrate. All samples exhibit a dual magnetic response composed of a weak ferromagnetic signal and a diamagnetic signal. The ferromagnetic contribution increases with the ion fluence. When the carbon film is removed by diamond polishing, the ferromagnetic signal vanishes. The sample irradiated with Ar ions at a fluence of 5×10^{16} ions/cm^2 also exhibited a ferromagnetic response as shown in Fig. 2, with saturation magnetization magnitude independent of the temperature and of the same order of magnitude as in the case of Si ion irradiation at a fluence of 10^{13} ions/cm^2. The enlarged part of the first quadrant is shown in the inset for better clarity. It is worth noting that a small paramagnetic signal adds to the ferromagnetic one when the temperature increases. Similar unconventional magnetic behavior was reported by Rode *et al.*,[12] which is possibly due to molecular oxygen attachment. The saturation magnetization of the film (volume of 1.5×10^{-5} cm^3) reaches 3×10^{-3} μB/atom for the fluence of 10^{13} Si ions/cm^2, which is quite comparable to reported values[27,28] and is higher than the magnetization values reported for ion implanted graphite or diamond.[20,21]

It can be noticed from the comparison of the induced magnetization by the irradiation of 250 keV Ar and 92 MeV Si ions that the magnetization achieved by Si ion irradiation at fluence of 10^{13} ions/cm^2 is about two times than that of obtained by Ar ion irradiation ($\sim$1 emu/cm^3 for a volume of 1.9×10^{-5} cm^{-3}) at a fluence of 5×10^{16} ions/cm^2. It implies that the electronic excitation has higher efficiency of creating magnetization than that of the collision cascade.

The experimentally determined amount of magnetic impurities were less than 20 ppm in 5×10^{18} carbon atoms per cm^2 (for a 500 nm fullerene film), which is equivalent to 10^{14} atoms of magnetic impurity. Therefore the maximum possible contribution to magnetization due to impurities is less than 10^{-6} emu, which is insignificant in comparison to the observed magnetization (3×10^{-5} emu or 2.25 emu/cm^3) Si ion irradiated fullerene films.

Some images of the topography (left) and magnetic force gradients (right) of pristine and Si ion irradiated fullerene

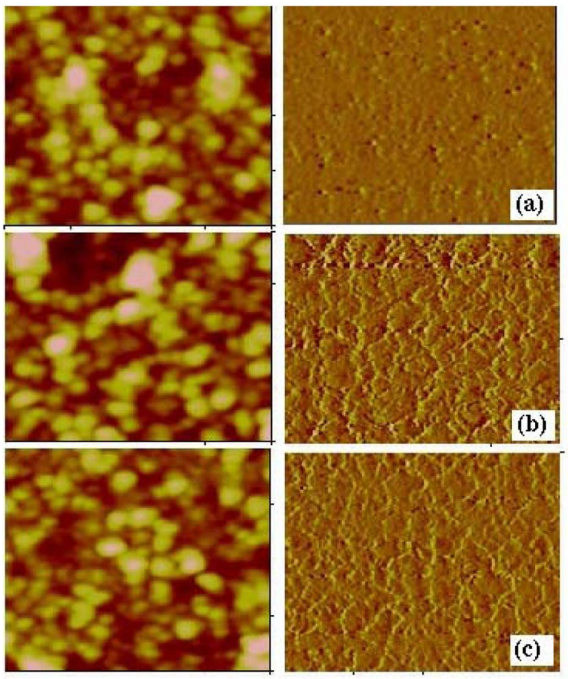

FIG. 3. (Color online) Topographic (left) and magnetic force gradient (right) images of un-irradiated and ion irradiated fullerene films for (a) pristine, (b) 1×10^{12} ions/cm^2, and (c) 1×10^{13} ions/cm^2 fluence. The scanned area was of 1×1 μm^2 and tip to sample distance was 20 nm. The ordinate scale is 100 nm for topographic images and 2° for images of magnetic gradients.

films are shown in Fig. 3. In the case of the pristine film, the topography is quite smooth and the root mean square roughness is 3.5 nm. We did not observe any contrast in the MFM images of the pristine film, indicating its nonmagnetic nature. On the contrary, the images of ion irradiated films clearly show a magnetic ordering. The images were recorded on a same area with different distances between tip and sample to verify that the contrast observed in magnetic images is not purely of topographic origin. Figure 4 shows a line scan on one of the analyzed areas giving an evidence that the magnetic signal is stronger between the islands with a more homogeneous magnetization. In fact, we suppose that spins exhibiting a ferromagnetic correlation are localized principally along these boundaries.

It is well established by Raman studies[17,24] that ion irradiation of fullerenes leads to the formation of amorphous carbon and polymerized fullerene. It has been shown earlier[24] that the signal of the polymer increases up to Si ion fluence of about 10^{11} ions/cm^2, beyond which it decreases. The polymerization vanishes around fluence of 10^{13} ions/cm^2 and complete damage of fullerene film occurs, transforming it to *a-C*. Similar trend[16] has been observed in the case of heavier ion irradiation. It can be reasonably assumed that the *a-C* phase is formed in the track surrounded by the polymerized fullerene in the track halo. The yield of magnetization increases with fluence up to 10^{13} ions/cm^2 for Si ions, while the polymerized C_{60} decreases at the fluences above of 10^{11} ions/cm^2. Thus we can conclude that the magnetic phase is made of amorphous carbon and not due to polymerization.

Similarly in case of Ar ion irradiation, it has been shown by Kastner *et al.*[19] that polymerization of fullerene occurs at 10^{13} ions/cm^2 and complete transformation to *a-C* occurs at a fluence $\sim5\times10^{14}$ ions/cm^2 of 220 keV Ar ions. Therefore it is reasonable to assume that the fullerene film will be completely transformed to *a-C* at a fluence of 5×10^{16} ions/cm^2 of 250 keV Ar ions. This leads us to the conclusion that the *a-C* is the cause of magnetization and the polymerization is not responsible for magnetization. Therefore the low energy as well as high energy experiments lead us to the same conclusion.

The magnetization of polymerized C_{60} observed by other authors was correlated to a doping with oxygen, by photoassisted diffusion, and ascribed to defects decorated with oxygen, mainly in grain boundaries.[25] It has been shown by calculations that polymerized fullerenes free of defects are not magnetic.[26,27] The contamination of as-deposited films with O (at most 1% for the films 200 nm thick used in SQUID measurements) and their imperfect structure may explain that they are already a little ferromagnetic before irradiation. The increase of magnetization with irradiation may also be partly due to the further contamination after exposure to air of the damaged films. The attachment of oxygen creates spin localization.[25]

The magnetization of other carbon allotropes is also generally ascribed to defects and often correlated to a decoration of these defects with impurities. In the case of pure graphite, the magnetization was explained by the trapping of unpaired electrons on atoms with dangling bonds or vacancies at the edges of crystals.[28–31] But the doping of pyrolytic graphite or nanostructured diamond by implantation with species such as hydrogen or nitrogen, seems to favor their magnetization.[20,21] It has been observed that the saturation magnetization of pyrolytic graphite increased with the fluence of H implantation, whereas implantation with similar fluences of He induced no

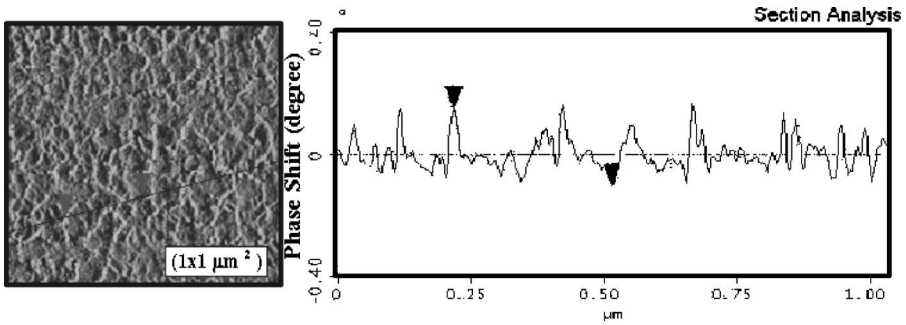

FIG. 4. Diagonal profile section of magnetic force gradient in the MFM images of irradiated fullerene film at the fluence of 1×10^{13} ions/cm^2.

significant magnetization, probably because of the neutral nature of these ions.[20] The origin of the magnetization of C_{60} films amorphized by irradiation may be the existence of some topological order in the stacking of sp^2 and sp^3 bonded atoms, favoring the correlation between unpaired spins. Indeed, amorphous materials often exhibit a certain topological order and some imperfectly localized defects (local density defects which are the equivalent of vacancies in crystalline materials).[32] This order may be stronger at the periphery of ion tracks. MFM images seem to indicate that magnetic electrons are localized mainly at boundaries between nanometric islands with irregular shapes. We suppose that the lines with a stronger magnetization seen in Figs. 3 and 4 correspond to intersections between overlapping tracks, which may be decorated with trapped O atoms.

In conclusion, we have demonstrated that a significant magnetization arises from irradiation of fullerene films with 250 keV Ar and 92 MeV Si ions. The saturation magnetization of films irradiated with Si ions increases with the ion fluence. The present work shows that the electronic excitation has higher efficiency of creating magnetization than that of the collision cascade. The magnetization of the amorphous phase may be due to some ordering of the sp^2 and sp^3 bonded atoms favoring the correlation between unpaired spins or the trapping of O atoms in regions with a lower density.

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