Universal infrared conductivity of graphite

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The conductivity of graphite is analytically evaluated in the range of 0.1–1.5 eV, where the electron relaxation processes can be neglected and the low-energy excitations at the "Dirac" points are most essential. The value of conductivity calculated per one graphite layer is close to the universal conductivity of graphene. The features of the conductivity are explained in terms of singularities of the electron dispersion in graphite.

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Since the pioneering experimental investigations of a single atomic layer of graphite (graphene),[1,2] its properties attract much attention. Among them, the optical response is of particular interest. Recently the transmittance of light throw the graphene monolayer has been measured.[3–5] The transmittance

$$T = 1 - \pi\alpha$$

was found to be frequency independent in a broad range of photon energy. The result of the experiments is remarkable because it involves the fine structure constant α. It was discovered that the real part of the optical conductance of graphene takes the universal value,

$$G = \frac{e^2}{4\hbar},$$

which does not depend on any parameters of graphene. This value agrees perfectly with the calculations[6,7] ignoring the Coulomb interactions between electrons. The agreement shows that the poorly screened Coulomb interaction does not play any role in graphene for infrared photon frequencies.[8,9]

The intermediate place between two-dimensional graphene and three-dimensional semiconductors belongs to multilayer graphenes[10] and graphite, which have a layered structure with the interlayer distance $c_0=3.35$ Å much larger than the nearest-neighbor distance $a_0=1.42$ Å in the layer. In the study of graphite,[11] it was found that its optical conductivity per one layer is very closed to the universal conductivity of graphene and has evident peculiarities. The analytic calculation of the in-plane optical response of graphite done previously[12] has ignored coupling between layers and no peculiarities have appeared for the infrared region.

In the present Brief Report, we evaluate analytically the conductance of graphite in the infrared region of the photon frequencies. It is known that the low-energy electron excitations in graphite can be described very well with the Slonczewski-Weiss-McClure theory.[13] The largest parameter of the theory, $\gamma_0=3.1$ eV,[14] describes the electron dispersion for in-layer directions $\mathbf{k}$. If the photon energy is less than γ_0, we can use the linear expansion of the in-layer hopping term in the Hamiltonian and introduce the constant velocity parameter $v=10^8$ cm/s. The next in size is the interlayer hopping γ_1 on the order of 0.4 eV which is known from experiments on bilayer graphene.[15,16] The parameters γ_3 and γ_4 give the corrections of the order of 10% to the in-layer velocity v. The electron-hole overlap on the order of 0.02 eV is determined by parameters γ_2 and γ_5 (see Fig. 1). Therefore, for the photon frequencies larger than 0.1 eV, we can neglect the terms with γ_2 and γ_5. Calculating such the integral property as conductivity in the region of the infrared frequencies between 0.1 and 1.5 eV, we can, first, neglect the small parameters of the theory and, second, use the linear k expansion of the in-layer hopping term. Our results have the evident analytic form.

In this approximation, the effective Hamiltonian writes near the K-G-H lines of the Brillouin zone in the simple form

$$H(\mathbf{k}) = \begin{pmatrix} 0 & k_+ & \gamma(z) & 0 \\ k_- & 0 & 0 & 0 \\ \gamma(z) & 0 & 0 & k_- \\ 0 & 0 & k_+ & 0 \end{pmatrix} \tag{1}$$

determined only by two constants. One is $v=10^8$ cm/s included in the definition of the in-plane momentum compo-

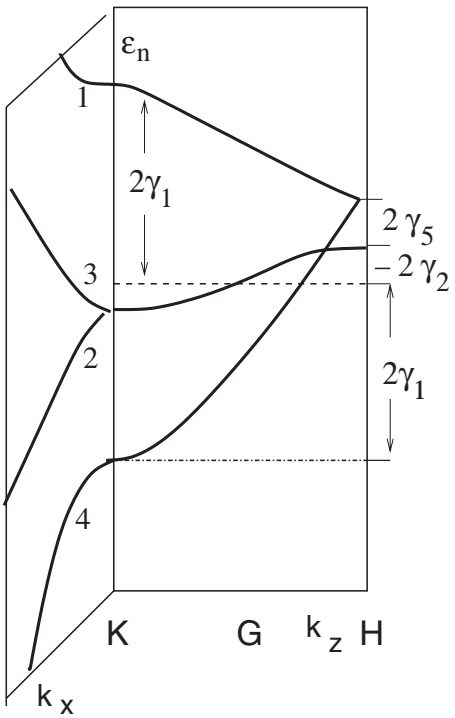

FIG. 1. The dispersion of the low-energy electron bands in graphite.

nents, $k_{\pm}=v(\mp ik_x-k_y)$, and another is the interlayer interaction γ_1 involved in the function $\gamma(z)=2\gamma_1 \cos z$. The momentum component $z=k_z c_0$ is limited by the Brillouin half zone, $0<z<\pi/2$ in relative units.

The corresponding eigenenergies are

$$\varepsilon_{1,2}=\frac{\gamma(z)}{2}\pm\sqrt{\frac{1}{4}\gamma^2(z)+k^2},$$

$$\varepsilon_{3,4}=-\frac{\gamma(z)}{2}\pm\sqrt{\frac{1}{4}\gamma^2(z)+k^2}.$$

On the K-G-H lines, $k=0$, these equations determine two bands $\varepsilon_{1,4}=\pm\gamma(z)$ and two degenerate (electron and hole) bands with the energy $\varepsilon_{2,3}=0$. We have to emphasize that this degeneracy results from C_{3v} symmetry on the K-G-H line.

In order to calculate the conductivity, we use the general expression

$$\sigma^{ij}(\omega)=\frac{2ie^2}{(2\pi)^3}\int d^3k\sum_{n\geq m}\left\{-\frac{df}{d\varepsilon_n}\frac{v_n^i v_n^j}{\omega+i\nu}+2\omega\frac{v_{nm}^i v_{mn}^j\{f[\varepsilon_n(\mathbf{k})]-f[\varepsilon_m(\mathbf{k})]\}}{[\varepsilon_m(\mathbf{k})-\varepsilon_n(\mathbf{k})]\{(\omega+i\nu)^2-[\varepsilon_n(\mathbf{k})-\varepsilon_m(\mathbf{k})]^2\}}\right\},\tag{2}$$

valid in the collisionless limit $\omega\gg\nu$, where ν is the collision rate of the carriers, $f(\varepsilon)=[\exp(\frac{\varepsilon-\mu}{T})-1]^{-1}$ is the Fermi-Dirac distribution function, and the integral is over the Brillouin zone.

Here, the first term is the Drude-Boltzmann conductivity negligible for frequencies larger than the electron-hole overlap. The second term represents the optical interband transitions of electrons from the valence 2, 4 to conductive 1, 3 bands. The real part of the interband contributions into conductivity arises from the bypass around the pole at $\varepsilon_n(\mathbf{k})-\varepsilon_m(\mathbf{k})=\pm\omega$. The imaginary part is given by the principal value of the integral.

The velocity operator

$$\mathbf{v}=\frac{\partial H(\mathbf{k})}{\partial\mathbf{k}}$$

near the K-G-H lines is determined by Hamiltonian (1). The corresponding matrix elements should be calculated in the representation, where the Hamiltonian has a diagonal form. The operator transforming the Hamiltonian to this form can be written as follows:

$$U=\begin{pmatrix}\varepsilon_1/N_1 & \varepsilon_2/N_2 & -\varepsilon_3/N_3 & -\varepsilon_4/N_4\\ k_-/N_1 & k_-/N_2 & -k_-/N_3 & -k_-/N_4\\ \varepsilon_1/N_1 & \varepsilon_2/N_2 & \varepsilon_3/N_3 & \varepsilon_4/N_4\\ k_+/N_1 & k_+/N_2 & k_+/N_3 & k_+/N_4\end{pmatrix},$$

where $N_n^2=2(\varepsilon_n^2+k^2)$. In this representation, the velocity operator

$$U^{-1}\mathbf{v}U$$

has the matrix elements

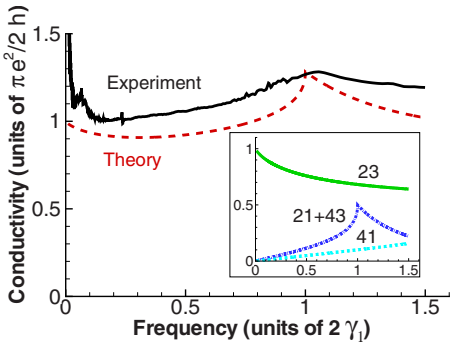

FIG. 2. (Color online) The real part of the graphite conductivity per layer (in units of $e^2/4\hbar$) versus the frequency (in units of $2\gamma_1=0.84$ eV); the experimental data (Ref. 11) are shown in the solid line, results of the present theory in the dashed line. The insert shows the contributions of various electron transitions.

$$\mathbf{v}_{nn}=\partial\varepsilon_n/\partial\mathbf{k},$$

$$\mathbf{v}_{23}=2i(\varepsilon_3-\varepsilon_2)(-k_x\mathbf{e}_y+k_y\mathbf{e}_x)]/N_2N_3,$$

$$\mathbf{v}_{12}=2(\varepsilon_1+\varepsilon_2)(k_x\mathbf{e}_x+k_y\mathbf{e}_y)]/N_1N_2,$$

$$\mathbf{v}_{14}=2i(\varepsilon_4-\varepsilon_1)(-k_x\mathbf{e}_y+k_y\mathbf{e}_x)]/N_1N_4,$$

where $\mathbf{e}_i$ are the unit vectors directed along the coordinate axes. For the real part of conductivity, the integration in Eq. (2) is easily taken at zero temperatures $T=0$ in cylindrical coordinates (k_z,k,ϕ) over the angle ϕ and over k with the help of the δ function, $(\omega-x+i\nu)^{-1}\to-i\pi\delta(\omega-x)$. One obtains for contributions of the transitions between the corresponding valence and conduction bands into the diagonal components of conductivity (off-diagonal ones equal zero) the following integrals over $z=k_z/c_0$:

$$\mathrm{Re}\ \sigma_{23}=\frac{e^2}{4\pi\hbar c_0}\int_0^{\pi/2}dz\frac{2\gamma(z)+\omega}{\gamma(z)+\omega},$$

$$\mathrm{Re}\ \sigma_{21}=\frac{e^2}{4\pi\hbar c_0}\int_0^{\pi/2}dz\frac{\gamma^2(z)}{\omega^2}\theta[\omega-\gamma(z)],$$

$$\mathrm{Re}\ \sigma_{41}=\frac{e^2}{4\pi\hbar c_0}\int_0^{\pi/2}dz\frac{2\gamma(z)-\omega}{\gamma(z)-\omega}\theta[\omega-2\gamma(z)],$$

$$\sigma_{43}=\sigma_{21},\tag{3}$$

where $\gamma(z)=2\gamma_1\cos z$ and $\theta(x)$ is the step function.

It is evident from Eq. (3) (see also Fig. 2) that the conductivity σ_{23} tends to $e^2/4\hbar c_0$ at the low frequencies $\omega\ll 2\gamma_1$, whereas other contributions go to zero in the limit of low frequencies. At larger frequencies $\omega\gg 2\gamma_1$, the total conductivity (the sum of σ_{23} and σ_{41}) tends again to $e^2/4\hbar c_0$. Therefore, $\sigma_0=e^2/4\hbar c_0$ can be considered as the universal conductivity of graphite, where $e^2/4\hbar$ is the conductivity of monolayer graphene and the factor $1/c_0$ is the number of the layers per the length unit in the z direction of graphite.

Integrating in Eq. (3) we get finally

$$\mathrm{Re}\frac{\sigma_{23}}{\sigma_0} = 1 - \frac{2t}{\pi\sqrt{t^2-1}}\arctan\sqrt{\frac{t-1}{t+1}}, \quad t>1,$$

$$\mathrm{Re}\frac{\sigma_{23}}{\sigma_0} = 1 - \frac{t}{\pi\sqrt{1-t^2}}\ln\frac{\sqrt{1+t}+\sqrt{1-t}}{\sqrt{1+t}-\sqrt{1-t}}, \quad t<1, \qquad (4)$$

$$\mathrm{Re}\frac{\sigma_{21}}{\sigma_0} = \frac{1}{4t^2}\begin{cases} 1, & t>1, \\ 1-\dfrac{2}{\pi}(\arccos t + t\sqrt{1-t^2}), & t<1, \end{cases}$$

$$\mathrm{Re}\frac{\sigma_{41}}{\sigma_0} = 1 - \frac{2t}{\pi\sqrt{t^2-1}}\arctan\sqrt{\frac{t+1}{t-1}}, \quad t>2,$$

$$\mathrm{Re}\frac{\sigma_{41}}{\sigma_0} = 1 - \frac{2z_1}{\pi} - \frac{2t}{\pi\sqrt{t^2-1}}\left[\arctan\sqrt{\frac{t+1}{t-1}} - \arctan\left(\sqrt{\frac{t+1}{t-1}}\tan\frac{z_1}{2}\right)\right], \quad 1<t<2,$$

$$\mathrm{Re}\frac{\sigma_{41}}{\sigma_0} = 1 - \frac{2z_1}{\pi} + \frac{t}{\pi\sqrt{1-t^2}}\left[\ln\frac{\sqrt{1+t}+\sqrt{1-t}}{\sqrt{1+t}-\sqrt{1-t}} + \ln\frac{\sqrt{1+t}\tan\frac{z_1}{2}-\sqrt{1-t}}{\sqrt{1+t}\tan\frac{z_1}{2}+\sqrt{1-t}}\right], \quad t<1, \qquad (5)$$

where $t=\omega/2\gamma_1$ and $z_1=\arccos(t/2)$.

The peculiarity as a kink can be seen in Fig. 1. Expression (5) shows that this kink is located at $\omega=2\gamma_1$. Taking into account the kink position $\omega=0.84$ eV determined experimentally, the value of $\gamma_1=0.42$ eV is found in excellent agreement with experiments on bilayer graphene.

The contributions of the electron interband transitions in the imaginary part of conductivity can be integrated over k at the zero temperature. The results are obtained in the form of integrals over k_z,

$$\mathrm{Im}\frac{\sigma_{23}}{\sigma_0} = \frac{2}{\pi^2}\int_0^{\pi/2} dz \frac{\omega\gamma(z)}{\gamma^2(z)-\omega^2}\ln[\gamma(z)/\omega],$$

$$\mathrm{Im}\frac{\sigma_{21}}{\sigma_0} = \frac{1}{\pi^2}\int_0^{\pi/2} dz \frac{\gamma(z)}{\omega}\left[2+\frac{\gamma(z)}{\omega}\ln\frac{|\gamma(z)-\omega|}{\gamma(z)+\omega}\right],$$

$$\mathrm{Im}\frac{\sigma_{41}}{\sigma_0} = \frac{1}{\pi^2}\int_0^{\pi/2} dz\left\{\frac{2\gamma(z)-\omega}{\gamma(z)-\omega}\ln|2-\omega/\gamma(z)| - \frac{2\gamma(z)+\omega}{\gamma(z)+\omega}\ln[2+\omega/\gamma(z)]\right\}$$

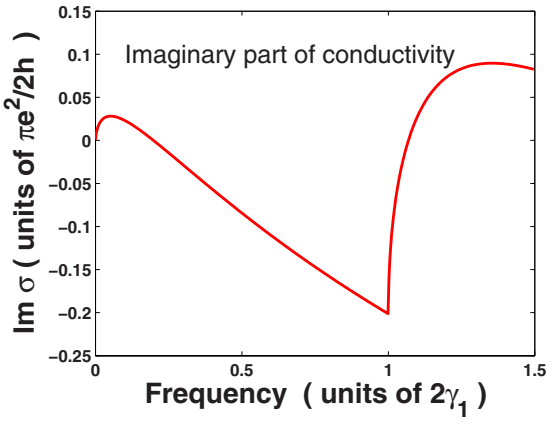

FIG. 3. (Color online) The imaginary part of the graphite conductivity per layer (in units of $e^2/4\hbar$) versus the frequency (in units of $2\gamma_1=0.84$ eV).

and shown in Fig. 3. Here, the peculiarity looks like a threshold at $\omega=2\gamma_1$ and it is more clearly marked in comparison with the kink in the real conductivity. Both peculiarities result from the electron transitions between the bands $2\rightarrow1$ and $4\rightarrow3$. We should emphasize that the peculiarities become broader with the temperatures and the collision processes included.

So far the in-layer conductivity was considered. The estimate of the interlayer conductivity can be also done. Since the conductivity is determined by the ratio of the corresponding velocities squared, we have to write

$$v_z = \frac{\partial\varepsilon_3}{\partial k_z} \sim \gamma_1 c_0 \sin(k_z c_0).$$

Then, integrating over k_z, we get

$$\sigma_z/\sigma_0 \sim (\gamma_1 c_0/\hbar v)^2/2 \sim 0.05.$$

In conclusion, our calculations reveal that the optical conductance of graphite can be estimated for frequencies between 0.1 and 1.5 eV multiplying the graphene conductivity $e^2/4\hbar$ by the number of the layers $1/c_0$ per the length unit. The Drude-Boltzmann contribution is essential at lower frequencies, whereas others interband transitions, e.g., at the M point of the Brillouin zone contribute into the conductivity at higher frequencies. Similar estimates are applicable for other graphite materials such as nanoribbons. The kink in the real part of conductivity and the threshold in the imaginary part appear at the frequency $\omega=2\gamma_1$ determined by the interlayer coupling. The sharpness of the features are smeared with the relaxation processes and temperatures included.

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[1] K. S. Novoselov *et al.*, Science **306**, 666 (2004); K. S. Novoselov *et al.*, Nature (London) **438**, 197 (2005).
[2] Y. Zhang, J. P. Small, M. E. S. Amori, and P. Kim, Phys. Rev. Lett. **94**, 176803 (2005).
[3] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, Science **320**, 1308 (2008).
[4] Z. Q. Li, E. A. Henriksen, Z. Jiang, Z. Hao, M. C. Martin, P. Kim, H. L. Stormer, and D. N. Basov, Nat. Phys. **4**, 532 (2008).
[5] K. F. Mak, M. Y. Sfeir, Y. Wu, C. H. Lui, J. A. Misewich, and Tony F. Heinz, Phys. Rev. Lett. **101**, 196405 (2008).
[6] V. P. Gusynin, S. G. Sharapov, and J. P. Carbotte, Phys. Rev. Lett. **96**, 256802 (2006).
[7] L. A. Falkovsky and A. A. Varlamov, Eur. Phys. J. B **56**, 281 (2007).
[8] E. G. Mishchenko, EPL **83**, 17005 (2008).
[9] D. Sheehy and J. Scmalian, Phys. Rev. B **80**, 193411 (2009).
[10] M. Koshino and T. Ando, Solid State Commun. **149**, 1123 (2009).
[11] A. B. Kuzmenko, E. van Heumen, F. Carbone, and D. van der Marel, Phys. Rev. Lett. **100**, 117401 (2008).
[12] T. G. Pedersen, Phys. Rev. B **67**, 113106 (2003).
[13] J. W. McClure, Phys. Rev. **108**, 612 (1957); J. C. Slonczewski and P. R. Weiss, *ibid.* **109**, 272 (1958).
[14] B. Partoens and F. M. Peeters, Phys. Rev. B **74**, 075404 (2006).
[15] A. B. Kuzmenko, I. Crassee, D. van der Marel, P. Blake, and K. S. Novoselov, Phys. Rev. B **80**, 165406 (2009).
[16] Z. Q. Li, E. A. Henriksen, Z. Jiang, Z. Hao, M. C. Martin, P. Kim, H. L. Stormer, and D. N. Basov, Phys. Rev. Lett. **102**, 037403 (2009).