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Magnetoabsorption study of Landau levels in graphite

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We report far-infrared magnetoabsorption measurements of thin graphite samples exfoliated from highly ordered pyrolytic graphite showing transitions originating from the *K* and the *H* points. For the *K* point, both cyclotron resonance and interband transitions are measured which are not described well by the currently accepted values of the parameters in the Slonczewski-Weiss-McClure tight-binding model. We demonstrate that the observed data can be better described using an effective bilayer graphite model which has been modified to include an electron-hole asymmetry.

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The recent surge in interest in two-dimensional electronic systems formed from monolayer[1–4] and bilayer graphenes[5–7] has prompted a re-examination of the properties of bulk graphite.[8–12] Traditionally the band structure of graphite has been described by the Slonczewski-Weiss-McClure (SWM) tight-binding model[13,14] which requires the use of seven tight-binding parameters $\gamma_0, \ldots, \gamma_5, \Delta$. 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. It has been suggested recently[9,10,15] 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 model to describe the behavior of the holes as massless Dirac fermions at the *H* point and a bilayer model to describe the massive electrons and holes at the *K* point.

In general the most accurate method to study the band structure of graphite has proved to be a study of the Landau levels through experiments such as magneto-optics[8,9,16–21] and magnetotransport.[22–26] In practice the magnetotransport provides information predominantly at the Fermi energy as does the low-field cyclotron resonance. In addition the majority of the magneto-optical work has used the derivative of the magnetoreflectivity to deduce the resonance positions, which introduces a significant degree of uncertainty since, as remarked by Doezema *et al.*[19] this means that "it is not clear where the resonances are to be marked." Despite these limitations the SWM model[13,14] has in general provided a good fit to the measured properties. A characteristic of this model, however is that it predicts a large electron-hole asymmetry for the *K*-point carriers which is quite difficult to measure.[18] In this Rapid Communication we examine the low-energy magnetoabsorption of thin bulk graphite and show that the degree of asymmetry is significantly less than predicted by the currently accepted values of the SWM parameters and that the band structure can be fitted by a simplified model using only an asymmetry of the electron and hole velocities.

The thin graphite samples measured here are produced by repeatedly cleaving highly oriented pyrolitic graphite (HOPG) with the scotch tape method,[1] until the samples showed significant transmission ($\sim$10%) in the visible. Electrical measurements on similar samples suggest that they correspond to a total of approximately 100 monolayers. The samples were then left on the tape to act as a supporting medium for the thin graphite. Absorption spectra were taken using a Bruker IFS113 Fourier transform spectrometer. Illumination was by light guide and a parabolic focusing cone and the sample was mounted in a superconducting magnet. The transmitted signal was measured by a silicon bolometer. In order to produce the highest sensitivity over a large energy range the spectra were all ratioed against the zero-field transmission spectrum in order to display only the magnetic field induced changes in transmission.

The ratio $T(0)/T(B)$ spectra in which absorption features appear as peaks are shown in Fig. 1 as both a waterfall graph and as a false color map. The positions of the absorption peaks as a function of magnetic field are shown in Fig. 2. It is clear that the majority of the peaks increase approximately linearly with magnetic field as is expected from cyclotron and interband resonances associated with the *K* point.[8,9,16–20,28] In addition there is a single resonance, labeled A, which increases as $\sqrt{B}$. This is characteristic of Dirac fermions as found in both monolayer graphene[2,8,29–31] and for *H*-point holes in bulk graphite or multilayer graphene.[8,10,15,18,30] This can be fitted with the conventional expression:

$$E_{0-1} = v^* \sqrt{2e\hbar B}, \tag{1}$$

where B is the magnetic field, giving a velocity of 1.03×10^6 m/s, in good agreement with values reported previously.[8,18,30]

Our main interest here is the analysis of the *K*-point resonances, which are significantly stronger than those from the *H* point. We first consider electron cyclotron resonance. It has long been known that the presence of trigonal warping leads to the selection rule for low-field electron cyclotron resonance of

$$\omega = |3N + 1| \times \omega_c, \tag{2}$$

where transitions are observed for both $N=0,1,2,3\ldots$ and $N=0,-1,-2\ldots$ for opposite circular polarizations. ω_c is the cyclotron frequency, as was first measured by Galt *et al.*[28] and analyzed by Nozieres[32] and again by Suematsu and Tanuma[17] who found $m^*/m_e=0.058$ in the low-field limit. At high magnetic fields the effects of trigonal warping become less and the strength of the higher harmonics decreases, as is also expected for pure bilayers.[33] The cyclotron resonance transitions observed in Fig. 2 are identified as transitions

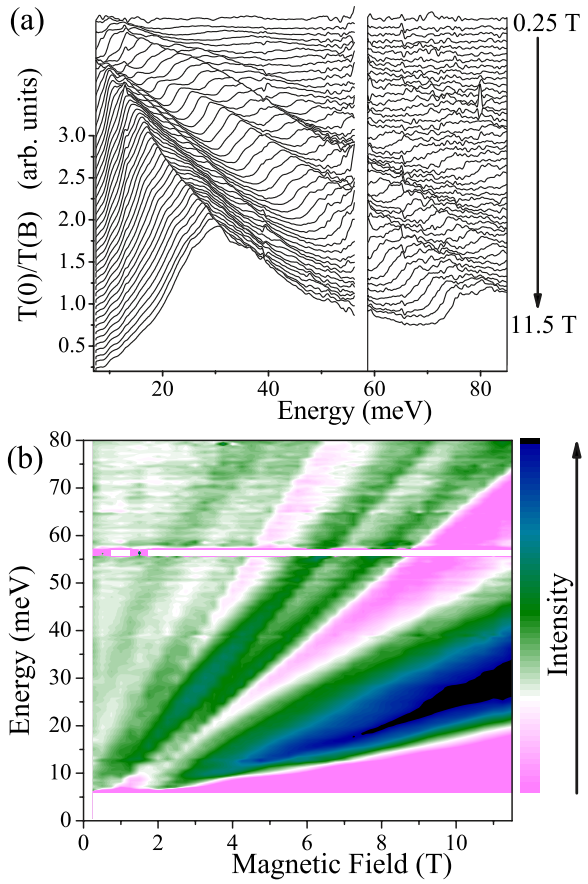

FIG. 1. (Color online) (a) Waterfall plot and (b) contour plot of the magnetotransmission resonance spectra from 0.25 to 11.5 T. Spectra are the ratios of the transmission at zero field $[T(0)]$ to the transmission at field $[T(B)]$ so that decreases in transmission due to absorption appear as peaks. A strong absorption obscures the spectra around 57 meV.

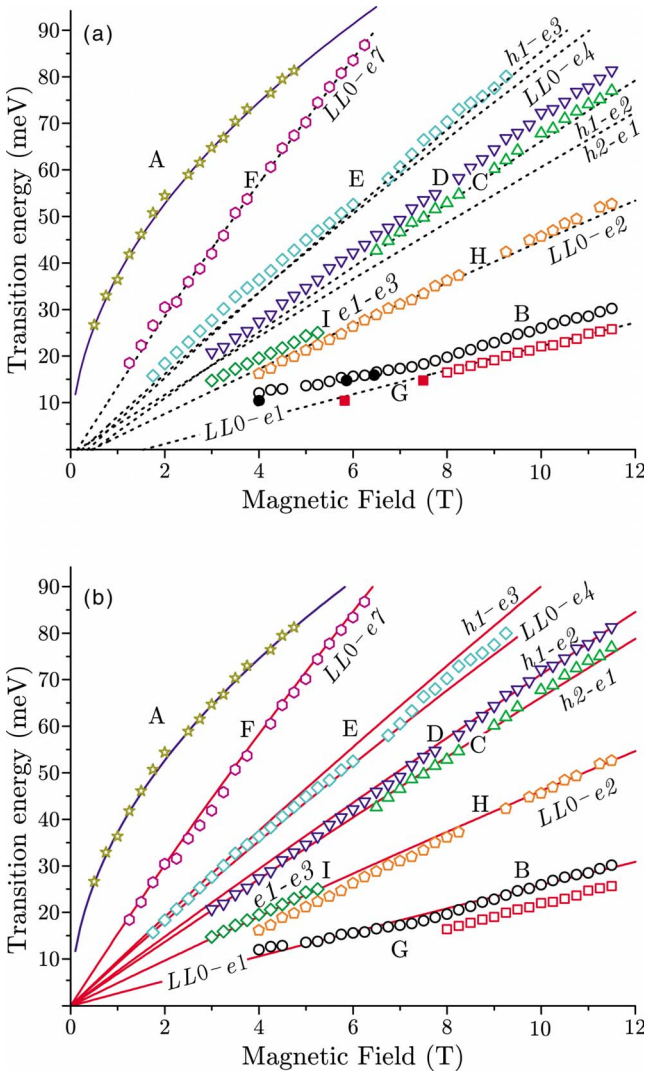

FIG. 2. (Color online) (a) Plot of the observed transition energies as a function of magnetic field. The black dashed lines represent fitting to the transitions from Nakao's (Ref. 27) calculations. The solid symbols represent resonance positions measured in Doezema *et al.* (Ref. 19). (b) Same data with red solid lines represent fitting using the method described in text.

$B(N=0)$, $E(N=1)$, and $F(N=2)$, with both the $N=1$ and $N=2$ transitions weakening considerably at higher fields. By contrast the $N=0$ transition strengthens and narrows considerably once the quantum limit is reached, where the resonance is dominated by transitions between the two lowest Landau levels and the effective mass falls to $m^*/m_e=0.045$. Individually resolved transitions were first reported by Doezema *et al.*[19] who used them to make a careful fit of the Landau level structure up to 7 T, using energies up to 16 meV and deducing SWM parameters with the calculation methods of Nakao.[27]

The Nakao[27] results are compared with the present data in Fig. 2(a) which identifies the different transitions using the nomenclature *en* and *hn* to identify the *n*th electron and hole Landau level and LL0 and LL-1 to identify the hole-electron mixed Landau level. It is clear that the agreement is not particularly good, other than for the higher harmonics which are observed at lower field. This is particularly noticeable for the dominant LL0-$e1$ transition at high fields. The reason for this discrepancy is probably due to the use of the derivative technique combined with magnetoreflectivity, which makes it significantly more difficult to identify the peak positions. The magnetoabsorption shown in Fig. 1 is dominated by a very strong LL0-$e1$ peak, particularly above the quantum limit at 7 T, when $e1$ is depopulated. This resonance shows a sharp peak, and a small shoulder [transition G in Fig. 2(a)] on the low-energy size, as well as a further shoulder at higher energies [transition H in Fig. 2(a)]. Comparison with the data from Doezema *et al.*[19] shows that this weak shoulder was fitted to the $e1$-LL0 position due to its strength in the derivative spectra.

We now turn to the interband transitions which follow the selection rule $\Delta n=1$. These have been studied at higher energies recently by Orlita *et al.*[9] and previously by several other authors.[16,18–20] In the present data the most prominent of these are the doublet [transitions C and D in Fig. 2] which increase in strength steadily with magnetic field and reach ~80 meV at 11.5 T (Fig. 1). This consists of the $h1-e2$ transition above 3 T, where it becomes allowed due to the emptying of $e2$, and $h2-e1$ which becomes allowed above

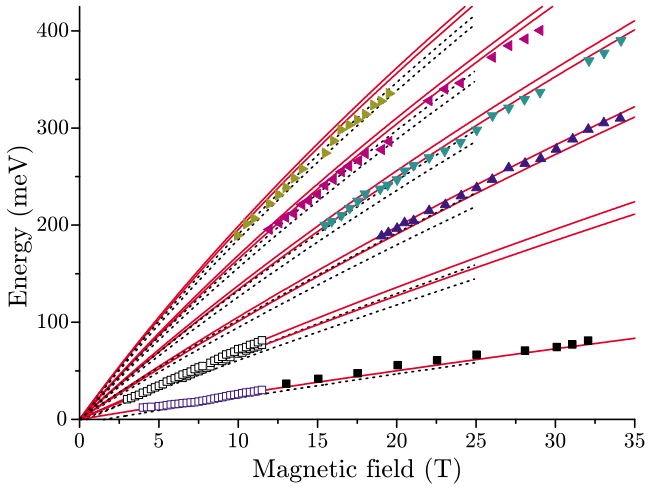

FIG. 3. (Color online) Interband transitions at high magnetic field as observed by Orlita *et al.* (Ref. 9) (solid symbols) compared to the approach used in the text (red solid lines) and the calculations of Nakao (Ref. 27) extended from 15 to 25 T using an adjusted the bilayer formula (black dashed lines). Data from the present work are shown as open symbols.

7 T. Once again it can be seen that the experimental transition energies are significantly higher than the predicted values. Overall therefore we conclude that the currently used parameters in the SWM model do not give an entirely satisfactory fit.

In order to produce the simplest approach which will fit the current and previously reported data we follow the method used by Orlita *et al.*[9] that the K point can be described by fitting the data using a graphene bilayer formalism. This was based on the work of Koshino and Ando[10] for thin multilayer graphenes, who showed that by considering only nearest-neighbor intralayer coupling of strength γ_0 and the strongest interlayer coupling parameter γ_1 the properties of the K point can be described by fitting the data using a graphene bilayer formula[6] with a coupling parameter given by $\lambda\gamma_1$ where,

$$\lambda = 2\cos\kappa, \tag{3}$$

and κ approaches zero as the number of graphene layers becomes large. One significant omission from this approach, however, is the nonvertical coupling term γ_4 which introduces electron-hole asymmetry since it is clear that the existing data and that reported previously on both graphite[18,20] and bilayer graphene[34] requires that there is a significant asymmetry in the electron and hole Landau levels at the K point. In order to provide a simple parameterized description of this we follow the suggestion of Henriksen *et al.*[34] and fit the data using a bilayer dispersion modified by introducing different velocities for the electron and hole. Thus we use

$$\varepsilon_n^{e,h} = \frac{s}{\sqrt{2}}[(\lambda\gamma_1)^2 + (2n+1)\Delta_B^{e,h^2} - \sqrt{(\lambda\gamma_1)^4 + 2(2n+1)(\lambda\gamma_1)^2\Delta_B^{e,h^2} + \Delta_B^{e,h^4}}]^{1/2}, \tag{4}$$

where Δ_B is the appropriate magnetic energy for either electrons or holes given by

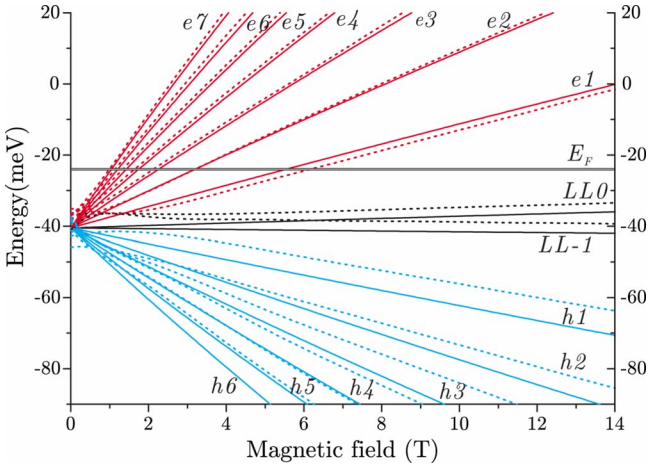

FIG. 4. (Color online) Landau energies as a function of magnetic field calculated using the asymmetric bilayer model (solid line) and from Nakao's SWM model (Ref. 27) (dotted line).

$$\Delta_B^{e,h} = v_{e,h}\sqrt{2\hbar eB}, \tag{5}$$

and $s=\pm$ for the electrons and holes respectively. In this approach there are two degenerate levels, usually denoted LL0 and LL-1 at $\epsilon=0$. In the SWM model these are split by second nearest-neighbor hopping, related to the terms γ_2 and γ_5. Transitions between these two levels have been resolved very clearly at very low energy in the reflectivity data of Li *et al.*[21] and so using a simplified version of the approach of McCann[33,35] we fit these levels with the expression

$$\varepsilon_{\mathrm{LL0}} = \frac{3}{2}\beta\hbar\omega_c, \tag{6}$$

$$\varepsilon_{\mathrm{LL\text{-}0}} = -\frac{1}{2}\beta\hbar\omega_c, \tag{7}$$

where $\hbar\omega_c$ is the cyclotron energy of the $e1$ level and $\beta=0.075$. The value of β is chosen to fit the splitting of LL0 and LL-1 as measured by Li *et al.*[21] and apart from a constant shift this functional form also to fits the energy levels as calculated by Nakao[27] at high fields to better than 0.5 meV.

We now fit the observed transition energies for both the cyclotron resonance and interband transitions as shown in Fig. 2(b) by varying the parameters v_e, v_h, and $\lambda\gamma_1$. The electron velocity is constrained mainly by fitting the cyclotron resonance transitions which leads us to the value $v_e=1.109\times10^6$ ms^{-1}. The weak shoulder H is also found to be well described as a weakly allowed LLO-$e2$ transition. Fitting the interband transitions then gives $v_h=0.951\times10^6$ ms^{-1} with the asymmetry leading to a splitting of the transitions in good agreement with the observed behavior. The choice of these values gives an average velocity $(v_e+v_h)/2=v^*=1.03\times10^6$ ms^{-1} in good agreement with the value determined here and earlier[8,9,30] for the Fermi velocity of the H-point holes and requires us to use $\lambda\gamma_1=0.75$ eV. Using the value of $v^*=\sqrt{3}/2\gamma_0 a_0/\hbar$, where $a_0=0.246$, gives a value for $\gamma_0=3.18$ eV. The value for $\lambda\gamma_1$ is also in good agreement with the value used by Orlita *et*

al.,[9] suggesting that the measurements are dominated by multilayer graphene with a large number of layers. Further confirmation of these fitting parameters can be seen by comparison of the predictions of the asymmetric bilayer model with the higher field, higher energy measurements of Orlita *et al.*[9] in Fig. 3. Unfortunately, although some features show asymmetric line shapes, the linewidth in these measurements is too large (15–30 meV) to resolve the predicted splittings which are of order 10 meV. Also shown in this figure are the calculations of Nakao,[27] extrapolated to higher field using the functional form of Eq. (4), which demonstrate that the SWM model with the currently accepted parameters provides a noticeably poorer fit to these data. The asymmetry between the electron and hole velocities of 16.6% is also consistent with that deduced by Henriksen *et al.*[34] for purely bilayer graphene who found an asymmetry in the velocities of the electrons and holes of 13%. Figure 4 shows a comparison of the Landau levels as calculated by Nakao[27] with those as calculated using the asymmetric bilayer model. This demonstrates that the main differences occur for the lowest Landau levels and all of the hole Landau levels, which show significantly less asymmetry than for the conventional SWM model.

In conclusion therefore we have measured magnetoabsorption in thin layers of bulk graphite and observed both cyclotron resonance and interband transitions at the K point of the Brillouin zone. We have demonstrated that it is possible to produce a good description of the observed transition energies using a simplified model based on the effective bilayer approximation[10,15] for multilayer graphite, modified to include electron-hole asymmetry. This asymmetric bilayer model provides a better description of the dispersion than provided by the accepted SWM model with currently accepted values of the tight-binding fitting parameters.

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