Magnetism in Disordered Graphene and Irradiated Graphite

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The magnetic properties of disordered graphene and irradiated graphite are systematically studied using a combination of mean-field Hubbard model and first principles calculations. By considering large-scale disordered models of graphene I conclude that only single-atom defects can induce ferromagnetism in graphene-based materials. Preserved stacking order of graphene layers is shown to be another necessary condition for achieving a finite net magnetic moment of irradiated graphite. Ab initio calculations of hydrogen binding and diffusion and of interstitial-vacancy recombination further confirm the crucial role of stacking order in π-electron ferromagnetism of proton bombarded graphite.

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Graphene and related nanostructured materials are recognized as possible building blocks for prospective electronics technologies [1] among which spintronics [2] occupy a special place. Extraordinary magnetic properties of carbon nanostructures resulting from their reduced dimensions have been predicted theoretically [3, 4, 5]. This progress allowed to think of novel devices realizing extraordinary magnetic properties are still awaiting their experimental confirmation, a discovery of room-temperature ferromagnetism in proton irradiated graphite [7] continues to stimulate research in the field of magnetic carbon. Recent experimental investigations have revealed that the magnetic order in proton bombarded graphite has two-dimensional (i.e. graphene-like) character [8] and originates from the carbon π-electron system rather than from intrinsic or introduced impurities [9]. These results are supported by theoretical calculations [10, 11] which show the crucial role of defect-induced quasilocalized states [12, 13] in producing a magnetic order stable at high temperatures. Although magnetic properties of defects in graphene have been widely studied by first principles methods, the use of different periodic models of limited size often resulted in varying outcomes [10, 14, 15, 16, 17]. This calls for a study employing realistic disordered models. The origin of ferromagnetic order in graphene which generally favors antiferromagnetic coupling between the neighboring atoms [14, 10] as well as the role of various possible defects in inducing magnetism remain elusive.

In this Letter, I address magnetic properties of disordered graphene and irradiated graphite by using a combination of mean-field Hubbard model and first principles calculations. The Hubbard model calculations of realistic models of disordered graphene show that only single-atom defects such as vacancies or chemical functionalizations unequally distributed over the two sublattices may result in a net magnetic moment. Further first principles calculations point out that the stacking order of graphite lies at the origin of ferromagnetism in proton bombarded graphite. To study the magnetic properties of disordered graphene I employ the mean-field approximation of the Hubbard model which proved to describe carbon π-electron systems in good agreement with first principles calculations [6]. The corresponding Hamiltonian reads

\[ \hat{H} = -t \sum_{\langle i,j \rangle, \sigma} [c_{i\sigma}^\dagger c_{j\sigma} + v.c.] + U \sum_{i, \sigma} n_{i\sigma} \langle n_{i-\sigma} \rangle, \]

where the first part is the single-orbital tight-binding Hamiltonian while the second part accounts for the on-site Coulomb repulsion. In this expression \( c_{i\sigma} (c_{i\sigma}^\dagger) \) annihilates (creates) an electron with spin \( \sigma \) at site \( i \) and \( \langle i,j \rangle \) stands for the pairs of bonded atoms. The expectation values of the spin-resolved density \( n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \) on atom \( i \) are obtained from the eigenvectors of \( \hat{H} \). The self-consistent solution of the problem provides the spin densities \( M_i = (n_{i\uparrow} - n_{i\downarrow})/2 \) on each atom \( i \).

The models of disordered graphene are generated by distributing randomly point defects in a large 20 \times 20 supercell (800 atoms). The calculations are performed for 64 different random distributions in order to provide reliable statistical sampling. This computational protocol yields the mean magnetic moments converged within ~1% both with respect to the supercell size and the number of configurations. Similar approach was successfully applied to study vacancy-induced magnetism in oxide materials [18]. I consider the range of defect concentration \( x = N_d/N = 0.01 - 0.1 \) with \( N_d \) out of \( N \) atoms or bonds being affected. The values \( U/t \approx 1.0, 1.33, 1.67, 2.0 \) are studied in order to investigate the role of on-site Coulomb repulsion magnitude. While the value of hopping integral \( t \approx 2.7 \) eV is well established for graphene, there is a growing debate regarding the on-site Coulomb repulsion \( U \). It is worth pointing out that the magnitude of \( U \) was inferred from
magnetic resonance studies of neutral soliton states in trans-polyacetylene [19], a one-dimensional bipartite sp² carbon system closely related to graphene. The estimated \( U = 3.0 - 3.5 \) eV \( (U/t = 1.1 - 1.3) \) [20] closely corresponds to \( U/t = 1.33 \) considered here.

The empirical value of \( U/t \) can also be compared to the values obtained by establishing a relation between the results of first principles and mean-field Hubbard model calculations [21]. The local density approximation (LDA) leads to \( U/t \approx 0.9 \) while the generalized gradient approximation (GGA) gives \( U/t \approx 1.3 \) in good agreement with the empirical value. It is somewhat cautionary that the results provided by generally more accurate hybrid density functionals correspond to \( U/t \approx 2.0 \) which is very close to the critical value \( U/t \approx 2.2 \) at which graphene accepts an antiferromagnetic ground state [22]. Discrepancies between the results of hybrid density functional calculations and experimental data for trans-polyacetylene have also been reported [23]. This urges to reconsider performance of these methods for describing magnetic sp² carbon systems.

Disorder in graphene induced by chemical treatment or irradiation with ions or electrons can be conveniently classified by the following three types of point defects. A carbon atom removed from the sp² lattice (i) ('vacancy') corresponds to either true vacancy [10, 14] or the rehybridization into the sp³ configuration. Such rehybridization may result from chemical functionalization (e.g. hydrogen chemisorption [10, 24]) or binding of the interstitial carbon atoms in irradiated graphite [25, 26]. A multiple-atom 'vacancy' can be viewed as an ensemble of neighboring single-atom 'vacancies'. In some cases a bivalent chemical functionalization results in breaking the bond between the pairs of adjacent atoms without their rehybridization [27]. This leads to so-called bond dilution (ii). While (i) and (ii) give rise to undercoordinated carbon atoms, topological defects (iii) such as the Stone-Wales defect [28] maintain the coordination number. This type of disorder can be described as a permutation of connectivity involving two or more neighboring atoms. However, no magnetic moments due to the presence of the Stone-Wales defects were observed in this study as well as in previous ab initio calculations [13]. Below, I focus only on the magnetism induced by the 'vacancies' and the bond dilution disorder.

The Hubbard model solutions for all configurations considered are characterized by the antiparallel orientation of magnetic moments on the two sublattices. Figs. 1a,b show the sublattice-resolved average magnetic moments \( \langle M_i^\eta \rangle \) \( (\eta = A, B) \) induced by varying concentrations of 'vacancies' for different values of \( U/t \). For the case of defects equally distributed over the two sublattices [Fig. 1a] \( \langle M_A \rangle \) and \( \langle M_B \rangle \) compensate each other resulting in an antiferromagnetic state with zero total magnetic moment \( M = N ((\langle M_A^A \rangle + \langle M_B^B \rangle))/2 = 0. \) This result can be understood within the Lieb theorem [29] which relates the total magnetic moment of a half-filled bipartite system to the difference of number of atoms in the two sublattices. In our case the two sublattices contain equal number of atoms resulting in zero net magnetic moment. The sublattice-resolved magnetic moments \( \langle M_i^\eta \rangle \propto x^\gamma \) \( (0 < \gamma < 1) \) show sub-linear dependence on \( x \) and tend to increase with increasing the magnitude of \( U/t \). In particular, for \( U/t = 1.33 \) the dependence on 'vacancy' concentration \( x \) can be accurately fitted by \( \langle M_i^\eta \rangle \approx 0.234 \cdot x^{0.78} \). For the case of 'vacancies' in sublattice \( B \) only the total magnetic moment per unit cell \( M = x \) [open circles in Fig. 1b)]. This is again in strict agreement with the Lieb theorem predicting \( 2M = N_A - N_B \). The magnetic state originates from the Hund's rule population of \( N_A - N_B \) zero-energy defect-induced quasilocalized states in sublattice \( A \). However, these singly-occupied states induce exchange polarization of the fully-occupied ones leading to a significant antiparallel magnetization of the atoms in sublattice \( B \). The induced magnetic moments follow an approximate dependence \( \langle M_i^B \rangle \approx -0.159 \cdot x^{0.69} \).

Figure 1c illustrates the distribution of magnetic moments induced by the 'vacancy' disorder in a representative configuration \( (x = 0.03) \) with defects in both sublattices. Magnetic moments develop in the nanometer-size regions characterized by the local domination of 'vacancies' in one of the sublattices [1 and 2 in Fig. 1c)]. In these regions one can trace distinctive triangular patterns associated with individual quasilocalized states [12].
The sublattices are inequivalent due to the stacking order of graphite. In bulk graphite and multilayer graphene, magnetic correlations develop as a result of bond dilution for different $U/t$ values and (b) spin density distribution in a representative configuration ($x = 0.10$; $U/t = 1.33$).

In contrast, the proximity of two defects pertaining to opposite sublattices (paths $A \rightarrow B$ and $A' \rightarrow B'$ in Fig. 3(b,c)) defined by the lowest barrier of path $A \rightarrow B$ is $1.04$ eV. Diffusion in the direction of $c$-axis requires much higher activation energy of $\sim 4$ eV. Free diffusion of protons in graphite will result in either saturation of vacancy dangling bonds or in the formation of energetically favorable aggregates with both sublattices being populated. Magnetic moments of the hydrogen aggregates quench due to the large splitting of quasilocalized states in the complementary sublattices. In addition, the condition of preserving the stacking order of graphite limits the maximum irradiation dose and intensity. Subsequently, there exist only

![FIG. 2: (Color online) (a) Average magnetic moments of carbon atoms in A and B sublattices of graphene as a function of bond dilution for different $U/t$ values and (b) spin density distribution in a representative configuration ($x = 0.10$; $U/t = 1.33$).](image)

![FIG. 3: (a) Inequivalent carbon atoms (A and B) in graphite. (b) Possible pathways for the diffusion of chemisorbed hydrogen in the $ab$ plane of graphite. (c) Relative energies of the potential energy surface minima and transition states for the diffusion of chemisorbed hydrogen in graphite.](image)
relatively narrow range of conditions at the sublattice-discriminating hydrogen chemisorption can be achieved. This accords with the fact magnetic moments are induced only in the narrow ring surrounding the irradiated spot.

Similarly to hydrogen chemisorption, single-atom vacancies produced by the knock-on recoils induce low-energy quasilocalized states \[10\]. In contrast, interstitial carbon atoms in the energetically preferred configuration \[25\] lead to the rehybridization of the pairs of neighboring atoms in the adjacent graphene layers. This situation is equivalent to the case of di-vacancies providing no low-energy states required for developing magnetic moments. Cross-sections for the momentum transfer due to knock-on collisions are likely to be equal for both A and B carbon atoms in graphite. However, the stacking order of graphite has strong influence on the kinetics of interstitial-vacancy recombination. Instantaneous recombination of low-energy recoils was found to be significantly more likely for the atoms in position A \[26\]. At longer time scales, diffusing interstitials encounter different barriers for the recombination with vacancies in these two positions. First principles calculations show different minimum transition barriers of 0.04 eV and 0.22 eV for A and B vacancies, respectively. Both values are below the diffusion barrier of interstitial atoms \[0.5 \text{ eV} \] suggesting that only very small difference in populations of the two sublattices by vacancy defects can be achieved in practice. Nevertheless, both vacancies and chemisorbed hydrogen atoms are found to populate preferably sublattice B thus producing ferrimagnetic order with the spin polarization larger for sublattice A.

In conclusion, I have shown the crucial role of single-atom defects in combination with a sublattice-discriminating mechanism for developing ferromagnetic order in graphene-based materials. In graphite the role of such mechanism is played by the stacking order of graphene layers. This suggestion is confirmed by the ab initio investigation of hydrogen chemisorption and vacancy defects in proton bombarded graphite. The results of this study pave a way for tailoring carbon based magnetic materials by means of irradiation and chemical treatment of graphite and other graphene derivatives.

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