Observation of Anomalous Phonon Softening in Bilayer Graphene

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The interaction of electron-hole pairs with lattice vibrations exhibits a wealth of intriguing physical phenomena such as the renowned Kohn anomaly. Here we report the observation in bilayer graphene of an unusual phonon softening that provides the first experimental proof for another type of phonon anomaly. Similar to the Kohn anomaly, which is a logarithmic singularity in the phonon group velocity [W. Kohn, Phys. Rev. Lett. 2, 393 (1959)], the observed phonon anomaly exhibits a logarithmic singularity in the optical-phonon energy. Arising from a resonant electron-phonon coupling effect, the anomaly was also expected, albeit not observed, in monolayer graphene. We propose an explanation for why it is easier to observe in bilayer samples.

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Graphene is an experimentally realized two-dimensional (2D) crystal [1]. Extensive work in this atomic carbon layer system exploits the continuous tunability of the Fermi energy ($E_F$) of Dirac fermions by the electric field effect (EFE) to create unprecedented venues for the investigation of electrons and phonons that are confined to an extreme 2D atomic limit [2–6]. One of the most intriguing fundamental predictions in recent theoretical studies is that the interaction of electron-hole pairs with lattice vibrations leads to a logarithmically divergent renormalization to the long-wavelength optical-phonon energy, when $|E_F|$ is tuned to half the phonon energy [4–6]. This effect, known as a phonon anomaly [6], was theoretically discussed in the case of single layer [6] and bilayer graphene [7]. The predicted signature of this phenomenon is that the optical-phonon mode first softens, and then stiffens, with increasing positive or negative charge density [4]. Experimentally, however, only stiffening of the phonon energy has been reported so far [8–11], and there is no clear evidence that confirms the phonon anomaly.

In this Letter we demonstrate that the phonon anomaly, proposed initially for single layer graphene [6], is a generic consequence of a tunable resonant electron-phonon coupling when the particle-hole pair energy is close to the phonon energy (Fig. 1). We report experimental observation of the anomalous phonon softening, a clear signature of this phonon anomaly, in bilayer graphene using Raman spectroscopy. The observation of the resonant phonon softening is facilitated in bilayer graphene. The reason is that the coupling between the two graphene layers results in a nearly parabolic dispersion and a relatively large density of states near the vanishing band gap. These unique properties of bilayer graphene make the phonon anomaly robust even in the presence of relatively large charge density nonuniformity.

Rather than being a special property unique to monolayer graphene, this anomaly is anticipated to occur in any multiband electron system where the zero momentum optical phonon can create resonant electron-hole pairs across the conduction and/or valence bands. Figure 1 illustrates the concept of the phonon anomaly in a model system of a 2D gapless semiconductor with particle-hole symmetry. A system which exhibits such a low energy band structure is in fact bilayer graphene, where the conduction and valence bands meet at the $K$ and $K'$ corner points of the Brillouin zone [12,13]. In graphene, the deformation-potential interaction couples vertical electron-hole interband excitations with long-wavelength optical phonons [14,15]. This coupling contributes to the renormalization of the phonon energy [16]. Within the second order time-dependent perturbation theory, the change of phonon energy $\omega_{ph}$ with tuning of the Fermi energy is given by

$$
\hbar\omega_{ph}(E_F) - \hbar\omega_{ph}(0) \sim -\lambda \int_0^{2|E_F|} dE_{e-h} \frac{2E_{e-h}}{\hbar\omega_{ph}^2 - E_{e-h}^2} \sim \lambda \ln \left( 1 - \frac{2|E_F|}{\hbar\omega_{ph}} \right),
$$

(1)

where $\lambda$ is the electron-phonon coupling parameter with dimensions of energy. The integrand represents an

![FIG. 1 (color online). (a)–(c) Vertical interband electron-hole pair transitions in a gapless 2D semiconductor with three different Fermi levels. Regions with green (or gray) shading are filled with electrons. The transition indicated by the blue (or dark gray) arrow is the resonance with the long-wavelength optical phonon. (d) Predicted change of phonon energy as a function of the Fermi energy. The two phonon anomalies show up at $E_F = \pm \hbar\omega_{ph}/2$.](image-url)
electron-phonon interaction correction to the phonon energy, due to an electron-hole pair with energy $E_{e-h}$. The integration from 0 to $2|E_F|$ and the negative sign in front reflects the fact that, for $0 < E_{e-h} < 2|E_F|$, the forbidden electron-hole pair transitions became allowed if the Fermi energy were at 0 [17]. Because of the resonant denominator $\frac{1}{\hbar \omega_{ph} - E_{e-h}}$ in Eq. (1), the perturbative contributions to $\omega_{ph}$ have a sign change at $E_{e-h} = \hbar \omega_{ph}$ and are markedly enhanced near the resonance [the interband transition indicated with a blue arrow in Fig. 1(a)]. When $|E_F|$ is increased, the positive and negative enhanced perturbations to $\omega_{ph}$ are switched off due to restrictions placed by the Pauli principle [illustrations for the case of electron doping are shown in Figs. 1(b) and 1(c)]. For this reason, the modulation of carrier density in the system results in marked changes in the optical-phonon energy around $|E_F| = \hbar \omega_{ph}/2$, as shown in Fig. 1(d).

In the derivation of Eq. (1), no assumptions of system dimensionality or band dispersion curvature are made. In principle, the phonon anomaly should show up in 1D systems like metallic or near zero gap semiconducting carbon nanotubes [18], graphene nanoribbons [19], 2D systems like graphene thin films [6,7], and 3D systems like silicon and germanium [20,21]. In fact, similar to single layer graphene [6], a log divergence was predicted, albeit not observed, in studies of chemically doped silicon [20].

In the present work, we use EFE and low temperature Raman spectroscopy to study the effects of the phonon anomaly in bilayer graphene. Previous experiments have revealed that bilayer graphene, with crystal lattice and electron band structure as shown in Figs. 2(a) and 2(b), is very different from the monolayer. For example, its quantum Hall effect is quite unique and cannot be viewed as a simple extension from that of the monolayer [22]. Another important difference is that the electrons and holes in bilayer graphene are not only chiral but also massive [12]. Because of this, the low energy electron density of states in a bilayer is much more than twice that of a monolayer. This is the key reason why intrinsic properties of bilayer graphene, such as the anomalous phonon softening, are much more robust in the presence of large nonuniformity of the charge density.

Here, we focus on the zero momentum optical phonon, known as the $G$ band in graphite and graphene thin films. Its energy $\hbar \omega_G = 1580 \text{ cm}^{-1} = 196 \text{ meV}$. Figure 2(c) schematically shows our experimental setup. A back gate voltage $V_g$ is applied across a thin layer of SiO$_2$ dielectric sandwiched between bilayer graphene and doped silicon to induce charge carriers in the sample. The gating efficiency is about $7.2 \times 10^{10} \text{ cm}^{-2}/\text{V} [23]$. For Stokes Raman scattering, $\omega_{Stokes} = \omega_{L} - \omega_{S}$, where $\omega_{L}$ and $\omega_{S}$ are frequencies of the incident and scattered light, respectively. The experiment is performed with the sample mounted inside a variable temperature cryostat with optical access. Data shown in this work are taken at 12 K.

The evolution of the bilayer $G$ band with gate voltage $V_g$ is displayed in Fig. 3. The EFE induced changes in the spectra are nearly symmetric about $V_g = 10 \text{ V}$ [Fig. 3(a)]. As in single layer graphene [8], this symmetry, which determines the charge-neutral point of the sample, reflects the underlying particle-hole symmetry in the band structure of bilayer graphene. Another important feature in the data is that the phonon bands have smaller linewidth at large charge doping with electrons or holes, indicating longer lifetime. This change of width is due to Landau damping of the $G$ phonon into electron-hole pairs when $|E_F| < \hbar \omega_G/2$ at small charge doping. Similar effects were observed in EFE tuned Raman spectra in single layer graphene [8].

While the observed $G$ phonon linewidth evolution in the bilayer sample is similar to that of a single layer, changes in the phonon energy are rather different. In single layer graphene, the $G$ phonon frequency exhibits only one minimum as the EFE tuned charge density $n$ passes through the charge-neutral Dirac point, and the phonon monotonically stiffens with increasing $|n|$ [8–10]. In contrast, when charge carriers are added into the bilayer sample, $\hbar \omega_G$ first decreases for smaller $|n|$ and then increases at larger doping [square symbols in Fig. 3(b)]. As expected from the particle-hole symmetry in the system, two distinct minima are clearly resolved in $\hbar \omega_G(n)$. These minima...
hopping energy [23,24], we found from
or dark gray) arrows in Figs.1(a) and 1(b) is allowed of the minima, indicating that Landau damping of the
two minimal points, Fermi energy, the charge density difference between these
electron-hole pair, respectively.
mum) and the electron (right minimum) in the resonant
anomaly positions correspond to the hole (left mini-
region [8]. This is consistent with the fact that
the anomaly positions correspond to the hole (left mini-
mum) and the electron (right minimum) in the resonant
electron-hole pair, respectively.

Since the phonon anomaly can only occur at a specific
Fermi energy, the charge density difference between these
two minimal points, \( \Delta n_A = 6 \times 10^{12} \text{ cm}^{-2} \), is linked to
the electronic band parameters that determine the low
energy dispersion of the bilayer graphene. Within the
tight-binding model [12], using the known \( A-B \) intralayer
hopping energy [23,24], we found from \( \Delta n_A \) the interlayer
\( A_B-B \), hopping energy \( \gamma_1 = 0.35 \pm 0.06 \text{ eV} \). As a com-
parison, photoemission experiments reveal that \( \gamma_1 = 0.43 \pm 0.03 \text{ eV} \) in epitaxial bilayer graphene [25]. Recent
infrared spectroscopy of mechanically exfoliated bilayer
graphene gives \( \gamma_1 = 0.404 \pm 0.010 \text{ eV} \) [26].

We expect the phonon anomaly to show up in single
layer graphene if sample quality is improved. In previous
measurements [8,11], single layer graphene samples con-
tained large charge inhomogeneity, which yields electron
and hole puddles of size \( \delta n = (3-10) \times 10^{11} \text{ cm}^{-2} \). This
inhomogeneity corresponds to the mesoscopic Fermi en-
ergy broadening \( \delta E_F \sim 100 \text{ meV} \) near the Dirac point in
single layer graphene, a value large enough to wash out the
anomalous phonon softening completely. In bilayer gra-
phene, however, similar \( \delta n \) results in much smaller \( \delta E_F \),
because bilayer \( E_F \) changes much slower with \( n \) than the
monolayer \( (n \) versus \( \sqrt{n} \) dependence in the low density
regime), as shown in Fig. 4(a). For this reason, the phonon
anomaly is more robust and easier to observe in bilayer
graphene.

To be more quantitative we numerically evaluated the
effect of charge inhomogeneity on \( \hbar \omega_G(E_F) \), assuming a
Gaussian distribution of the charge density \( f(n) = \frac{1}{\sqrt{2\pi\delta n}} e^{-\frac{(n-n_0)^2}{2\delta n^2}} \), where \( n_0 \) is the average charge density
in the sample, \( \delta n \) represents the size of the charge density
nonuniformity. Figure 4(b) exemplifies several such evo-
lutions for different \( \delta n \). As expected, the larger \( \delta n \), the
smaller the phonon anomaly size \( \Delta E_A = \hbar \omega_G(E_F = 0) -
\hbar \omega_G(E_F = \hbar \omega_G/2) \). Figure 4(c) displays \( \Delta E_A \) as a function
of \( \delta n \). Comparing with the experimental observation,
we estimate that \( \delta n = 1 \times 10^{12} \text{ cm}^{-2} \) for 1 \text{ cm}^{-1} \( \Delta E_A \) in
a bilayer. This size charge density nonuniformity agrees
well with results obtained from other experimental meth-
ods [24,27,28]. Note that similarly sized charge density
nonuniformity in single layer graphene is enough to
smooth out the phonon anomaly completely [inset of
Fig. 4(c)].

In conclusion, we have observed the anomalous softening
of the long-wavelength optical phonon in bilayer gra-
phonon anomaly in graphene, showing that EFE-Raman spectroscopy can access fundamental interaction effects near the charge-neutral point of graphene layers even in the presence of an inhomogeneous charge density distribution.

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FIG. 4 (color online). (a) Comparison of $E_F \sim n$ relation in bilayer and monolayer graphene. The Fermi energy goes up much faster with charge density in the monolayer. (b) Fits of the evolution of the $G$ phonon energy with $E_F$. The best fit has charge density nonuniformity $\delta n = 1 \times 10^{12}$ cm$^{-2}$. Blue (or dark gray) squares are experimental data taken from Fig. 3(b). (c) Phonon anomaly $\Delta E_A$ as a function of charge density nonuniformity in the bilayer (main panel) and the monolayer (inset). The anomaly is more robust in bilayer graphene.

[17] In Eq. (1), analytic terms like $\ln |1 + \frac{\Delta E_A}{h\nu}|$ are not written explicitly because near the resonance, the effects are dominated by the log-divergent term.