Magnetophonon resonance in graphite: High-field Raman measurements and electron-phonon coupling contributions

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Electron-phonon coupling in graphene and graphite has been investigated for several years. The zone-centre, doubly degenerate $E_{2g}$ phonon, strongly interacts with electrons, resulting in renormalization of phonon frequencies and line broadening. These are tunable by electric and magnetic fields, through Fermi-energy shifts and Landau quantization. The Raman $G$ peak is predicted to exhibit anti-crossings when the $E_{2g}$ phonon energy matches the separation of two Landau levels (LLs). Both intraband (i.e., cyclotron resonance-like) and interband (i.e., magneto-excitonic) transitions are allowed both in single layer graphene (SLG) and bilayer graphene (BLG). Interband magneto-phonon resonance (MPR) has indeed been observed in magneto-Raman scattering on SLG on the surface of graphite. Graphite, a semimetal containing both electrons and holes even at zero temperature, is expected to exhibit even richer carrier-phonon coupling phenomena. Indeed, Ref. 17 recently reported magneto-Raman measurements on graphite up to 28 T, and observed inter-LL transitions and signatures of MPR. As described via the Slonczewski-Weiss-McChure (SWM) model, graphite has a linear (“massless”) dispersion for the hole pocket around the $H$-point of the Brillouin Zone and a parabolic (“massive”) dispersion for the electron pocket around the $K$-point. Angle-resolved photoemission measurements provided evidence of such massless and massive quasiparticles in graphite. Near these high symmetry points, graphite’s band structure can be approximated as a combination of SLG, describing the $H$-point massless holes, and BLG, describing the $K$-point massive electrons.

Here, we report low-temperature magneto-Raman measurements of natural graphite in a magnetic field ($B$) up to 45 T, a range of fields much broader than any previous study. We demonstrate a rich picture of MPR effects caused by coupling of the $E_{2g}$ phonon to both $H$-point (SLG-like) and $K$-point (BLG-like) interband excitations. We also observe a series of electronic Raman excitations (i.e., emission of electron-hole pairs instead of phonons), including transitions involving the lowest, electron-hole mixed, LLs. We explain the entire, complex set of Raman-active interband excitations within a SWM approach. Furthermore, through quantitative analysis of the observed anti-crossing behaviors, we determine the strengths of electron-phonon coupling (EPC) for both $H$-point holes and $K$-point electrons. Finally, in the highest magnetic-field range (>35 T), where all transition energies are far away from the $E_{2g}$ phonon energy, the $G$ peak narrows, due to suppression of the EPC contribution to the linewidth.

Raman spectra were collected on natural graphite (NGS Naturgraphit GmbH) in a backscattering geometry, with $B$ up to 45 T [see Fig. 1(a)]. A 532-nm laser is coupled via an optical fiber to the low-temperature probe, and focused to a spot of $\sim 20 \mu$m, with a power of $\sim 13$ mW. The probe is inserted into a helium cryostat and placed in a 31 T resistive magnet or 45 T hybrid magnet. Under laser illumination, the temperature of the sample is stabilized at $\sim 10$ K. The unpolarized Stokes component of the scattered light is directed into the collection fiber and guided to a spectrometer equipped with a charge coupled device camera. Most of the data were collected with a spectral resolution of $\sim 3.4$ cm$^{-1}$. However, we used a spectral resolution $\sim 0.5$ cm$^{-1}$ to accurately measure the full width at half maximum of the $G$ peak, FWHM(G), at selected magnetic fields between 32 T and 45 T. Raw data contains the signal of interest from the sample in a smooth background coming from the fibers. At frequencies $\gtrsim 1300$ cm$^{-1}$, the background is featureless and much smaller than the signal from the sample. We performed numerous tests to characterize the
of peaks emerge, as shown in Fig. 1(c). These peaks were scanned to find SLG Raman signatures.

is opposite to that of Refs. 14 and 15, where the samples increase up to 45T, we observe small broad-band changes reaching 1% at ~650cm⁻¹. However, these could be due to other factors, such as long-term variation of the laser power or temperature drifts. Thus, we assume the background to be field-independent, at least within our signal to noise ratio and use zero field reference spectra to remove spurious signals due to scattering in the fibers. Decoupled SLG may exist on the surface of bulk graphite, as observed in Ref. 26, where Raman scattering of bulk graphite was measured in magnetic fields up to 6.5 T, but assigned to LLs in BLG.

Figure 2 displays a set of spectra taken at 10 K as a function of B up to 45 T. The observed nearly-linear B-dependence suggests these features to be related to inter-LL excitations of massive carriers in the vicinity of the K-point. The most intense peaks are attributed to the so-called “symmetric” inter-LL excitations, hn → e(n) or (n,n), i.e., the transitions from the n-th hole to the n-th electron LLs. Indeed, Ref. 28 and 29 theoretically showed that symmetric inter-LL excitations are Raman active in both SLG and BLG. These symmetric transitions were previously observed and analyzed through an effective BLG model.

In addition, we detect two extra electronic features below the (1,1) transition, indicated by open circles in Fig. 2. They are resolved at 45 T, as shown by gray arrows in Fig. 1, although their intensity is less than 10% of the (1,1) peak. We attribute them to the lowest inter-LL transitions, (1,0) and (−1,1), at the K point. They can be considered as a special case of the weak lowest-energy Raman-active transition in BLG predicted in Ref. 29.

To validate our peak assignments, we calculate the energies of interband, inter-LL transitions within the SWM model. This has seven tight-binding parameters, γ₀ to γ₅ and Δ. Despite its extensive use over the past 50 years, the precise values of these parameters are still under debate. Without the trigonal warping effect represented by...
TABLE I. SWM band parameters (in eV) extracted from results in Fig. 2, in comparison with previously reported values.

<table>
<thead>
<tr>
<th></th>
<th>This work</th>
<th>Ref. 30</th>
<th>Ref. 31</th>
<th>Ref. 17</th>
<th>Ref. 32</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_0$</td>
<td>3.06 (1)</td>
<td>3.1</td>
<td>3.18 (3)</td>
<td>3.08 (1)</td>
<td>3.16 (5)</td>
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<tr>
<td>$\gamma_1$</td>
<td>0.370 (5)</td>
<td>0.39</td>
<td>0.38 (1)</td>
<td>0.380 (2)</td>
<td>0.39 (1)</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>-0.028 (3)</td>
<td>-0.028 (4)</td>
<td>-0.02</td>
<td>- -0.020 (2)</td>
<td></td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>0.33 (1)</td>
<td>0.315</td>
<td>-</td>
<td>0.315 (1)</td>
<td>0.315 (15)</td>
</tr>
<tr>
<td>$\gamma_4$</td>
<td>0.080 (5)</td>
<td>0.041 (10)</td>
<td>0.08 (3)</td>
<td>0.044 (5)</td>
<td>0.044 (24)</td>
</tr>
<tr>
<td>$\Delta + 2\gamma_5$</td>
<td>0.130 (3)</td>
<td>0.15 (3)</td>
<td>0.064 (3)</td>
<td>-</td>
<td>0.068 (7)</td>
</tr>
</tbody>
</table>

$^a \Delta + 2\gamma_5 - 2\gamma_2 = 0.22 (1)$

$\gamma_3$, each LL can be obtained through a $4 \times 4$ Hamiltonian, which can be diagonalized for each $n$. Adding the $\gamma_3$ term mixes different LLs with indices $n$ and $n \pm 3$, making the dimension of the Hamiltonian infinite. We numerically calculate the LL energies by truncating this Hamiltonian into a finite $\sim 400 \times 400$ matrix. We note that, for matrix sizes larger than $100 \times 100$, the gaps between energy levels at $B=10$ T change less than 0.1 cm$^{-1}$. For higher magnetic fields, the results converge even faster. We obtained $\gamma_0$ from the position of the $H$-point MPR and used the SWM parameters from Ref. 30 as the initial guesses for our fitting. To reduce the number of parameters, we fixed $\gamma_0$ and $\gamma_2$ and varied the others to fit the data.

Table I compares our results with values extracted from magneto-transport experiments$^{30}$, infrared magneto-reflectance spectroscopy$^{31}$, magneto-Raman measurements$^{17}$, as well as values deduced from earlier experiments$^{32}$. Though the tight-binding parameters are not significantly different, our spectroscopic observation of both symmetric and asymmetric transitions, including the low-energy transitions involving the electron-hole mixed $1 \text{ and } 0$ LLs, enables an accurate determination of the SWM parameters.

Close examination of the $G$ peak in Fig. 2 reveals peak position modulations as a function of $B$. At a certain $B$, the resonance condition $E_{n,n'} = \hbar \Omega_F$ is met, where $E_{n,n'}$ is the $(n,n')$ transition energy and $\Omega_F$ is the $E_{2g}$ phonon frequency, and the phonon is “dressed” by the electronic transition$^{11-13}$. This coupling manifests itself as a series of avoided crossings$^{14-16}$. Specifically, the $E_{2g}$ phonon is allowed to couple with an $(n,n')$ transition only when $|n| - |n'| = \pm 1$. To examine the data more closely, we fit the $G$ peak with Lorentzians and plot the extracted peak positions and the second derivative Raman intensity in Fig. 3(a). The data reveals anti-crossings at 34 T, 31 T, 21 T, and 19 T, corresponding to the (2,1), (1,2), (3,2), and (2,3) transitions, respectively. At lower fields, the doublet structure due to the (3,4) and (4,3) transitions is smeared out and appears as a weak modulation of the $G$ peak. Note that, when the symmetric $(n,n)$ peaks cross the $G$ peak, they appear unchanged, indicating the absence of coupling. Furthermore, the central position of the $G$ peak is also $B$-dependent, exhibiting a modulation and broadening at $\sim 30$ T (Fig. 4), which we interpret as a signature of MPR of the asymmetric $h1 \rightarrow 0$ and $h1 \rightarrow -1$ $H$-point excitation with the $E_{2g}$ phonon. Finally, above 35 T, where the decay of $E_{2g}$ phonons into electron-hole pairs is quenched by Landau quantization and electron-phonon interaction is suppressed, the $G$ peak narrows to $\sim 4.4$ cm$^{-1}$. Our high-field value FWHM(G) is about twice the phonon-lifetime-limited linewidth at $B = 0$, $\gamma^2_{\text{ph}} \sim 2.5$ cm$^{-1}$ (Refs. 34 and 35), indicating the presence of another, probably disorder-induced, broadening mechanism.

To analyze the observed MPR, we first focus on the $G$-peak sidebands, corresponding to coupled electron-phonon modes associated with $K$-point electron asymmetric transitions [Fig. 3(a)]. The doublet anti-crossings at 34 T and 31 T, corresponding to the (2,1) and (1,2) transitions, respectively, is most accurately resolved [Fig. 3(b)], and therefore, most suitable for quantitative analysis. Following Refs. 12 and 14, we analyze the data via a two-coupled-mode model,

$$E_{\pm} = \frac{E_G + E_{n,n'}}{2} \pm \sqrt{\frac{(E_G - E_{n,n'})^2}{2}} + g^2,$$

where $E_G = \hbar \Omega_F - i \gamma_{1}/2$, $E_{n,n'} = \hbar \Omega_{n,n'} - i \gamma_{n,n'}/2$, $\gamma_T$ ($\gamma_{n,n'}$) is FWHM(G) [(n,n') transition], and $g$ is the coupling parameter. Expressing the magnetic energy $\hbar \Omega_F$ at the $K$ point within an effective BLG model, the coupling
using the SWM parameters described previously. Fit-
calculate the energies of asymmetric inter-LL transitions
\[ \langle E \rangle \text{ coupling energy} \]
where
\[ A_{\text{Pos}(G)} = 1582.6 \text{ cm}^{-1} \]
\[ B < 30 \text{ T} \] is a signature of the MPR effect involving (2,3)

Finally, we analyze the \( B \)-induced modulation of the
central component of the \( G \) peak, shown in Fig. 4. The
total peak-position modulation is \(~6\text{ cm}^{-1}\), while the
FWHM increases more than twice at \(~30\text{ T}\). This is con-
sistent with MPR due to \( H \)-point inter-LL transitions,
(1,0) or (1,−1), assuming that the LL widths are larger
than the coupling strength. The \( G \) peak modulation at
\(~20\text{ T}\) is a signature of the MPR effect involving (2,3)
\( K \)-point excitations. To deduce the EPC strength for the
\( H \)-point, we model the 30 T resonance with Eq. (1) using
a SLG-like expression for \( g^{(H)} \):

\[ g^{(H)} = \sqrt{\frac{3}{2}} \sqrt{\frac{\lambda}{4\pi l_B} \gamma_0 \equiv g_0^{(H)} \sqrt{B}.} \] (4)

The right side of the resonance \((B > 30 \text{ T})\) fits well
with the model with \( \gamma_T = 100 \pm 10 \text{ cm}^{-1} \), \( g_0^{(H)} = 3.2 \pm
0.2 \text{ cm}^{-1}/\text{T}^{1/2} \), and \( \lambda_{\text{EPC}}^{(H)} \approx 1.6 \times 10^{-3} \). The discrepancy
at lower fields is likely be due to the \( E_{2g} \) renormalization
via interaction with multiple inter-LL excitations, which
cannot be spectrally resolved for \( B < 30 \text{ T} \). We note that
\( \lambda_{\text{EPC}}^{(H)} \) is almost 20 times smaller than \( \lambda_{\text{EPC}}^{(K)} \).

In summary, we performed high-field magneto-Raman
experiments on graphite, observing strong magneto-
phonon resonances. The \( G \) peak shifts and splits as a
function of magnetic field as it sequentially resonates
with certain electronic transitions. Analysis of the ob-
served magneto-phonon resonance effects allowed us to
determine the strengths of electron-phonon coupling for both
\( H \)- and \( K \)-point carriers. The Slonzcewski-Weiss-
McCurn model provides an accurate description of all
observed interband electronic excitations. In the highest
field range \((>35 \text{ T})\), the \( G \) peak narrows through reduced
electron-phonon interaction.

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