Irradiation-Induced Magnetism in Graphite: A Density Functional Study

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Recent experiments indicate that proton irradiation triggers ferromagnetism in originally nonmagnetic graphite samples while He ion bombardment has a much smaller effect. To understand the origin of irradiation-induced magnetism, we have performed spin-polarized density functional theory calculations of the magnetic properties of the defects which are most likely to appear under irradiation vacancies and vacancy-hydrogen complexes. Both defects are magnetic, but as for the latter we find that H adsorption on one of the vacancy dangling bonds gives rise to a magnetic moment double that of the naked vacancy. We show that for small irradiation doses vacancy-hydrogen complexes result in a macroscopic magnetic signal which agrees well with the experimental values.

Experimental observations of magnetism in polymerized fullerenes [1] and graphite [2] have stimulated much research [3] on the magnetic properties of all-carbon systems, as light nonmetallic magnets with a Curie point well above room temperature appear to be very promising for many practical applications. However, despite considerable effort, there is not complete comprehension of the magnetism observed. Moreover, it is not clear if the mechanism of magnetic state formation is common for all the carbon systems or if it is different for different allotropes.

Presently, a number of factors are thought to possibly give rise to the magnetic state in all-carbon systems: defects in the atomic network such as undercoordinated atoms [4–9], itinerant ferromagnetism [10,11], and negatively curved sp^2-bonded nanoregions in the carbon structures [12]. Among these factors the defect-mediated mechanism appears to be the most general one because negatively curved regions can hardly be found in graphite. As for the second scenario, although itinerant magnetism resulting from strong electron-elecron interactions and the low dimensionality of the electron system can give rise to magnetism in carbon systems, direct experimental evidence supporting such a mechanism is still lacking. Note that magnetic atom impurities (e.g., Fe) can also result in a magnetic signal, but careful analysis [2,13] of the samples seems to exclude impurities as the origin of ferromagnetism.

The defect-mediated mechanism has been addressed in a considerable number of works [4–9]. Although the details can be different for different carbon systems (polymeric fullerenes, graphite, nanotubes), the common feature is the presence of undercoordinated atoms, e.g., vacancies [7], atoms on the edges of graphitic nanofragments with dangling bonds either passivated with hydrogen atoms [8,9,14] or free [6,9]. Structural defects, in general, give rise to localized electronic states, a net magnetic moment, flat bands associated with defects and thus to an increase in the density of states at the

Fermi level, and eventually to the development of magnetic ordering. At the same time, it is well known that irradiation of carbon systems with energetic electrons and ions should give rise to such defects, and their number could be controlled by choosing the right irradiation dose, particle energy, and irradiation temperature. Thus, if irradiation of the originally nonmagnetic carbon samples gave rise to magnetism, this would be strong evidence for the defect scenario.

Graphite samples were recently irradiated with 1.5 MeV He and 2.25 MeV H ions [15,16]. It was found that proton bombardment produced a significant magnetic signal, while bombardment with helium ions produced a signal which was only slightly larger than background. In this Letter, to understand the origin of irradiation-induced magnetism, we employ the spin-polarized density functional theory to calculate the magnetic properties of irradiation-induced defects and demonstrate that, due to the different interaction between C and H/He atoms, proton irradiation should indeed give rise to a stronger magnetic signal.

The calculations have been performed using the plane wave basis Vienna *ab initio* simulation pack (VASP) code [17,18], implementing the spin-polarized density functional theory (DFT) and the generalized gradient approximation. We have used projected augmented wave potentials [19] to describe the core $(1s^2)$ electrons of carbon. A kinetic energy cutoff of 400 eV was found to converge the total energy of our systems to within meV. All atoms were fully relaxed until the change in energy upon ionic displacement was less than 0.1 meV. Adequate k-point sampling of the Brillouin zone was checked for all systems calculated. As the interlayer spacing in graphite is 3.4 Å and the interaction between the layers is only weak van der Waals, the behavior of graphitic sheets with *in-plane* defects can be understood within the framework of a single graphene sheet model. A 128-atom graphene sheet was found to be large enough to make size-effect errors less than the method accuracy. This calculation

scheme has proved to be successful in previous studies [20–22].

Collisions of energetic ions with graphite give rise to the formation of atomic vacancies in the graphene sheets and carbon interstitials in the interlayer regions. The implanted atoms (neutralized ions) should also be present amidst layers. Note that for the ion energies used in the experiments [16] the number of vacancies is much larger than the number of implanted ions; TRIM [23] simulations indicate that one H ion gives rise to 15 vacancies and, correspondingly, the same number of interstitials, and one He ion to 70 vacancies. The interstitials in the interlayer regions are highly mobile [20] and the vast majority of them recombine with vacancies, although some of them form clusters which are much less mobile and can remain in the sample. Hydrogen atoms can easily adsorb on vacancy dangling bonds, as we show below, while He atoms, as one can expect, do not form any bonds with carbon atoms. Thus, the most prolific defects which appear under irradiation are vacancies, H-vacancy complexes, and small carbon clusters. Below we calculate their magnetic properties and compare their relative abundance.

Initially we consider those defects which will be common to irradiation with both H and He ions, vacancies and interstitials. Although the magnetic properties of vacancies have not yet been addressed, their structural properties in graphite have been discussed in detail previously [24], thus here we highlight only the issues important for the discussion. The vacancy undergoes a Jahn-Teller distortion upon relaxation, where two of the nearest atoms to the vacancy site form a weak covalent bond [see Fig. 1(a)], resulting in a pentagonlike structure, with the final atom displacing 0.18 Å out of the surface plane [22]. Contrary to previous DFT studies, we found that the ground state of the vacancy has a magnetic moment of $1.04\mu_B$, and the spin density is shown in Fig. 1(b). Upon removal of one atom, each of the three neighboring atoms now has one sp^2 dangling bond. Formation of the pentagon saturates two of these bonds, but the remaining unsaturated bond is responsible for the magnetic moment. Note that the difference between magnetic and nonmagnetic solutions is only about 0.1 eV, which is comparable to the energy of interlayer van der Waals interaction (a detailed compari-

son of magnetic and nonmagnetic solutions for graphene and nanotubes will be published elsewhere [22]). Thus, interlayer interactions and finite temperatures can decrease or, in principle, even destroy the vacancy contribution to the sample magnetic signal. One can also expect that saturation of dangling bonds of vacancies in adjacent layers by forming interlayer bonds [25] may also result in a nonmagnetic ground state, although large C atom displacements may induce ferrimagnetism [26].

Because of the large interlayer separation, carbon interstitials between graphitic layers can qualitatively be treated as adatoms on graphene layer. Although adatoms themselves do have a magnetic moment [20], their high mobility means that they are highly likely to recombine with vacancies. The theoretical barrier of 0.45 eV [20] for adatom migration appears to be higher than the barrier for interstitial diffusion, as the presence of a nearby layer should also facilitate migration; experimental estimates put it as low as 0.1 eV [27]. A further possibility for any residual interstitials is to form clusters in the interlayer regions [28]. Our calculations predict that clustering on the surface is energetically favorable, and that clusters with even numbers of carbon atoms (e.g., dimer, etc.) are nonmagnetic, and that odd clusters show rapidly decaying moments. Since the irradiation doses in experiments are not that high, clustering between layers would be dominated by dimer formation and can be excluded from our discussion of magnetic defects.

With these results in mind, we now consider the interaction of helium with graphite. As one would expect, helium shows very little interest in bonding with graphite. Our calculations for the ideal graphene sheet give an adsorption energy of −15 meV and no magnetic signal. If we introduce a vacancy, the equilibrium adsorption site is 3.06 Å above the vacancy with an adsorption energy of only 16 meV; in this case, we recover the magnetic moment of the vacancy itself, about $1\mu_B$. Helium does have a metastable position in the vacancy, which destroys the magnetic moment, but in practice this configuration is extremely unlikely as it costs 3.29 eV to introduce He to the vacancy. Basically, helium's role in the process is just to create the initial defects; most of these are then healed at room temperature via recombination or clustering, leaving only a weak magnetic signal due to residual vacancies.

Similar to He irradiation, energetic H ions create Frenkel pairs, but, unlike He, H can form covalent bonds with carbon, and specifically with vacancy dangling bonds. The interaction of H with graphite has been studied at length, as this issue is important for H storage, fusion devices, and in understanding the mechanism of H_2 formation in the interstellar region [29]. When a H atom is slowed down to thermal energies, it occupies an interstitial position between the graphite planes, bonding on top of a carbon site.

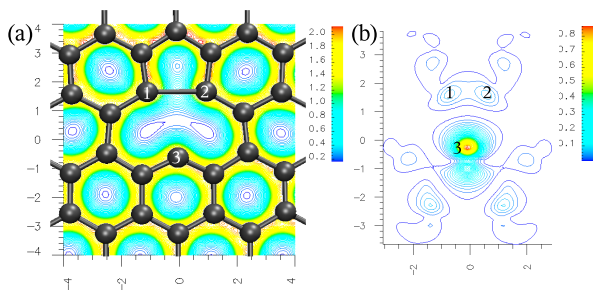The adsorption energy of H on perfect graphene is 0.87 eV (0.76 eV [29], 0.76 eV [30], and 0.67 eV [31]) and

FIG. 1 (color online). (a) Structure, charge density ($e/\text{Å}^3$), and (b) spin density ($e/\text{Å}^3$) of the graphite vacancy. Density plots are slices in the graphene plane.

the adsorption position is above a carbon atom. This configuration has no magnetic moment unless the density of hydrogen on the surface is very high, i.e., approaching a few percent [30]. In any case, above a graphene sheet the hydrogen is quite mobile (barrier 1.30 eV for an isolated H on graphene, but reducing to 0.48 eV near other H atoms [29]) and does not form a dimer easily since the barrier for recombination is 2.82 eV [29]. Hence it is highly probable that hydrogen migrates on the plane until it is pinned by another defect.

If the hydrogen encounters an empty vacancy, then it saturates the dangling bond and is pinned at a height of 1.25 Å above the plane, with an adsorption energy of 4.36 eV. This configuration is nonmagnetic—contrasting with studies of the effect of a hydrogen on a vacancylike defect in fullerenes [32], where a magnetic moment of $3.0\mu_B$ was observed. However, the local structure in the fullerenes is different, and the undercoordinated carbons cannot saturate bonds with each other due to the increased curvature-induced mechanical strain. Hence, hydrogen saturates only one dangling bond and the local moment is provided by the other two sites. A similar configuration can be considered in graphene, where hydrogen adsorbs directly into the vacancy, in plane with the graphene sheet, providing a moment of $2.3\mu_B$. However, this configuration is metastable with an energy about 1.3 eV higher than the previous structure, and also a very small barrier between the two states. It is possible that the van der Waals interaction from other layers in graphite may stabilize this structure, or at least increase the barrier, but other configurations seem more likely.

Two stable magnetic configurations involving hydrogen do exist in graphite. First, if an hydrogen atom encounters a vacancy which has already been saturated by hydrogen, it will bond to the other side of the vacancy [see Fig. 2(a)] with an adsorption energy of 3.2 eV, at a distance of 0.76 Å below the plane; the original H moves to 0.89 Å above the plane. This configuration has a magnetic moment of $1.2\mu_B$ localized on the dangling sp^2 bond [see Fig. 2(b)]. Addition of a third hydrogen completes the decoration of the vacancy edges, saturates the remaining dangling bond, and thus destroys the magne-
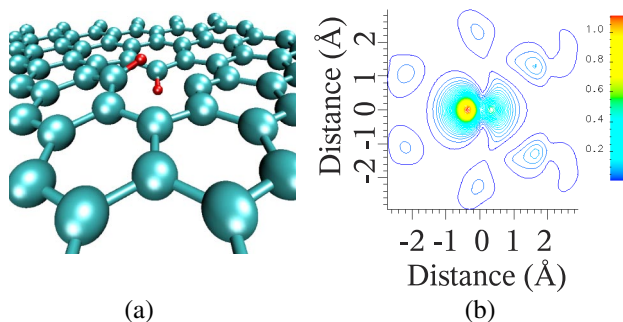
tism of the vacancy. Adsorption energy to a system already occupied by two hydrogens is 4.0 eV, but steric hindrance is likely to provide a barrier for this configuration.

Second, if an hydrogen atom encounters a carbon adatom, they will pin each other [see Fig. 3(a)]. The C-H bond is tilted due to interaction with the second graphene layer (which must be considered for such a "tall" defect), and H is 2.1 Å above the plane. The adsorption energy of this complex is 3.8 eV. The resulting C-H group has a magnetic moment of $0.9\mu_B$ [see Fig. 3(b)].

If we assume that every hydrogen atom introduced by proton irradiation eventually will saturate a carbon dangling bond, then we can predict a rough estimate of the measurable magnetic signal. Two hydrogen atoms at a vacancy result in a moment of $1.2\mu_B$, and an adatom-hydrogen group provides a moment of $0.9\mu_B$ from the C-H itself, and $1.0\mu_B$ from the uncompensated vacancy. Hence, we can consider each hydrogen as providing an average moment of $1.25\mu_B$. For an experimental dose of 3 μC (cf. Fig. 2 in Ref. [16]) of protons, we get a signal of 0.2 μemu, which is in an agreement with the experimental signal 0.3 ± 0.2 μemu and with higher dose of 10 μC the predicted signal is 0.8 μemu in agreement with 1 μemu. Obviously, it is very difficult to specify exactly the ratio of different defects that would actually be present in the irradiated material, but the agreement with the experimental magnetic signal strongly suggests that the H-vacancy complex plays a dominant role. Note that at small doses the experimental signal should be directly proportional to the irradiation dose, but at higher doses this is not the case due to H outgasing and damage accumulation (scales as a square root of the dose [16]). Also, in this analysis we have implicitly assumed that, due to defect-defect interactions, there will be magnetic ordering of the H-vacancy complexes. Although we cannot demonstrate this in our DFT calculations, previous results for adsorbed hydrogen [33] indicate that coupling on graphite can be very long ranged (up to 25 lattice constants).

As specific attention has recently been paid to possible magnetism in carbon nanotubes [9,14], we have also considered the interaction of hydrogen with vacancies
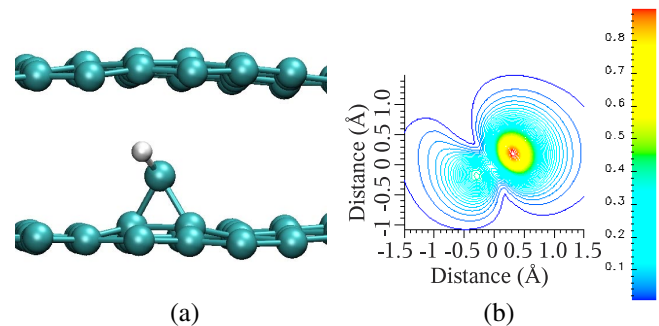

FIG. 2 (color online). (a) Structure and (b) spin density $(\mu_B/\text{Å}^2)$ of a vacancy surrounded by two hydrogens.

FIG. 3 (color online). (a) Structure and (b) spin density $(\mu_B/\text{Å}^2)$ of a C-H group adsorbed between two layers of graphene.

in nanotubes. We found that such defects are also magnetic in nanotubes, but the story is complicated by curvature and chirality. The "parallel" (the pentagon bond lying parallel to the tube axis) configuration on the $(5, 0)$ tube and the "perpendicular" configuration on the $(7, 0)$, $(8, 0)$, and $(10, 0)$ tubes are magnetic, with magnetic moments of about $1.0\mu_B$. For other armchair and zigzag nanotubes, the moment is zero. The details of these results are still being analyzed and will be published separately [34].

In conclusion, we have investigated the magnetic properties of the most prolific defects which appear in graphite under irradiation—vacancies and vacancy-hydrogen complexes. Our calculations demonstrate that vacancies are magnetic, but, due to the high mobility of carbon interstitials at room temperature, vacancies will mostly annihilate with interstitials. We further show that hydrogen will strongly adsorb at vacancies in graphite, maintaining the magnetic moment of the defect, and that for small irradiation doses vacancy-hydrogen complexes should give rise to a macroscopic magnetic signal, which agrees very well with the experimental values. At the same time, H adsorption should suppress recombination of Frenkel pairs. Thus, our results stress the importance of hydrogen for the development of the magnetic state [35] and offer a possible explanation for the results of experiments on graphite irradiation with H and He ions: hydrogen irradiation should result in a much stronger magnetic signal. It is worth noting that the large moment of H at a vacancy predicted here implies that H impurities are as important as Fe impurities for carbon systems [36]. Finite magnetic moments of naked vacancies also indicate that a weakly magnetic sample could be produced by irradiating with He ions, but at very low temperatures, when recombination of Frenkel pairs is suppressed.

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