Upper Bound for the Magnetic Force Gradient in Graphite

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In this work we investigate possible ferromagnetic order on the graphite surface by using magnetic force microscopy (MFM). Our data show that the tip-sample interaction along the steps is independent of an external magnetic field. Moreover, by combining kelvin probe force microscopy and MFM, we are able to separate the electrostatic and magnetic interactions along the steps obtaining an upper bound for the magnetic force gradient of 16 μN/m. Our experiments suggest the absence of ferromagnetic signal in graphite at room temperature.

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Ferromagnetism in carbon based materials [1–4] is a current hot topic with relevant implications in material science [5], nanotechnology [6], physics [7,8] and even economy [9]. Ferromagnetism is usually associated with partially filled $3d$ and $4f$ shells but, in the case of pure carbon materials, it has been suggested that the presence of defects can be also at the origin of this phenomenon. Defects break the translational symmetry of the lattice, creating localized states at the Fermi energy. Scanning tunneling microscopy (STM) has been used to characterize these states in isolated vacancies on the graphite surface [8]. DFT studies of clean and hydrogen-terminated surface vacancies have shown that these defects support local magnetic moments larger than $1\mu_B$ [10,11].

Most of the experiments to prove ferromagnetic order in carbon materials are based on superconducting quantum interference devices (SQUID) used to measure extremely weak magnetic fields located in the sample volume [1–3,12]. In fact, this technique is so sensitive that it is very easy to detect spurious magnetic signals giving raise to different and, sometimes, contradictory results not only in graphite but also in graphene [13,14]. Magnetic force microscopy (MFM) [15,16], a variation of atomic force microscopy (AFM) where magnetic probes are used, has the important advantage over SQUID of producing images where the presence of defects and the spatial distribution of the magnetic signal can be resolved at the nanometer scale [4,17,18]. In MFM, a very sharp tip attached to the end of an oscillating micro-cantilever is used as the force sensor. The change in the resonance frequency due to the total tip-sample interaction, F, is tracked using phase-lock-loop techniques [19–21]. This frequency shift, Δf, can be calculated, for small oscillation amplitudes, with the linear approximation $\Delta f = -\frac{f_0}{2k} \cdot \frac{\partial F}{\partial z}$, with f_0 and k the free resonance frequency and stiffness of the cantilever, and z the tip-sample distance.

The magnetic contrast comes from the dipolar interaction between the magnetic moments on the tip and sample. Defects supporting magnetic moments with the same orientation as the tip (parallel configuration, attractive interaction) will appear dark in the images, while those with antiparallel configuration (repulsive interaction) will appear bright. Since steps are always related to defects in the crystalline order, it is natural to assume that they could exhibit ferromagnetic character. In particular, grain boundaries in highly oriented pyrolytic graphite (HOPG) are characterized by a plane of defects that propagates almost perpendicular to the graphite surface. Guided by this idea, Cervenka *et al.* [4] have recently reported MFM images on HOPG that show contrast inversion along the steps when the magnetization of the tip is reversed and concluded that these defects support ferromagnetic domains. However, clear evidence of magnetic order in the sample can only be achieved if the weak magnetic contribution can be separated from the rest of the forces. Although short-range chemical forces and van der Waals (vdW) interactions can be removed operating at large tip-sample distances, to split the magnetic and electrostatic contributions is not an easy task. The metal-covered tips used in MFM are also very sensitive to electrostatic interactions with the charge density variations associated with defects.

In this Letter, we use MFM measurements to show that the contrast along the steps in HOPG is independent of the external magnetic field and tip magnetization state. Furthermore, combining MFM and Kelvin Probe Force Microscopy (KPFM) [22,23], we demonstrate that most of the signal at the steps has an electrostatic origin. KPFM minimizes the electrostatic interaction by compensating the local contact potential between tip and sample, assuring that the frequency shift measured comes exclusively from the magnetic interaction. This remaining contrast, that we can detect with our accurate phase-lock-loop setup, provides an upper bound for the magnetic force gradient of 16 μN/m, 6 times lower than the lowest theoretical estimate [4].

Our experiments have been carried out using Cobalt-coated PPP-MFMR NanoSensors ($k \simeq 1.5$ N/m, see supplementary material [24]) on HOPG samples of ZYH and ZYA quality cleaved by an adhesive tape. We have used two experimental setups: (i) An AFM in air ambient conditions with the capability to apply an out-of-plane external magnetic field H_E between ± 60 mT [25], enough to reverse both the magnetization of the sample (assuming $H_c \approx 20$ mT [2–4]) and the tip ($H_c = 45$ mT, see Fig. SM1 in [24]); and (ii) A high-sensitivity AFM inside of a vacuum chamber, which combines KPFM simultaneously with MFM. Each of them uses a Dulcinea control unit (Nanotec Electronica SL) [26]. The magnetic signal is recorded in retrace mode (equivalent to lift mode^{TM}): first a topography line is acquired, then using the information obtained in this first scan, a second scan is performed where the topography feedback is disable and the tip follows the topography contour far away from the surface (20–70 nm). The frequency shift images shown in Figs. 1 and 2 were acquired at a lift distance of 50 nm, with oscillation amplitudes ranging between 4–7 nm where the linear approximation for Δf is clearly valid.

Figure 1 portrays the main result using the first experimental setup. Figure 1(a) is an edge enhanced AFM topographic image of a ZYH-HOPG surface. The magnetic states of both tip and sample were initially prepared as represented in the inset of Fig. 1(b) using a magnet. Figures 1(b)–1(f) are the corresponding frequency shift signal taken at different external magnetic fields, H_E. Any long-range interaction, such as the tip-sample magnetic force, should be reflected in this magnitude. The insets of these figures represent the tip-sample magnetic states, according to the coercitive fields H_c discussed above, for the corresponding H_E values. At first glance, Fig. 1(b), taken in remanence ($H_E = 0$), suggests that the origin of the contrast observed along the steps is not magnetic, or at least not exclusively magnetic, since it only shows bright steps and not a distribution of dark and bright steps associated with the presence of both parallel and antiparallel domains expected for the sample in remanence. After measuring on many different areas on the HOPG surface, we have always observed just bright steps on the MFM images. As we vary the external magnetic field [see snapshots in Figs. 1(b)–1(f)], overcoming, first the sample coercitive field [Fig. 1(c) $H_E = +35$ mT] and then the tip one [Fig. 1(d) $H_E = +60$ mT], the contrast along the steps remains constant, in obvious contradiction with the expected orientation of the magnetization assumed in the insets. A similar situation is observed when the external magnetic field is reversed [Figs. 1(e) and 1(f)]. Thus, this experiment suggests that the contrast observed along the steps is not of magnetic origin.

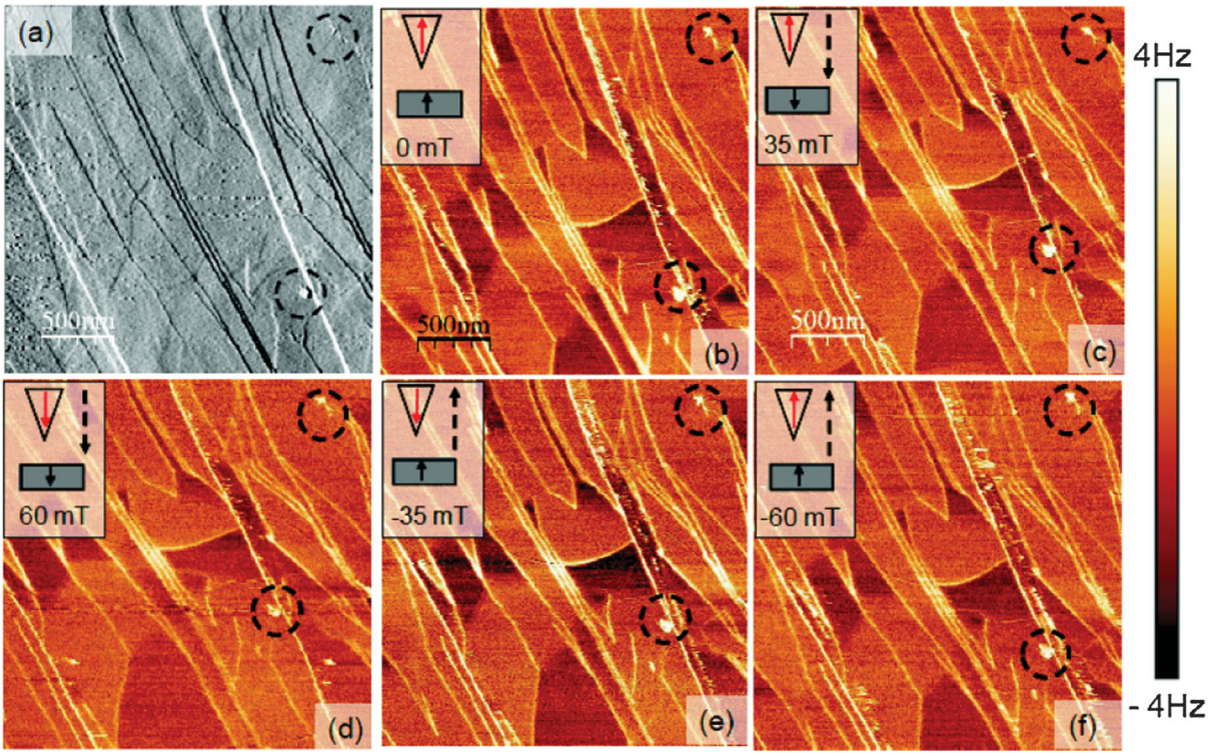

FIG. 1 (color). AFM images in ambient conditions under an external magnetic field. (a) Edge enhanced topography showing a 2.5 μm $\times$ 2.5 μm ZYH-HOPG typical area with a large density of steps. (b–f) MFM images taken at a lift distance of 50 nm using 5 nm oscillation amplitude. As the external magnetic field (H_E) is scanned [inset (a) as the external magnetic field (HE) is scanned, the contrast along the steps remains unmodified] the contrast along the steps remains unmodified. The insets of figures (b)–(f) indicate the expected magnetic configuration for tip and sample as H_E is varied.

As a general rule, measuring MFM signals along steps is always a difficult task. The origin of the contrast observed in graphite with MFM could be a combination of (i) artifacts due to the crosstalk with the topography [27], and (ii) electrostatic interactions. (i) The retrace mode may introduce an spurious contrast along the steps associated with the different force gradient near and far away from the surface. However, as we shall see, this effect is not the relevant one for a surface as flat as HOPG. (ii) Steps in conducting surfaces exhibit an electrostatic dipole [28] that locally changes the surface potential along them. Moreover, nucleation preferentially occurs along the steps, and therefore, we expect adsorption of molecules that can also vary the surface potential. These factors, together with the experimental results discussed above, suggest that the most relevant contribution to the measured Δf along the steps comes from electrostatic interactions.

In order to test this hypothesis with an improved sensitivity, we have carried out experiments which combine both KPFM and MFM techniques in a high vacuum chamber with a base pressure of 10^{-6} mbar. The cantilever quality factor Q at this pressure is 6850, 49 times higher than in air ambient conditions. This Q enhancement results in an better sensitivity to the different tip-sample interactions [19]. Figure 2(a) is a topographic image of a freshly cleaved ZYH-HOPG surface. In order to enhance the step edges we are showing the derivative of the topography image [Fig. 2(b)]. For reasons still under discussion, graphite exhibits a marked distribution of electrostatic potential on its surface [29–31] that can be easily measured by KPFM using metallic cantilevers. Figure 2(c) is a KPFM image taken simultaneously with the topographic image. An advantage of KPFM with respect to MFM is that it can provide electrostatic potential images of the sample surface at distances where the vdW interactions are still relevant. Figure 2(d) is again a KPFM image of the surface where the tip is lifted 50 nm to avoid short-range and vdW interactions. The electrostatic signal is basically the same as in Fig. 2(c) but slightly smoothed by the 50 nm lift distance. Figure 2(e) is the frequency shift, simultaneously measured with Fig. 2(d), that gives no signal within our experimental error.

The point to be stressed in this measurement is that we are separating the electrostatic interaction, that goes to the KPFM image [Fig. 2(d)], from the magnetic one, that should be exclusively present in the frequency shift image [Fig. 2(e)]. Since we are not able to measure any significant signal, we conclude that graphite does not exhibit ferromagnetic interaction along the step edges. The clear electrostatic signal measured at lift distance confirms our high sensitivity and discards any artifact due to tip damage.

The magnitude of our noise can be estimated by measuring an ''empty'' image [32]. The root-mean-square (rms) resonance-frequency noise so evaluated is about

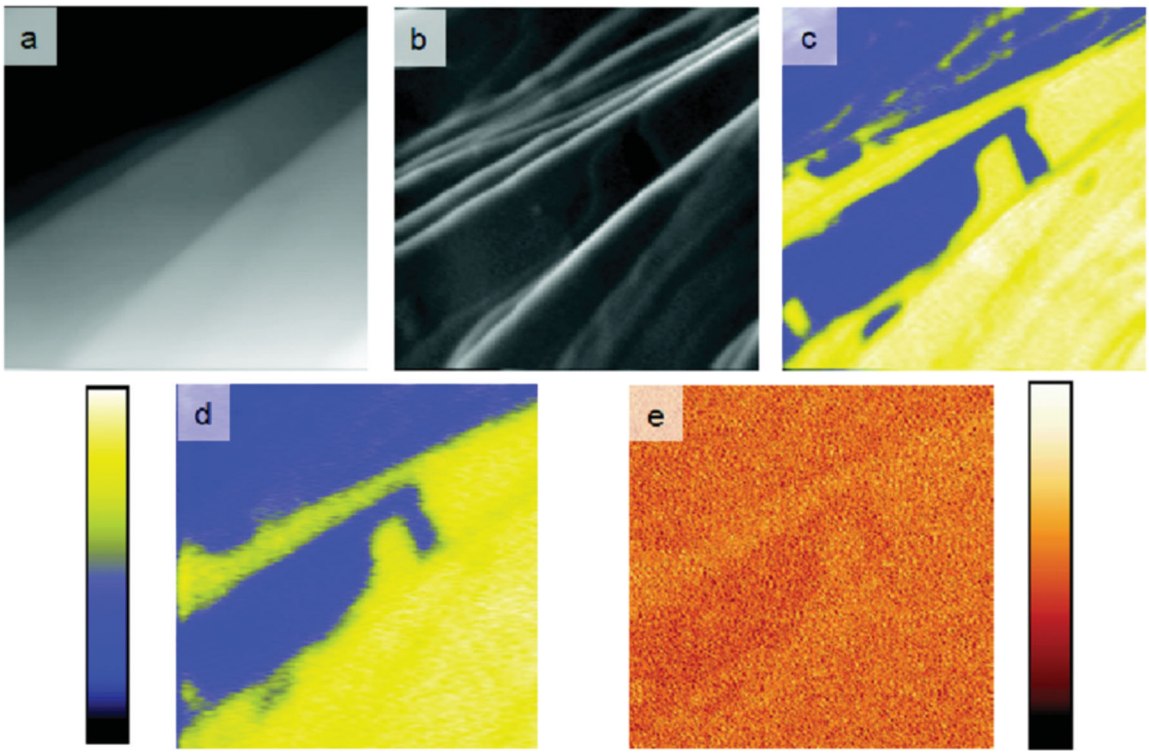

FIG. 2 (color). 3 μm $\times$ 3 μm AFM, KPFM, and MFM images taken in high vacuum with a cobalt-coated probe on ZYH-HOPG. (a) Topography. (b) Edge enhanced image of (a) showing the surface steps. (c) KPFM image simultaneously taken with (a), showing electrostatic domains and steps on the sample surface (the potential difference between bright and dark areas is 200 mV). (d) KPFM image taken in retrace at 50 nm lift distance. (e) Frequency shift image taken simultaneously with (d). The total frequency shift variation in figure (e) is 0.4 Hz.

0.2 Hz, which translates into a minimum detectable magnetic signal of 8 μN/m (in good agreement with Ref. [27]). Since Fig. 2(e) does not show any signal along the steps, this would be the upper bound for the magnetic force gradient. We can determine an even more cautious upper bound taking advantage of an instrumental artifact seen in Fig. 2(e): the ''shadows'' that follow the shape of the KPFM domains. While most of the electrostatic signal goes to the KPFM channel, there is still some signal that leaks to the frequency shift image. The origin of this artifact is the KPFM feedback, that cannot perfectly compensate the electrostatic signal. This is also seen when using Pt-covered tips, discarding again any magnetic origin. The frequency shift of this region is 0.4 Hz, so we know that the sensitivity of the frequency shift image is at least this one. The corresponding force gradient is 16 μN/m. We consider this a very prudent upper bound for the force gradient produced by any possible magnetic field on the HOPG surface.

The results discussed above are in clear contrast with a recent report by Cervenka *et al.* [4] for the same type of AFM probes and HOPG samples. In particular, the magnetic force gradient obtained in our experiments is an order of magnitude lower than their corresponding experimental value (244 μN/m at 50 nm). Besides, we do not observe contrast inversion along the graphite steps even at relatively high external magnetic fields. We attribute the origin of the discrepancy to the inadequate operating mode used to obtain the MFM data. First, they do not use the best instrumental option, a phase-lock-loop, to track Δf. Second, and more important, their images were taken with a very large amplitude (100 nm at 50 nm lift distance) [33], that implies tip-sample contact and, therefore, the linear approximation that they use to relate phase and force gradient is obviously not valid any longer [24]. Using these large oscillation amplitudes, we observe contrast inversion along the graphite steps by slight changes in the working conditions [24]. Furthermore, the authors reported in the supplementary information of their work [34] an image where all step edges are brighter than the substrate. The different brightness is attributed to opposite magnetic domain orientations. This is a clear misinterpretation since opposite magnetic domains should show contrast above the substrate (positive frequency shift) and below (negative frequency shift). Finally, they did not discount properly the electrostatic signal that, as we have shown, is the basic component of the long-range interaction on HOPG.

To conclude, our careful separation of the magnetic and electrostatic signal suggests absence of ferromagnetic interactions on HOPG. Furthermore, our work demonstrates the importance of combining KPFM and MFM as a general method to obtain reliable results for magnetic measurements.

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