Tuning the Electron-Phonon Coupling in Multilayer Graphene with Magnetic Fields

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Magneto-Raman scattering study of the E_{2g} optical phonons in multilayer epitaxial graphene grown on a carbon face of SiC is presented. At 4.2 K in magnetic field up to 33 T, we observe a series of well-pronounced avoided crossings each time the optically active inter-Landau level transition is tuned in resonance with the E_{2g} phonon excitation (at 196 meV). The width of the phonon Raman scattering response also shows pronounced variations and is enhanced in conditions of resonance. The experimental results are well reproduced by a model that gives directly the strength of the electron-phonon interaction.

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Lattice vibrations in solids can be effectively modified via their coupling to electronic excitations, as, for example, evidenced by observations of Kohn anomalies in metals [1,2], of coupled phonon-plasmon modes in polar semiconductors [3,4], or of different phonon spectra in metallic and semiconducting carbon nanotubes [5]. The electron-phonon interaction is currently intensively studied in graphene [6–9], which is a two-dimensional crystal of carbon atoms arranged in a honeycomb lattice and a semimetal with characteristic dispersions of electronic states displaying Dirac cones near the Fermi energy [10,11]. The case of the long wavelength optical E_{2g}-phonons at the Γ point of the Brillouin zone, which correspond to the relative displacement of two nonequivalent carbon atoms in the unit cell of graphene [6,7], is of particular interest. The perturbation due to this displacement is effective in inducing the direct ($\Delta k = 0$) electronic transitions across the Dirac point: E_{2g} phonons efficiently couple to those low energy interband excitations [6,7] that are unique to graphene. The spectrum of these excitations (its $2E_F$ low energy onset) can be modified by tuning the Fermi energy E_F. This was achieved in gated graphene flakes on Si/SiO_2 substrates where the electrically modified E_{2g}-phonon spectrum was traced with Raman scattering methods [8,9].

The spectrum of the graphene E_{2g} phonon is expected to be even more severely modified by applying a magnetic field perpendicular to the 2D plane [12,13], i.e., when a continuous spectrum of electronic excitations is transformed into a series of quasidiscrete inter-Landau level excitations characteristic of a 2D system. In conditions of Landau quantization, the electron-phonon coupling has a resonant character which is expected between the E_{2g} phonon and properly selected inter-Landau level excitations. The observation of magneto-phonon resonance in graphene structures, which we present in this Letter, has been an experimental challenge [14] aiming at verification of theoretical predictions [12,13].

We report here on magneto-Raman scattering studies of the E_{2g}-phonon band of multilayer epitaxial graphene on the carbon face of a SiC substrate (MEG), in fields up to 33 T, and low, liquid helium temperatures. The measured E_{2g} band is observed to be composed of two components: one fixed and another oscillating with the applied field. The extracted oscillatory component of the E_{2g} band shows the theoretically anticipated magnetophonon multiresonance [12,13]. Pronounced variations of the energy position and width of this line reflect a series of avoided crossings each time the E_{2g}-phonon energy tends to match the energy of the specific (defined by appropriate selection rules) inter-Landau level excitations. Comparison of the experimental results to existing models allows us to analyze the characteristic strength of the electron-phonon interaction in the investigated graphene system. Possible origin of the field-independent component of the E_{2g} band is discussed.

Raman scattering spectra were measured using the Ti:sapphire laser setup, tuned at accurately controlled wavelength in the range $\sim\lambda = 720$ nm, in order to minimize the superfluous Raman signal of optical fibers which were used to transmit the excitation light to, and to collect the scattered photons from the sample. The sample was immersed in a helium gas kept at $T = 4.2$ K and placed in a resistive magnet delivering fields up to 33 T. The non-polarized Raman scattering spectra were measured in nearly backscattering Faraday geometry: the arrangement of the excitation and collection fibers (both with core diameters of 200 μm) with respect to sample surface is sketched in the inset of Fig. 1(a). Typical excitation power was $\sim$100 mW, spread over 600 μm-diameter laser spot on the sample. The collected light was dispersed with a single grating spectrometer (spectral resolution

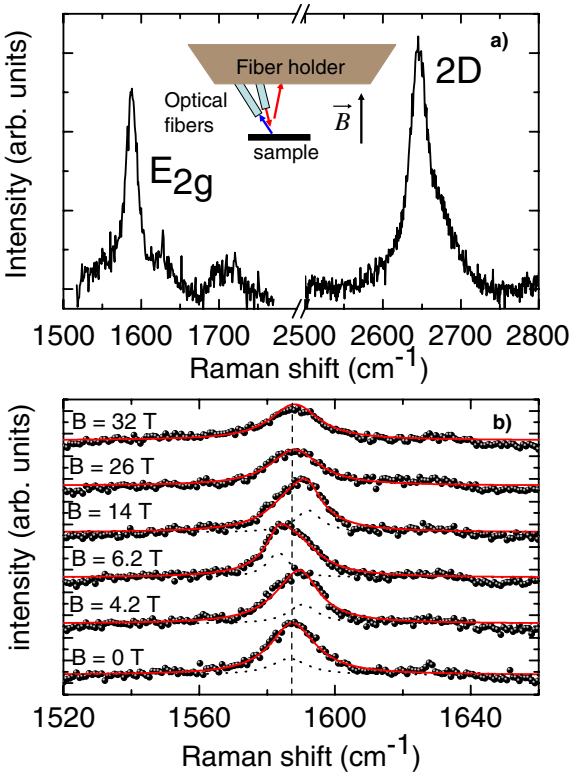

FIG. 1 (color online). (a) The E_{2g} and 2D Raman scattering bands measured at $T = 4.2$ K and $\lambda = 720.7$ nm laser excitation at zero magnetic field. The scheme of the experimental configuration is shown in the inset. (b) Background corrected spectra of the E_{2g} band, measured at different magnetic fields. The solid red lines represent the fitted two-Lorentzian components shape. One of these components is field independent and solely reproduces the spectra at $B \geq 26$ T. The oscillatory with field component is shown with dotted black lines.

$\Delta\lambda = 0.3$ nm) equipped with nitrogen cooled CCD detector and band pass filters were used to reject the stray light.

The MEG structures which we have used for experiments were fabricated by thermal decomposition of the carbon face of a 4H–SiC substrate [15]. Two investigated structures, both with a relatively large number of graphene layers, show similar data and we present here the results obtained for the sample which contains ~70 layers. We used strongly graphitized samples to enhance the Raman scattering signal, particularly because the E_{2g}-phonon band in MEG samples appears on the background of the two-phonon Raman scattering processes in the SiC substrate. A number of experimental studies, including magnetoabsorption [16,17] and micro-Raman scattering measurements [18], show that Dirac-like electronic bands, which are genuine of a single graphene sheet, persist in MEG structures and that a large part of these layers is practically neutral, with carrier densities as low as 5×10^9 cm^{-2} and fairly high mobilites up to 250 000 cm^2/(V s) [17]. The electronic bands in MEG grown on the carbon face of SiC are alike those of a single layer because of preferentially rotational and not Bernal-type layer stacking in this material [19–22]. Although we believe that the majority of the structure probed in our experiments displays neutral graphenelike electronic system, the MEG samples and, in particular, the strongly graphitized specimens are not expected to be uniform on the scale of 600 μm defined by the actual size of the laser spot on the sample. For example, the presence of Bernal-stacked minority inclusions in these structures has been seen with micro-Raman scattering experiments [18].

The representative Raman scattering bands observed for our ~70 layers MEG sample in the absence of magnetic field are shown in Fig. 1(a). The so-called "2D" band, which is frequently analyzed to characterize different graphene structures [23,24], appears at 2646 cm^{-1} as a 35 cm^{-1}-wide, slightly asymmetric line. A pure Lorentzian shape of the "2D" line is a signature of the electronic system with simple Dirac-like electronic states, such as those characteristic of graphene or of the majority part of the MEG structures. We understand that the observation of the high energy asymmetry in the "2D" line under the present experimental conditions is a consequence of signal averaging from a relatively large portion of the sample, which includes other than simple graphenelike structures (i.e., Bernal-stacked residues).

The focus of this Letter is on the E_{2g}-phonon line which clearly dominates over the background of two-phonon signal from SiC substrate and peaks at 1586.5 cm^{-1} in the Raman scattering spectrum measured at zero magnetic field [Fig. 1(a)]. As shown in Fig. 1(b) with background corrected spectra, the E_{2g}-phonon line is visibly affected by the application of the magnetic field, but distinctly it is practically field independent at high fields, above $B = 25$ T. Hence, one may anticipate that the observed magneto-Raman spectrum of the E_{2g} phonon is composed of two components: one oscillating with field and the second one which is field independent and dominant at $B > 25$ T. Indeed, as illustrated in Fig. 1(b), the E_{2g} spectrum measured at any magnetic field can be fairly well fit with two-Lorentzian functions (solid red lines). The field-independent component $I_{B=26\ \mathrm{T}}(h\nu)$ has been set to fit the spectrum at $B = 26$ T. The resulting oscillatory component is shown with dashed lines in Fig. 1(b). To present the full data collection, the $I_{B=26\ \mathrm{T}}(h\nu)$ Lorentzian function has been extracted from each measured spectrum and the resulting differential spectra (oscillatory part) are shown in Fig. 2, in form of the intensity false color map. Full points in this figure denote the peak position (center) of the Lorentzian functions which fit the oscillatory component.

The magnetic field evolution of the spectra shown in Fig. 2 can be clearly seen as resulting from a series of avoided crossings between the E_{2g} phonon excitation and the specific inter-Landau level electronic transitions. The energy ladder of Landau levels (L_n; $n = 0, \pm 1, \pm 2, \ldots$) of the two-dimensional Dirac-like electronic system is given by $E_n = \mathrm{sgn}(n)\tilde{c}\sqrt{2e\hbar B|n|}$, where the measured slope of

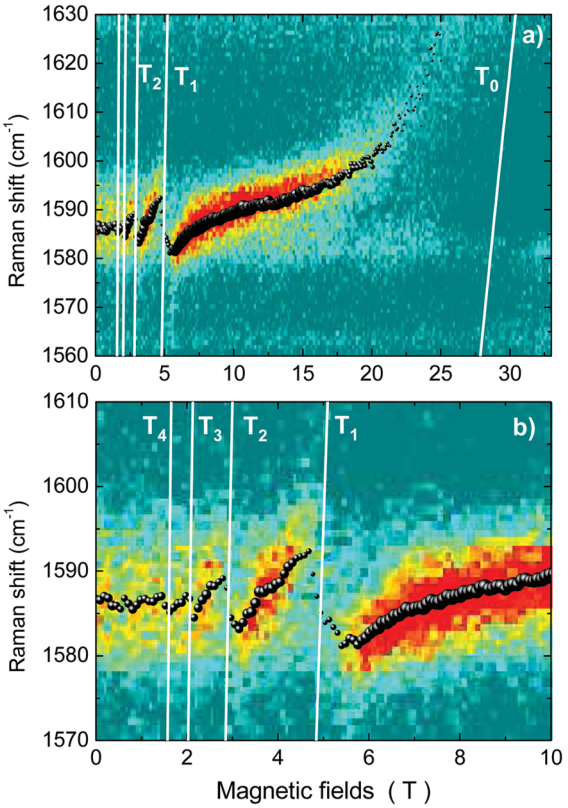

FIG. 2 (color). (a) Color map of the magneto-oscillatory component of Raman scattering spectra of E_{2g} band phonons as a function of the magnetic field measured at $T = 4.2$ K under $\lambda = 720.7$ nm laser excitation. The extracted peak position of this line is shown with full dots. Their size is proportional to the line amplitude. Solid lines T_k represent the energies of the series of inter-Landau level transitions: $L_{-k,(-k-1)} \rightarrow L_{k+1,(k)}$, which couple to E_{2g} phonon ($\tilde{c} = 1.02 \times 10^6$ m s^{-1} is assumed). (b) Zoom on the 0 to 10 T range of magnetic fields.

the Dirac cone (Fermi velocity) $\tilde{c} = 1.02 \times 10^6$ m/s in the investigated structures [16,17]. As illustrated in Fig. 2, the E_{2g}-phonon couples to a series of $L_n \rightarrow L_m$ transitions which fulfill the $|n| - |m| = \pm 1$ selection rules and therefore appear at energies $T_k = (\sqrt{k} + \sqrt{k+1})E_1$ ($k = 0, 1, 2, \ldots$). Notable, the same selection rules apply to optically active inter-Landau level transitions which are observed in far-infrared magnetotransmission spectra [12,13,16,25]. The amplitude of the observed "anticrossings" grows with the magnetic field because, as a rule, the splitting (Δ) between coupled modes is proportional to the square root of the oscillator strength of the uncoupled excitations and to the square root of interaction parameter λ. In our case, these are electronic excitations which become enhanced by the magnetic field. This is primarily due to the increasing with B-field Landau level occupation (eB/h degeneracy). If broadening is neglected we roughly expect $\Delta \sim \sqrt{\lambda B}$ and derive more rigorously [13]: $\Delta = \sqrt{2\lambda}E_1$, for our neutral Dirac-like system.

For the sake of more quantitative data analysis we consider both the characteristic phonon energy as well as its broadening which is another inherent element of mode coupling effects. In Fig. 3 we replot the center and add the extracted linewidth (HWHM) of the Lorentzian peak which fits the magneto-oscillatory component of the measured E_{2g} line. The magneto-oscillations in the peak position are accompanied by oscillations in the linewidth which, as expected, is enhanced under resonant conditions. To reproduce the data of Fig. 3, we adopt the approach of Ando [12] to our neutral Dirac-like system and derive the phonon energy ϵ and broadening parameter Γ by extracting $\tilde{\epsilon} = \epsilon - i\Gamma$ from the equation which defines the poles of the phonon Green's function:

$$\tilde{\epsilon}^2 - \epsilon_0^2 = 2\epsilon_0 \lambda E_1^2 \sum_{k=0}^{\infty} \left\{ \frac{T_k}{(\tilde{\epsilon} + i\delta)^2 - T_k^2} + \frac{1}{T_k} \right\},$$

where ϵ_0 stands for the phonon energy of the neutral system at $B = 0$ T and δ accounts for the broadening characteristic for electronic excitations. The measured linewidth has been assumed as a convolution sum $\sqrt{\delta_0^2 + \Gamma^2}$, where δ_0 accounts for other, than electron-phonon coupling, broadening mechanisms.

To calculate the energy and broadening of the E_{2g}-phonon spectrum we fix the value of $\tilde{c} = 1.02 \times 10^6$ m/s as derived from far-infrared magnetoabsorption experiments on MEG samples [16,17]. Working effectively

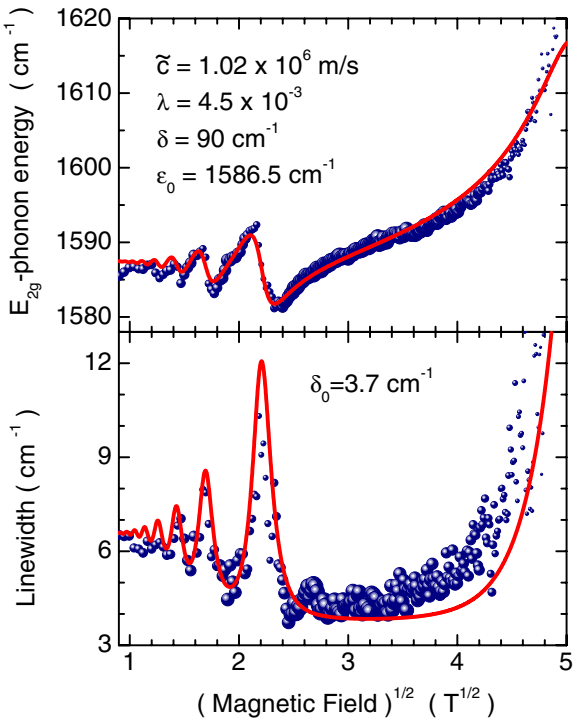

FIG. 3 (color online). Magnetic field evolution of the peak position (upper part) and the linewidth (HWHM) of the magneto-oscillatory component of the measured E_{2g} Raman band. Solid lines represent the result of modeling of the data (with the parameters specified in the figure) along the procedure described in the text.

with only two adjustable parameters δ and λ ($\delta_0 = 3.7\ \mathrm{cm}^{-1}$ is the background correction to the linewidth oscillations) the experimental data can be fairly well reproduced. Optimal choice of parameters is $\delta = 90\ \mathrm{cm}^{-1}$ and $\lambda = 4.5 \times 10^{-3}$. The extracted strength of electron-phonon coupling is in excellent agreement with estimations of λ in the range of $(4–5.5) \times 10^{-3}$ from the detailed analysis of the dispersions of the E_{2g} in graphite [26] and/or measurements of electrically tuned E_{2g} phonon in graphene [8,9]. We also note that the width δ_0 which is measured in between well separated resonances, i.e., when the effects of electron-phonon interaction are switched off, appears to be practically identical to its value measured under corresponding conditions ($2E_F > \epsilon_0$) on graphene flakes on Si/SiO_2 [8]. The parameter δ accounts for broadening of electronic states and its actual value reasonable matches the width of magnetoabsorption transitions expected in our sample at high magnetic fields [27]. For simplicity δ is assumed constant, thought its increase with field ($\sim\sqrt{B}$) which is expected from magnetoabsorption experiments [17] could improve the data simulation (larger broadening of the high field resonance). Direct detection of electronic excitations in Raman scattering experiments would be desirable, however, this is another experimental challenge since the expected signals are very weak [28] though possibly already observed in bulk graphite [29].

The puzzle of the presented results is the origin of the field-independent component of the E_{2g} spectrum which, we note, represents the significant portion of the total spectral weight. The Bernal-stacked inclusions are first possible candidates to account for this contribution (we have checked that in fields up to 14 T the magneto-Raman spectrum of the E_{2g} band of natural graphite sample is practically field independent). However, inspecting the shape of the measured 2D band, we can rule out that the contribution from these inclusions is as large as 65% (extracted for the $B = 0$ T spectrum). Another candidate is a signal from highly doped layers close to the interface. This is also scarcely probable since such a signal should be significantly shifted in frequency from that of the majority neutral graphene layers, which is not seen. We speculate the field-independent component of the E_{2g} line is an inherent property of the graphenelike systems [14] what remains to be understood.

In conclusion, we have investigated the magnetic field evolution of the Raman scattering response of the E_{2g} phonons in a graphenelike system in fields up to 33 T. A pronounced avoided crossing behavior of the phonon energy and oscillations of the linewidth are observed each time the optically active inter-Landau level excitation is tuned in resonance with the phonon energy. The experimental results are well accounted for by existing theoretical models [12,13] of electron-phonon coupling in graphene, with the estimated electron-phonon coupling constant $\lambda = 4.5 \times 10^{-3}$.

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