Sublattice ordering in a dilute ensemble of monovalent adatoms on graphene

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received 14 October 2009; accepted in final form 22 February 2010
published online 26 March 2010

PACS 64.70.Jd – Structural transitions in nanoscale materials
PACS 73.22.-f – Electronic structure of nanoscale materials and related systems
PACS 05.60.Gg – Quantum transport

Abstract – When adsorbents attach themselves to carbons in the honeycomb lattice of graphene, they may preferentially take positions on one of its two sublattices, thus breaking the global lattice symmetry. This leads to opening a gap in the electronic spectrum. We show that such a sublattice ordering may spontaneously occur in a low-density ensemble of adatoms adsorbed on graphene, due to the long-range interaction between them mediated by electrons. As a result sublattice-ordered domains may form, with electronic properties characteristic of a two-dimensional topological insulator.

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The flatland of graphene [1] turned out to be a laboratory where fundamental ideas of particle physics and cosmology [2] find an on-table realization. The low-energy spectrum of charge carriers in graphene resembles that of massless relativistic particles [3]; it directly follows from the symmetry of its hexagonal lattice [3,4] that the spectrum is gapless and linear. In pristine graphene, the lattice symmetry is so robust and resilient against spontaneous symmetry breaking that no gap-generation mechanism has yet been proposed. Here we show that a relatively low concentration of adsorbents sprinkled over graphene flake can reverse the situation. It turns out that even at relatively low concentration the adsorbents may self-organize into the partially ordered state. The ordering generates a gap in the electronic spectrum and converts graphene into a topological insulator.

The honeycomb lattice of graphene with two carbons in the unit cell can be considered as a combination of two overlaying triangular sublattices, A and B —see fig. 1. It is the symmetry between the sublattices that prevents formation of the gap in pristine graphene [3,4]. Consider now one-sided chemisorption of atoms on a flake deposited on an isolating substrate. Some adsorbents, such as fluorine, hydrogen, or hydroxyl group are known to form a covalent bond with a particular carbon [5–8], thus violating the symmetry between the sublattices locally. As long as the density $\rho$ of the adsorbents is low ($\rho \ll a^{-2}$, where $a$ is the lattice constant of graphene) and their locations are random, one should expect approximately equal occupation of the sublattices, $\rho_A \approx \rho_B$ (here, $\rho_A/B$ is density of adsorbents on A/B sublattice, and $\rho = \rho_A + \rho_B$). Effect of the local symmetry violation is, then, limited to the scattering of electrons.

However, under certain conditions the global sublattice symmetry can be spontaneously violated ($\rho_A \neq \rho_B$), leading to the correlations between sublattice affiliations of adatoms. These correlations between adsorbents’ positions are electron-mediated: each adsorbent creates a sublattice-asymmetric perturbation in the electronic density (which is equivalent to the polarization of the electron states inside the unit cell), which in turn interacts with other adsorbents. The effective long-range pair interaction between the adsorbents depends on whether they reside on the same sublattice, or on different ones. This situation can be described in terms of the two-dimensional Ising model with the direction of an Ising “spin”, $m = \pm 1$ identifying to which sublattice each given adsorbent belongs. The finite difference $\rho_A - \rho_B = \rho M$ between the sublattice occupations emerges, then, as an analog of the spontaneous spin polarization $M = \langle m \rangle$ in

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the Ising model, and spontaneous breaking of sublattice symmetry over mesoscopic scale areas in a flake gives rise to the gap in the electronic spectrum, fig. 1.

Effect of the partial ordering illustrated in fig. 1 is determined by the relation between the electronic de Broglie wavelength $\lambda = \hbar / p$ and the mean distance, $\rho^{-1/2}$ between the adsorbents. While “high-energy” electrons with short wavelength $\lambda \ll \rho^{-1/2}$ are insensitive to the ordering (for them the adsorbents act as individual scatterers), for electrons with long wavelength $\lambda \gg \rho^{-1/2}$ the ordering implies global symmetry-breaking field, which opens the spectral gap, $\Delta$ (see fig. 1):

$$\varepsilon = \pm \sqrt{v^2 p^2 + \Delta^2}, \quad \Delta = Mu^2 \rho. \quad (1)$$

Here, $v$ is the Dirac velocity of electrons, and $u$ is the electron-adatom coupling constant. The density of states (DoS) corresponding to the gapped spectrum eq. (1) is

$$\gamma = \gamma_0 \theta(\varepsilon - \Delta)$$

(where $\theta(z)$ is the step function and $\gamma_0 = 2\varepsilon / \pi v^2 \hbar^2$ is DoS in pristine graphene, which takes into account the spin and valley degeneracy). One can say that in a unit area of the graphene flake as many as $\Delta^2 / (\pi v^2 \hbar^2)$ states that originally resided within the gap $\varepsilon < \Delta$ have been transferred by the ordering to the higher energies, $|\varepsilon| > \hbar \sqrt{\rho}$. In the absence of carriers the conduction band is empty, while the valence band is full. The gap formation thus reduces the sheet density of the energy by, approximately, $\Delta^2 / \sqrt{\rho} / \hbar v \sim M^2 u^2 (a^2 \rho)^3 / (\sqrt{\rho} / \hbar v)$. For the ordering to be thermodynamically favorable, the energy gain should exceed the free energy cost, $k_B T M^2 \rho$ related to the entropy drop upon ordering. We therefore predict a phase transition with the sublattice symmetry breaking at $T = T_c$,

$$T_c = C \frac{u^2}{\hbar v \alpha^2} (a^2 \rho)^{3/2}, \quad \text{(2)}$$

where $C \sim 1$ is a numerical factor which will be evaluated below. The formation of the gap in the electronic spectrum due to the partial ordering of adsorbents (see fig. 1) should manifest itself in ARPES and in a suppressed infrared light absorption.

To describe the sublattice ordering transition we use the RKKY-like approach [9] to the pair correlations between adsorbents (adatoms) and map the problem onto the Ising model. The Hamiltonian of graphene with adsorbents residing on carbons has the form [8,10]

$$\hat{H} = v \sigma \cdot \mathbf{p} + u a^2 \sum_i [\hat{\sigma}_x m_i + \hat{V}_{res}] \delta(\mathbf{r} - \mathbf{r}_i). \quad (3)$$

The first term $\hat{H}$ describes free electrons with linear spectrum. The second term accounts for the interaction of the electrons with the adsorbents. It is responsible for the A-B symmetry breaking. Three Pauli matrices, $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$ act on the sublattice components of the electronic Bloch function. Ising “spin” $m_i$ determines the sublattice A ($m_i = +1$) or B ($m_i = -1$) that hosts given adsorbent. The residual term $\hat{V}_{res}$ contains two contributions, which do not affect sublattice ordering. Firstly, there are two electronic valleys in graphene, and $V_{res}$ takes into account intervalley scattering. Although we dropped the valley indices in eq. (3), everywhere below the valley degeneracy is taken into account. Secondly, $V_{res}$ contains a “scalar” contribution describing the sublattice- and valley-independent channel of electron scattering. Although such a contribution does not affect sublattice ordering directly, it is helpful to notice that it leads to a repulsive interaction between adatoms and precludes adatom clustering discussed in [11].

A remark is due here concerning the Hamiltonian (3). Strictly speaking, the interaction term in the (3) is not well defined due to ultraviolet problems and is written in this form for illustrative purposes. In a more rigorous approach $\hat{\sigma}_x m_i + \hat{V}_{res}$ should be replaced by an energy-dependent $\hat{T}$-matrix defining the long-distance asymptotic form of the electron wave scattered off the defect at point $\mathbf{r}_i$. The typical energy of electrons involved in the RKKY exchange between impurity atoms is $\Delta \varepsilon \sim \hbar v \sqrt{\rho}$. If $T(\varepsilon)$ is a slowly varying function of energy for $|\varepsilon| < \Delta \varepsilon$, one can neglect its energy dependence altogether. Technically, this amounts to treating the scattering terms in eq. (3) in the Born approximation. Under special circumstances, for instance in the presence of resonant impurity levels at energies comparable to $\Delta \varepsilon$, such an approximation breaks down and an alternative approach is to be used, e.g. such as in [11].

An adsorbent “i” attached to one of carbons redistributes the electron density between A and B sites. The density redistribution creates a sublattice-asymmetric potential landscape for another adatom “j” at a distance $r_{ij}$. We have found that energy of two adatoms is lower when they reside at the same sublattice than when
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Sublattices are different:

\[ E_{\text{int}} = -J \sum_{i \neq j} \frac{m_i m_j}{r_{ij}^3/2}, \quad J = \frac{u^2}{4\pi \hbar v F(a^2 \rho)^{3/2}} \quad (4) \]

and \( r_{ij} = |r_i - r_j| \). The electron-mediated interaction \( E_{\text{int}} \) between adatoms can be derived using the standard diagrammatic technique [9]. The interaction eq. (4) resembles the RKKY interaction between spins in dilute ferromagnetic semiconductors [12]. A similar interaction has also been investigated for surface adsorbates on metals [13–17]. There is an important peculiarity of undoped graphene [18]: coupling \( \text{metals} \) [13–17]. There is an important peculiarity of undoped graphene [18]: coupling \( \text{metals} \) [13–17]. There is an important peculiarity of undoped graphene [18]: coupling \( \text{metals} \) [13–17]. There is an important peculiarity of undoped graphene [18]: coupling \( \text{metals} \) [13–17].

Conventional RKKY interaction is caused by Friedel oscillations — the electron density around a point defect oscillating in space with the wave vector equal to the momentum transfer upon scattering between the extreme points of the Fermi surface. In graphene the hexagonal Brillouin zone (BZ) is characterized by two triads of equivalent corners, \( K \) and \( K' \) related within each triad by the reciprocal lattice vectors, \( \mathbf{G}, \mathbf{G}', \mathbf{G''} \) (see fig. 1(b)). In the absence of charge carriers the Fermi line is shrank to the points \( K \) and \( K' \) which become its extremes. Perturbation of the electron Vanier functions by an adsorbent creates oscillating charge redistribution analogous to the Friedel oscillations. The wave numbers in this case are equal to the reciprocal lattice vectors, \( e.g. \) \( \mathbf{G}, \mathbf{G}', \mathbf{G''} \). Usually the amplitude of Friedel oscillations is proportional to the Fermi level DoS of electrons. The latter, formally, vanishes: in neutral graphene \( \gamma \propto \varepsilon = \epsilon p \), \( e.g. \), \( \gamma(0) = 0 \). Nevertheless the charge density modulation still takes place. Indeed, according to the Heisenberg uncertainty principle, given the distance \( r_{ij} \) between the two adsorbents, the characteristic electron momentum counted from the BZ corner is \( p \sim h/r_{ij} \). Therefore, for the estimation of RKKY coupling we should use \( \gamma \sim (\hbar v r_{ij})^{-1} \). This is the source of the additional \( 1/r_{ij} \) factor in the RKKY interaction between spinfull-on-site impurities in graphene [18] and in eq. (4) describing the distance dependence of the effective interaction between adsorbents.

Equation (4) determines the Ising model in the ensemble of randomly distributed “spins” with a long-range interaction. To evaluate the critical temperature \( T_c \), we simulated the transition numerically: we used 10 realizations of random Poisson distributions of \( N = 2 \times 10^4 \) Ising spins on a plane interacting according to eq. (4). The thermodynamic average, \( M \) of the polarization for each realization was computed by the cluster Monte Carlo algorithm [19]. Results of this computation presented on fig. 2 suggest that

\[ T_c \approx 13J, \quad (5) \]

i.e. factor \( C \) in eq. (2) is \( C \approx 1 \).

It should be noted that, strictly speaking, eqs. (4) and (5) only apply in the absence of charge carriers. If doping is heavy as, \( e.g. \), in graphene on SiC [20], it suppresses the transition. Indeed, at finite carrier density \( n_e \) the RKKY interaction develops Friedel oscillations [21], \( E_{\text{int}}(n_e) \propto (m_i m_j) \sin(2\sqrt{\pi n_e} r)/r^2 \), which lead to a random sign of the exchange coupling between adatoms at distance \( r > \sqrt{1/n_e} \). As the typical distance between adatoms is \( r \sim 1/\sqrt{\rho}, \) no ordering should be expected for \( n_e > \rho \). In order to observe the predicted transition in such heavily doped systems the carrier density has to be tuned to sufficiently small values by electrostatic gates.

Two important remarks on the ordering transition are due here. One has to deal with competing interactions between the adsorbents. In addition to Ising interaction in eq. (4) between the adsorbents, each of them causes Friedel-like oscillations of a different type: with the wave vector equal to the distance between non-equivalent BZ corners \( K \) and \( K' \). The amplitude is decaying as inverse cube of the distance from the adsorbent. From the symmetry point of view these oscillations can be regarded as a charge density wave superlattice with a supercell three times as big as the unit cell. They generate an effective interaction between adsorbents which favors an AB configuration (rather than AA or BB ones) of the closest neighbor. Such interaction is anisotropic: when projected onto one supercell, two adsorbents determine one of the three possible directions of A-B bonds. Due to this anisotropy for a low-density \( \rho \ll a^{-2} \) random coverage the supercell correlations are unavoidably frustrated and would not lead to ordering. This behavior should be contrasted to that of adsorbents which reside in the middle of honeycomb lattice hexagons (such as alkali atoms) or adatoms residing over the C-C bonds: such adsorbents cannot distinguish between two sublattices, but they can establish partial ordering into a superlattice with a triple-size Kekule-type unit cell [22].
Another remark concerns the kinetics of the transition. The ordered state arises only if adsorbents can hop along a flake. This is possible only if the activation barrier for the adsorbent’s hop between A and B is less than the desorption barrier. Recent studies of hydrogen on graphite [23] suggest that desorption barrier for H on graphite is lower than its diffusion barrier. Therefore hydrogenated graphene [24] may not be the likeliest candidate to observe the suggested sublattice ordering. The alternatives are represented by halogens, e.g., fluorine. The best atom/group for realization of the proposed ordering is yet to be identified.

Let us discuss electronic properties of the graphene with partially sublattice-ordered adsorbents. Opening of the spectral gap offers an attractive route to control the transport properties. It is quite likely however that the Ising-type spontaneous symmetry breaking would result in splitting of the flake into domains of opposite “polarization” $M = \pm 1$—regions where adsorbents occupy a particular (A or B) sublattice. Such a domain can be viewed as a “weak” topological insulator [25–27]. Indeed, while inside each domain the electron spectrum is gapped, the boundary between them supports a mid-gap one-dimensional band of chiral electronic states [28]—domain wall states (DWS), which are similar to the quantum Hall edge states [29]. Even in the absence of magnetic field DWS electrons in one valley, e.g. K, propagate only in one direction, whereas in the other valley, $K'$, the DWS on the same boundary propagate in the opposite direction. Without intervalley scattering, the DWS would make a domain wall an ideal ballistic “wire”, with the width $w_{DW} \sim h\nu/\Delta \sim (h\nu/u)(a^2\rho)^{-1}$ and conductance $\alpha^2/h$.

Note that the sublattice-ordered adsorbents still scatter electrons between the valleys, at a rate

$$\tau_{\text{ee}}^{-1} \sim pu^2a^4\gamma(\varepsilon)/h, \quad \gamma(\varepsilon) = 2\pi/e\hbar^2\alpha^2. \quad (6)$$

Interaction between the oppositely propagating one-dimensional DWS leads to their localization, at the length scale of the order of the mean free path $l$ for intervalley scattering. For the energies we can substitute $\varepsilon \sim \Delta$, eq. (1) into eq. (6) and estimate the mean free path of a DWS as

$$l \sim \frac{h\nu}{u} \frac{(h\nu/u)a^2}{(a^2\rho)^2} \gg w_{DW}.$$

An immediate consequence of this would be the high resistivity of graphene flake, with characteristic for hopping resistivity temperature dependence, $R \propto \frac{2}{\Delta} \exp\left\{ (T/\Delta)^{\gamma} \right\}$ ($x = \frac{1}{2}$ for the Mott hoping law [30], and $x = \frac{1}{3}$ for the Efros-Shklovskii law [31]). As long as $l$ exceeds a typical domain size, this system should also display a strong positive magnetoresistivity $B/R(B_c)$ over a broad magnetic field range, $B_c \sim h/eI^2$. The above-described modification of transport characteristics of graphene accompanied by opening of a gap in its optical absorption spectrum would be natural manifestations of self-organization of a dilute ensemble of on-site adsorbents into a sublattice-ordered state.

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This study was supported by the EPSRC grant EP/G041954, US DOE contract No. DE-AC02-06CH11357, and Notur project of the Norwegian Research Council.

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