PHYSICAL REVIEW B **71**, 100404(R) (2005)

Multilevel ferromagnetic behavior of room-temperature bulk magnetic graphite

A. W. Mombrú, H. Pardo, and R. Faccio
Crystallography, Solid State and Materials Laboratory (Cryssmat-Lab), DEQUIFIM, Facultad de Química, Universidad de la República, P.O. Box 1157, Montevideo, Uruguay

O. F. de Lima
Instituto de Física "Gleb Wataghin," UNICAMP, 13083-970, Campinas São Paulo, Brazil

E. R. Leite
Laboratório Interdisciplinar de Eletroquímica e Cerâmica-CMDMC, Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905, São Carlos São Paulo, Brazil

G. Zanelatto
Grupo de Semicondutores, Departamento de Física e Engenharia Física, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905, São Carlos São Paulo, Brazil

A. J. C. Lanfredi, C. A. Cardoso, and F. M. Araújo-Moreira*
Grupo de Materiais e Dispositivos-CMDMC, Departamento de Física e Engenharia Física, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905, São Carlos São Paulo, Brazil

(Received 13 December 2004; published 11 March 2005)

In this paper we report on the magnetic properties of pure bulk ferromagnetic graphite, obtained by a chemical route previously described. This magnetic graphite has been obtained by a vapor reaction consisting of a controlled etching on the graphite structure. By magnetic force microscopy we have verified that its magnetic properties are related to the topographic defects introduced in the pristine material. Also, the magnetic properties have been verified through magnetization measurements as a function of temperature and applied magnetic field. At low temperatures (2 K) the saturation magnetization reaches a value of 0.58 emu/g, leading to a defect concentration of 1250 ppm. The system is highly irreversible due to the inhomogeneity of the distribution of defects in the material. Two transition temperatures are detected, $T_{c1}=115(5)$ K and $T_{c2}=315(5)$ K. These transitions could be associated to the weak coupling between ferromagnetic regions related to defects and to the ferromagnetism inside the defect regions.

DOI: 10.1103/PhysRevB.71.100404 PACS number(s): 75.50.Dd, 78.70.−g, 81.05.Uw

I. INTRODUCTION

Over the last years, the survey for macroscopic magnetic ordering phenomena in organic materials has been one of the most exciting and interesting subjects in science. Nanostructured carbon materials have increasingly attracted the interest of the scientific community, not only because of their physical properties but mainly because of their potential applications in *high-tech* devices. The possibility of achieving striking properties in macroscopic carbon—such as room-temperature magnetic properties and even superconductivity—open up a plethora of possible and striking applications. To cite just a few of them, these carbon-based materials could be used in nanotechnology, sensors, detectors, actuators, among others, for applications in medicine—magnetic imaging—or even applications in telecommunications, electronics, biosensors, magnetic materials separation, etc. For these reasons, obtaining macroscopic quantities of bulk room-temperature ferromagnetic carbon (like graphite) would be of fundamental and general interest, not only for a wide number of natural sciences, but mainly for technological applications of this material in engineering, as well as in medicine and biology, as a biocompatible magnetic material.[1]

The existence of pure carbon materials exhibiting ferromagnetic properties has hardly been believed to be true for many years. However, more than 100 articles, and about 30 patents, have been reported for ferromagnetic carbon-based materials consisting only of carbon or including elements of the first rows of the periodic table such as B, N, and S. Recent reports indicate that the ferromagnetic phase in those materials originates in the form of magnetic islands in a nonmagnetic matrix.[2] In the last few years, this field of research has been renewed after the discovery of allotropic forms of carbon, in particular after the discovery of ferromagnetism in the charge-transfer salt $[\mathrm{TDAE}]^{+}\mathrm{C}_{60}$ and in polymerized fullerenes.[3–5] Also, some other reports have proved the existence of weak ferromagneticlike magnetization loops in highly oriented pyrolytic graphite (HOPG).[6,7] On the other side, experiments performed on extraterrestrial graphite obtained from a meteorite[8] have pointed to the presence of ferromagnetic graphite. In this case, the total experimental magnetization exceeded the calculated magnetization by a factor of 1.5 what had been attributed to ferromagnetic graphite, which constituted more than half of the meteorite mass. To demonstrate that the existence of ferromagnetism in pure carbon is unambiguously possible, very recently there have been reported two remarkable papers. In the first one, Esquinazi *et al.*[9] report the induction of magnetic ordering by proton irradiation performed on HOPG samples. After the irradiation, the material exhibits stable magnetic ordering at room temperature. In the second paper, Rode *et al.*[10] report the synthesis of an allotropic form of carbon—an all-carbon nanofoam—that exhibits ferromagneticlike behavior up to 90 K, with a narrow hysteresis curve and a high saturation magnetization.

In this paper, we report on the magnetic properties of pure *bulk* ferromagnetic graphite, obtained by a chemical route we have recently reported.[11] This method consists of a controlled etching on the graphite structure by a vapor phase *redox* reaction in a closed nitrogen atmosphere with copper oxide. This modified graphite has a strong magnetic response even at room temperature, where it can be attracted by any commercial magnet. Several samples have been prepared and all of them exhibited stable magnetic behavior.

II. EXPERIMENTAL PROCEDURE

We have performed experiments of magnetization as a function of the absolute temperature, T (for a fixed value of the external magnetic field, H) and also as a function of H, for fixed values of temperature. These measurements were performed using a MPMS-5T Quantum Design magnetometer. To study the correlation between the defects introduced in the pristine graphite by the chemical vapor reaction previously mentioned, we have also used the magnetic force microscopy (MFM) technique. These measurements were performed using a Nanoscope III, by Digital Instruments. Finally, to double check the presence of induced defects in the pristine graphite, we have performed Raman spectroscopy experiments. In this case, Raman spectra were recorded with a J-Y T64000 triple (subtractive) Micro-Raman spectrometer, using a 50×, 0.5 n.a. objective, to focus 3 mW of the 514.5-nm line of an Ar^+ laser (laser spot put over a similar graphite crystal in both samples, the pristine and the modified graphite, far from the crystal border).

III. RESULTS AND DISCUSSION

Micro Raman analysis (Fig. 1) of the pristine graphite exhibited a peak at 1580 cm^{-1}, showing the good quality of the reagent used in this procedure. The modified magnetic graphite clearly showed the occurrence of the 1350-cm^{-1} peak, well known as the "disordered" D band. A broadening of the 1580-cm^{-1} peak was also observed. Both signals are indicative that the crystal could no longer be regarded as infinite, and that the presence of defects is clearly significant. The presence of magnetic regions at the microscale has been verified by MFM. Also, the role of the pores and the microstructural features were studied simultaneously with atomic force (AFM) and magnetic force microscopy (MFM), trying to correlate the topography to the magnetic signal. Figure 2 shows a 10 μm × 10 μm picture of the topography (upper-left image) of one of the magnetic graphite samples, and the corresponding magnetic behavior (MFM, upper-right image). A large pore can be seen at the topography image, and a grid scheme typical of magnetic systems is clearly seen surrounding it, where magnetic domains are fairly homogeneously distributed. The periodicity of the domains is approximately 1 μm. At the bottom of those figures we show the corresponding three-dimensional (3D) images. Figure 3 shows the diagonal profile section (corresponding to the lines depicted on top images of Fig. 2) of both the topography and the magnetic signal (keeping outside most of the pore). Its analysis clearly allows us to stress that the magnetic signal is not correlated to the roughness of the sample surface outside the pore, i.e., the origin of the magnetic grid is genuinely intrinsic.

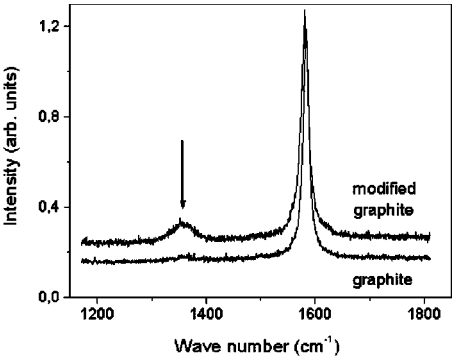

FIG. 1. Raman spectra of the pristine and modified magnetic graphite samples.

Figure 4 shows the magnetic behavior of magnetic graphite as a function of temperature [zero field cooled (ZFC) and field cooled (FC) for $H = 1000$ Oe]. Two clear magnetic transitions are observed: $T_{c1} = 115(5)$ K and $T_{c2} = 315(5)$ K. The irreversibility of the system is clear and can be better seen in the inset, where the difference between the magnetization values at the FC and ZFC branches is plotted against temperature. The arrows in the inset show changes in slopes, which are a few degrees below the magnetic transitions. There is evidence of the persistence of ferromagnetism even at 350 K, where a weak loop can still be observed at the upper-left inset of Fig. 5. This multilevel ferromagnetic be-

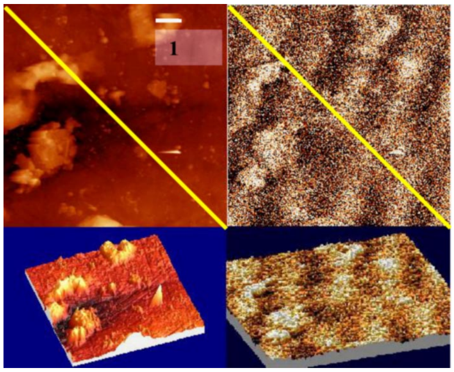

FIG. 2. Set of images of an area of a magnetic graphite sample of 10 μm × 10 μm, corresponding to the topography (AFM, upper-left image) and the magnetic behavior (MFM, upper-right image). At the bottom we show the corresponding 3D images.

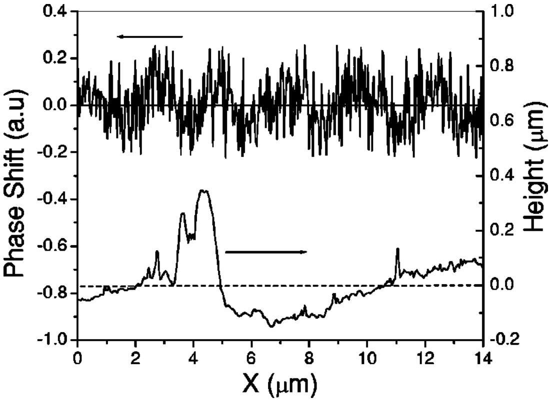

FIG. 3. Diagonal profile section corresponding to the lines depicted on the top images of Fig. 2 and related to the height (topography) and to the phase-shift (magnetic) signals.

havior, evidenced by several Curie temperatures, could be explained through the inhomogeneity of the modified magnetic carbon specimen derived from the presence of defects, as stated by both MFM and Raman experiments. As a consequence of the defects created by the procedure reported in Ref. 11, the material becomes inhomogeneous, which seems to be an essential feature of the magnetic graphite samples. X-ray diffraction analysis on this material suggested the coexistence of a nonmagnetic pristine graphite matrix and foamy graphite with decrease of the d spacing of the (00l) reflections.[11] The presence of ferromagnetic islands, related to the inhomogeneity of defects, is supported by the high irreversibility observed in the m vs T plot. In principle, the complex magnetic behavior should be intrinsic and could not be avoided. Due to the defects created, the material enhances the intrinsic magnetic behavior previously reported.[2,3] The use of powder graphite as a reagent seems to be crucial because of the high reactivity to chemical attacks, due to the highly exposed surface, and the previous existence of defects. Thus, the concentration of defects produced by chemical attack could be the cause of producing the strong magnetic response reported here. Figure 5 exhibits the hysteresis cycles for the m vs H curves at 2, 200, 300, and 350 K. The lower right inset also shows the m vs H loop at 2 K without the subtraction of the diamagnetic background. We assumed that the material at 2 K lacked the paramagnetic phases and used this curve to establish the diamagnetic contribution to be subtracted at all temperatures (approximately -3×10^{-5} emu/g). Then, a paramagnetic contribution was also subtracted at 200, 300, and 350 K. The saturation magnetic moment was strong, 0.58, 0.28, 0.25, 0.19 emu/g, for $T=2$, 200, 300, and 350 K, respectively. The saturation magnetization at 2 K, leads to a defect concentration of 1250 ppm, assuming that each defect has a magnetic moment $g\mu_B S(g=2,\ S=\frac{1}{2})$. This value is higher than others previously reported, such as the 78–840 ppm range for nanographite-based carbon materials.[12]

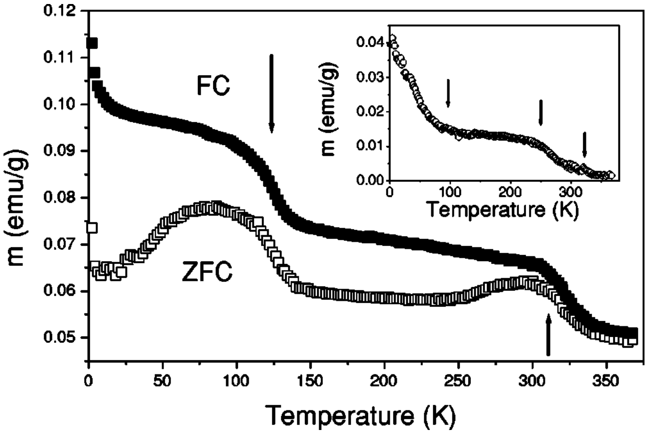

FIG. 4. ZFC and FC magnetization vs temperature. The arrows show the magnetic transition temperatures. Inset: the difference in the magnetization FC-ZFC vs temperature. The arrows show changes of slopes.

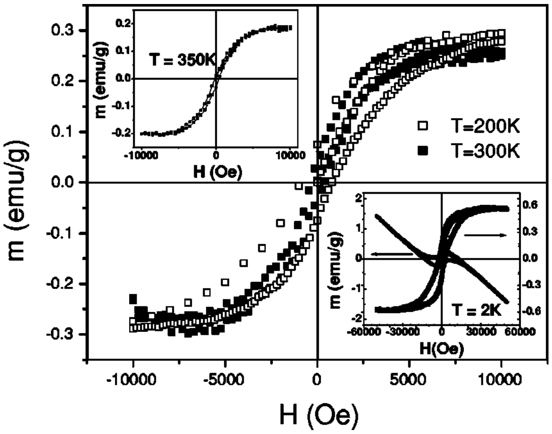

FIG. 5. Hysteresis curves, m vs H, for the magnetic graphite material for $T=200$ and 300 K. Lower right inset: m vs H at 2 K, with and without the diamagnetic background subtraction. Upper left inset: m vs H at 350 K.

To justify those values of the saturation magnetic moment through the role of magnetic impurities by assuming that all these impurities behave as bulk ferromagnetic material—which most probably would not be the case—it would require a ferromagnetic cluster of about 2600 ppm of Fe. As previously reported,[11] the total content of iron in our samples was determined to be around 40–60 ppm range. Other ferromagnetic metals such as nickel and cobalt were detected at concentrations around 1 ppm. Since this value is much lower than the one required, the presence of ferromagnetic impurities cannot be responsible for the magnetic behavior of this material, and this hypothesis can be ruled out. A strong decrease in the coercive field was observed when temperature increases, $Hc=2200$, 850, 350, and 170 Oe at 2, 200, 300, and 350 K, respectively. The remnant magnetization was 0.17, 0.075, 0.04, and 0.01 emu/g for 2, 200, 300, and 350 K, respectively. These values correspond to 29, 27, 16, and 5 % of the saturation magnetic moment for 2, 200, 300, and 350 K, respectively.

IV. CONCLUSIONS

We have shown that bulk stable magnetic graphite prepared by the procedure described by Pardo *et al.*[11] intrinsically exhibits a multilevel ferromagnetic behavior derived from the presence of defects. This is in agreement to the fact that the magnetic ordering can be caused by the appearance of a curvature in the surface, grain boundaries, and particularly when there is structural disorder in the graphene planes. In this case, our results give strong experimental evidences to support that, when high topological disorder has been introduced into the material, ferromagnetism is preferable to antiferromagnetism.[1,7] Thus, the multilevel ferromagnetic behavior here reported would be associated with microstructural features observed in the attacked sample that produced an inhomogeneous material with enhanced magnetism. This outstanding behavior is postulated to be associated to those microstructural characteristics by breaking the continuity of the delocalized pi-electron clouds of the graphitic material and where the sp^3 and sp^2 bonds could play an important role, as stated elsewhere.[13] This allows the existence of magnetic centers related to the topology, which could be the origin of a multilevel ferromagnetic behavior. The observed magnetic transitions could be postulated to be the ferromagnetic transition inside the defect regions (T_{c2}) and the weak coupling between these regions (T_{c1}). The high irreversibility of the system would support the representation of the material as a coexistence of a nonmagnetic pristine graphite matrix and magnetic foamy graphite.

ACKNOWLEDGMENTS

We gratefully acknowledge PEDECIBA and CSIC (Uruguayan organizations) and CNPq and FAPESP (Brazilian organizations) for partial financial support. We are grateful to E. Longo, I. G. Gobato, A. Vercik, J. A. Chiquito, E. Marega, A. V. Narlikar, P. F. S. Moraes (deceased), and J. C. Ortega for valuable discussions and help in the initial steps of this work. We also thank the technical help of R. L. Almeida (magnetization measurements) and F. C. Rangel (MFM).

---

*Corresponding author. Electronic address: faraujo@df.ufscar.br

[1] T. L. Makarova, Semiconductors **38**, 615 (2004).

[2] P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama, and M. Kinoshita, Chem. Phys. Lett. **180**, 327 (1991).

[3] P. M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, and J. D. Thomson, Science **253**, 301 (1991).

[4] T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevichk, P. Scharff, V. A. Davydov, L. S. Kashevarova, and A. V. Rakhmanina, Nature (London) **413**, 716 (2001).

[5] R. A. Wood, M. H. Lewis, M. R. Lees, S. M. Bennington, M. G. Cain, and N. Kitamura, J. Phys.: Condens. Matter **14**, L385 (2002).

[6] Y. Kopelevich, P. Esquinazi, J. H. S. Torres, and S. Moehlecke, J. Low Temp. Phys. **119**, 691 (2000).

[7] P. Esquinazi, A. Setzer, R. Höhne, C. Semmelhack, Y. Kopelevich, D. Spemann, T. Butz, B. Kohlstrunk, and M. Losche, Phys. Rev. B **66**, 024429 (2002).

[8] J. M. D. Coey, M. Venkatesan, C. B. Fitzgerald, A. P. Douvalis, and I. S. Sanders, Nature (London) **420**, 156 (2002).

[9] P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K. H. Han, and T. Butz, Phys. Rev. Lett. **91**, 227201 (2003).

[10] A. V. Rode, E. G. Gamaly, A. G. Christy, J. G. Fitz Gerald, S. T. Hyde, R. G. Elliman, B. Luther-Davies, A. I. Veinger, J. Androulakis, and J. Giapintzakis, Phys. Rev. B **70**, 054407 (2004).

[11] H. Pardo, R. Faccio, A. W. Mombrú, F. M. Araújo-Moreira, and O. F. de Lima (unpublished).

[12] Y. Shibayama, H. Sato, T. Enoki, and M. Endo, Phys. Rev. Lett. **84**, 1744 (2000).

[13] K. Kusakabe and M. Maruyama, Phys. Rev. B **67**, 092106 (2003).