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Magnetism in C_{60} films induced by proton irradiation

S. Mathew, B. Satpati, and B. Joseph
Institute of Physics, Sachivalaya Marg, Bhubaneswar 751 005, India

B. N. Dev*
Institute of Physics, Sachivalaya Marg, Bhubaneswar 751 005, India
and Indian Association for the Cultivation of Science, 2A & 2B Raja S.C. Mullick Road, Jadavpur,
Kolokata 700 032, India

R. Nirmala and S. K. Malik†
Tata Institute of Fundamental Research, Mumbai 400 005, India

R. Kesavamoorthy
Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India
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It is shown that polycrystalline fullerene thin films on hydrogen-passivated Si(111) substrates irradiated by 2 MeV protons display ferromagneticlike behavior at 5 K. At 300 K, both the pristine and the irradiated film show diamagnetic behavior. Magnetization data in the temperature range of 2–300 K in 1 T applied field, for the irradiated film show much stronger temperature dependence compared to the pristine film. Possible origins of ferromagneticlike signals in the irradiated films are discussed.

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Recent observation of the occurrence of ferromagnetism in materials purely of carbon origin[1] has created enormous interest in these materials. Since 1991, it has been known that some organic molecules with unpaired π electrons show magnetic order below 20 K.[2] An antiferromagnetic ordering has been found in a *s*-*p* electron system below 50 K.[3] Wood *et al.*[4] showed the occurrence of ferromagnetic ordering in two dimensionally polymerized highly oriented rhombohedral C_{60} (Rh-C_{60}) phase. Tetra-kis(diemethylamino)ethylene (TDAE)-doped fullerides are known to be ferromagnetic below a Curie temperature (T_c) of 17 K.[5,6] Ferromagnetic behavior has also been observed in microcrystalline carbon[7] and micrographite structures.[8] Theoretical efforts in understanding magnetism in C-based systems are being made. A ferromagnetic phase of mixed sp^2 and sp^3 pure carbons has been predicted theoretically.[9] Understanding the basic mechanism behind magnetic behavior of carbon-based materials and engineering ferromagnetic carbon structures are of prime importance.

Recently, Esquinazi *et al.*[10] reported ferromagnetic (or ferrimagnetic) ordering of highly oriented pyrolitic graphite (HOPG) with T_c above 300 K when irradiated with 2.25 MeV protons. The possibility of the occurrence of ferromagnetic, antiferromagentic, and superconducting instabilities due to topological disorder in graphene sheets has also been predicted theoretically.[11] It has been suggested that topological defects can be used to explain the observed ferromagnetism in Rh-C_{60}. According to a recent theoretical investigation by Vozmediano *et al.*,[12] proton irradiation can produce large local defects, which give rise to the appearance of local moments whose interaction can induce ferromagnetism in a large portion of the graphite sample.

The discovery of ferromagnetism in rhombohedral C_{60} polymers has opened up the possibility of a whole family of magnetic fullerenes and fullerides. Here, we present the results of magnetization measurements on pristine and 2 MeV proton irradiated C_{60} films deposited on hydrogen-passivated Si(111) surfaces. We find that magnetism is induced in proton irradiated C_{60} films. Transmission electron microscopy (TEM), Raman spectroscopy, nuclear resonant scattering (NRS), and proton-induced x-ray emission (PIXE) measurements were used to characterize the samples. Magnetic measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer.

The hydrogen passivation of Si(111) surfaces involves the following: degreasing of the Si substrate, removal of native oxide, and then growth of a thin uniform oxide, etching the oxide produced, and passivating the surface with H using 40% NH_4F solution. The detailed procedure is given in Ref. 13. The passivated substrates [H-Si(111)] were loaded into a high-vacuum (4×10^{-6} mbar) chamber and deposition of the fullerene film was carried out by evaporating 99.9% pure C_{60} (MER Inc., USA) from a tantalum boat.

NRS measurements and ion irradiation were carried out using the 3 MV 9SDH2 tandem Pelletron accelerator facility in our laboratory. We usually use Rutherford backscattering spectrometry (RBS) experiments to determine the film thickness. However, for C, the Rutherford scattering cross section is rather small. To enhance the scattering cross section, we choose appropriate energy of the incident ions and use a resonant scattering condition. A beam of 4.265 MeV alpha particles was used for the NRS experiments to determine the film thickness. These measurements were carried out on a sample area of 8 mm^2 and the thickness was estimated to be 1.88 μm from NRS. Then, the C_{60} films were irradiated uniformly with a 2 MeV H^+ beam by rastering the ion beam on the sample. The pressure in the irradiation chamber during

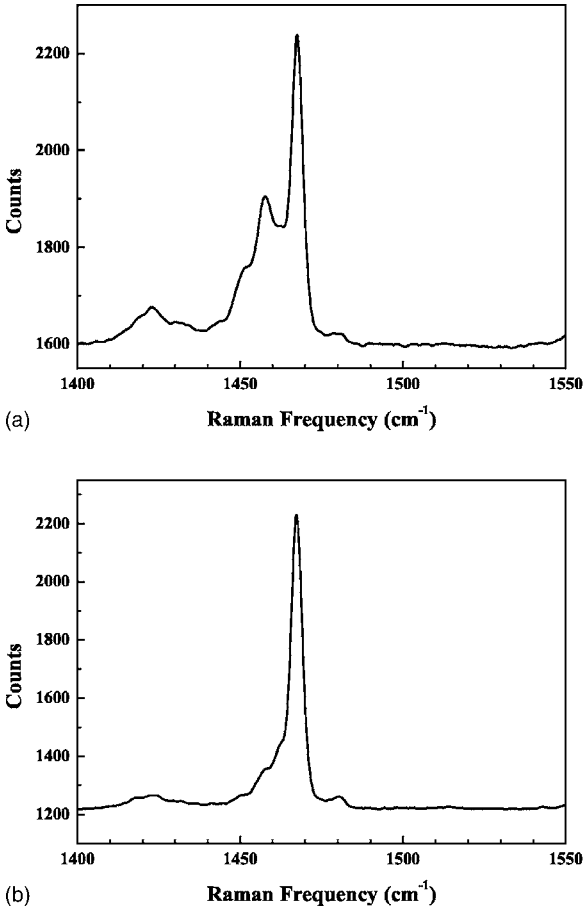

FIG. 1. Raman spectrum of (a) pristine C_{60}/H-Si(111) film and (b) C_{60}/H-Si(111) film irradiated with 2 MeV H^+ at a fluence of 6×10^{15} cm^{-2}.

irradiation was 2×10^{-6} mbar. The ion fluence in the irradiated sample was 6×10^{15} H^+/cm^2. The beam current during irradiation was kept at ~50 nA. Plan view TEM measurements were carried out using 200 KV (JEOL 2010) high-resolution TEM (HRTEM) with point to point resolution of 0.19 nm and lattice resolution of 0.14 nm. Raman spectra were recorded at room temperature in the backscattering geometry using a 514.5 nm line from an Ar ion laser and a charge-coupled device (CCD) detector (Jobin Yvon U100 spectrometer); 2.16 mW laser power was focused on to the sample to a 100 μm spot size. Magnetization was measured using the reciprocating sample option (RSO) in a SQUID magnetometer (MPMS XL, Quantum Design) in the temperature range of 2–300 K in applied fields up to 7 T.

Results of Raman spectroscopy measurements on pristine and irradiated samples are shown in Fig. 1. In the pristine sample, two dominant peaks are seen at 1458 and 1467 cm^{-1}. In the irradiated sample, the first peak height is reduced, while the second is enhanced. Sauvajol *et al.*[14] showed that the appearance of a mode at 1458 cm^{-1} was due to phototransformation (partial polymerization) of pure C_{60}. However, in the irradiated film, the intensity of this mode is reduced along with an enhancement of the 1467 cm^{-1} vibrational mode. The reduction of intensity of the 1458 cm^{-1} mode in the irradiated sample in Fig. 2 may be due to the fact that irradiation has caused enough disorder so that the fraction of the phototransformed component is reduced in comparison with the pristine film.

Another explanation for the appearance of mode at 1458 cm^{-1} is given by Duclos *et al.*[15] They showed that a C_{60} film grown under vacuum and kept under vacuum shows only a broad peak at 1458 cm^{-1}. Exposure of the film to O_2 or air gives rise to the peak at 1467 cm^{-1}. Although the authors could not confirm the origin of the peak at 1467 cm^{-1}, they tend to believe that the structural perturbation of the C_{60} molecule itself is the origin of this peak. This conclusion was based on, besides other reasons, the fact that a total of 16 modes were observed, while the icosahedral symmetry of C_{60} predicts only 10, signifying a lowering of symmetry of the C_{60} molecule in the O_2- or air-exposed film. With ion irradiation, a fraction of C atoms is displaced from the C_{60} cage and thus contributes to symmetry lowering.

Displacement of C atoms might be responsible for the enhancement of the intensity of the peak at 1467 cm^{-1} in the irradiated film. We believe this is why the intensity of the peak at 1467 cm^{-1} increases in the irradiated film. The perturbation of the C_{60} molecular cage can be inferred from the HRTEM image in Fig. 2(c), although the overall crystalline structure, such as the crystalline planes and the diffraction spots [Fig. 2(d)], remain that of the fcc C_{60} crystals. HRTEM lattice images of as-deposited and irradiated samples with corresponding diffraction patterns are shown in Fig. 2. The transmission electron diffraction (TED) and HRTEM images confirm the crystalline nature of the C_{60} film in the fcc structure. Twin structures are seen in Fig. 2(a). The presence of defect structures in the irradiated film is evident from Fig. 2(c). The (111) planar spacing of an fcc fullerene film is seen in Figs. 2(a) and 2(c).

Results of magnetization vs field (*M*-*H*) measurements at 5 K for the film irradiated at a fluence of 6×10^{15} H^+/cm^2 show a marked increase of magnetization and a tendency toward saturation (Fig. 3). A weak remanent magnetization of the order of a few tens of μemu is observed (data not shown). At 300 K, both the as-deposited and the irradiated sample show diamagnetic behavior. Magnetization data in the temperature range of 2–300 K in 1 T applied field for the irradiated film show much stronger temperature dependence when compared with that of the pristine film (Fig. 4). The magnetization (*M*) vs field (*H*) isotherm of irradiated C_{60} obtained at 5 K clearly shows a tendency toward saturation, which is a signature of ferromagnetism. The hysteresis associated with *M*-*H* curve is feeble, as expected for a soft ferromagnetic material. Similar soft ferromagnetism has indeed been observed earlier in an organic fullerene C_{60} material, namely, C_{60} $TDAE_{0.86}$, where the ferromagnetic state shows no remanence.[6]

An alternative explanation of the *M*-*H* curve for the irradiated sample in Fig. 3 is that it arises from superparamagnetism. In order to demonstrate that the observed *M*-*H* curve is not due to superparamagnetism and the observed magnetic behavior in the irradiated C_{60} film is stable over a long period, in Fig. 5 we present the results of measurements made on the same sample one year after the original measurements (Fig. 3) had been made. Measurements at three different temperatures (5, 20, and 30 K) have been made to test one cri-

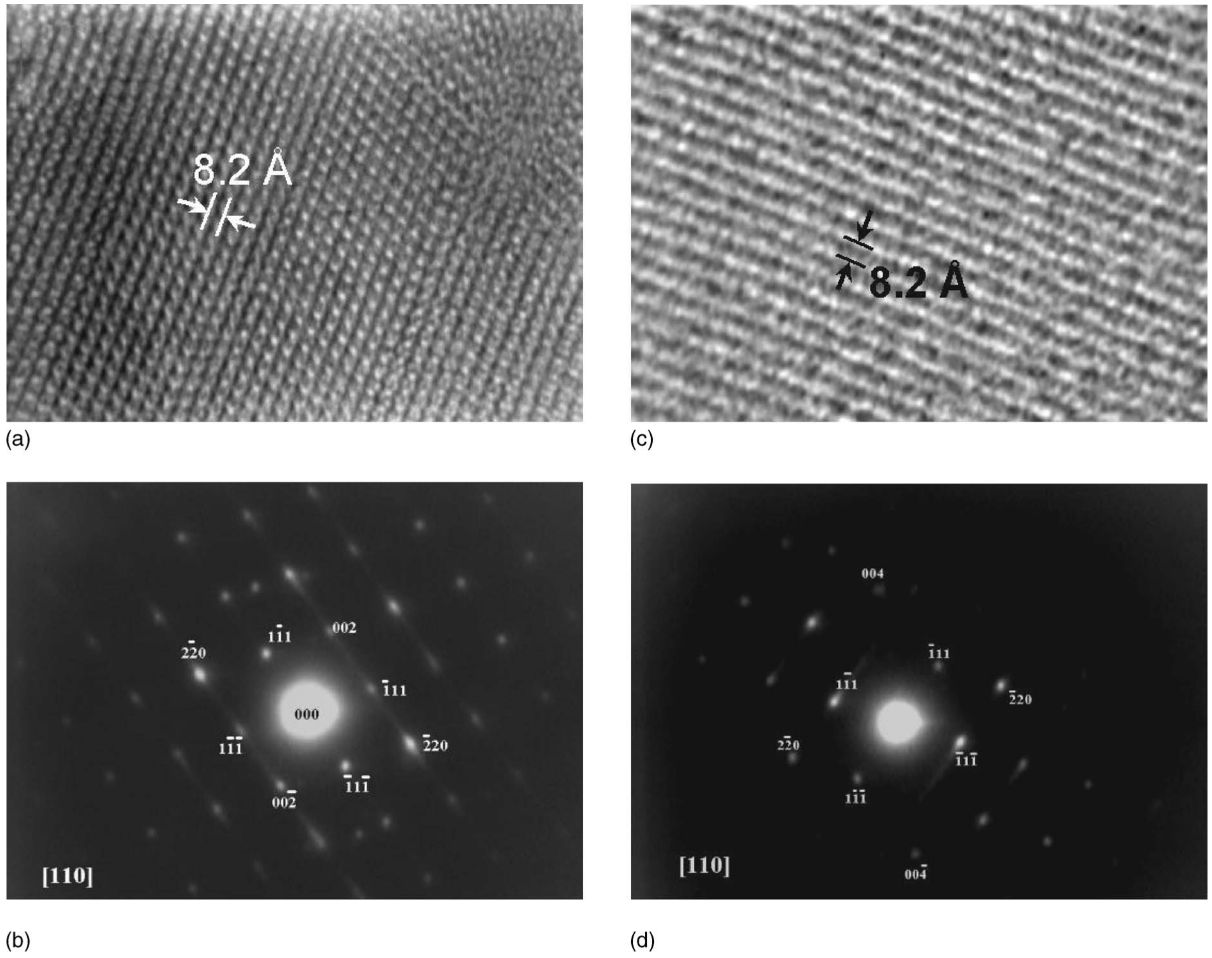

FIG. 2. (a) A high-resolution TEM (HRTEM) lattice image from an as-deposited C_{60} film and (b) the corresponding selected area transmission electron diffraction (TED) pattern. (c) A HRTEM image from an irradiated C_{60} film and (d) the corresponding TED pattern. The (111) planar spacing of fcc fullerene is marked in (a) and (c).

terion for superparamagnetism, that is, M-H isotherms should scale as H/T.[16] The magnetization vs H/T curves for different temperatures are shown in Fig. 5, and from the figure, it is clear that they do not superimpose. These isotherms should superimpose for paramagnetic or superparamagnetic materials. From these results, in conjunction with the observed feeble remanent magnetization, we conclude that the irradiated C_{60} films are soft ferromagnets. The results also show that the ferromagnetic behavior in the irradiated film is stable over a long period of time.

The magnetic moment observed for the irradiated sample in an applied field of 7 T is about 5×10^{-3} emu with a tendency toward saturation. The magnetization curve of the irradiated film in high fields at 5 K compared with that of the as-deposited film and the empty substrate (the latter not

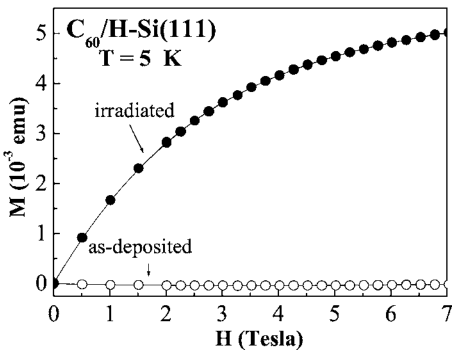

FIG. 3. M vs H at 5 K for an as-deposited and an irradiated C_{60} film after subtracting the substrate [H-Si(111)] contribution (substrate data not shown here).

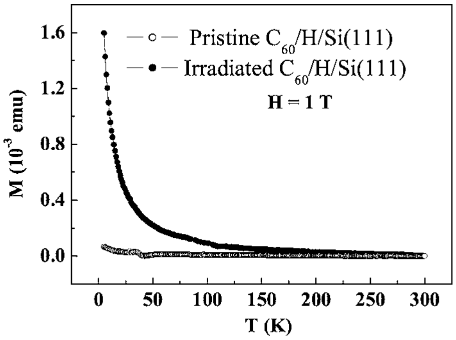

FIG. 4. M vs T for an as-deposited and an irradiated C_{60} film in an applied field of 1 T (substrate [H-Si(111)] contribution subtracted).

shown here) gives clear evidence for the irradiation-induced magnetism in C_{60} films. The total amount of magnetic impurities (Fe, Cr, and Ni) was determined by postirradiation PIXE experiments and estimated to be ~50 ppm and the maximum magnetic moment contribution due to all these impurities in our film will be less than 5×10^{-7} emu. Thus, the contribution to observed magnetization due to these impurities is negligible.

The range of 2 MeV protons, calculated by using SRIM (Ref. 17) simulation program for an amorphous carbon target having the density of C_{60}, is found to be ~50 μm. Since our C_{60} film is only ~1.9 μm thick, the protons pass through the film and get buried deep into the Si substrate. The total-energy loss of the proton beam in the present 1.9-μm-thick C_{60} film is ~45 keV. The energy losses of the protons at the top and at the bottom of the C_{60} film are 24.4 and 24.8 eV/nm, respectively. As the proton energy loss is uniform over the whole depth of the film, it is reasonable to assume that the irradiation damage is uniformly produced over the whole depth of the film. We have used the total thickness of the film in order to determine the magnetization value in emu/g.

The magnetization curve of the irradiated sample in Fig. 3 has a tendency toward saturation at high fields. The magnetization at 7 T is about 200 emu/g. [Similar large magnetization value (400 emu/g) had been reported for proton-irradiated HOPG samples[18]]. In the proton-irradiated C_{60} films, although defects are created, the observation of ordered periodic lattice fringes in the irradiated sample and corresponding TED pattern indicate that irradiation did not cause disintegration of C_{60} cage leading to amorphization.

Regarding the mechanism for the formation of magnetic state in all-carbon systems, among others, the defect mediated mechanism appears to be the most general one. The defect-mediated mechanism has been addressed in a number of publications.[4,11,12] The possible origins of magnetism in these irradiated C_{60} films could be the following: (i) irradiation-induced carbon vacancy in the system could lead to a singly occupied dangling sp^2 orbital that can give rise to a magnetic moment. (ii) The presence of nanographitic fragments that have zigzag edges could lead to splitting up of the flat energy bands and lower the energy of spin-up band than the spin-down band and hence ferromagnetism in the material. Recent theoretical studies have predicted that magnetic ground states are stable in the edges of the isolated graphene sheets whether they are hydrogen passivated or not.[19] In the present work, 2 MeV protons (range 50 μm) were used to irradiate a film of thickness of ≈2 μm and hence the possibility of H-terminated edges are negligible. The proton irradiation on C_{60} films could lead to formation of nanographitic fragments and hence the observed magnetism. (iii) Broken cagelike structure of polymerized fullerene and consequent broken interfragment C–C bonds could also lead to magnetic moment. However, the Raman spectrum of irradiated film does not reveal any significant damage to the cagelike structure of C_{60}. On the other hand, the possible presence of magnetic moments in a hexagonal polymeric C_{60} layer is predicted by the formation of radical centers in polymerized C_{60}, with partially broken intermolecular bonds, without damage to the fullerene cages.[20] Although the details may be different for different carbon systems (graphite, polymeric fullerene, nanotubes, etc.), the common feature is the presence of undercoordinated atoms, such as vacancies,[21] and atoms in the edges of graphitic nanofragments.[19,22,23] Ion irradiation of any material generates vacancies. The enhancement in magnetization observed in H^+-irradiated C_{60} samples may be due to defect moments from vacancies and/or deformation and partial destruction of fullerene cage. The HRTEM image in Fig. 2(c) points to this possibility. Raman spectroscopy and HRTEM measurements on the irradiated sample show the stability of the fullerene crystal structure under the present irradiation condition. There are reports[19,22,23] that nanographitic fragments can trigger ferromagnetism. The formation of graphitic nanofragments in ion-irradiation of fullerene cannot be ruled out. Further studies such as estimating the presence of nanographitic fragments and carbon vacancies in such systems will provide deeper insight into the understanding of the origin of magnetism in the ion-irradiated C_{60} films.

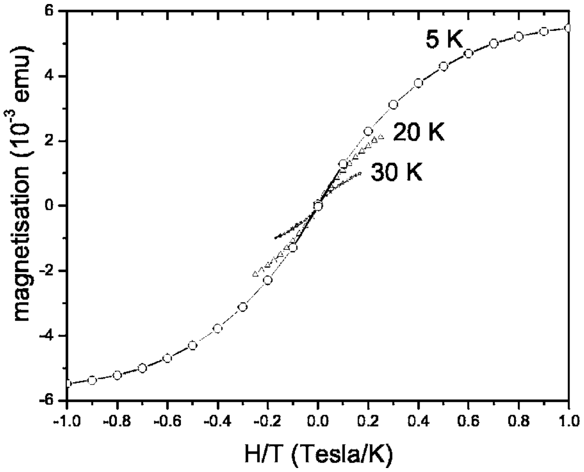

FIG. 5. M vs H/T at 5, 20, and 30 K for the same irradiated C_{60} film as in Fig. 3 measured again one year after the first measurement (Fig. 3).

According to a recent density functional study[21] of magnetism in proton-irradiated graphite,[10] it is shown that the H-vacancy complex plays a dominant role for the observed magnetic signal. For a fluence of 10 μC, the predicted signal is 0.8 μemu, which is in agreement with the experimental signal.[10] The implanted proton fluence in our sample is 77μC (6×10^{15} ions cm^{-2}) and all the protons are buried into silicon. So far we have not come across any report showing magnetic ordering in proton irradiated silicon. Even if we assume the same kind of magnetism due to the H-vacancy complex in proton-irradiated silicon as in proton-irradiated graphite, the expected magnetic signal would be 3 orders of magnitude smaller than our observed result. Considering the above fact, we can safely ignore the contribution of implanted protons in the Si substrate to the observed magnetism, which is predominantly due to atomic displacements caused by energetic protons while passing through the film.

In conclusion, we have observed soft ferromagnetic behavior in 2 MeV proton-irradiated C_{60} films. Magnetism in this irradiated film arises due to atomic displacements caused by the energetic protons as they pass through the film. Possible sources of magnetization are isolated vacancies, vacancy clusters, or formation of nanographitic fragments. Further investigations are necessary to estimate their relative contribution.

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[*] Electronic address: bhupen@iopb.res.in; msbnd@iacs.res.in

[†] Present address: International Center for Condensed Matter Physics (ICCMP), University of Brasilia, 70904–970 Brasilia DF, Brazil.

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