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Electronic Spectrum and Conductivity in Graphene with Impurities

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In the tight-binding one-electron model, the influence of substitutional impurity atoms on the energy spectrum and electrical conductance of graphene is studied. It is established that the ordering of substitutional impurity atoms on nodes of the crystal lattice causes the appearance of a gap in the energy spectrum of graphene $\eta|\delta|$ in width centered at the point $y\delta$, where η is the parameter of ordering, δ is the difference of the scattering potentials of impurity atoms and carbon atoms, and y is the impurity concentration. If the Fermi level is located outside the gap, then the electrical conductance increases with the parameter of order η.
It is shown that an increase in the electrical conductance with the order parameter is a result of both the growth of the density of states at the Fermi level and the time of relaxation of electron states. We have demonstrated the presence of a domain of localized states on the edges of the energy gap arising at the ordering of atoms of the admixture.

KEYWORDS: graphene, energy gap, density of states, impurity concentration, ordering parameter, Green's function, metal-insulator transition, region of localization of electronic impurity states

1. Introduction

Theoretical studies of the energy spectrum of graphene are mainly based on the density functional theory. It should be noted that the success of this theory is associated with a self-consistent meta-generalized gradient approximation within the projector-augmented-wave method [1], implemented using VASP software. Quantitative studies performed by this method showed the opening of a gap in the energy spectrum of graphene due to the presence of impurities. Calculations of the electronic structure of graphene with impurities were performed in works [2-5], where the appears of the gap in The possibility of a metal-insulator transition and the dominant role of a quasi-gap with localized states caused by scattering by pairs and triplets of impurity centers were assumed. In the works [6-11] in the tight-binding one-electron model, which allows accurate analytical solutions, in the extreme case of weak scattering $|\delta/w| \ll 1$ it was

first analytically predicted that when ordering the substitution impurity atoms in the energy spectrum of graphene there is a gap width $\eta|\delta|$ with center at point $y\delta$ Here η is the ordering parameter, y is the impurity concentration, δ is the difference between the scattering potentials of the impurity atom and carbon, w is the half-width of the energy zone of pure graphene.

It is worth noting the other nature of the gap in the energy spectrum of graphene, associated with edge effects. In works [12-14], study of the appearance of an energy gap in graphene nanoribbons, which increases with decreasing width of the nanoribbons, was performed. Recently, several dozen papers have been published on the effect of different types of deformation on the electronic properties of (mostly defect-free) graphene (see, for example, a review [15]). The results of the first calculations in the theory of the density functional [16] claimed that even small deformations can cause the appearance of a band gap. Calculations in the model of strong bonding and linear theory of elasticity [17] showed that the band gap occurs only at tensile deformations (~23%).

2. Theoretical Model

The Hamiltonian in the Lifshits tight-binding one-electron model describing the one-electron states of graphene with substitutional impurity atoms can be written in the form [10]

$$H = \sum_{ni}|ni\rangle v^{ni}\langle ni| + \sum_{ni,n'i'\neq ni}|ni\rangle h_{ni,n'i'}\langle n'i'|, \quad (1)$$

where $h_{ni,n'i'}$ is a matrix element (hopping integral) of the Hamiltonian that is nondiagonal in the Wannier representation and is independent of the random distribution of atoms in the accepted approximation of diagonal disorder; v^{ni} is a diagonal matrix element taking the value v^A or v^B if atom A or B is located, respectively, at node ni; i is the number of a sublattice, and n is the number of a node of the sublattice.

The retarded Green's function of graphene, which is an analytic function in the upper half-plane of values of the complex energy z, is defined as

$$G(z) = (z - H)^{-1}. \quad (2)$$

It was shown [6] that the contributions of electron scattering processes to the density of states and electrical conductivity decrease with an increase in the number of atoms in a cluster in powers of some small parameter $\gamma_i(\varepsilon)$. The study of this parameter shows [10] that it can be small in a wide range of changes in the characteristics of the crystal, with the exception of narrow intervals of the value of the electron energy, located at the edges of the energy band and the edges of the gap that occurs when the impurity is ordered.

Neglecting the contribution of the processes of scattering on clusters composed of three and more atoms, being small by parameter γ, we present the density of one-electron states of graphene as [6]:

$$g_e(\varepsilon) = \frac{1}{\nu}\sum_{i_1,\gamma_1,\lambda} P_{ni}^{\lambda} g_{i_1\gamma_1}^{\lambda ni}(\varepsilon), \quad (3)$$

where the conditional partial density of states is

$$g_{i_1\gamma_1}^{\lambda ni}(\varepsilon) =$$

$$-\frac{1}{\pi}\,\mathrm{Im}\left\{\tilde{G}_{ni_1\gamma_1,ni_1\gamma_1}+\sum_{n_1}\left[\tilde{G}\,t^{\lambda ni}\tilde{G}+\sum_{\substack{(lj)\neq(ni)\\ \lambda',Z_{\lambda'},m_{\lambda'}}}P_{ljni}^{\lambda'/\lambda}\times\tilde{G}T^{(2)\lambda\,ni,\lambda' lj}\,\tilde{G}\right]_{n_1i_1\gamma_1,n_1i_1\gamma_1}\right\} \tag{4}$$

$\tilde{G}=\tilde{G}(\varepsilon)$ is the retarded Green's function of the effective medium described by coherent potentials σ^i $(i=1,2)$, where

$$T^{(2)n_1i_1,n_2i_2}=\left[I-t^{n_1i_1}\tilde{G}t^{n_2i_2}\tilde{G}\right]t^{n_1i_1}\tilde{G}t^{n_2i_2}\left[I+\tilde{G}t^{n_1i_1}\right], \tag{5}$$

$$t^{n_1i_1}=\left[I-\tilde{v}^{n_1i_1}\tilde{G}\right]^{-1}\tilde{v}^{n_1i_1}, \tag{6}$$

$$\tilde{v}^{n_1i_1}=|n_1i_1\rangle\left(v^{n_1i_1}-\sigma^{i_1}\right)\langle n_1i_1|. \tag{7}$$

Here, $t^{n_1i_1}$ is the operator of scattering on one node.

Detailed calculations of conductance σ_{xx} are given in [6].

3. Results

In the limiting case of weak scattering $|\delta/w|\ll 1$, where w is the half-width of the energy zone of pure graphene, δ is the difference of the scattering potentials of impurity atoms and carbon atoms, the given theoretical model admits analytic solutions [6]. It was established that the arising gap ηδ in width is centered at the point $y\delta$, where η is the parameter of ordering and y is the impurity concentration.

Near the edges of the gap, the density of electron states as a function of the energy has the characteristic peaks related to electron impurity states. Outside the energy gap, the density of electron states $g(\varepsilon)$ increases by a linear law with the distance to the gap edge [6]:

$$g(\varepsilon)=\frac{S_1(\varepsilon-y\delta)}{\pi\hbar^2v_F^2},\ \left|\frac{\Delta\varepsilon(\eta)}{w}\right|<\left|\frac{\varepsilon-\sigma'_i}{w}\right|\le\left|\frac{\delta}{w}\right|. \tag{13}$$

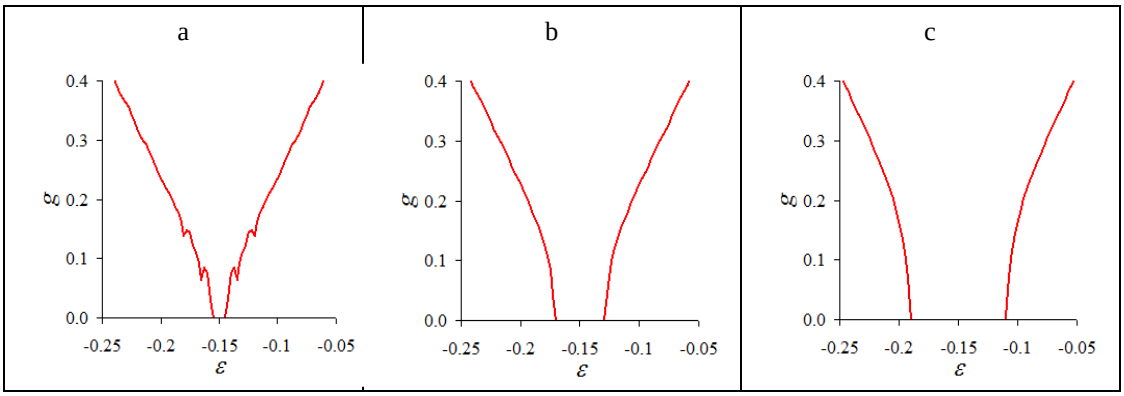

Fig. 1. Dependence of the density of electron states on the energy at values of the scattering potential $\delta/w=-0.3$ and the impurity concentration $y=0.2$ with different order parameters $\eta=0.1$ (a), $\eta=0.25$ (b), $\eta=0.4$ (c). The energy region in a vicinity of the gap is shown.

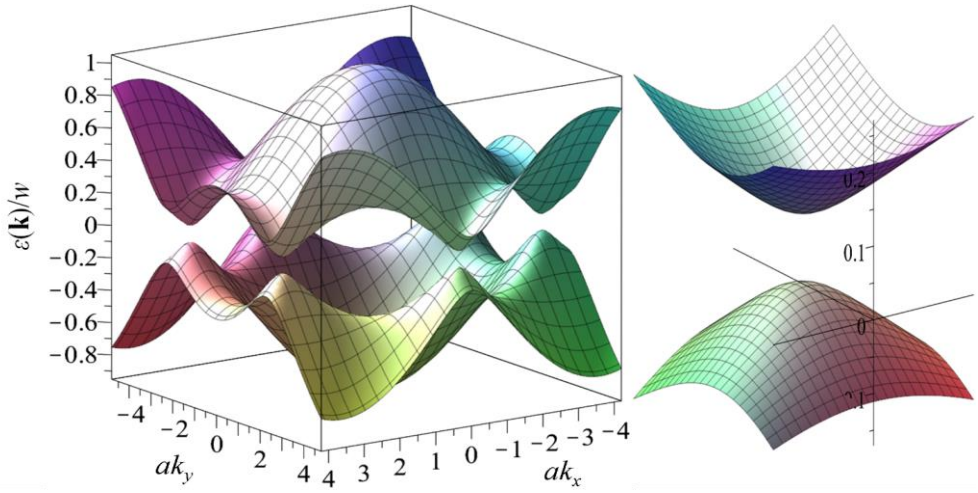

Fig. 2. Dependence of the electron energy on the wave vector for graphene with completely ordered impurity with the concentration $y = 1/2$ and scattering parameter $\delta/w = 0.1$. On the right, the region of the Dirac point is shown.

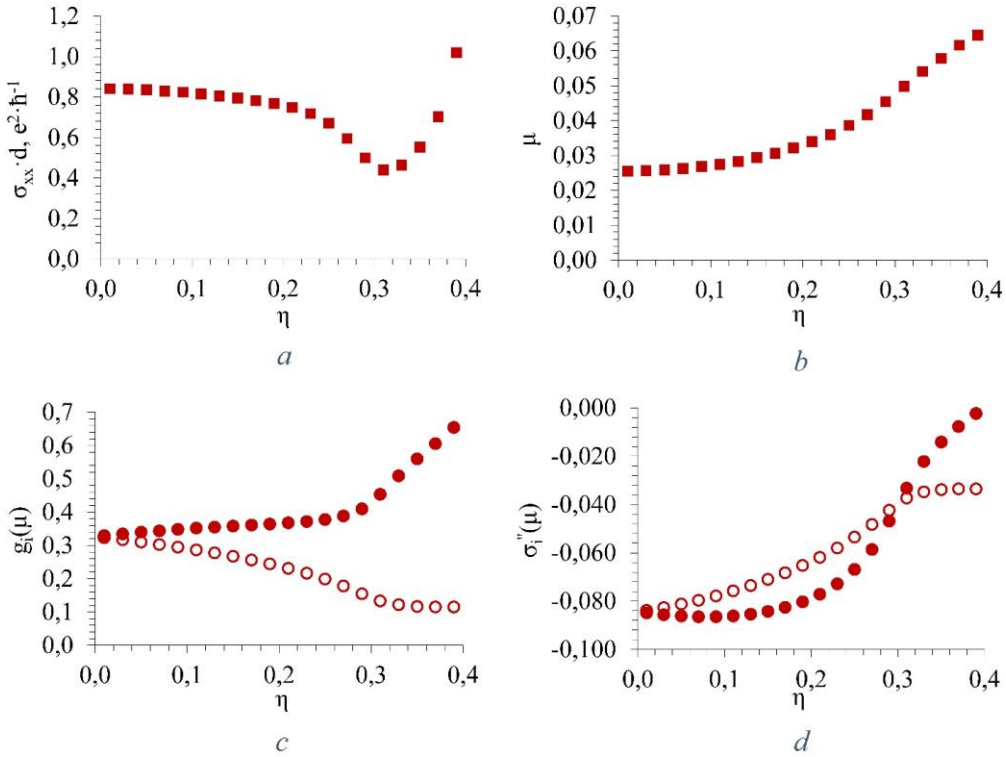

Fig. 3. Dependence of a) the electrical conductance of graphene σ_{xx}; b) the Fermi level μ; c) the partial density of states $g_i(\mu)$ at the Fermi level; d) the imaginary part of the coherent potential $\sigma_i''(\mu)$ at the Fermi level on the order parameter of impurity atoms η. The substitutional impurity concentration $y = 0.2$, the scattering potential $\delta/w = -0.6$. Circles correspond to $g_1(\mu)$ and $\sigma_1''(\mu)$ of the first sublattice, in which the impurity atoms are located in the case of full order. Filled circles show $g_2(\mu)$ and $\sigma_2''(\mu)$ for the second sublattice.

We recall that the contributions of the processes of scattering of electrons on clusters to the density of states and to the electrical conductance decrease and are guided by some small parameter $\gamma_i(\varepsilon)$, as the number of atoms in a cluster increases [6].

In Fig. 1 we show the results of numerical calculations of the density of states of graphene. Numerical calculations are performed according to the formulas (3), (4).

It is seen from Fig. 1, that the gap width increases with the order parameter, which agrees qualitatively with the conclusions obtained in the limiting case of weak scattering $|\delta/w| \ll 1$.

In Fig. 2, we present the dependence of the energy of an electron on the wave vector for graphene with completely ordered substitutional impurity ($\eta = 1$) with the hypothetical concentration $y = 1/2$ in case where the scattering potential: $\delta > 0$. The dependence of the energy of an electron on the wave vector for the completely ordered arrangement of an impurity is given by the formula following from the equation for poles of Green's function.

At the ordering of a substitutional impurity with the stoichiometric concentration $y = 1/2$, the gap appears in the energy spectrum of graphene.

The results of studying the dependence of the electrical conductivity of graphene on the impurity ordering parameter η are shown in Fig. 3. Numerical calculations are performed using formula (8). Here, *d* is the thickness of graphene. The azis *x* is directed from a carbon atom to its nearest neighbour. The $\sigma_{xx} \cdot d$ are given in units $e^2 \cdot \hbar^{-1}$.

It is seen from Fig. 3 that the electrical conductance of graphene increases with the order parameter of an impurity η.

4. Conclusions

We have established that, at the ordering of impurity atoms, a gap appears in the energy spectrum of graphene. In the limiting case of weak scattering $|\delta/w| \ll 1$, we have shown that the gap arising at the ordering of impurity atoms in the energy spectrum of graphene has a width of $\eta|\delta|$ and is centered at the point $y\delta$, $w = 3|\gamma_1|$, where w is the half-width of the energy zone of pure graphene. It is shown that at values of the order parameter η close to the maximum $\eta_{max} = 2y$, $y < 1/2$, the curve of the density of electronic states at the edges of the energy gap that occurs when the impurity is ordered has peaks corresponding to impurity levels. As the order parameter η decreases, the impurity levels split into impurity bands.

At the electron concentration, when the Fermi level falls in the arising gap, the electrical conductance tends to zero at the ordering of an impurity, $\sigma_{xx} \to 0$, i.e., a metal-dielectric transition arises.

If the Fermi level lies outside the gap, the electrical conductance σ_{xx} increases with the order parameter η and tends to infinity, as the order parameter $\eta \to \eta_{\max} = 2y$.

An increase in the electrical conductance σ_{xx} of graphene with the order parameter η of impurity atoms is caused by an increase in the density of states at the Fermi level, $g(\mu)$, and by an increase in the relaxation time of electron states, $\tau(\mu)$.

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References

[1] J. Sun, M. Marsman, G. I. Csonka, A. Ruzsinszky, P. Hao, Y.-S. Kim, G. Kresse and J.P. Perdew. Self-consistent meta-generalized gradient approximation within the projector-augmented-wave method. Phys. Rev. B **84**, 035117 (2011). DOI: https://doi.org/10.1103/PhysRevB.84.035117.

[2] C. Yelgel and G. P. Srivastava. Ab initio studies of electronic and optical properties of graphene and graphene–BN interface. Applied Surface Science **258**, 8338 (2012). DOI: https://doi.org/10.1016 /j.apsusc.2012.03.167.

[3] P. A. Denis. Band gap opening of monolayer and bilayer graphene doped with aluminium, silicon, phosphorus, and Sulphur. Chem. Phys. Lett. **492**, 251 (2010). DOI: https://doi.org/10.1016 /j.cplett.2010.04.038.

[4] D. Xiaohui, W. Yanqun, D. Jiayu, K. Dongdong and Z. Dengyu. Electronic structure tuning and band gap opening of graphene by hole/electron cooping. Phys. Lett. A **365**, 3890 (2011). https://doi:10.1016/j.physleta.2011.08.070.

[5] T. M. Radchenko, V. A. Tatarenko, I. Yu. Sagalianov and Yu. I. Prylutskyy. Effects of nitrogen-doping configurations with vacancies on conductivity in grapheme. Phys. Lett. A **378** (Nos. 30-31), 2270 (2014). DOI: https://doi.org/10.1016/j.physleta.2014.05.022.

[6] S. P. Repetsky, I. G. Vyshyvana, S. P. Kruchinin and S. Bellucci. Influence of the ordering of impurities on the appearance of an energy gap and on the electrical conductance of graphene. Scientific Reports **8**, Article number: 9123 (2018). DOI: https://doi.org/10.1038/s41598-018-26925-0. https: //www.nature.com/articles/s41598-018-26925-0.

[7] S. P. Repetsky, I. G. Vyshyvana, S. P. Kruchinin, B. Vlahovica and S. Bellucci. Effect of impurities ordering in the electronic spectrum and conductivity of graphene. Physics Letters A **384** (No. 19**)**, 126401 (2020). DOI: https://doi.org/10.1016/j.physleta.2020.126401

[8] S. Bellucci, S. Kruchinin, S. P. Repetsky, I. G. Vyshyvana and R. Melnyk. Behavior of the energy spectrum and electric conduction of doped graphene. Materials **13**, 1718 (2020). DOI: https://doi.org/10.3390/ma13071718.

[9] S. P. Repetsky, I. G. Vyshyvana, S. P. Kruchinin, O. Ya. Kuznetsova and R. M. Melnyk. Influence of the impurity ordering on the energy spectrum and electrical conductivity of graphene. Metallofiz. Noveishie Tekhnol., **41**, No. 4: 427 (2019) (in Ukrainian). https://doi.org/10.15407/mfint.41.04.0427.

[10] S. P. Repetsky, I. G. Vyshyvana, S. P. Kruchinin, R. M. Melnyk and A. P. Polishchuk. The energy spektrum and the electrical conductivity of graphene with substitution impurity. Condensed Matter Physics **23** (No. 1), 13704 (2020). https://doi.org/10.5488/CMP.23.13704.

[11] S. P. Repetsky, I. G. Vyshyvana, S. P. Kruchinin, R. M. Melnyk, and A. P. Polishchuk. Impurity ordering effects on graphene electron properties. In: *Conf. Proc. "Advanced Nanomaterials for Detection of CBRN", NATO Science for Peace and Security Series A: Chemistry and Biology*. Editors: J. Bonča, S. Kruchinin. (Springer 2020), Chp. 3. https://doi.org/10.1007/978-94-024-2030-2.

[12] V. A. Saroka, M. V. Shuba, M. E. Portnoi. Optical selection rules of zigzag graphene nanoribbons. Phys. Rev. B **95**, 155438 (2017). https://doi.org/10.1103/PhysRevB.95.155438.

[13] H.-C. Chung, Y.-T. Lin, S.-Y. Lina, C.-H.Ho, C.-P. Chang and M.-F. Lin. Magnetoelectronic and optical properties of nonuniform graphene nanoribbons. Carbon **109**, 883 (2016). https://doi.org /10.1016/j.carbon.2016.08.091.

[14] C. Si, Z. Sun and F. Liu. Strain engineering of graphene: A review. Nanoscale **8**, 3207 (2016). https://doi.org/10.1039/c5nr07755a.

[15] G. Gui, J. Li and J. Zhong. Band structure engineering of graphene by strain: First-principles calculations. Phys. Rev. B **78**, 075435 (2008). https://doi.org/10.1103/PhysRevB.78.075435.

[16] V. M. Pereira, A. H. Castro Neto and N. M. R. Peres. Tight-binding approach to uniaxial strain in grapheme. Phys. Rev. B **80**, 045401 (2009). https://doi.org/10.1103/PhysRevB.80.045401.