Exploring the charge dynamics in graphite nanoplatelets by THz and infrared spectroscopy

H L Liu\textsuperscript{1,6}, G L Carr\textsuperscript{2}, K A Worsley\textsuperscript{3}, M E Itkis\textsuperscript{3}, R C Haddon\textsuperscript{3}, A N Caruso\textsuperscript{4}, L-C Tung\textsuperscript{5} and Y J Wang\textsuperscript{5}

\textsuperscript{1} Department of Physics, National Taiwan Normal University, Taipei 11677, Taiwan
\textsuperscript{2} National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973-5000, USA
\textsuperscript{3} Center for Nanoscale Science and Engineering, Department of Chemistry and Chemical and Environmental Engineering, University of California Riverside, Riverside, CA 92521, USA
\textsuperscript{4} Department of Physics, University of Missouri—Kansas City, Kansas City, MO 64110, USA
\textsuperscript{5} National High Magnetic Field Laboratory, Tallahassee, FL 32310, USA

E-mail: hliu@phy.ntnu.edu.tw

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Abstract. We present the results of THz, infrared and magneto-optical measurements performed on graphite nanoplatelet films as a function of temperature (4.2–300 K) and magnetic field (0–17.5 T). An effective medium analysis of the low-energy spectral response indicates that the nanoplatelet material is well described by a Drude function plus two infrared absorption bands. Interestingly, the Drude plasma frequency (\(\sim 1675 \text{ cm}^{-1}\)) decreases slowly with temperature, whereas the carrier scattering rate (\(\sim 175 \text{ cm}^{-1}\)) is temperature independent. Furthermore, measurements in an applied magnetic field at 4.2 K show that a large portion of the Drude spectral weight is transferred to finite frequency features corresponding to various Landau-level transitions. Some of these transition energies scale as \(\sqrt{B}\), as expected for Dirac-like quasi-particles in graphene and observed in other graphene-like materials. Thus, our results are consistent with recent theoretical calculations indicating that the spectrum of multilayer graphene can be decomposed into subsystems effectively identical to monolayer or bilayer graphene.

\textsuperscript{6} Author to whom any correspondence should be addressed.
1. Introduction

After the atomically thin graphene film was experimentally discovered in 2004 [1], intensive studies directed toward the understanding of this new and unique material [2, 3] have led to a new and excited physics community. The main framework has been set by both its potential technological usefulness and a fundamental physics point of view. Graphene is a two-dimensional (2D) hexagonal network of carbon atoms connected by strong covalent $\sigma$–$\sigma$ bonds, and is the basic building block for graphitic materials of all other dimensionalities. The electron velocity in graphene is about $10^8 \text{ cm s}^{-1}$ and the mobility can be larger than 15 000 cm$^2$ Vs$^{-1}$ at room temperature [4, 5], many orders higher than that found in most semiconductor materials. These properties make possible a new class of carbon-based high-speed electronics.

Furthermore, the linear dispersion at the $K$ and $K'$ points of the graphene band structure gives rise to a relativistic like behavior of free carriers that has many implications for the observed quantum electrodynamics, such as the anomalous quantum Hall effect [4]–[6], a Klein paradox [7] and coherent transport [8].

There has been particular interest recently in the infrared spectral studies of graphene layers. Infrared spectroscopy can probe the dynamical properties of quasi-particles over a wide energy range and therefore provide important information about the transport and electrodynamic properties of this material. Sadowski et al [9] reported the first infrared measurements of Landau level spectra of a few (3–5) graphene layers. Jiang et al [10] examined the infrared spectra of the Landau level transitions in single-layer graphene. In monolayer graphene, the low-energy spectrum of the quasi-particle excitation becomes linear in the vicinity of the two conical points located at the opposite corners of the 2D Brillouin zone, where the conduction and valence bands touch each other [11]. In the presence of a magnetic field $B$, this perfect linearity leads to the observed spacing proportional to $\sqrt{Bn}$ for the Landau levels indexed by the integer $n$ [12]. Their experimental data compare well with the existing single-particle model of Dirac fermions in graphene. Similar infrared experiments were also undertaken with bilayer graphene [13], multilayer graphene [14] and bulk graphite [15]. More recently, gate tunable infrared properties of graphene allowed detailed investigations of its band structure [16]–[19]. All these results suggest that many-body interactions play an important role in the excited-state properties of graphene.

Currently, the most widely used method for preparing samples of single-layer graphene involves mechanical exfoliation [1]. Whereas the ideal case of a single, isolated graphene sheet having macroscopic dimensions is difficult to realize, systems comprising multiple graphene sheets can still show some of the extraordinary electronic properties of individual graphene sheets. Such films can now be prepared by a relatively efficient process where natural
Graphite is converted into few-layer graphite nanoplatelets by a process of acid intercalation, thermal exfoliation, physical separation and dispersion [20]. The resulting nanoplatelets can be deposited to form macroscopically thick layers on common substrate materials such as silicon. In this paper, we report a comprehensive THz, infrared and magneto-optical study of such moderately thick graphene films consisting of nanoplatelet structures. Our THz and infrared results yield an electronic scattering rate of 175 cm$^{-1}$ and a plasma frequency of 1675 cm$^{-1}$, the latter decreasing slowly with temperature. Magnetospectroscopy measurements at 4.2 K and in magnetic fields up to $B = 17.5$ T show several sets of Landau-level transitions (cyclotron resonance). The frequencies for some of these transitions show a conventional linear dependence on $B$, while others scale as $\sqrt{B}$, indicating a significant contribution from nearly massless Dirac fermions (quasi-particles obeying a linear dispersion relation). Such behavior is consistent with the existence of an effective monolayer-like subband in this system.

2. Experimental

High-density graphite nanoplatelet films were deposited onto high-resistivity ($\sim 5000$ Ω cm) silicon substrates using a chemical process described elsewhere [20]. Atomic force microscopy images show individual nanoplatelets having a nominal thickness of 1.7 nm, with most containing four graphene layers [20]. Raman spectra on the films are consistent with this few-layer graphene character [21]–[23]. The inset of figure 1 shows a typical scanning electron microscopy (SEM) image of the film. It is interesting to note the relatively even stacking of nanoplatelets in the film, consistent with a dense distribution over large areas of the substrate.

THz and far-infrared transmission measurements were carried out at the U4IR beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. A Bruker IFS 66v Fourier transform infrared spectrometer and a 1.5 K bolometer detector were used over the range 10–120 cm$^{-1}$. The frequency region above 120 cm$^{-1}$ was covered with a Bruker Vertex 80v spectrometer. Our transmission reference was a blank (open) aperture. To determine the film conductivity, knowledge of the index of refraction $n$ and the extinction coefficient of the substrate, which is measured separately, is required. A 10 T superconducting magnet was employed for this part of the magnetic-field work, and temperature-dependent spectra were also obtained from 2 to 300 K. Infrared studies in higher magnetic fields were carried out at the National High Magnetic Field Laboratory in Tallahassee, using a Bruker 113v spectrometer with custom light-pipe optics to carry the infrared radiation through a 20 T superconducting magnet and a 4.2 K bolometer detector. In all measurements, the unpolarized light was incident normal to the film, and the magnetic field $B$ was applied either perpendicular (Faraday geometry) or parallel (Voigt geometry) to the film.

3. Results and discussion

Figure 1 shows the measured zero-field optical transmission spectra of a bare silicon substrate and a graphite nanoplatelet film having a thickness of about 340 nm over the entire frequency range at 300 K. Measurements made on another film with a thickness of about 325 nm gave similar results. The low-frequency transmission spectrum of the silicon substrate is essentially flat. Absorption bands in the 500–1050 cm$^{-1}$ spectral range are well-known silicon multi-phonon vibrational modes; otherwise the substrate transmission is about 50% owing to reflection losses. Notably, the overall transmission intensity of the graphite nanoplatelet film is up to
40% lower than that of the silicon substrate, indicating strong absorption in the film. More interestingly, the frequency dependence of the transmission of the graphite nanoplatelet film can be divided into two regions. Below 100 cm$^{-1}$, there is a strong frequency dependence of the transmission as it increases by a factor of 2.2 as the frequency decreases. Above 100 cm$^{-1}$, the transmission varies by less than 5%.

As shown in the SEM images, the preparation technique yields inhomogeneous films of stacked nanoplatelets. The films are found to be mechanically fragile, consistent with rather weak nanoplatelet adhesion (and limited inter-grain contact). For our infrared analysis, we assume that the films consist of individual nanoplatelets surrounded by a non-conducting (dielectric) host and adopt the Garnett (or Maxwell–Garnett) theory [24] to describe the optical properties. This theory relates the effective dielectric constant of the overall film, $\epsilon_{\text{eff}}$, to the dielectric constant of the host material, $\epsilon_m$, and the graphite nanoplatelet inclusions, $\epsilon$, to an adjustable parameter for the volume fraction occupied by the nanoplatelet component, $\eta$:

$$\frac{\epsilon_{\text{eff}} - \epsilon_m}{\epsilon_{\text{eff}} + 2\epsilon_m} = \eta \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}. \quad (1)$$

Note that, for simplicity, we have chosen the ‘3D’ version of the Garnett theory, which assumes randomly situated spherical inclusions. Although a sophisticated ‘2D’ model is more appropriate (at present unavailable), our simple analysis contains the salient features of densely packed grains with extremely weak inter-grain conductivity.
Figure 2. Real part of the room-temperature optical conductivity spectrum of an individual nanoplatelet (solid line). The dashed line is the effective conductivity of the film, calculated within the Garnett theory. The inset shows the temperature dependence of the Drude plasma frequency and the scattering rate.

The dielectric function for the nanoplatelets was analyzed using the Drude–Lorentz model [25],

$$\epsilon(\omega) = -\frac{\omega_p^2}{\omega^2 + i\omega/\tau_D} + \sum_{j=1}^{N} \frac{\omega_{p,j}^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j} + \epsilon_\infty,$$

(2)

where $\omega_p$ and $1/\tau_D$ are the plasma frequency and the scattering rate of the Drude component; $\omega_j$, $\gamma_j$, and $\omega_{p,j}$ are the frequency, damping and oscillator strength of the $j$th Lorentzian contribution; and $\epsilon_\infty$ is the high-frequency limit of $\tilde{\epsilon}(\omega)$, which includes interband transitions at frequencies above the measured range.

For the case of a film thickness $d \ll \delta < \lambda$, where $\delta$ is the skin or penetration depth and $\lambda$ is the wavelength of the far-infrared radiation, the transmission through the film into a non-absorbing substrate with index $n$ can be written as [26]

$$T = \frac{4n}{(n+1+y_1^2+y_2^2)},$$

(3)

where $y_1 + iy_2 = (4\pi/c)d(\sigma_1 + i\sigma_2)$ is the film admittance. In figure 1, we show the fit to the transmission obtained by first determining the effective dielectric constant or conductivity using equations (1) and (2) and then finding $T$ from equation (3).

Figure 2 displays the calculated 300 K real part of the optical conductivity up to 2000 cm$^{-1}$ for the individual nanoplatelets along with the effective conductivity of the film based on the Garnett theory. The room-temperature $\sigma_1(\omega)$ of an individual nanoplatelet exhibits a Drude
peak that describes free (mobile) carriers, plus two absorption components around 240 and 1980 cm⁻¹. This is in contrast with the gap-like feature below 100 cm⁻¹ in the overall (effective) conductivity of the film. This stems from the Garnett theory that, for metallic inclusions imbedded in a dielectric host, shows no dc conductivity until the inclusions occupy 100% of the volume. The percolation threshold is not predicted by the Garnett theory. Our Garnett theory fit parameters for η are close to 94% with an εₘ of about 4 (i.e. an insulator). Thus, the gap-like feature at low frequencies is not a true gap but rather a consequence of the film’s granularity, consisting of poorly connected nanoplatelets with micro area that prevent inter-platelet conductivity. The lack of any temperature dependence to this feature (i.e. no evidence for thermal excitations across such a small gap) plus the inability to sense dc transport support this picture based on granularity. Returning to the conductivity for the nanoplatelet inclusions, our fits yield a Drude plasma frequency of ωₚₓ and scattering rates 1/τₓ of 1675 and 175 cm⁻¹, respectively, whereas ε∞ is 15.4. This plasma frequency is slightly smaller than that obtained in highly oriented pyrolytic graphite (HOPG) [27, 28] and an epitaxial graphene film [29]. In contrast, our scattering rate is by a factor of 2 larger than the value reported in HOPG [27, 28], but is comparable to that obtained in epitaxial graphene films [29]. This increased scattering can be attributed to the effects of impurities, defects, disorders and nanoplatelet boundaries. The estimated Drude conductivity [σₓ = ωₓ²/τₓ/60] is about 267 Ω⁻¹ cm⁻¹. The absorption bands near 240 and 1980 cm⁻¹ can be associated with interband transitions between the π bands near K and H points of the Brillouin zone [27]. When the sample is cooled from 300 to 4.2 K, the low-frequency transmission below 120 cm⁻¹ increases with decreasing temperature, corresponding to a decrease in conductivity. We obtain a good fit for the low-temperature transmission by adjusting only the Drude parameters (the plasma frequency in particular), while keeping the others fixed at their T = 300 K values. Separate measurements on the bare Si substrate showed no temperature dependence, as expected. The temperature evolution of ω xp and 1/τ xp is shown in the inset of figure 2. One first observes that the scattering rate exhibits very little temperature dependence, whereas the Drude plasma frequency monotonically decreases with decreasing temperature. This reveals that the decreased conductivity is mainly due to changes in the free carrier concentration (thermally excited electron–hole pairs) and not changes in the scattering rate. Furthermore, the lack of a major change in Drude plasma frequency down to 4.2 K implies that band gaps in a graphite nanoplatelet are less than 1 meV [30].

Figure 3 shows the magneto-transmission ratio of a graphite nanoplatelet film, T(H) / T(H = 0 T), at 4.2 K in the Faraday geometry. The spectra display rich and surprisingly strong field dependence over the full frequency range. There are two important features to these spectra: (i) the transmission at low frequency is strongly enhanced as the field increases and (ii) the transmission spectra display a series of field-dependent resonances extending up to 2800 cm⁻¹. The dramatic increase in the low-frequency transmission is an infrared counterpart of the positive magnetoresistance effect. The resonance features in transmission originate from the absorption by quasi-particles transitioning between Landau levels that shift as a function of applied field. Below, we discuss these two striking magneto-optical response aspects in more detail. It should also be noted that the spectra do not show any field dependence when measured in the Voigt geometry. Therefore our discussion pertains only to the Faraday orientation.

7 Basically, the Garnett theory is fitting only the very low frequency up-turn in transmission. The quality of the fit above 150 cm⁻¹ is hardly affected by different values of η. Thus the fit values for the nanoplatelet plasma frequency and scattering rate are mostly independent of the Garnett theory.
To illustrate more clearly the effect of a magnetic field, we plot the ratio of the transmission at a given field to the transmission at $B = 0$ T. Figure 4 shows this transmission ratio in the THz region (frequencies below 120 cm$^{-1}$). Here, the field-induced spectral changes occur gradually and smoothly as the applied field is increased, with the ratio reaching 1.35 at 10 T and no evidence for saturation. These changes correspond to decreasing absorption and therefore a positive magnetoresistance effect within the nanoplatelets. This positive magnetoresistance is unusual and noteworthy in several respects. First, the magnitude is surprisingly large from the viewpoint of a typical metal where the effect is usually a few per cent or lower. Its scale is determined by $\omega_c \tau$, where $\omega_c$ is the cyclotron frequency and $\tau$ is the scattering time, and so we may conclude that in our sample $\omega_c$ is quite large, especially in light of the small value for $\tau$. We note that this magnetoresistance effect is still smaller than the enormous positive magnetoresistance ratio of perfect single-crystal graphite (exceeding $10^4$ at 4.2 K and 16 T), an effect that has been known for nearly 40 years \[31\].

The magnetoresistance field dependence also differs from that of most metals. Whereas the conventional magnetoresistance is quadratic in field, our graphene nanoplatelet films display a linear dependence on field. Nonetheless, this strong positive magnetoresistance is clearly related to the transfer of electronic spectral weight from the Drude component to higher frequencies as the magnetic field is applied, with the spectral weight appearing in various transitions between Landau levels. Similar behavior has also been inferred from magnetoreflectance measurements of HOPG \[27\].
Next, we discuss magneto-spectral features in the mid-infrared, consisting of a collection of transmission minima (absorptions) whose shape and position vary with the applied magnetic field, suggestive of Landau-level transitions. How these Landau levels change in a field is indicative of the electronic band structure in the material. To better quantify this field dependence in the presence of other broad features (e.g. the depletion of the Drude response at low frequencies), we calculated the transmission ratio second derivatives and, from this, assembled the field-frequency-dependent trends of five absorption peaks, shown in figure 5.

Clearly, the behavior of three low-energy absorption peaks shifts linearly with $B$, while two higher-energy peaks follow $\sqrt{B}$. We assign the $B$-linear modes to Landau-level transitions of conventional quasi-particles. In traditional 2D materials with parabolic dispersion, this is tantamount to measuring the effective mass of quasi-particles $m^*$, because transitions between the equally spaced Landau levels at energy $E_n = (n + \frac{1}{2}){\hbar}eB/m^*$ ($n \geq 0$) reflect the same $m^*$ as in a classical cyclotron resonance at $\omega_c = eB/m^*$. Here, $m^* \sim 0.05m_e$ ($m_e$ is a free-electron mass) is slightly smaller than that of bulk graphite [32]–[34]. The other two significant modes that vary with $\sqrt{B}$ are assigned to a ‘Dirac’ energy spectrum similar to the one that occurs in single-layer graphene. Here, the quasi-particle’s linear dispersion leads to unequally spaced Landau levels at energy $E_n = \text{sgn}(n)\tilde{c}\sqrt{2e\hbar B|m|}$, where $\tilde{c}$ is the band velocity, and $n > 0$ or $n < 0$ represents electrons or holes. Thus, the two $\sqrt{B}$-dependent features correspond to transitions $L_0 \rightarrow L_1 (L_{-1} \rightarrow L_0)$ and $L_{-1} \rightarrow L_2 (L_{-2} \rightarrow L_1)$, respectively. Quantitatively, this assignment yields a value of $\tilde{c} \sim 1.03 \times 10^6$ m s$^{-1}$, the same velocity as for single-layer graphene.

Significantly, the presence of both $B$-linear and $\sqrt{B}$-dependent mode frequencies suggests that the graphite nanoplatelet is typified by two kinds of quasi-particles, i.e. one having a
conventional band mass and the other nearly massless with linear dispersion. This observation is consistent with recent theoretical predictions [35]. The magneto-optical absorption spectra of multilayer graphene can be decomposed into sub-components effectively representing the monolayer or bilayer graphene. Specifically, odd-layered graphene always exhibits absorption peaks that shift in proportion to $\sqrt{B}$ owing to the existence of an effective monolayer-like subband. We can infer that both monolayer graphene and bilayer graphene contribute to the anomalous behavior of cyclotron resonance in graphite nanoplatelets. Indeed, very similar behavior has been observed in samples containing a large number of graphene layers (between 70 and 100) grown in a SiC substrate [14] and in a thin graphite sample of thickness $\sim 100$ nm exfoliated from an HOPG [15].

4. Conclusion

In conclusion, the THz, infrared and magneto-optical spectra of graphite nanoplatelet films provide substantial insight into the low-energy charge dynamics in this system. Firstly, the optical conductivity of a single nanoplatelet consists of a free carrier absorption and two infrared absorption bands near 240 and 1980 cm$^{-1}$. The absolute value of the room-temperature Drude plasma frequency implies a carrier density of $n \sim 1.6 \times 10^{18}$ cm$^{-3}$, assuming $m^* \sim 0.05m_e$. Using the experimental value of the carrier scattering rate $\sim 175$ cm$^{-1}$, we estimate the carrier mean free path $\ell = \tau_0 h (3\pi^2 n)^{1/3}/m^*$ $\sim 25.4$ nm at room temperature. A similar value of 31.2 nm is obtained using a graphene quasi-particle velocity of $10^8$ cm s$^{-1}$. As the temperature is lowered, the Drude plasma frequency decreases. The lack of a major change in Drude plasma frequency down to 4.2 K implies that band gaps in a graphite nanoplatelet are less than 1 meV. In contrast, the scattering rate does not show much temperature variation. Secondly, in a magnetic

Figure 5. Positions of the absorption peaks related to the Landau level transitions as a function of applied magnetic field. The solid symbols are data obtained from the transmission second derivative. The solid lines are the best $B$ linear or $\sqrt{B}$ fit.
field, the Drude oscillator strength is suppressed and transferred to various finite frequency transitions between the Landau levels. The frequencies for some of the Landau-level transitions display a clear \( \sqrt{B} \) dependence, indicating a significant contribution from nearly massless Dirac fermions with a band velocity of \( \tilde{c} \sim 1.03 \times 10^{6} \text{ m s}^{-1} \) owing to the existence of an effective monolayer-like subband. Most importantly, these results demonstrate that the intriguing quasi-particle dynamics of graphene can be obtained in these readily prepared nanoplatelet films.

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