The origin of electron-hole asymmetry in graphite

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The electron hole asymmetry has been measured in natural graphite using magneto-optical absorption measurements. A splitting is observed for the transitions at both the $K$-point and the $H$-point of the Brillouin zone of graphite where the effect of trigonal warping vanishes. This result is fully consistent with the SWM Hamiltonian providing the free electron kinetic energy terms are taken into account. An identical electron-hole asymmetry should be present in graphene.

The band structure of graphite has been calculated by Slonczewski and Weiss (SW) in the late fifties [1]. Based upon detailed group theoretical considerations the SW Hamiltonian, with its seven tight binding parameters $\gamma_0, \gamma_5, \Delta$, can be exactly diagonalized to give the band structure. Due to the inter layer coupling the in-plane dispersion depends on the momentum $k_z$ parallel to the $c$-axis. McClure derived the magnetic Hamiltonian for the case when the magnetic field is applied parallel to the $c$-axis [2]. The so called Slonczewski, Weiss and McClure (SWM) Hamiltonian has infinite order since the trigonal warping term $\gamma_3$ couples Landau levels with orbital quantum number $n$ to Landau levels with quantum number $n + 3$. This coupling breaks the dipole selection rule and gives rise to a large number of harmonics in the cyclotron resonance. Nakao showed that the infinite Hamiltonian can be successfully truncated to a reasonable size and numerically diagonalized to find the eigenvalues [3]. At the $H$-point the effect of $\gamma_3$ vanishes and the SWM Hamiltonian can be analytically solved to give a Landau level energy spectrum which depends only on $\gamma_0$. This is the origin of a widespread misconception in the literature, including our own work, that there is no electron-hole asymmetry at the $H$-point.

The electronic properties of graphite are well documented in the literature [4][8]. In particular, magneto-optical techniques have been extensively used to probe the Landau level energy spectrum at the $H$ and $K$-points where there is a joint maximum in the optical density of states [19][24]. This data was for the most part analyzed using the effective bi-layer model [25] for graphite with only two parameters, $\gamma_0$ and an effective inter layer coupling $2\gamma_1$. The splitting of the $K$-point transitions in the magneto-reflectance data was analyzed within the effective bi-layer model by including electron-hole asymmetry due to the non vertical coupling term $\gamma_4$ phenomenologically [22]. In our previous work [23] the observed splitting of the $H$-point transitions was not assigned to electron-hole asymmetry as there is no trigonal warping at the $H$-point, so the effect of $\gamma_4$ vanishes.

In this letter we show that electron-hole asymmetry exists for all values of $k_z$ and is an inherent part of the SWM Hamiltonian through the often neglected free electron kinetic energy terms. The asymmetry should lead to an observable splitting of both the $H$ and $K$-point optical transitions. Extending our previous magneto-optical on natural graphite to lower energies, lower temperatures, and higher magnetic fields we show that a splitting of both the $H$ and $K$-point transitions due to the electron-hole asymmetry is observed. The size of the splitting at the $H$-point is in good agreement with the predicted electron-hole asymmetry. The splitting of the $K$-point transitions is also found to be dominated by the free electron terms with $\gamma_4$ and $\gamma_5$ playing only a secondary role.

Nakao [3] derived an explicit form for Landau level energy spectrum at the $H$-point. Unfortunately, when writing the expression Nakao neglected for simplicity the small free electron kinetic energy terms $h^2k^2/2m$, where $k$ is the in plane wave vector and $m$ is the free electron mass. The free electron terms are quantized in a magnetic field and their values are significant for all magnetic fields. The SWM Hamiltonian can easily be diagonalized at the $H$-point and the correct expression for the Landau level spectrum, including the free electron terms is,

$$E_{3\pm}^n = \frac{\Delta \pm \sqrt{\left(\Delta + h^2s/2m\right)^2 + 3ns^2a_0^2}}{2} + \frac{nh^2s}{2m},$$

$$E_{1,2}^n = \frac{\Delta \pm \sqrt{\left(\Delta - h^2s/2m\right)^2 + 3(n+1)s^2a_0^2}}{2} + \frac{(n+1)h^2s}{2m},$$

where $n = 0, 1, 2, \ldots$ is the orbital quantum number, $s = 2eB/h$ and $a_0 = 0.246$ nm. The Zeeman term has been omitted since it simply shifts the energies by $\pm g\mu_B B/2$ and can easily be added if required. At the $H$-point the electron hole asymmetry is provided by the free electron term $nh^2s/2m$. Thus the dipole allowed transitions, $E_{3\pm}^n \rightarrow E_{3\pm}^n + 1$ and $E_{3\pm}^{n+1} \rightarrow E_{3\pm}^n$ will
be split by $\delta E = \hbar^2 s^2/2m \simeq 0.23$ meV/T. Note that
$\hbar^2 s^2/2m \ll \gamma_0^2 s_0^2$ so that to a very good approximation
$E_{3n+1}^n = E_{1,2}^n$, i.e. the Landau ladders remain doubly
degenerate at the $H$-point. Note that the free electron term
has the expected phase (0) for massless Dirac fermions.

In a similar way, the bilayer expression [25] can be
modified phenomenologically to include the free electron
term for massive fermions with a phase of (1/2) at the
$K$-point

$$E_{3n}^{n} = \pm \frac{1}{\sqrt{2}} \left[ (\lambda \gamma_1)^2 + (2n + 1)\varepsilon^2 
- \sqrt{(\lambda \gamma_1)^4 + 2(2n + 1)\varepsilon^2(\lambda \gamma_1)^2 + \varepsilon^4} \right]^{1/2}
+ \frac{(n+\frac{1}{2})\hbar^2 s}{2m}, \quad (2)$$

where $n = 0, 1, 2, \ldots$, $\lambda = 2$, $\varepsilon = v_f \sqrt{2eH}/E$ is the
characteristic magnetic energy, $v_f = \sqrt{3e\alpha \gamma_1/2h}$ is the
Fermi velocity. Eq. (2) has not been derived explicitly, however, we have verified that the predicted behavior
is in exact agreement with the SWM calculation with
$\gamma_3, \ldots, \gamma_5, \Delta = 0$. The full SWM model has quantum numbers
$-1, 0, 1, 2, \ldots$ and there are two special Landau levels
(LL0 and LL-1) whose energy remains close to zero. The
fields neglected in the numerical calculations of Nakao.

Before presenting the experimental data, the impor-
tance of the free electron kinetic energy terms is dem-
s trated by numerically diagonalizing the truncated 600 $\times$
600 SWM matrix for a magnetic field $B = 0.3$ T using
the SWM parameters of Nakao [3] to allow a compar-
ison. The calculated Landau level dispersion along $k_z$
is shown in Fig. 1(a) including the free electron terms.
The symbols (circles and triangles) in Fig. 1(a) are taken
from the calculations of Nakao at the same magnetic field
(Fig. 3 of Ref. [3]). The triangles distinguish the triply
degenerate Landau levels, which have a markedly different
dispersion along $k_z$ and correspond to leg orbits. Clearly
there is perfect agreement between the two calculations.
On the other hand, the calculations in Fig. 1(b) which
neglect the free electron terms are significantly different.
Notably, the electron cyclotron energy is underestimated,
while the hole cyclotron energy is overestimated. Thus,
the free electron terms have to be included in the SWM
Hamiltonian if the correct energy spectrum is to be ob-
tained. As our SWM calculations agree perfectly with
the results of Nakao, we conclude that the free electron
terms were omitted from Eq. (9) of Ref. [3], but included
in the numerical calculations of Nakao.

For the magneto-transmission measurements suitably
thin samples were fabricated by exfoliating natural
graphite. The measurements were performed in pulsed
fields $\leq 60$ T ($\simeq 400$ mS). A tungsten halogen lamp pro-
vides a broad spectrum in the visible and near infra-red
range and the absorption is measured in the Faraday con-
f iguration with the $c$-axis of the graphite sample paral-
lel to magnetic field. A nitrogen cooled InGaAs photodi-
eode array, or an extended InGaAs detector analyzed
the transmitted light dispersed by a spectrometer. The
use of two detectors allows us to cover a wide energy
range 0.6–1.1 eV. Differential transmission spectra were
produced by normalizing all the acquired spectra by the
zero field transmission. Measurements to higher fields
$\leq 150$ T were performed using a semi-destructive tech-
nique and pulse lengths of $\sim 10$ ms and the transmission
of a polarized CO laser (0.229 eV) measured as a func-
tion of the magnetic field using a nitrogen cooled HgCdTe
photodiode coupled with a 200 MHz low noise amplifier
and an infrared tunable wave plate.

Representative differential absorption spectra mea-
sured at $T \simeq 1.8$ K in magnetic fields $B = 55–59$ T are
shown in Fig. 2(a). The spectra contains a large number of
lines reflecting the large number of $K$ and $H$ point
transitions which cross in this energy region. Neverthe-
less, a clear splitting of the $H$-point and the $K$-point
transitions is observed (arrows). The energy of the ob-
served transitions are plotted as a function of magnetic
field in Fig. 2(b). Before discussing these results it is use-
ful to consider the possible transitions at the $H$-point.
Dipole allowed transitions have a change in the orbital
quantum number of $\pm 1$. Due to the doubly degenerate
Landau level spectrum at the $H$-point with $E_{3n+1}^{n} = E_{1,2}^{n}$
there are a large number of allowed transitions between
the valence band ($E_{3-}$ or $E_2$) and the conduction band
($E_{3+}$ or $E_1$). However, the understanding of the prob-
FIG. 2. (Color online) (a) Differential magneto-transmission spectra of natural graphite measured at magnetic fields in the range 55 − 59 T at T ≃ 1.8 K. (b) Magnetic field dependence of the observed optical transitions in natural graphite. The calculated SWM energies of the transitions are shown as lines: $H$-point $\Delta n = \pm 1$ (thin blue lines), “effective” $H$-point $\Delta n = \pm 2$ (dashed red lines), $\Delta n = 0$ (dotted green lines) and $K$-point $\Delta n = \pm 1$ (thick black lines).

The problem is greatly facilitated by fact that all transitions involving bands $E_2$ or $E_1$ are degenerate with $E_{3-} \rightarrow E_{3+}$ transitions with “apparent” selection rules $\Delta n = 0$ and $\Delta n = \pm 2$. This is shown schematically in Fig. 3. The electron hole asymmetry, also shown schematically here, splits both the $\Delta n = \pm 1$ and the $\Delta n = \pm 2$ transitions, while the $\Delta n = 0$ transitions remain unaffected. From Eq.(1) the splitting of the $\Delta n = \pm 2$ transitions is $\delta E = h^2 s/m$ i.e. twice the size of the splitting of the $\Delta n = \pm 1$ transitions.

The energy of the observed $H$ and $K$-point transitions are plotted as a function of magnetic field in Fig. 2(b). As seen in the raw data, a splitting of the $H$-point and the $K$-point transitions is observed. The calculated SWM transitions energies are indicated by the solid and broken lines.

The energy of the $H$-point transitions depends only on $\gamma_0 = 3.15$ eV and the calculated splitting is independent of all other SWM parameters and vanishes only if the free electron terms are not included in the Hamiltonian. We have verified that the predictions of Eq.(1) are exact. The observed splitting of the $H$-point $E_3^{n(n+1)} \rightarrow E_3^{n+1(n)}$ transitions (blue solid lines) is beautifully reproduced by the calculations. We stress that in either approach there are no fitting parameters; the size of the splitting is simply given by $h^2 s/2m \approx 0.23$ meV/T. In addition, the observed splitting of the “effective” $E_{3-} \rightarrow E_{3+}$ transitions with “apparent” selection rules $\Delta n = \pm 2$ (dashed red lines) is twice as large in agreement with the predictions for electron hole asymmetry in Eq.(2).

The calculated splitting of the $K$-point transitions depends on the SWM parameters used, notably $\gamma_4$ and $\gamma_5$. We adjust very slightly $\gamma_1 = 0.37$ eV to fit the observed transitions (slope of the magnetic field dependence) and use the accepted values for the other SWM parameters which are summarized in Table I. The agreement turns out to be very good making a further refinement of the parameters unnecessary. A comparison of the SWM splitting $\approx 23$ meV at $B = 60$ T with $h^2 s/2m \approx 14$ meV suggests that $\gamma_4$ and $\gamma_5$ are responsible for approximately

$$\begin{align*}
\gamma_0 &= 3.15 \text{ eV} \\
\gamma_1 &= 0.37 \text{ eV} \\
\gamma_2 &= -0.0243 \text{ eV} \\
\gamma_3 &= 0.31 \text{ eV} \\
\gamma_4 &= 0.07 \text{ eV} \\
\gamma_5 &= 0.05 \text{ eV} \\
\Delta &= -0.002
\end{align*}$$

| $\Delta n = 1$ | $\Delta n = 0$ | $\Delta n = 2$ |
|----------------|----------------|----------------|
| $E_3^+$       | $E_3^-$        | $E_3^+$        |
| $E_3^+$       | $E_3^-$        | $E_3^+$        |
| $E_3^+$       | $E_3^-$        | $E_3^+$        |
| $E_3^+$       | $E_3^-$        | $E_3^+$        |
| $E_3^+$       | $E_3^-$        | $E_3^+$        |

**TABLE I. Summary of the SWM parameters used.**
FIG. 4. (Color online) (a) Magneto-transmission of natural graphite showing mainly K-point transitions. (b) Calculated SWM transitions together with the measured splitting (symbols). There is no electron-hole asymmetry for the $0 \rightarrow 1$ K-point transition which splits due to the Zeeman term.

40% of the splitting. The relative importance of the contribution of the free electron kinetic energy terms to the electron-hole asymmetry means that any data analysis which neglects them would lead to a significant over estimation of size of $\gamma_4$ or $\gamma_5$.

Polarization resolved magneto-transmission, in fields up to $\pm 140$ T are shown in Fig. 4(a). Mainly K-point transitions are observed in this energy range. The different field directions corresponds to different polarizations and the features are shifted in field due to the different energy of the $n \rightarrow n+1$ and $n+1 \rightarrow n$ transitions. The feature around 100 T is the fundamental $0 \rightarrow 1$ transition, which should not be split (shifted) since the LL0 is special and has a free electron term $\gamma s/2m$. Nevertheless, the position is shifted by $\gamma s/2m$ at 10 T between the two polarizations. However, this can be understood when spin splitting is taken into account. The SWM prediction for the transitions are shown in Fig. 4(b) together with the measured field splitting. It can be seen that there is indeed no effect of electron-hole asymmetry for the $0 \rightarrow 1$ K-point transition (solid and broken lines). However, including the Zeeman term $\pm g\mu B/2$ with $g = 2$ the calculated splitting of the $0 \rightarrow 1$ transition, is comparable with the observed splitting. The Zeeman term is important here due to the very high magnetic field, and the fact that the $0 \rightarrow 1$ transition evolves very slowly with magnetic field so that a small energy splitting can generate a large field splitting in the data.

Finally, we note that the Landau level energy spectrum of graphene can be derived from the SWM Hamiltonian simply by setting all the inter-layer coupling parameters $\gamma_1, ..., \gamma_5 = 0$. The analytic solution of this simplified Hamiltonian is nothing other than Eq. (1). This implies that the electron-hole asymmetry observed in the cyclotron resonance of exfoliated graphene [26] also originates from the neglected free electron kinetic energy terms.

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