Measurement of graphite tight-binding parameters using high field magneto-reflectance

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Magnetic subbands of graphite have been investigated by magneto-infrared reflectance spectroscopy at 4K in fields up to 31T. Both Schrödinger-like (K-point) and Dirac-like (H-point) Landau level transitions have been observed, and their magnetic field dispersion are analyzed by a newly-derived limiting case of the Slonczewski-Weiss-McClure model. The values of the band parameters are evaluated without using sophisticated conductivity peak lineshape analysis. In this work, several less-explored band parameters are determined from the experimental results and they are known to result in electron-hole asymmetry and the opening of an energy gap between the electron and hole bands in multilayer and bilayer graphene systems.

The tight-binding model of graphite’s band structure, first calculated by Wallace, and later extended by Slonczewski, Weiss, and McClure, has enjoyed a renaissance in recent years due to its successful application in understanding many properties of single and few-layer graphene. The model, known as Slonczewski-Weiss-McClure (SWMc) band theory, rests on seven tight binding parameters, $\gamma_0$ to $\gamma_5$ and $\Delta$, characterizing interactions between near neighbor atoms in the lattice. The physical representations and estimated values of these parameters have been illustrated and organized by Dresselhaus et al. and Zhang et al. While the SWMc model has been used in understanding graphitic materials for the last 60 years, the values of less-explored band parameters ($\gamma_4$, $\gamma_5$, and $\Delta$) remain uncertain. As these parameters may play an expanded role in interpreting observed asymmetries in the electronics of graphene, there is an increased incentive to accurately measure them.

Infrared (IR) (magneto)-spectroscopy is a powerful tool in resolving energies in the band structure of graphitic materials, and has already been employed to study the unique electronic states of massless Dirac-like fermion in monolayer graphene, massive chiral fermions in bilayer graphene, and rich spectral features in graphite, where effects attributed to both massless holes and massive electrons have been seen. The results in graphite have been modeled by assuming that its band structure is a combination of a monolayer model, where the holes at the Brillouin zone H-point behave like massless fermions, and an effective bilayer model (EBM), where the electrons at the K-point behave like massive fermions with an adjusted coupling constant between layers. However, the EBM ignores the band parameters governing the interlayer hoppings between unstacked and stacked/unstacked sublattices ($\gamma_3$, $\gamma_4$), next-nearest interlayer hoppings ($\gamma_2$, $\gamma_5$), and the on-site energy difference between the stacked and unstacked sublattices ($\Delta$). Excluding these parameters removes the possibility of electron-hole ($e-h$) asymmetry, which has been observed to be significant in bilayer graphene and graphite.

The interlayer hoppings can also drastically change the band structure near the charge neutrality point (CNP), i.e., the point where the electron and hole bands touch, and lift the degeneracy of the doubly degenerate $e-h$ mixed Landau level (LL-1) and (LL0). Here, we use the level indexing notation of ref. $[11]$. The (LL-1) and (LL0) refer to the two LLs near the CNP, and the term, $hn-ecm$, refers to a transition from the $n$-th hole LL to the $m$-th electron LL. The splitting of the two $e-h$ mixed LLs was observed recently by Li et al. and the transition between these two states exhibits a potential 3D to 1D crossover due to graphite’s anisotropic properties.

In this communication, we use IR spectroscopy to measure the magnetic-field dispersion of graphite’s LLs and fit our measurements to a newly-derived limit of the SWMc model that includes higher-order band parameters. The intense magnetic fields applied distinguish the two $e-h$ mixed LLs and split of the $e-h$ symmetry of several interband transitions. These lifted degeneracies are accounted for by our modified SWMc model, and values for the set of band parameters are found consistent with those previously reported.

Our measurement set-up uses Kish graphite flakes stabilized on the Scotch tape and placed in a cryostat held at 4K subjected to magnetic fields of up to 31T. IR reflectance spectra are measured by a Fourier transform IR interferometer using light pipe optics. The reflectance is then normalized by taking the ratio of the sample spectra to that of a gold mirror. The acquired reflectance spectra are modeled by Drude-Lorentz functions using RefFit. Sharp or minute features attributable to noise were smoothed prior to modeling. To show the quality of the modeling, the smoothed reflectance spectra are plotted in Fig. 1 overlaid with the original spectra at every other Tesla. Further analysis reveals that the observed...
The sheet conductance of our sample, calculated using $G_0 = e^2/4h$ for photon energies between 0.1 to 0.6eV at zero magnetic field.\textsuperscript{26} (1eV = 8065cm$^{-1}$) The sheet conductance of our sample, calculated using $G(\omega) = c_0 \sigma(\omega)$ with interlayer distance $c_0 = 3.35\text{Å}$, is shown in the inset of Fig. 2 (b). The calculated value is found larger than $G_0 = e^2/4h$, but closer to $4e^2/h$. Accounting for this discrepancy, one should note that the conductivity is not calculated from a true Kramer-Kronig transform, but a result of modeling the reflectance spectra using finite numbers of Drude-Lorentz functions. As one cannot precisely assign Lorentz modes outside the measurement range, the optical weight for the modes located within the measurement range tends to be overestimated. Moreover, the incident angle and the misalignment (between the sample and the gold reference) can also affect the result. On the other hand, the universal conductance is dependent on the short-range disorder, "ripples" in graphene’s atomic structure and the presence of charged impurities\textsuperscript{27, 28}, all of which are likely to be present in Kish graphite. The focus of this work is the magnetic-field dispersion of the LLs, which are not impacted by the frequency-independent universal conductance.

Mode energies extracted from the conductivity peaks of Fig. 2 are plotted in Fig. 3, with modes following $\sqrt{B}$-dependence shown in (a) and those following linear dependence shown in (b). The (LL0)-e1 transition follows linear dependence below 12T, but $\sqrt{B}$- dependence at higher fields, and thus is plotted in both panels. Anomalies in mode energies can be found around the characteristic phonon energies of graphite\textsuperscript{29, 30}, particularly along several LL transitions (H: -1 to 0, K: (LL0)-e2, h1-e2), which will be further investigated elsewhere.

In order to invoke the SWMc model, we start with the theoretical observation that the LL structures for $\gamma_3 = 0$ and $\gamma_3 \neq 0$ are similar at high fields\textsuperscript{11, 21}, and so set $\gamma_3 = 0$, which ignores the trigonal warping in the band structure. The energy of the magnetic subbands can then
be obtained using the following self-consistent Eq. (9),

\[
(n + \frac{1}{2})\bar{E}^2 = \varepsilon^2(1 + \nu^2) + \frac{\delta\omega}{(\omega^2 - \delta\omega^2)} + \frac{2\varepsilon\nu}{(1 - \nu^2)^2} - \frac{\omega}{(\omega^2 - \delta\omega^2)\nu} \pm \sqrt{\left[\varepsilon^2(1 + \nu^2) + \frac{\delta\omega}{(\omega^2 - \delta\omega^2)} + \frac{2\varepsilon\nu}{(1 - \nu^2)^2} - \frac{\omega}{(\omega^2 - \delta\omega^2)\nu}\right]^2 + \frac{\bar{E}^2}{2}},
\]

where integer \( n \) is the LL index, \( \varepsilon = E - E_0, \bar{E}^2 = e^22e\hbar B = qB \) with \( \varepsilon = \frac{\sqrt{3}\nu\omega_0}{2\hbar}, \nu = \frac{3\gamma}{\gamma_0} \) with \( \Gamma = 2\cos(\frac{c_0a_0}{a_0}), \omega = \frac{1}{2}\left[\frac{1 + \nu^2}{E_2 - E_1} - \frac{1 + \nu^2}{E_2 - E_3}\right] \) and \( \delta\omega = \frac{1}{2}\left(\frac{1 + \nu^2}{E_2 - E_3} - \frac{1 + \nu^2}{E_2 - E_1}\right) \), in which \( c_0 \) and \( a_0 \) are lattice parameters. In SWMc model, \( E_1, E_2, \) and \( E_3 \) can be represented as [9],

\[
E_1,2 = \Delta + \gamma_1\Gamma + \frac{1}{2}\gamma_3\Gamma^2 \quad \text{and} \quad E_3 = \frac{1}{2}\gamma_2\Gamma^2.
\]

Using the modes following \( \sqrt{B} \)-dependence, we find that the data agree well with the Fermi velocity \( \tilde{c} = 1.03 \times 10^6 \) m/s (\( \gamma_0 = 3.18 \text{eV} \)) and assign the two highest energy modes to the \( n = -1 \) to \( n = 0 \) and \( n = -1(-2) \) to \( n = 2(1) \) transitions. To see if the parameter \( \Delta \) is finite, the energy \( E_{-1,0} \) for \( n = -1 \) to \( n = 0 \) transition is scaled by a factor of \( 1 + \sqrt{2} \), and plotted in a dotted line in Fig. 3 (a). If \( \Delta \) is finite, the scaled energy \( (1 + \sqrt{2})E_{-1,0} \) would be larger than the interband transition energy \( E_{-1,2} \). From the difference, \( |\Delta| \) is estimated to be 60 cm\(^{-1}\).

For K-point transitions, the levels follow a linear in \( B \) dependence when \( \tilde{E} \) is small, and can be written as [9]

\[
\varepsilon_{e,h} = [\pm\sqrt{n(n+1)\omega^2 + \frac{1}{4}\delta\omega^2 - (n + \frac{1}{2})\delta\omega}]\hbar B,
\]

in which \( \omega \) determines the energy separation between the LLs and \( \delta\omega \) results in the \( e - h \) asymmetry. It is clear from the data that most K-point modes are not linear at high fields. Though having a nonlinear magnetic field dispersion, the EBM [20, 21] ignores the \( e - h \) asymmetry; an effect one cannot sufficiently account for by using two different Fermi velocities [21], since the correction is apparently dependent on the LL index \( n \). On the other hand, it worths noting that the EBM [20, 21], and the bilayer model [51] (\( \Gamma = 1 \)) can be obtained by approximating the self-consistent Eq. (1) of the SWMc model as,

\[
\varepsilon^2 \approx \frac{2n + 1}{2}\bar{E}^2 + \frac{1}{2}\omega^2 - \frac{1}{2}\sqrt{\frac{1}{\omega^4} + \frac{4\varepsilon^2}{\omega^2}} + \bar{E}^4.
\]

and use a trial \( \varepsilon^2 = \frac{2n + 1}{2}\bar{E}^2 \) on the right-hand side.

![FIG. 3: Transition energies as a function of magnetic field: Three green dotted horizontal lines mark the characteristic phonon energies in graphite. Black solid lines are fittings using Eq. (3) for panel (a) and Eq. (6) for panel (b). The purpose of the dashed lines is explained in the text. Inset: Schematic energy diagram at the H- and K-point.](image)
achieved using $\omega q = 14.5 \text{ cm}^{-1}/\text{T}$, $\delta \omega q = -3.4 \text{ cm}^{-1}/\text{T}$ and $\nu = 0.05$. The calculated transition energies are shown in solid lines in Fig. 3 (b) and the higher-energy modes are assigned to the transitions that best describe the magnetic-field dispersion of the transition energies. Near the K-point, i.e. $\gamma_1 \Gamma \gg \Delta + \frac{1}{2} \gamma_5 \Gamma^2 - \frac{1}{7} \gamma_2 \Gamma^2$, the fitting parameters, $\omega$ and $\delta \omega$, are related to the band parameters as

$$\omega \sim \frac{1}{\gamma_1 \Gamma}; \delta \omega \sim -\frac{\Delta}{\gamma_1 \Gamma} + 2 \gamma_4 \frac{\omega_0}{\gamma_1 \Gamma} + \frac{1}{2} \gamma_5 - \frac{1}{7} \gamma_2 \gamma_1^2.$$  \hspace{1cm} (8)

From the values of fitting parameters, we extract $\gamma_1 = 0.38 \text{ eV}$, $\gamma_4 = 0.08 \text{ eV}$ and $\gamma_2 + \gamma_5 = 0.048 \text{ eV}$. It is generally agreed\cite{6, 7} that $\gamma_2 = -0.02 \text{ eV}$, so $\gamma_5$ is estimated to be $0.028 \text{ eV}$.

For the (LL-1) and (LL0) levels (i.e. $n = 0$), one can solve the cubic Eq. in Ref. 10 to find

$$\varepsilon = 0 \text{ and } \varepsilon \sim -\delta \omega q B,$$  \hspace{1cm} (9)

respectively. Since the (LL0) level will be partially occupied by electrons, the transition between the (LL-1) and (LL0) levels are made by those electrons away from the K-point. The parameter $\delta \omega (k_z \sim k F q)$ is found to be $-3.7 \text{ cm}^{-1}/\text{T}$, which is slightly larger than $\delta \omega (k_z = 0) q = -3.4 \text{ cm}^{-1}/\text{T}$; therefore, the sublattice energy difference $\Delta$ is likely to be positive.

The (LL0)-e1 transition exhibits an unusual crossover. At lower fields, its energy agrees with the prediction of the linear SWMc model with a slope of $17 \text{ cm}^{-1}/\text{T}$. (dashed line in Fig. 3 (b)) At higher fields, the peak broadens quickly with increasing magnetic field, and the magnetic-field dispersion becomes Dirac-like with a slope of $54 \text{ cm}^{-1}/\text{T}^{1/2}$. (dashed line in Fig. 3 (a)) A similar behavior has been reported previously\cite{18}, where the (LL0)-e1 mode has a larger slope for $B \leq 8.5 \text{ T}$, but a smaller slope for $B \geq 8.5 \text{ T}$. In addition, we find that $E_{(LL-1)-(LL0)} + E_{(LL0)-e1} < E_{(LL-1)-e1}$, a discrepancy that cannot be accounted for by simple pictures assuming LLs are independent with each other. Except for the (LL0)-e1 transition, all other transitions are well described by the modified SWMc model (Eq. (6)), so the underlying mechanism for this anomaly is specific to the (LL0) level. Anomalous phenomena have been observed pertaining to this level, and it has been conjectured that a charge density wave\cite{33, 35} has an effect specific to it, though it should be noted that these anomalies were found at lower temperatures and at higher fields.

In summary, magnetic subbands in Kish graphite are investigated using magneto-infrared reflectance spectroscopy up to 31T. The high magnetic field distinguishes the two $e - h$ mixing LLs near the CNP and the splitting of the interband transitions. We propose a new limit of the SWMc model to describe the K-point transitions and use it to estimate the values of the band parameters,

$$\gamma_0 = 3.18 \text{ eV}, \gamma_1 = 0.38 \text{ eV}, \gamma_2 = -0.02 \text{ eV}, \gamma_3 = 0,$$

$$\gamma_4 = 0.08 \text{ eV}, \gamma_5 = 0.028 \text{ eV}, \text{ and } |\Delta| = 0.028 \text{ eV}.$$

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