Local defects and ferromagnetism in graphene layers.

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We study the changes in the electronic structure induced by lattice defects in graphene planes. In many cases, lattice distortions give rise to localized states at the Fermi level. Electron-electron interactions lead to the existence of local moments. The RKKY interaction between these moments is always ferromagnetic, due to the semimetallic properties of graphene.

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Introduction. A number of recent experiments suggest that pure graphite behaves as a highly correlated electron system. In particular it shows a metal-insulator transition in magnetic fields and insulating behavior in the direction perpendicular to the planes in different samples. Recent results show ferromagnetic behavior, enhanced by proton bombardment, what opens up a new way to the creation of organic magnets. In this paper we study the formation of local moments near simple defects. It is shown that many types of lattice distortions, like cracks and vacancies, can induce localized states at the Fermi level, leading to the existence of local moments. The RKKY interaction between these moments is always ferromagnetic due to the semimetallic properties of graphite. Hence, the RKKY interaction does not lead to frustration and spin glass features.

The model. The conduction band of graphite is well described by a tight binding model which includes the π orbitals which are perpendicular to the graphite planes at each C atom. If the interplane hopping is neglected, this model describes a semimetal, with zero density of states at the Fermi energy, and where the Fermi surface is reduced to two inequivalent K-points located at the corner of the hexagonal Brillouin Zone. The low-energy excitations with momenta in the vicinity of the Fermi points have a linear dispersion and can be described by a continuum model which reduces to the Dirac equation in two dimensions. The Hamiltonian density of the system is

\[
\mathcal{H}_0 = \hbar v_F \int d^2r \Psi^\dagger(r) (i \sigma_x \partial_x + i \sigma_y \partial_y) \Psi(r),
\]

where the components of the two-dimensional spinor \( \Psi(\mathbf{r}) = (\Psi_1(\mathbf{r}), \Psi_2(\mathbf{r})) \) correspond to the Bloch states of the two sublattices in the honeycomb structure, independent of the absence of interactions. In the clean two-dimensional system there is no room for low energy electronic instabilities, the short range interactions being irrelevant due to the vanishing density of states at the Fermi level.

It is known that disorder significantly changes the states described by the two dimensional Dirac equation, and, usually, the density of states at low energies is increased. Lattice defects, such as pentagons and heptagons, or dislocations, can be included in the continuum model by means of a non-abelian gauge field that reproduces the effects of the curvature of the lattice and the possible exchange of Fermi points. Within the same theoretical scheme it has also been shown that certain types of disorder randomly distributed in the graphene lattice enhances the effect of the interactions and can stabilize new phases. In addition, a graphene plane can show states localized at interfaces, which, in the absence of other types of disorder lie at the Fermi energy. Structures with mixed \( sp^2 \) and \( sp^3 \) bonding can also lead to localized states.

The tight binding model defined by the π orbitals at the lattice sites can have edge states when the sites at the edge belong all to the same sublattice (zigzag edge). These states lie at zero energy which for neutral graphene planes correspond to the Fermi energy. In the continuum model described earlier localized states are normalizable solutions \( (\Psi_1(\mathbf{\bar{r}}), \Psi_2(\mathbf{\bar{r}})) \) of the Dirac equation:

\[
(\partial_x + i \partial_y) \Psi_1(\mathbf{\bar{r}}) = 0
\]

\[
(\partial_x - i \partial_y) \Psi_2(\mathbf{\bar{r}}) = 0
\]

These equations are satisfied if \( \Psi_1(\mathbf{\bar{r}}) \) is an analytic function of \( z = x - iy \) and \( \Psi_2(\mathbf{\bar{r}}) \) is an analytic function of \( \bar{z} = x + iy \). Zigzag edge states can be obtained as follows. Consider a semi-infinite honeycomb lattice with an edge at \( y = 0 \) and which occupies the half plane \( x > 0 \). A possible solution which decays as \( x \to \infty \) is

\[
\Psi_1(x, y) \propto e^{-kz} = e^{iky} e^{-kx}, \Psi_2(\mathbf{\bar{r}}) = 0 .
\]

These solutions satisfy the boundary conditions at \( y = 0 \) if the last column of carbon atoms belong to the sublattice where the component \( \Psi_1 \) is defined. Then, the next column belongs to the other sublattice, where the amplitude of the state is, by construction, zero.

This kind of solutions can be generalized to describe other types of extended defects that will be produced in experiments where graphite samples are bombarded by protons. In a strongly disordered sample, large defects
A similar solution is obtained by exchanging the upper by the lower spinor component, and replacing \( z \leftrightarrow \bar{z} \).

Because of the discreteness of the lattice, the allowed values of \( n \) should be smaller than the number of lattice units spanned by the crack.

We have checked numerically the existence of these localized states by diagonalizing the tight binding Hamiltonian in finite lattices of different sizes. The dependence of some of the states close to the chemical potential (zero energy) on the cluster size is shown in Fig. 2. The delocalized states show a dependence \( \epsilon_{\text{del}} \propto L^{-1} \), consistent with the properties of the Dirac equation from which they can be derived. The states closest to \( \epsilon = 0 \), show a dependence \( \epsilon_{\text{loc}} \propto L^{-2} \), which suggest a power law localization, in agreement with the previous analysis.

These states are half filled in a neutral graphene plane. In the absence of electron interactions, this leads to a large degeneracy in the ground state. A finite local repulsion will tend to induce a ferromagnetic alignment of the electrons occupying these states, as in similar cases with degenerate bands [26].

To verify this behavior and to compare with previous results we have performed an unrestricted Hartree Fock calculation of the graphene cluster with different types of defects including large vacancies as the one shown in Fig. 1. Similar calculations done in graphene ribbons have shown non-bonding molecular orbitals localized mainly along the zigzag edges (edge states) [27, 28]. These edges have partly flat bands which give rise to a sharp peak in the density of states at the Fermi energy. A finite on-site Coulomb interaction leads to an instability of these flat bands and to the existence of spin-polarized states. We have verified that the similar behavior can
The on-site interaction term is \( U = 0 \). The defect with zig-zag boundary as the one shown in Fig. 1. The on-site interaction term is \( U = 0 \).

![Fig. 3: Density of states of a 26 \times 26 cluster with a large defect with zig-zag boundary as the one shown in Fig. 1. The on-site interaction term is \( U = 0 \).](image)

![Fig. 4: Same as Fig. 3 with an on-site interaction \( U = 0 \).](image)

also be obtained near the boundary of a large defect as the one shown in Fig. 1. We have performed calculations in a honeycomb lattice of various sizes with a maximum of 26\( \times \)26 unit cells, i.e. a cluster of 52 \( \times \) 52 sites. In the absence of defects the density of states is zero at the Fermi level, Fig. 2 shows the charge density distribution of a lattice with an extended vacancy shaped as shown in Fig. 1, without on-site interaction. The Fermi level is located at zero. A peak in the Fermi level is formed due to the presence of defects. The total magnetization of the cluster is zero. When the on-site interaction is switched on, a spin polarization arises of a magnitude proportional to the size of the defect. Fig. 4 shows the density profile of the polarized cluster obtained with \( U = 0.5t \).

Next we will analyze the influence of these magnetic moments on the conduction band. The hopping between the states involved in the formation of these moments and the delocalized states in the conduction band vanishes by definition, if the localized states lie at zero energy. Hence, a Kondo-like coupling mediated by the hopping will not be induced. The localized electrons act as a reservoir of localized moments, which interact with the valence electrons via the on-site Hubbard repulsion, \( U \). The wavefunction of the localized electrons overlaps on many sites with the valence electrons. On these sites, the valence electrons will tend to be polarized with their spins parallel to the spins of the localized electrons. The change in the energy at a given site for the valence electrons near the defect is of order \( U \), distributed over \( N \) sites. Then, the valence electrons will induce long range RKKY interactions between the localized moments, which can be estimated by adding the contributions from all sites. We find:

\[
J_{\text{RKKY}}(\mathbf{r}) \sim U^2 N^2 \int d^2k e^{i\mathbf{k}\cdot\mathbf{r}} \chi(\mathbf{k}) \sim U^2 N^2 \frac{a^4}{v_F |\mathbf{r}|^3} \tag{3}
\]

Where \( a \) is the lattice constant, and the static susceptibility is given by: \( \chi(\mathbf{k}) \propto |\mathbf{k}|^{12} \), and \( a \) is the lattice constant.

Due to the absence of a finite Fermi surface, the RKKY interaction in eq. (3) does not have oscillations. Hence, there are no competing ferro- and antiferromagnetic couplings, and the magnetic moments will tend to be ferromagnetically aligned. The total polarization per unit area at low temperatures is proportional to \( N_c \), where \( c \) is the concentration of defects, and \( N \) is proportional to the average size.

We can make an estimate of the Curie temperature from the coupling between the local magnetic moments given in eq. (3). The entropy cost of aligning ferromagnetically moments is \( S \sim T \) per moment. The average distance between moments is \( |\mathbf{r}| \sim c^{-1/2} \). Hence, the free energy per moment in the ferromagnetic phase can be written as:

\[
\mathcal{F}(m) = \left(-c_1 \frac{U^2 N^2 a^4 c^{3/2}}{v_F} + c_2 T\right) m^2 + \cdots \tag{4}
\]

where \( c_1 \) and \( c_2 \) are numerical constants of order unity. The value of the free energy will be negative (and below the value in the paramagnetic phase) at a Curie temperature given by:

\[
T_c \sim \frac{U^2 N a^3}{3W} \sim \frac{U^2 Na}{W l^3} \tag{5}
\]

where \( W \) is the conduction electron bandwidth, \( W \sim v_F/a \), and \( l \) is the average distance between impurities.

The Curie temperature depends on the concentration and size of the defects. Assuming, as an example, that \( N \sim 10 \) and \( l \sim 10^2 a \), we obtain a saturation magnetization of \( 10^{-3} \) Bohr magnetons per unit cell, and a Curie temperature \( T_C \sim 10^{-4} U^2/W \). The value of \( U^2/W \) can be estimated to be \( \sim 1\text{eV} \). Then, these arguments give \( T_C \sim 1\text{K} \). This temperature is considerably lower than the experimentally observed ones. It is worth noting, however, that this analysis does not take into account the enhancement of the susceptibility of the conduction electrons, percolation effects due to the random distribution of impurities, and the finite extension of the localized states induced by the defects.
Conclusions. We have shown that, under very general circumstances, lattice defects, vacancies and voids in the graphene structure give rise to localized states at the Fermi energy. The number of these states scales roughly with the perimeter of the defect. Repulsive electron-electron interactions lead to the polarization of these states, and to the formation of local moments. The RKKY interaction mediated by the valence electrons decays as $r^{-3}$, where $r$ is the distance between defects, and shows no oscillations, due to the vanishing of the Fermi surface in a graphene layer. The interaction is ferromagnetic, and the system cannot show the frustration effects and spin glass features observed in other disordered systems with local moments. On the other hand, the Curie temperature estimated assuming a random distribution of local moments is low, $T_C \sim 1K$, for reasonable values of the defect concentration. It may happen that percolation effects, and the finite extension of the localized states which give rise to the local moments will increase the value of $T_C$.

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