Magneto-transmission of multi-layer epitaxial graphene and bulk graphite: A comparison

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Magneto-transmission of a thin layer of bulk graphite is compared with spectra taken on multi-layer epitaxial graphene prepared by thermal decomposition of a SiC crystal. We focus on the spectral features evolving as $\sqrt{B}$, which are evidence for the presence of Dirac fermions in both materials. Whereas the results on multi-layer epitaxial graphene can be interpreted within the model of 2D Dirac fermions, the data obtained on bulk graphite can only be explained taking into account the 3D nature of graphite, e.g. by using the standard Slonczewski-Weiss-McClure model.

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I. INTRODUCTION

Within the last few years, the properties of massless fermions and massive “relativistic” particles have been probed in magneto-optical experiments carried out on several carbon-based systems: graphene monolayer14 and bilayer,15 multi-layer epitaxial graphene,14-16 as well as bulk graphite.3,9,10,11 These experiments offer an important insight into the electronic structure of these materials, in particular, they directly demonstrate the unusual $\sqrt{B}$-scaling of Landau levels (LLs) of Dirac fermions. Naturally, these experiments stimulated intensive theoretical work in this area.12,13,14,15,16

Recently, remarkable experiments have been performed on the same systems without applied magnetic field. A universal value of optical conductivity was demonstrated in graphene12 as well as in bulk graphite.18 The optical response of graphene monolayer and bilayer samples as a function of the gate voltage was reported in several experimental works, see Refs. 19,20,21,22 and this topic was addressed also theoretically.23,24,25 First results of time-resolved optical experiments on multi-layer graphene are also available.26,27

In this paper, we present a direct comparison of the magneto-transmission spectra taken on a thin layer of bulk graphite and multi-layer epitaxial graphene. We focus on spectral features exhibiting a $\sqrt{B}$-dependence, which corresponds to the optical response of Dirac fermions, and show that there are essential differences in the spectra of both materials.

II. EXPERIMENTAL DETAILS

The investigated multi-layer graphene sample was prepared by thermal decomposition on the carbon face of a 4H-SiC substrate28,29 and contains around $\sim$100 graphene layers. The thin layer of bulk graphite was prepared by simple exfoliation as described in Ref. 30. As no significant difference in FIR optical response of natural graphite and HOPG was found,31 we present only results taken on natural graphite due to its higher crystalline quality. Both samples were characterized using micro-Raman. In the case of multi-layer epitaxial graphene, the Raman signature of decoupled layers, equivalent to a single flake of exfoliated graphene,24 as well as of additional graphite residuals were found, see Ref. 31. The Raman spectra taken on a thin graphite layer dominantly showed a multi-component 2D band typical of many Bernal-stacked sheets, but some minor traces of decoupled layers were found, see the discussion in Ref. 10.

To measure the FIR transmittance of the sample, the radiation of globar, delivered via light-pipe optics to the sample and detected by a Si bolometer placed directly below the sample, was analyzed by a Fourier transform spectrometer. All measurements were performed in the Faraday configuration with the magnetic field applied normal to graphene/graphite layers. All the spectra were taken with non-polarized light in the spectral range of 5-350 meV, limited further by several regions of low tape transmissivity or the SiC opacity, see grey areas in Fig. 1.

III. RESULTS AND DISCUSSION

A comparison of the transmission spectra taken on multi-layer epitaxial graphene and a thin layer of bulk graphite is presented in Fig. 1. Starting with results taken on multi-layer layer graphene in Fig. 1b, a series of absorption lines is observed and denoted by Roman letters, following the notation introduced in Ref. 14. Assuming the LL spectrum of graphene, $E_n = \hbar c \sqrt{2eHn}$, together with the corresponding selection rules for dipole-allowed transitions $\Delta n = \pm 1$, the observed absorption
lines B,C,D,E and F can be clearly identified as inter-
LL transitions \(L_{-m} \rightarrow L_{m+1} \) and \(L_{-(m+1)} \rightarrow L_{m} \) with 
\( m = 0,1,2,3 \) and 4, respectively. The Fermi velocity
is found to be \( \tilde{c} = (1.02 \pm 0.01) \times 10^{6} \text{ m.s}^{-1} \). Hence, these
results are fully consistent with a model of 2D Dirac
fermions and individual sheets in multi-layer epitaxial
graphene indeed behave as if they are electronically
decoupled. This was recently explained by a random mu-
tual rotation of adjacent sheets in this material.13

Similar spectra were also measured on a single sheet of exfoli-
ated graphene, however, the Fermi velocity seems to be
enhanced by amount of \( \approx 10\% \) and these data also sug-

gest some influence of electron-electron interaction, not
observed in transmission spectra of multi-layer epitaxial
graphene.

The results obtained on a thin layer of bulk graphite,
see Fig. 1b, are more complex. Basically, all the ab-
sorption lines observed in multi-layer graphene are also
found in spectra of bulk graphite with practically the
same Fermi velocity \( \tilde{c} = (1.02 \pm 0.02) \times 10^{6} \text{ m.s}^{-1} \). This
justifies the same notation using the Roman letters. In
addition to these lines, another series of transitions, de-
noted by Greek letters and clearly exhibiting the \( \sqrt{B} \-
dependence, is present in transmission spectra. These
lines cannot be assigned to any dipole-allowed transitions
between LLs in graphene. Nevertheless, the energies of
the additional lines \( \alpha, \gamma, \delta \) and \( \varepsilon \) exactly match to tran-
sitions symmetric around the Dirac point, \( L_{-m} \rightarrow L_{m} \),
with indices \( m = 1,2,3 \) and 4, respectively. The \( \beta \) line

can be identified as transitions \( L_{-1(-3)} \rightarrow L_{3(1)} \).

To explain the absorption lines denoted by the Greek
letters we have to abandon the simplified model of
2D Dirac fermions and consider the full band struc-
ture of bulk graphite. According to the standard SWM
model, Dirac fermions are located in the vicinity of the
\( H \) point, where the bands \( E_{1}, E_{2} \) and the doubly de-
generate \( E_{3} \) are close to the Fermi level. If the magnetic
field is applied along the \( c \)-axis of the crystal, Landau
levels or more accurately, Landau bands are created, see
Fig. 2, having at the \( H \) point (\( k_{z} = 0.5 \)) an analytical
form16,39 (\( n \geq 1 \)):

\[
\begin{align*}
E_{3}^{-1} &= 0 \\
E_{3}^{0} &= \Delta \\
E_{3}^{n} \pm &= E_{1,2}^{n-1} = \frac{\Delta}{2} \pm \sqrt{\frac{\Delta^{2}}{4} + \xi Bn},
\end{align*}
\]

where \( \Delta \) denotes the pseudogap, i.e. the distance of \( E_{1} \)
and also \( E_{2} \) and \( E_{3} \) bands at \( k_{z} = 0.5 \) and \( B = 0 \).
The parameter \( \xi \) is related to the Fermi velocity as \( \xi = 2\tilde{c}^{2} e h \).

The form of LLs implies several important \( H \) point-
related optical properties of graphite. It suggests that the
LL energy spectrum typical of graphene is present also
at the \( H \) point in graphite, when the pseudogap \( |\Delta| \) is
small in comparison to the energies of the LLs. Experimentally, \( |\Delta| \) is found to be significantly below 10 meV,
see Refs. [33,34] and therefore, the magnetic fields above
100 mT are sufficient to insure this condition. On the
other hand, each LL in Eq. (1) is (with the exception of \( E_{3}^{n} \))
doubly degenerate, \( E_{3}^{+} = E_{3}^{-1} \) and \( E_{3}^{0} = E_{2}^{-1} \), see Fig. 2. This double degeneracy is
in addition to the spin and valley degeneracies present
in graphite. Obviously, taking account of the same se-
lection rules \( \Delta n = \pm 1 \), we obtain a considerably richer
set of possible dipole-allowed transitions for graphite in
comparison to graphene. For instance, the transition
\( L_{-1} \rightarrow L_{1} \) is strictly forbidden in graphene, neverthe-
less the absorption line at this energy (\( \alpha \) transition) is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Transmissions spectra of multi-layer epitaxial
graphene (a) and bulk graphite (b) for selected magnetic fields
at \( T = 2 \text{ K} \). The absorption lines corresponding to dipole-
allowed transitions in graphene are denoted by Roman letters.
Greek letters are used for additional transitions which scale
as \( \sqrt{B} \) and are only found in spectra taken on bulk graphite.
For clarity, the spectra in part (a) and (b) were shifted by
0.18 and 0.10, respectively.}
\end{figure}
observed in bulk graphite at the \( H \) point due to the dipole-allowed transitions \( E_3^1 \rightarrow E_3^0 \) and \( E_2^0 \rightarrow E_3^{1+} \), see Fig. 2b. Similarly, the lines \( \gamma, \delta \) and \( \varepsilon \) are detected due to transitions \( E_3^{m+1} \rightarrow E_1^m \) and \( E_2^m \rightarrow E_3^{m+1} \) for \( m = 1, 2 \) and \( 3 \), respectively. The remaining \( \beta \) line can be identified as \( E_3^1 \rightarrow E_1^2 \) and \( E_2^2 \rightarrow E_3^1 \). Hence, the presence of absorption lines denoted by Greek letters is qualitatively consistent with the standard SWM model of graphite. Nevertheless, we are aware of inconsistency of our results with predictions of Koshino and Ando.\(^6\) They expect that for graphite layer with several tens or more Bernal-stacked sheets, the intensities of \( \sqrt{B} \)-dependent absorption lines should be negligible in comparison with spectral features arising in massive electrons around the \( K \) point, which evolve nearly linearly with \( B \).

Another difference of spectra Figs. 1a and b is an apparent asymmetry of the B line in bulk graphite at low magnetic fields, whereas the equivalent line in the spectra of multi-layer graphene remains perfectly symmetric. To explain this difference, we must extend our considerations to the near vicinity of the \( H \) point and take into account the \( k_z \)-dependence of LLs. Such LL structure calculated within the standard SWM model is shown in Fig. 2b, where the two components, \( B_0 \) and \( B_{-1} \) of which the B line consists, are denoted by arrows. Note that the relatively low value of the pseudogap \(|\Delta|\) does not allow to directly resolve the splitting of the B line into these components. At low magnetic field, when the Landau band \( E_3^1 \) is nearly parallel with \( E_3^0 \) and/or when it is partially or completely located above the Fermi level, we can expect rather asymmetrical shape of the B line with a well-pronounced high energy tail due to the transition \( E_3^0 \rightarrow E_3^{1+} \). With increasing magnetic field, this asymmetry should gradually disappear, as indeed observed experimentally, see Fig. 1b. From the lineshape, we roughly estimate the position of the Fermi level slightly below \( \approx 20 \) meV, but the situation is here complicated by the fact that also decoupled graphene layers in graphite, revealed by the Raman spectroscopy or detected in scanning tunneling spectroscopy experiments,\(^{28,29}\) can contribute to the final shape of the B line.

Note, that for the sample of multi-layer graphene investigated here, the fully symmetrical B line survives in transmission spectrum down to magnetic fields of 40 mT, when the Fermi level is located at \( \approx 7 \) meV from the Dirac point. The presented transmission experiment thus probes mainly undoped graphene sheets \((n_0 \approx 5 \times 10^9 \text{ cm}^{-2})\), which are located further from the SiC substrate. The layer(s) in the immediate vicinity of the substrate are highly conductive (above \( n_0 \approx 10^{12} \text{ cm}^{-2} \)) and can be probed in transport experiments.\(^{28,29}\)

Analogous considerations based on the shapes of Landau bands in the vicinity of the H point, can also qualitatively explain the significant differences in widths of individual absorption lines. For instance, the C line is roughly three times broader in comparison to the \( \alpha \) line, see Fig. 1b, in spite of the fact that they both originate in the same LLs. For a simple explanation of this fact, we just need to realize that the \( \alpha \) line is composed of transitions \( E_3^1 \rightarrow E_3^0 \) and \( E_2^0 \rightarrow E_3^{1+} \). If we take account of the near vicinity of \( k_z = 0 \), we find out that both pairs of these LLs are nearly parallel, see Fig. 2b, and give thus a rather sharp \( \alpha \) line in comparison to the C.

FIG. 2: LL structure of bulk graphite in the vicinity of the \( H \) point. Dipole-allowed transitions between LLs depicted in blue, dark yellow and red colors in part (a), (b) and (c) contribute to the B, \( \alpha \) and C lines in the transmission spectrum, respectively, cf. Fig. 1b. The parameters \( \Delta = -5 \) meV and \( \tilde{c} = 1.02 \times 10^9 \text{ m.s}^{-1} \) are used for this calculation. The effects of trigonal warping are neglected.
line. This line is composed of transitions $E_{\Delta}^{(2)} \rightarrow E_{\alpha}^{(1)}$ and $E_{\Gamma}^{(2)} \rightarrow E_{\Gamma}^{(1)}$, see Fig. 3, which occur between pairs of LLs having their derivatives of opposite signs, which causes the broadening of the C line. This explanation can be straightforwardly generalized for all transitions, giving qualitative explanation of the differences in linewidths simply using the standard SWM model.

In principle, another and even more appealing interpretation of our data could assume that we actually see the response of decoupled graphene layers instead of the $H$ point of bulk graphite. The presence of additional “Greek” lines in spectra could be then a consequence of some perturbation of the graphene system leading to a relaxation of the selection rules $\Delta n = \pm 1$. Even though the appearance of some decoupled graphene sheets in our sample is very likely, we have the following arguments to support our “bulk” interpretation: i) Our experiments were performed on several samples prepared from two different types of bulk graphite and the almost identical results, concerning the presence, position, lineshape and mainly mutual intensities of all the $\sqrt{\mathcal{B}}$-scaled absorption lines were obtained. ii) The “Greek” transitions show significantly smaller linewidth in comparison to “Roman” ones, e.g. compare lines $\alpha$ and $C$, which is unlikely to be caused by any perturbation relaxing the selection rules in graphene.

In both materials, spectral features evolving nearly linearly with $B$ are also observed, see low energy part of spectra in Figs. 1a and b, and represent thus an evidence for massive particles. In bulk graphite, the spectral features linear in $B$ cannot be explained unless some part of the sample is created from bulk graphite or at least from few-layer graphene stacks. Indeed, the traces of Bernal-stacked layers were found in micro-Raman experiment, as mentioned above.

**IV. CONCLUSIONS**

We have compared the optical response of Dirac fermions in bulk graphite and multi-layer epitaxial graphene in low magnetic fields. Whereas the results obtained on multi-layer graphene fully correspond to expectations for dipole-allowed transitions in a 2D gas of Dirac particles, the transmission spectra taken on bulk graphite appear to be more complex. The standard Slonczewski-Weiss-McClure model is found, in the latter case to be sufficient to explain the existence of all absorption lines scaling as $\sqrt{\mathcal{B}}$ as well as their individual lineshapes.

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