Landau levels in bulk graphite by Raman spectroscopy

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The electronic Raman scattering of bulk graphite at zero magnetic field reveals a structureless signal characteristic of a metal. For $B \gtrsim 2$ T, several peaks at energies scaling linearly with magnetic field were observed and ascribed to transitions from the lowest energy Landau level(s) [LL(s)] to excited states belonging to the same ladder. The LLs are equally (unequally) spaced for high (low) quantum numbers, being consistent with the LL sequence from massive chiral fermions $[m^* = 0.033(2)m_e]$ with Berry's phase 2π found in graphene bilayers. These results provide spectroscopic evidence that some of the physics recently revealed by graphene multilayers is also shared by bulk graphite.

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Despite being exhaustively investigated since the early days of condensed-matter physics, graphite has attracted renewed interest since the recognition that much in its physics was missed in the past.[1] Among the recently discovered phenomena are (i) the metal-insulator transition (MIT) driven by magnetic field applied perpendicular to graphene planes;[2–4] (ii) quasi-two-dimensional Dirac fermions occupying an unexpectedly large portion of the Fermi surface;[5] and (iii) the coexistence of quantum Hall effects originating from massless Dirac fermions and massive quasiparticles.[2,6] The occurrence of massless Dirac fermions is also characteristic of graphene monolayers,[7] indicating that much of the graphene physics may be found in graphite. This conclusion has been reinforced by a number of recent spectroscopic observations, such as angle-resolved photoemission spectroscopy (ARPES) (Ref. 8) and magnetotransmission[9] experiments, which showed coexisting massless Dirac holes and massive electrons at the H and K points of the Brillouin zone, respectively. The striking qualitative correspondence between the MIT found in graphite[2–4] and graphene[10] strongly suggests the same physical mechanism behind the observed phenomenon in both systems. Also, scanning tunneling spectroscopy (STS) experiments showed a Landau level (LL) spectrum characteristic of coexisting massless Dirac fermions and massive chiral fermions.[11] Since STS experiments probed the LLs at the surface, it is not clear which of such levels are bulk representative, and therefore direct spectroscopic observations of LLs from massive chiral fermions in bulk graphite are still missing.

For nonrelativistic band electrons within the effective-mass (m^*) approximation, the energy levels are quantized upon the action of a magnetic field in a series of equally spaced LLs,

$$E_n - E_0 = n\hbar\omega_c, \tag{1}$$

where $\omega_c = eB/m^*$ is the cyclotron frequency and $E_0 = \frac{1}{2}\hbar\omega_c$ is the lowest energy level. In this work, we denote the LL ladders satisfying Eq. (1) as "conventional" LLs. On the other hand, for a single graphene layer, the energy dispersion is linear with momentum, $E = v_F\hbar k$ (massless relativistic electrons), and the LLs follow a distinct B and n dependence,

$$E_n - E_0 = \sqrt{2e\hbar v_F^2 nB}. \tag{2}$$

Here $E_0 = 0$ is the lowest zero-energy level. Equations (1) and (2) are therefore associated with distinct kinds of quantum Hall effect (QHE), with Berry's phase 0 and π, respectively. A third member of the small family of QHE systems was recently found for graphene bilayers, with Berry's phase 2π and a LL structure given by[12,13]

$$E_n - E_0 = \hbar\omega_c\sqrt{n(n-1)}, \tag{3}$$

where $E_0 = E_1 = 0$.

Raman scattering (RS) from LLs has been known both theoretically[14–16] and experimentally[17–21] for more than 40 years, and has been mostly observed in semiconductor bulks and superstructures. In parallel, it is interesting to note that RS has been extensively used as a very powerful and versatile characterization tool of graphitic materials,[22–28] with a double-resonance mechanism[23] for activation of a second-harmonic phonon band, termed $2D$, connecting phononic and electronic structures. It is believed that RS measurements in graphite probes ~20 atomic layers,[26] being therefore bulk sensitive. In this paper, we present a magnetic-field-dependent RS study of graphite. Our data are consistent with a LL ladder following Eq. (3), providing insights into the LL structure of bulk graphite and its relationship with graphene bilayers.

The highly oriented pyrolitic graphite (HOPG) (from the Research Institute "Graphite," Moscow) and Kish graphite samples studied in this work were thoroughly characterized by means of x-ray, magnetotransport, magnetization, and ARPES.[2,5,6,8] Fresh surfaces were used, obtained by cleaving the samples in air. The RS spectra were excited with the 488 nm laser line from an argon-ion (Ar^+) laser, unless otherwise noted, with an average power of ~7 mW focused in a spot of ~100 μm diameter. The scattered light was analyzed by a triple 1800 mm^{-1} grating monochromator system in the subtractive mode equipped with a N_2-cooled charge-coupled device (CCD) detector. The exposition time for the electronic RS was 2 h for each field (6×20 min), except for $B=0$ and 5 T, in which the total integration time was 4 h. The phonon measurements were taken with collection times of 30 min. The studied samples were inserted within a commercial superconducting magnetocryostat. The magnetic field ($0 \leq B$

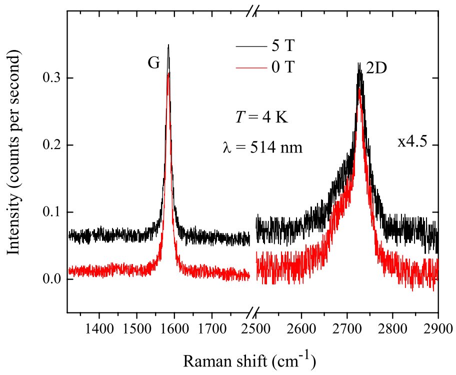

FIG. 1. (Color online) Phonon Raman spectra of HOPG at 4 K and $B=0$ and 5 T, showing its typical G mode and the 2D band. The spectrum at 5 T was vertically translated for clarity.

≤ 6.5 T) was applied parallel to the hexagonal c axis of graphite. All measurements were made in a near-backscattering configuration with the incident light propagating along the c axis, and the scattered light being captured within a solid angle of 0.15 sr. Polarized (depolarized) experiments were performed with parallel (perpendicular) incident and scattered light polarizations.

Characteristic RS modes of bulk graphite were detected, as shown in Fig. 1. The absence of the forbidden D peak at ~ 1355 cm^{-1} (Ref. 22) within our sensitivity is indicative of a small defect concentration. Also, the Raman G mode and 2D band did not present any significant change with the applied magnetic fields in the studied range. This indicates that the roughening of the electronic structure associated with the LL quantization caused by the field produces no observable effect in the vibrational properties and in the double-resonance mechanism,[23] within our experimental resolution.

The effect of the magnetic field can be most clearly seen in the electronic RS spectra shown in Fig. 2. Note that only the experiments with $B=0$, 2.5, and 5 T were performed down to the lowest attainable energies in our experimental conditions (~ 3 meV). At zero field, a structureless electronic continuous approaching null scattering as $\omega \to 0$ is observed, which is characteristic of a normal metal.[29] This observation indicates that the relatively low carrier density ($\sim 1 \times 10^{18}$ cm^{-3}) does not prevent the observation of a significant electronic Raman signal in graphite. Under application of a field, a roughening of the electronic RS can be initially onbserved, preceding the development of a clear sequence of well-defined peaks for the fields above ~ 3 T. The Raman shifts of these peaks are the same using the laser lines of 488 and 514 nm, excluding any possibility of fluorescence being the origin of this signal. The peaks with higher energies appear to be equally spaced, while the first couple of peaks seems to deviate from this pattern. A more quantitative analysis can be made when the energies of the observed features in Fig. 2 are plotted as a function of B (see Fig. 3). Here, linear field dependencies are noticed, allowing for an unambiguous identification of these Raman peaks as due to transitions between LLs. Again, a nearly constant separation between the more energetic LLs is seen, indicating that the observed LL transitions refer to a unique ladder, while a clear deviation from the equal spacings rule can be noticed for the less energetic levels in Fig. 3. Polarization measurements at 5 T indicate that the LL scattering is fully depolarized within our experimental sensitivity (see Fig. 4). For polarized scattering, only a broad maximum at ~ 55 meV was seen, also observed at 0 T (see also Fig. 2).

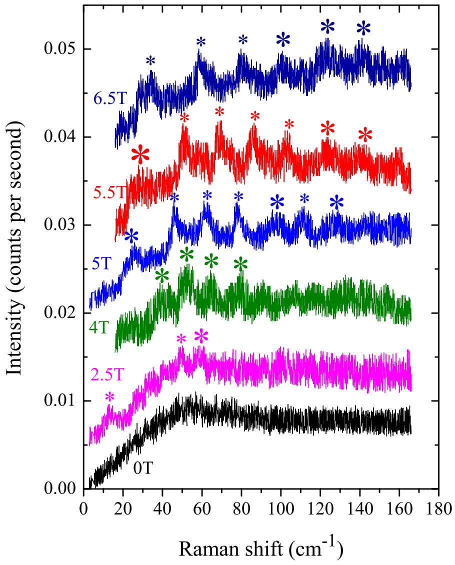

FIG. 2. (Color online) Unpolarized electronic Raman spectra of HOPG at 7 K for the studied applied magnetic fields. All Raman spectra, except at 0 T, were vertically translated for clarity. The most clearly observed peaks are marked by asterisks, in which their sizes indicate the experimental errors in the energy determination.

Since the observed Raman peaks appear to belong to the same LL ladder, indexing becomes straightforward. Figure 5(a) shows the slopes of the straight lines in Fig. 3 as a function of the level index n. Note that in a RS experiment, transitions between LLs are observed, and therefore E_n is not measured directly, but rather $\Delta E \equiv E_n - E_0$. For large n, a linear behavior is observed. Nonetheless, the extrapolation of the straight line does not meet the origin. This is a consequence of the deviation from the equal spacing law for small n, also evident in Fig. 5(a). Therefore the observed LL sequence cannot be associated with a conventional LL ladder given by Eq. (1). We should mention that other indexing possibilities, such as $n=2$ for the first observed peak, are possible but appear to be implausible. In fact, from the selected spectrum at 5 T in Fig. 2, it may be noticed that the LL intensities show a smooth n dependence. Thus, if the peak at ~ 24 meV was associated with $n=2$, then another peak (for $n=1$) of similar or higher intensity should appear at ~ 12 meV, which is not the case. From Figs. 3 and 5(a), it is evident that even if another mode existed at lower energies, the deviation from the equal spacings law [Eq. (1)] would remain beyond the experimental error. An alternative analysis of the observed features is given in Fig. 5(b), in which a plot of $\Delta E/B$ versus $\sqrt{n(n-1)}$ yields a straight line crossing the origin, indicating that the observed LL sequence is consistent with Eq. (3) (massive chiral fermions). Note that, in this case, the first observed level has to be indexed with $n=2$ since $E_0=E_1=0$ in Eq. (3). An effective mass $m^* = 0.033(2)m_e$ is extracted from the fit, in excellent agreement

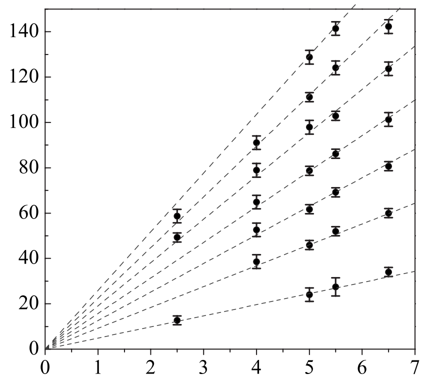

FIG. 3. Peak positions obtained from the spectra of Fig. 2 as a function of magnetic field. Dashed lines represent linear fits crossing the origin.

with $m^*=0.028(3)m_e$ obtained by STS for the massive chiral fermions.[11] In fact, there is a direct correspondence between the LLs observed by Raman and those observed by STS and ascribed to massive chiral fermions. Our results indicate that such LLs (and therefore the nature of the electrons causing such levels) are not restricted to the surface, being actually bulk representative.

The T and sample dependences of the LL spectra of graphite at 5 T were also studied (not shown). The LL peaks smear out as temperature increases and become nearly invisible at $T=100$ K, being in good agreement with a simple criterion $\hbar\omega_c \gg k_B T$ for the observability of the LLs. Also, a Kish graphite sample was found to show the same LL spectrum as HOPG, within our resolution, indicating no considerable sample dependence of our results. We mention that STS results showed largely different surface LL spectra between Kish graphite and HOPG.[30]

An important observation of this work is the purely depolarized scattering for the observed excitations (see Fig. 4). This is a clear indication that the mechanism behind the observation of inter-LL transitions by RS in graphite involves spin flip.[21,35–37] Nonetheless, this has little impact in the accuracy of the determination of LL energies in this work since the Zeeman splitting for spin 1/2 and $g=2$ is only 0.12 meV/T (see Fig. 5).

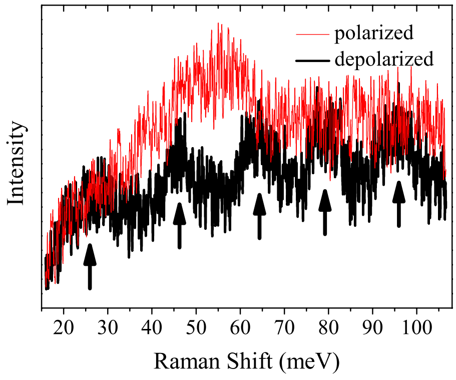

FIG. 4. (Color online) Polarized and depolarized electronic Raman scattering at $B=5$ T and $T=7$ K.

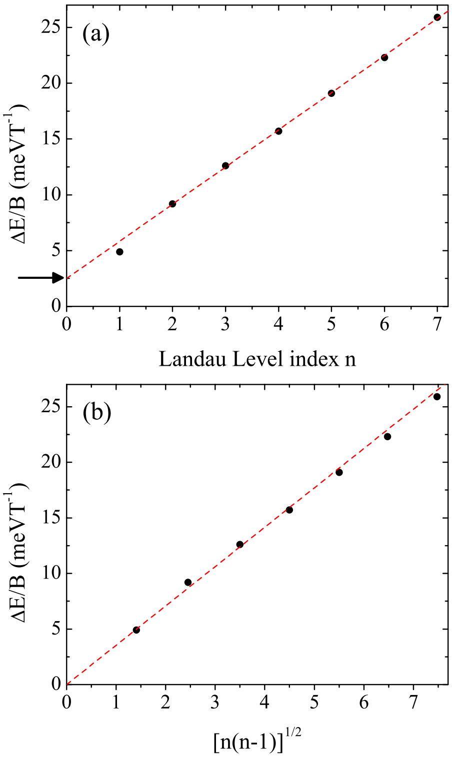

FIG. 5. (Color online) (a) $\Delta E/B \equiv (E_n - E_0)/B$ versus LL index n. Experimental errors are smaller than the symbol size. The dashed line is a linear fit obtained for high n, which should cross the origin for conventional Landau levels satisfying Eq. (1) in the text. The arrow indicates that this is not the case. (b) $\Delta E/B$ versus $[n(n-1)]^{1/2}$. The solid line represents the linear fit according to Eq. (3) in the text.

Comparing our results to previous band-structure calculations[31–33] and cyclotron resonance measurements,[34] the conventional LLs of graphite do not appear to show a straightforward association with our results. For instance, at the K point and $B=5$ T, the separation between adjacent levels is about 10 meV,[33,34] while in our measurements this separation is between 20 (for high n) and 30 meV (for low n) at this field. In addition, the presence of massless Dirac fermions with Berry's phase π in bulk graphite had been already demonstrated by de Haas–van Alphen and Shubnikov–de Haas oscillations[5,6] and magnetotransmission studies,[9] but the corresponding LLs were not observed in our experiments. It is therefore intriguing that only LLs arising from massive chiral fermions were observed by RS, while those from massless Dirac fermions and conventional carriers were not detected within our sensitivity. Further theoretical work on the Raman cross sections of LLs by chiral fermions is necessary to elucidate this point.

In summary, we observed LLs in graphite by RS, consistent with the predicted spectra by massive chiral fermions with Berry's phase 2π, characteristic of bilayer graphene.

The present results agree well with theoretical predictions by Koshino and Ando,[38] who showed that the calculated LLs of graphene multilayers may be identical to monolayer or bilayer graphene. On the other hand, these theoretical predictions are at odds with very recent infrared spectroscopy experiments.[39] Clearly, further theoretical and experimental work is needed to clarify this issue.

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