Ultrahigh Magnetic Field Study of Layer Split Bands in Graphite

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We report studies of the magnetospectroscopy of graphite into a new regime of high energies and ultrahigh magnetic fields which allows us to perform the first spectroscopic studies of the interlayer split-off bands, E_1 and E_2. These bands can be well described by an asymmetric bilayer model and have only a small interlayer band gap asymmetry. We show that all of the properties of the electrons and holes can be described by a simple relativistic behavior determined by γ_0 and γ_1.

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The recent surge in interest in two-dimensional electronic systems formed from monolayer [1–4] and bilayer graphene [5–7] is based on the properties of bulk graphite [8–13]. In particular, the many exciting properties of bilayer graphene are crucially dependent on understanding the interlayer coupling that originates in bulk graphite. There is mounting evidence [9,10,14,15] that the majority of the properties of graphite can be described quite simply at the high symmetry points of the Brillouin zone by a combination of a single layer graphene (SLG) model for massless Dirac fermions at the H point and a bilayer graphene (BLG) model for massive particles at the K point. Spectroscopic and theoretical estimates of the band parameters still remain controversial, however, particularly around the K point, as only very limited experimental evidence exists of the properties of the interlayer split-off bands E_1 and E_2 formed by the interlayer coupling which is dominated by the matrix element γ_1 in Bernal stacked layers. By using ultrahigh magnetic fields we now extend the magnetospectroscopy of graphene and graphite into a new regime of high energies which allows us to perform the first magnetospectroscopy of the interlayer split-off bands and show that their behavior can be modeled very well by the analog of relativistic behavior predicted by the BLG model.

Traditionally, the band structure of graphite has been described by the Slonczewski-Weiss-McClure (SWM) tight-binding model [16,17], which requires the use of seven tight-binding parameters $\gamma_0, \ldots, \gamma_5$, Δ determined by interlayer and intralayer matrix elements. This provides a description of the dispersion relations all around the Brillouin zone edge from the hole pocket centered at the H point to the electrons around the K point. By contrast, the SLG or BLG model uses γ_0 with only a single interlayer matrix element γ_1 and is found to provide a remarkably accurate [9] description of the magneto-optical properties of graphite by assuming that this is dominated by the H and K points. Even at low energies where the band structure is known to be more complex [12,18], the slight modification of introducing an asymmetric velocity for the K point fits the data very well [19] and can describe most of the behavior predicted in the SWM model. In the simplified bilayer picture the band structure is shown in Fig. 1(b), with the K point having two touching symmetric massive bands and split-off bands at $\pm 2\gamma_1$. Introduction of the asymmetric bilayer model (ABM) (as occurs due to the presence of γ_4 in the SWM) means that E_2-E_3^+ and E_1-E_3^- become symmetric pairs of bands each with their own respective Fermi velocity, v_F^+ and v_F^-, which are predicted to differ by $\sim$10% in both the SWM model and density functional theory [13,15–17].

Measurements were made of the transmission of thin ($\sim$ 20 nm) exfoliated natural crystalline graphite up to magnetic fields of 160 T at 300 K. Fields were generated using a semidestructive single-turn coil technique shown schematically in Fig. 1(a) that provides pulse lengths of 5 μs. The transmission of a series of lasers in the region 1550–630 nm was detected using high speed photodiodes and a 200 MHz low noise amplifier to follow complete cycles of the pulsed magnetic field, allowing the rising and falling parts of the magnetic field cycle to be compared and

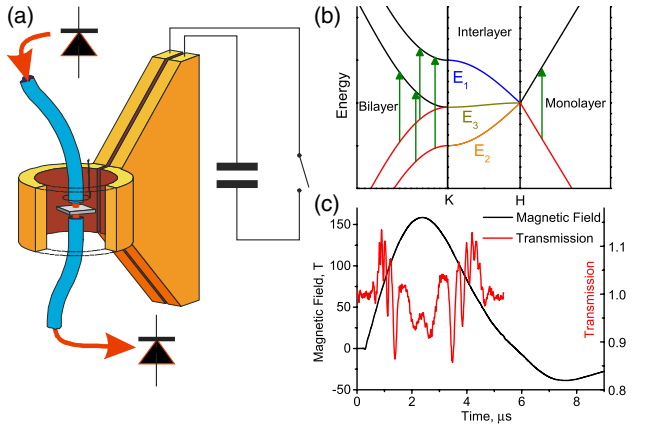

FIG. 1 (color online). (a) Schematic view of the experimental system, (b) graphite band structure, (c) typical time dependence of the magnetic field and sample transmission for 1220 nm radiation.

averaged. Typical recordings of the time-dependent magnetic field and transmission are shown in Fig. 1(c).

Typical experimental results are shown in Fig. 2, where there are a series of absorptions which we will show are periodic in $1/B$ with more than one periodicity, depending on the photon energy. The strongest high frequency series are assigned to the ($\Delta n = \pm 1$) transitions between the $E_3^{\pm}$ K-point Landau levels, by extrapolation from previous work [9,20]. The lower frequency resonances are, however, previously unreported, and are due to transitions from and to the split-off bands.

We analyze the magneto-optical response by introducing a Fourier analysis procedure which allows us to isolate the in-plane quantization effects and separate out the contributions from the different bands when working at fixed photon energy. The periodicity of the transitions in reciprocal magnetic field can be seen from an analysis starting from the bilayer approach for the K point [10,21], where the Landau level energies ε_n are given by

$$\varepsilon_n = \frac{s}{\sqrt{2}}\Big[(\lambda\gamma_1)^2 + (2n+1)\Delta_B^2 + \mu\sqrt{(\lambda\gamma_1)^4 + 2(2n+1)(\lambda\gamma_1)^2\Delta_B^2 + \Delta_B^4}\Big]^{1/2}, \quad (1)$$

where Δ_B is the magnetic energy for the graphenelike in-plane motion

$$\Delta_B = v^{\pm}\sqrt{2\hbar eB} = \sqrt{\alpha B}, \quad (2)$$

where $v^{\pm} = \sqrt{3}ea_0\gamma_0/2\hbar$ (with different values for the electrons and holes in the ABM), $s = \pm$ for the electrons and holes, and $\mu = \mp$ corresponds to the fundamental and split-off bands. For the K-point transitions in graphite $\lambda = 2$ due to the double-sided coupling as compared to a single bilayer where $\lambda = 1$. Rearranging Eq. (1) gives

$$(n^2+n)\alpha B = (n+1/2)\varepsilon_n^2 \pm \lambda\gamma_1\varepsilon_n(n^2+n)^{1/2} \times\sqrt{\left(1+\frac{\varepsilon_n^2}{4(n^2+n)(\lambda\gamma_1)^2}\right)}. \quad (3)$$

For the dominant interband optical transitions with a selection rule $\delta n = \pm 1$, the transition energies are

$$E = |\varepsilon_n^+| + |\varepsilon_{n\pm1}^-|. \quad (4)$$

Working at constant energy E for high Landau level indices n, Eqs. (3) and (4) approximate to give the magnetic field dependence of transitions between the nth and $(n-1)$th levels B_n as the remarkably simple expression

$$n\alpha B_n = E^2/4 + 2\gamma_1 E/2, \quad (5)$$

where α is chosen as the appropriate mean of the values deduced from v for the bands involved in the transitions.

The values for B_n predicted by Eq. (5) are within $<0.5\%$ of the values predicted by the full bilayer model for $n > 3$, using the same values for γ_0 and γ_1, suggesting that the observed behavior should be very accurately periodic in $1/B$ and can be used to determine these parameters without the need for qualitative judgements of the fitting accuracy for multiple peaks.

For transitions involving the layer split-off bands, we have a similar expression with similar accuracy:

$$n\alpha B_n = (E-\Gamma)^2/4 + 2\gamma_1(E-\Gamma)/2, \quad (6)$$

where $\Gamma = 2\gamma_1$ for transitions between the layer split-off bands and E_3 ($E_2 \rightarrow E_{3+}$, $E_{3-} \rightarrow E_1$) and $\Gamma = 4\gamma_1$ for transitions directly between the two layer split-off bands ($E_2 \rightarrow E_1$).

These simple expressions are a consequence of the intermediate energy zero field result [6] for a bilayer:

$$v^2p^2 = \varepsilon^2 + 2\gamma_1\varepsilon, \quad (7)$$

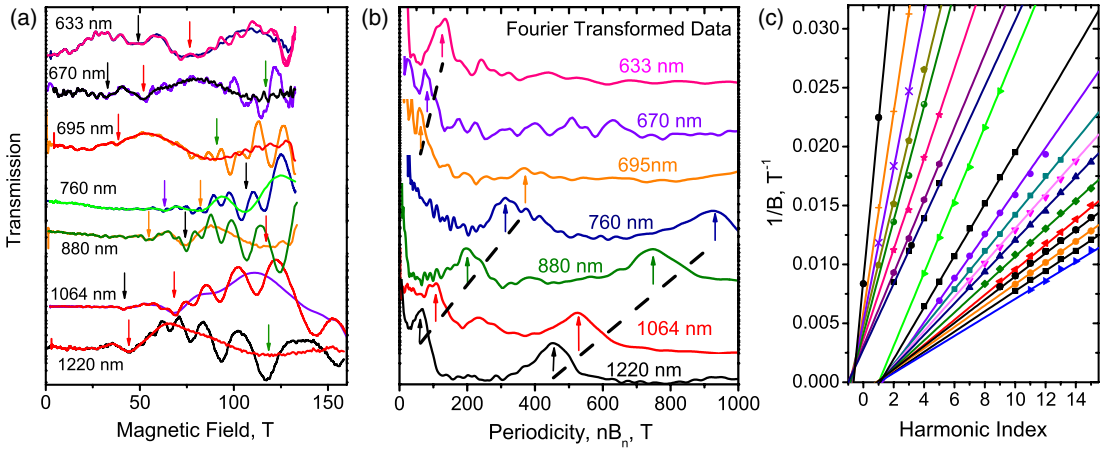

FIG. 2 (color online). (a) Magnetotransmission as a function of magnetic field (original data and spectra filtered to remove $E_3\pm$ transitions) for a series of wavelengths with arrows shown to denote the transitions to the split-off bands, (b) Fourier transforms as a function of $1/B$ for the traces shown in (a), (c) plots of the values of $1/B_n$ versus (arbitrary) harmonic index for the $E_3^- - E_3^+$ (right-hand group) and $E_2 - E_3^+$ (left-hand group) transitions for different photon wavelengths from 1550 to 633 nm, together with linear fits.

where the momentum p^2 has been quantized at $2ne\hbar B$, the transition energy $E = 2\varepsilon$, and the interlayer interaction $2\gamma_1$ is twice the result for the isolated bilayer. This expression is an exact analogy of the relativistic energy momentum relationship where γ_1/v^2 plays the role of the particle rest mass [22]. Including the split-off bands gives the set of relativistic dispersion relations:

$$\varepsilon_3^{\pm} = \pm\sqrt{\gamma_1^2 + p^2 v_{\pm}^2} \mp \gamma_1,$$
$$\varepsilon_{1,2}^{\pm} = \pm\sqrt{\gamma_1^2 + p^2 v_{\mp}^2} + \delta. \quad (8)$$

The pairs of bands are asymmetric, which is a feature of both the SWM and *ab initio* calculations using density functional theory [13] which predict $v_+/v_- \approx 1.12$. Both types of theory also predict that the $E_2 - E_3$ and $E_3 - E_1$ interlayer gaps should be asymmetric. The SWM model predicts, for example, that $(E_2 + E_1 - 2E_3) = 2(\Delta - 2\gamma_2 + 2\gamma_5) = 2\delta$, with typical fitting parameter values from the literature suggesting a wide range of values for 2δ in the region 0.06–0.3 eV [12,13,22,23] and tight-binding models predicting 0.1–0.2 eV [13]. All of the transition energies plotted in Fig. 3 can then be calculated from the differences of the energies in Eq. (8).

For a fixed photon energy the magnetic field values for the transitions are thus expected to show a very well defined periodic dependence on $1/B$ with a periodicity $[n\alpha B_n = 1/\Delta(1/B_n)]$ given by Eqs. (5) and (6). The experimental results demonstrate that this prediction holds extremely well. Plots of $1/B$ values for the absorption minima show [Fig. 2(c)] a very accurate harmonic series, and Fourier transforms of the traces in Fig. 2(a) as a function of $1/B$ [Fig. 2(b)] show well-defined peaks.

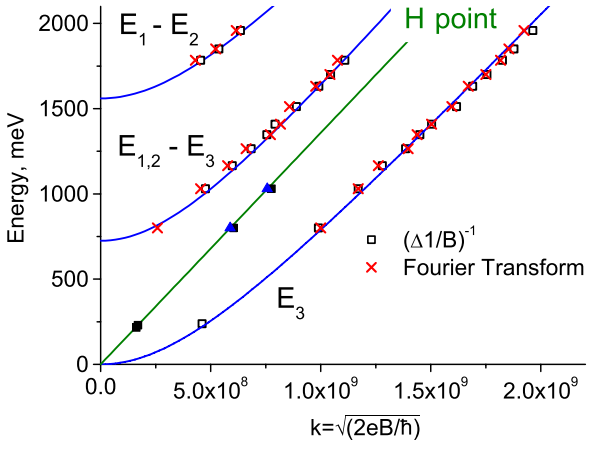

FIG. 3 (color online). Energy momentum relation for interband excitations in graphite deduced from the periodicity of the magneto-oscillations from Fourier transformation (points) and from fitting the values of $1/B_n$ compared with the values from Eq. (8) (lines), low energy (229 meV) data from [26]. The H-point dispersion comes from $n = 1$ to $n = 2$ interband transitions giving $v = 1.03 \times 10^6$ m/s [24].

The highest periodicity peak (300–1300 T) corresponds to the well-known K-point $E_3^{\pm}$ transitions. The transforms show the appearance of two new peaks for energies more than 1 eV (1220 nm) (100–400 T) and 1.8 eV (690 nm) (50–200 T), respectively. The new series correspond to transitions involving the split-off bands, the first from a combination of $E_2 \rightarrow E_3^+$ and $E_3^- \rightarrow E_1$, and the second directly from $E_2 \rightarrow E_1$. The periodicities of all three transitions are used to give the k vector $(= \sqrt{2enB_n/\hbar})$ and then plotted as energy–k-vector dispersions in Fig. 3 with the periodicities determined both from $1/B$ plots and from the Fourier transforms. The $E_3^- \rightarrow E_3^+$ transitions show excellent agreement with Eq. (5), using typical values for $\gamma_0 = 3.18$ eV ($v = 1.03 \times 10^6$ m/s) and $\gamma_1 = 0.39$ eV [9,24]. Since these transitions correspond to high quantum numbers n, they measure the average of the values for E_{3+} and E_{3-} (which we later show to be $v^+ = 1.14 \times 10^6$ m/s and $v_- = 0.92 \times 10^6$ m/s), and no electron-hole splitting can be resolved. These values give us rest masses for the two pairs of bands of $\gamma_1/v_{\pm}^2 = 0.081m_e$ and $0.053m_e$. Fitting the periodicities for the $E_2 \rightarrow E_1$ transitions with Eq. (6) also gives good agreement with the same parameter values for the average v and a total gap of $4\gamma_0$. The results for the $E_3 \rightarrow E_{1,2}$ transitions are more surprising, as these require a significantly higher value for v and a reduced value for the band gap of 0.725 eV. This suggests that transitions from $E_2 \rightarrow E_{3+}$ are dominant, where both bands have the higher Fermi velocity and the band gap is reduced due to the asymmetric interlayer coupling [13,16,17]. The Fermi level suggests that charge transfer should occur from the H to K points at high fields, leading to increased density in the $n = 0$ Landau level and changes to its exchange and correlation effects at high fields which might affect the transition intensities [25], although the transitions studied here are between states at least 100 meV away from the Fermi level.

The existence of a well-defined periodicity in $1/B$ allows us to examine the split-off band transitions in more detail by using a Fourier blocking filter in $1/B$ to remove the higher frequency oscillations from the $(E_3^{\pm})$ transitions, as shown in Fig. 2. For each recording a second trace is shown where the data have been processed with a Fourier blocking filter over the range $[nB_n(E_3^{\pm}) \pm 200$ T], which removes the oscillations associated with the $E_3^{\pm}$ transitions. We first analyze the $E_2 \rightarrow E_1$ transitions which are compared directly with the exact ABM predictions for low quantum numbers as shown in Fig. 4. This allows us to make an accurate fit for $\gamma_1 = 0.39 \pm 0.005$ eV, since this is the only parameter which enters into the $E_2 - E_1$ separation, even in the full SWM model.

As already suggested above, the second series of transitions from $E_3 \leftrightarrow E_{1,2}$ require an increased value of $\gamma_0 = 3.63$ eV ($v^+ = 1.14 \times 10^6$ m/s) when fitted with either Eq. (6) or the full asymmetric bilayer model Eq. (3), with a suitably reduced value of v_-. This suggests that at high

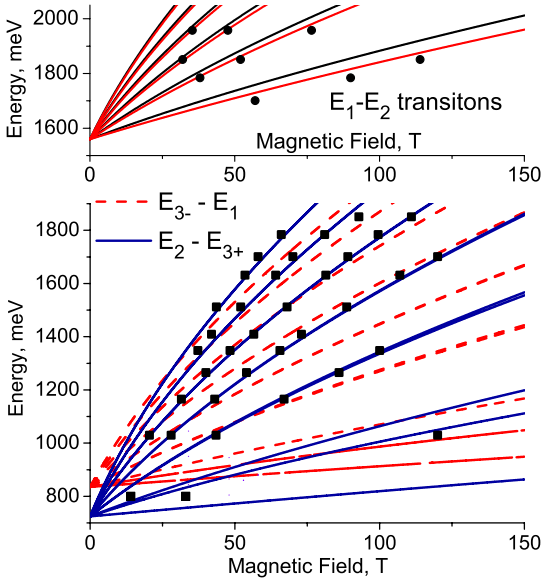

FIG. 4 (color online). Transition energies (points) as determined from the Fourier filtered plots shown in Fig. 2 and as calculated (lines) from the ABM for all possible split-off transitions from n to $n \pm 1$, including the asymmetry term δ and using asymmetric velocities v.

fields the transitions are dominated by the symmetric pair of bands E_2 and E_3^+, which have a higher electron velocity due to the band asymmetry associated with the γ_4 term and the free-electron contribution [26] in the SWM model. The two velocities are slightly more asymmetric than observed previously in low field measurements on graphite [19] and for monolayer [27] and bilayer [28] graphene, which is not unexpected given that our measurements use a larger range of energies. Another potential explanation is that Coulomb many-body interactions are becoming larger at higher energies [29]. Figure 4 illustrates the exact transition energies calculated using the asymmetric bilayer model for all of the layer split band transitions with a value for $(E_2 + E_1 - 2E_3) = 0.11 \pm 0.04$ eV. There are very few direct measurements of the asymmetry, but a value of 0.13 eV was observed by Bellodi *et al.* [30] from thermoreflectivity measurements at zero field. These measurements study transitions which are strongly influenced by the Fermi level occupancy of the states around the K point, which makes their interpretation difficult [31], but they are nevertheless in good agreement with our measurements, which suggests that the layer split band gaps $E_1 - E_3$ and $E_3 - E_2$ are significantly less asymmetric than often thought and should provide a good constraint for values used in fitting theoretical models of graphite. Our value for $E_3 - E_2$ of 0.725 ± 0.02 eV is also in good agreement with that reported from angle-resolved photoemission spectroscopy measurements (0.71 ± 0.015 eV) [12], although this method could not observe the upper band. Split-off band transitions have been observed with bilayer graphene where electroreflectance measurements [32] measure split-off bands at half the energy for graphite due to the single-sided coupling. The resonances at 0.363 and 0.393 eV are slightly less asymmetric than our graphite values where considerably more interlayer coupling is occurring.

Perhaps the most remarkable conclusion is that the dispersion relation for all of the interband excitations can be deduced from the simple quasirelativistic dispersion relations Eq. (8) with only slightly more asymmetric velocities than reported previously [19,27,28]. In the visible region of the spectrum, all of the excitations can be considered to be in the relativistic region of the dispersion relation with a similar rest mass in all four bands at the K point.

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