PHYSICAL REVIEW B **80**, 241417(R) (2009)

Optical phonon mixing in bilayer graphene with a broken inversion symmetry

Jun Yan,[1,2,*] Theresa Villarson,[1] Erik A. Henriksen,[1] Philip Kim,[1,3] and Aron Pinczuk[1,3,†]
[1]*Department of Physics, Columbia University, New York, New York 10027, USA*
[2]*Department of Physics, University of Maryland, College Park, Maryland 20742, USA*
[3]*Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA*
(Received 11 October 2009; revised manuscript received 29 November 2009; published 31 December 2009)

Pristine bilayer graphene is a centrosymmetric material in which parity is a conserved quantity. The high sensitivity of this atomic scale structure to external perturbations that break the inversion symmetry enables significant potentials for device applications. Raman spectroscopy is used here to probe the breakdown of parity conservation in a direct and quantitative manner via a phonon mixing phenomenon. The striking broken-symmetry effects display anticrossing coupling between two opposite parity long-wavelength optical phonons. The spectral intensity transfer between the two observed Raman peaks offers quantitative measurements of the evolution of the phonon wave function and demonstrates a manifestation of broken inversion symmetry in graphene layers.

DOI: 10.1103/PhysRevB.80.241417 PACS number(s): 78.30.Na, 63.20.kd, 63.20.kg, 78.66.Tr

The inversion center in a crystalline structure is linked to parity as a conserved quantity.[1] Pristine bilayer graphene is a prime contemporary example of such centrosymmetric materials. Breaking of parity conservation in this atomic scale structure can be achieved by external perturbations or by fabrication of specific structures at the atomic level. The removal of inversion symmetry in bilayer graphene has important consequences such as the opening of a tunable bandgap.[2,3] The expectation of remarkable fundamental physics, combined with the promising potential for atomic scale devices, has stimulated intense interest recently in studies of the electronic structure,[4–6] optical,[7–12] and vibrational[13–15] properties of bilayer-graphene structures.

Here we report the observation of an optical phonon mixing behavior in bilayer graphene. The effect induced by breaking of inversion symmetry of the pristine graphene bilayer has remarkable manifestations in Raman spectra. To achieve significant symmetry breaking we perform Raman-scattering experiments in a field-effect transistor with a transparent polymer-electrolyte top gate. The results reveal an unexpected anticrossing coupling (or mode repulsion) of the even- and odd-parity long-wavelength optical lattice vibrations of the unperturbed bilayer. This mode anticrossing and the associated striking spectral intensity transfer between the two modes demonstrate that the parity labeled modes are no longer true vibration eigenstates of a biased graphene bilayer. The mixing of the two long-wavelength optical phonon modes is easily tuned by a gate bias that induces large charge densities reaching well above 10^{13} cm^{-2}.

Figure 1 illustrates the rearrangements of carbon atoms and their displacement vectors in the bilayer-graphene structure after the inversion operation. In the long-wavelength limit, the in-plane optical phonons (G bands) of the two layers couple to an in-phase (IP) mode and an out-of-phase (OP) mode.[16] The IP motion is invariant under inversion [Fig. 1(a)] while the OP motion changes sign [Fig. 1(b)]. When parity is a good quantum number, as is the case in the unperturbed bilayer graphene, the IP phonon (G_{IP}) has even parity and the OP phonon (G_{OP}) has odd parity.

The breaking of inversion symmetry achievable with tuning the potential difference between two graphene layers[5,6,9,10] creates a state in which the even-parity (Raman-active) G_{IP} mode of the unperturbed graphene bilayer mixes with the odd-parity (infrared-active) G_{OP} mode.[17,18] It is this phonon mixing that is revealed in our experiment. The observed breakdown of parity conservation is a direct evidence for inversion-symmetry breaking. The marked sensitivity of the phonon spectrum to symmetry properties allows us to quantitatively monitor the degree of inversion-symmetry breaking in a bilayer-graphene field-effect transistor (FET).

The Raman experiment is performed at room temperature on a bilayer-graphene FET (Ref. 13) that is gated with a polymer electrolyte, as described in Figs. 2(a)–2(c). The transparent polymer electrolyte is composed of $LiClO_4$ dissolved in a poly-ethylene-oxide (PEO) polymer matrix (1:8 in weight ratio) and top gating is achieved with the insertion of a gold wire into the polymer electrolyte.[19] Figure 2(d) shows schematically the charge-density and electric-field dis-

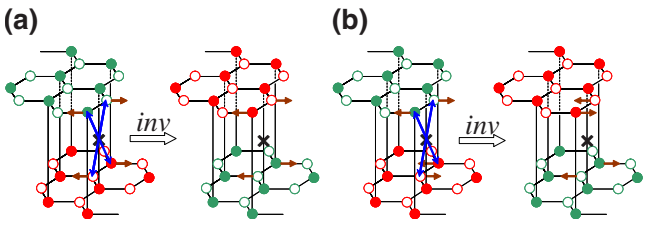

FIG. 1. (Color online) Inversion-symmetry operation on bilayer-graphene lattice and its long-wavelength in-plane optical phonons. The four sublattices of the structure are represented by filled and unfilled circles with different colors (gray scales). The inversion-symmetry operation exchanges carbon atoms about the inversion center (black cross). The blue (dark gray) arrows between the graphene layers exemplify such rearrangements: the green (light gray) filled atoms are inverted into the positions of the red (dark gray) filled atoms, and similar changes occur in the unfilled carbon atomic sites. The brown (dark gray) arrows attached to the carbon atoms represent the relative sublattice motion of the in-phase phonon G_{IP} (a) and the out-of-phase phonon G_{OP} (b). Inversion leaves G_{IP} invariant but flips the G_{OP} lattice vibration.

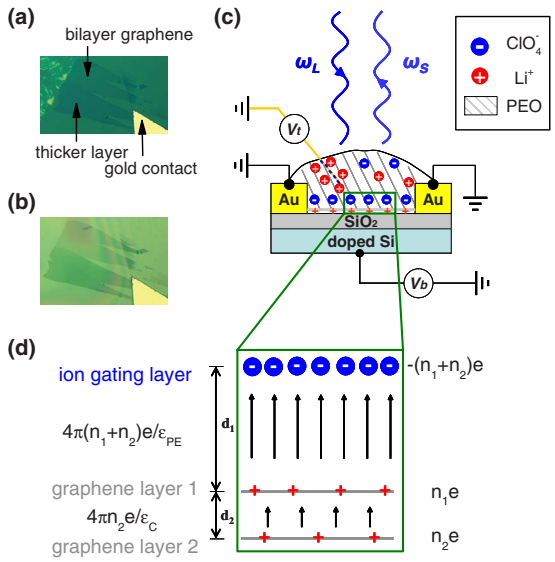

FIG. 2. (Color online) The bilayer-graphene field-effect transistor gated with polymer electrolyte. (a) and (b) Optical microscope images of the graphene sample before (a) and after (b) application of the polymer electrolyte. (c) A schematic illustration of the device and the experimental setup. ω_L and ω_S represent the incident and scattered light respectively. In the experiment, only the polymer-electrolyte top gate V_t is tuned and the Si/SiO_2 back gate V_b is set to zero. Here the device is illustrated for the case of hole doping. (d) The electric-field and charge-density distributions in the vicinity of the bilayer graphene. ε_{PE} and ε_C are static dielectric constants of the polymer electrolyte and graphene. $d_1 \approx 2$ nm, and $d_2 = 0.335$ nm.

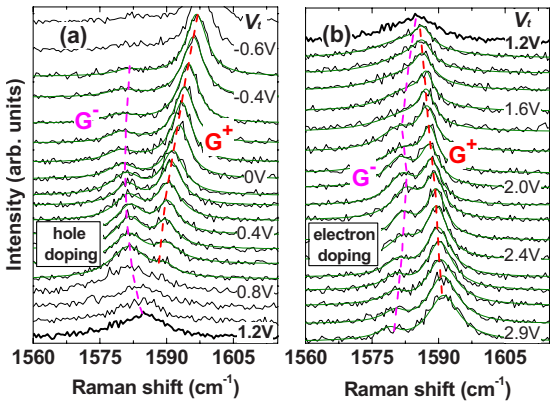

FIG. 3. (Color online) Room-temperature Raman spectra of bilayer graphene biased with the polymer-electrolyte top gate. (a) is for hole doping and (b) is for electron doping. $V_t = 1.2$ V is the approximate charge neutral position. The smooth overlapping curves are fits with the coupled-mode theory [Eq. (1)] using the parameters in Figs. 4(d)–4(f). Other spectra are fitted with a single Lorentzian (not shown). The dashed lines indicate the peak evolution of the G^+ and G^- modes.

tributions based on macroscopic Maxwell equations.[20] The electric field between the ion gating layer and bilayer graphene constitutes the capacitive coupling required for charge doping, while the field between the two graphene layers creates an electrostatic potential gradient that breaks the inversion symmetry of the electron system.

Figure 3 reveals the impact of a varying gate voltage (charge doping) on the long-wavelength in-plane optical phonons in bilayer graphene. The observed G band changes its position and line shape, eventually splitting into two modes G^+ and G^- with energy and spectral weight evolving as V_t is tuned. From the approximate symmetry of the spectra evolution with respect to electron and hole doping,[13,15,21,22] we estimate that the charge neutrality point occurs at a voltage close to $V_t \approx 1.2$ V. This relatively large value is attributed to chemical doping from the polymer electrolyte.[19] Near this neutral point, the only phonon mode in the spectra is the G band broadened by electron-phonon coupling.[13–15] This band derives from the G_{IP} lattice vibration shown in Fig. 1(a).

Figures 4(a)–4(c) display the intensities, half widths, and peak energies of the two modes in Fig. 3, as a function of carrier density n (or Fermi-level position E_F). These are extracted from simple fits of the G^+ and G^- bands with two Lorentzian peaks. The two normal modes are seen to repel each other in energy, while simultaneously a striking reversal of the resonance intensities takes place. At low charge doping, close to the neutral point, the lower energy mode G^- dominates. With increasing carrier density, the Raman intensity is gradually transferred into the higher energy mode G^+.

Since the OP lattice vibration [see Fig. 1(b)] has an energy close to the IP mode, it is quite tempting to assign the two peaks as G_{IP} and G_{OP}, respectively. In fact, such an interpretation was adopted by Malard *et al.* in Ref. 14 and the lower energy mode G^- was identified as G_{OP}. The argument was that G_{OP} becomes Raman active because of breaking of inversion symmetry.[14] However, when parity is not conserved it is not clear if G_{IP} and G_{OP} can still be viewed as eigenstates of bilayer graphene. Furthermore, with increasing charge doping, one would expect that the G_{OP} becomes more intense since there is a larger degree of inversion-symmetry breaking, while our data in Fig. 3 clearly shows that the intensity of G^- decreases with charge doping. Thus we believe that the breakdown of Raman selection rules is too weak an effect to account for the experimental observations, and that Raman scattering from the G_{OP} mode is negligibly small according to the experimental data. Instead, we propose, in agreement with Refs. 17 and 18, that the appearance of two peaks indicates that the carbon displacements in the IP lattice vibration are shared between the two normal modes, G^+ and G^-. The IP and OP lattice vibrations are no longer eigenstates of the system because the inversion symmetry is broken by the strong interlayer electric field. The resulting phonon eigenstates can be regarded as superpositions of G_{IP} and G_{OP} displacements. Consequently, both normal modes become Raman active and the peak intensity is determined by the size of G_{IP} content within each mode.

We quantitatively analyze the Raman spectra using a simple coupled-mode description,

$$\begin{vmatrix} E - E_{IP} & g \\ g & E - E_{OP} \end{vmatrix} = 0, \tag{1}$$

where $E_{IP} = \hbar\omega_{IP} - i\Gamma_{IP}$, $E_{OP} = \hbar\omega_{OP} - i\Gamma_{OP}$ (Γ is half width of the phonon), and g is the G_{IP}-G_{OP} coupling.[23] Solutions to Eq. (1) are given by

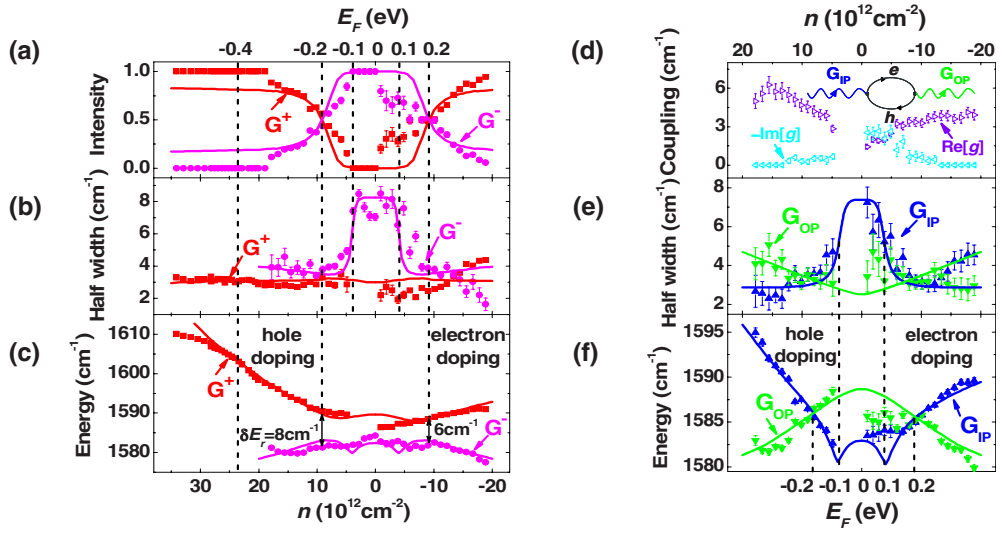

FIG. 4. (Color online) Inversion-symmetry-breaking induced phonon-phonon mixing and anticrossing. (a)–(c), Evolution of the G^+, G^- relative intensity, half width and energy with carrier density. The experimental data points are represented with symbols, while the smooth curves are fits adapted from theoretical calculations in Ref. 17. The vertical dashed lines indicate several special positions of the Fermi energy. 0.1eV is about half the G band energy. ± 0.2 eV are the approximate positions where mode anticrossing occurs and G^+ G^- have identical intensities. 0.4eV is the separation between the two nearly parallel conduction or valence π bands (Ref. 2). In (c), we indicate sizes of the resonant splitting δE_r at $\sim \pm 0.2$ eV. (d)–(f), Charge-density dependence of G_{IP}, G_{OP} and their coupling g. In (d), Re[g] and Im[g] stand for the real and imaginary parts of the G_{IP}-G_{OP} coupling. The inset diagrammatically describes the interaction between G_{IP} and G_{OP} via their mutual coupling to electron-hole pair transitions.

$$E^{\pm} = \frac{E_{IP} + E_{OP}}{2} \pm \sqrt{\left(\frac{E_{IP} - E_{OP}}{2}\right)^2 + g^2} \qquad (2)$$

so that the real and imaginary parts of $E^{\pm}$, respectively, describe the energy and broadening of the G^+ and G^- modes. Figures 4(d)–4(f) present an analysis of the data using this model, where we have extracted the coupling strength, g, as well as the half widths and energies of G_{IP} and G_{OP} that underlie the G^+ and G^- normal modes.[24] The relatively large width of G^- [Fig. 4(b)] and G_{IP} [Fig. 4(e)] for $-0.1 < E_F < 0.1$ eV is a result of Landau damping of lattice vibrations into electron-hole pairs, which was also observed in monolayer graphene.[21,22]

The evolution of G_{IP} band with charge doping in bilayer graphene has been studied in several Raman experiments,[13,15] with the results agreeing well with theoretical calculations.[16,25] The G_{OP} mode is infrared active by symmetry and two recent infrared spectroscopy studies of bilayer graphene did observe phonon signatures with a Fano shape.[11,12] However, while Ref. 11 attributed this mode to G_{OP}, Ref. 12 put forth that the relevant mode is G_{IP} instead.[12] Furthermore, the phonon energy found in Ref. 12 is less than 196 meV (1580 cm^{-1}), smaller than the observed G_{IP} energy,[15] while phonon energy renormalization calculations have predicted that G_{OP} should have a higher energy than G_{IP} at low charge densities.[16]

In light of such controversy, the analysis of our data offers a unique perspective into this intricate problem by giving a detailed evolution of the G_{IP} and G_{OP} energies. As shown in Fig. 4(f), it is clear that G_{OP} has a higher energy at low densities. This result is also consistent with past studies of graphite[26] which can be viewed as an infinite repetition of the bilayer graphene. This energy difference is an important property of bilayer graphene that reflects the different electron-phonon coupling for IP and OP processes.[16] In fact, this property plus the softening of G_{OP} and stiffening of G_{IP} with charge doping[16,17] are key elements that guarantee the degeneracy of the two modes at a certain Fermi energy: $\sim \pm 200$ meV as determined in Fig. 4(f). Such degeneracies, together with the inversion-symmetry-breaking induced coupling, result in the anticrossing behavior observed in our experiment.

At $E_F \approx \pm 200$ meV, the two peaks in the Raman spectrum have the same intensity as shown in Fig. 4(a) because the resonant coupling partitions the Raman-active G_{IP} equally to the G^+ and G^- modes. The resonant energy splitting δE_r, 8 cm^{-1} on the hole side and 6 cm^{-1} on the electron side [Fig. 4(c)], can be viewed as quantitative measurements of the broken inversion symmetry since the splitting vanishes in the limit of the unperturbed symmetric bilayer graphene.

Away from ± 200 meV, the two crossing branches of G_{IP} and G_{OP} energies evolve with charge doping. Their mutual coupling to electron-hole pairs with indefinite parity results in two anticrossing branches of G^+ and G^-. The relative intensities of G^+ and G^- reverse, reflecting the fact that G^- (G^+) is dominated by the IP vibration at low (high) charge densities. This further demonstrates that G_{IP} has a lower energy for charge neutral bilayer graphene, and that with charge doping, its energy eventually exceeds that of G_{OP}.[16,17]

The charge-density dependences of G_{IP}, G_{OP}, G^+, and G^- have been calculated by Ando and Koshino using a phonon renormalization approach.[17] We plot the results of their calculations (solid lines) along with our data in Fig. 4, and see that the theory agrees reasonably well with our experimental

results when an analysis that accounts for particle-hole asymmetry is employed.[27]

Note that in Fig. 4(d) we have experimentally determined both the imaginary and real parts of the G_{IP}-G_{OP} coupling strength g. While there is no theoretical calculation for g, conceptually the coupling can be represented with processes described by the diagram in the inset of Fig. 4(d). These second-order processes take place via intermediate electron-phonon interactions. Here the IP phonon creates an electron-hole pair that subsequently interacts again with the lattice to recombine and emit an OP phonon.[28] This phonon-phonon interaction mechanism is forbidden when parity is conserved and g vanishes in the unperturbed bilayer graphene. The size of G_{IP}-G_{OP} coupling can thus be viewed as a useful gauge for the degree of inversion-symmetry breaking.

To conclude, the breaking of inversion symmetry in bilayer graphene by application of a polymer-electrolyte top gate results in a striking mixing of the optical phonon modes, with remarkable manifestations in Raman spectra. Our work indicates that the experimental determination of phonon mixing comprises a very sensitive tool for investigations of symmetry breaking in atomically thin electronic systems.

We thank Chenguang Lu for help with the preparation of polymer electrolyte. This work is supported by ONR (Grant No. N000140610138), NSF (Grants No. CHE-0117752 and No. CHE-0641523), and the NYSTAR. P.K. acknowledges support from the FENA MARCO Center. A.P. is supported by NSF (Grants No. DMR-0352738 and No. 0803691) and DOE (Grant No. DE-AIO2-04ER46133).

*juny@umd.edu

†aron@phys.columbia.edu

[1] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley Publishing Company, Massachusetts, 1963), Vol. 3.

[2] E. McCann and V. I. Falko, Phys. Rev. Lett. **96**, 086805 (2006).

[3] E. McCann, Phys. Rev. B **74**, 161403(R) (2006).

[4] T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenberg, Science **313**, 951 (2006).

[5] E. V. Castro, K. S. Novoselov, S. V. Morozov, N. M. R. Peres, J. M. B. Lopes dos Santos, J. Nilsson, F. Guinea, A. K. Geim, and A. H. Castro Neto, Phys. Rev. Lett. **99**, 216802 (2007).

[6] J. B. Oostinga, H. B. Heersche, X. Liu, A. F. Morpurgo, and L. M. K. Vandersypen, Nature Mater. **7**, 151 (2007).

[7] E. A. Henriksen, Z. Jiang, L.-C. Tung, M. E. Schwartz, M. Takita, Y.-J. Wang, P. Kim, and H. L. Stormer, Phys. Rev. Lett. **100**, 087403 (2008).

[8] Z. Q. Li, E. A. Henriksen, Z. Jiang, Z. Hao, M. C. Martin, P. Kim, H. L. Stormer, and D. N. Basov, Phys. Rev. Lett. **102**, 037403 (2009).

[9] Y. Zhang, T. T. Tang, C. Girit1, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen, and F. Wang, Nature (London) **459**, 820 (2009).

[10] K. F. Mak, C. H. Lui, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **102**, 256405 (2009).

[11] A. B. Kuzmenko, L. Benfatto, E. Cappelluti, I. Crassee, D. van der Marel, P. Blake, K. S. Novoselov, and A. K. Geim, Phys. Rev. Lett. **103**, 116804 (2009).

[12] T. T. Tang, Y. Zhang, C.-H. Park, B. Geng, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, S. G. Louie, Y. R. Shen, and F. Wang, Nat. Nanotechnol. (to be published).

[13] J. Yan, E. A. Henriksen, P. Kim, and A. Pinczuk, Phys. Rev. Lett. **101**, 136804 (2008).

[14] L. M. Malard, D. C. Elias, E. S. Alves, and M. A. Pimenta, Phys. Rev. Lett. **101**, 257401 (2008).

[15] A. Das, B. Chakraborty, S. Piscanec, S. Pisana, A. K. Sood, and A. C. Ferrari, Phys. Rev. B **79**, 155417 (2009).

[16] T. Ando, J. Phys. Soc. Jpn. **76**, 104711 (2007).

[17] T. Ando and M. Koshino, J. Phys. Soc. Jpn. **78**, 034709 (2009).

[18] P. Gava, M. Lazzeri, A. M. Saitta, and F. Mauri, Phys. Rev. B **80**, 155422 (2009).

[19] C. Lu, Q. Fu, S. Huang, and J. Liu, Nano Lett. **4**, 623 (2004).

[20] E. McCann, D. S. L. Abergel, and V. I. Fal'ko, Solid State Commun. **143**, 110 (2007).

[21] J. Yan, Y. Zhang, P. Kim, and A. Pinczuk, Phys. Rev. Lett. **98**, 166802 (2007).

[22] S. Pisana, M. Lazzeri, C. Casiraghi, K. S. Novoselov, A. K. Geim, A. C. Ferrari, and F. Mauri, Nature Mater. **6**, 198 (2007).

[23] Note that Ref. 17 studied the problem from the perspective of interaction between G bands of the top and bottom graphene layers, while Eq. (1) considered coupling between G_{IP} and G_{OP}.

[24] To fit the spectra in Fig. 3, we use the phonon spectral function $\mathcal{I}(\omega)=-\mathrm{Im}[\frac{1}{\hbar\omega-E_{IP}-\frac{g^2}{\hbar\omega-E_{OP}}}]$ (Ref. 28). It is easy to notice that Eq. (1) is obtained if we let the denominator of the spectral function equal to zero.

[25] In this experiment we didn't observe the phonon anomaly of G_{IP} expected at ± 0.1 eV (Refs. 13 and 16). This is most likely due to the large charge nonuniformity created by the polymer electrolyte.

[26] R. J. Nemanich, G. Lucovsky, and S. A. Solin, Solid State Commun. **23**, 117 (1977).

[27] In the analysis of phonon energy evolution, we added a correction $(0.016n^2)$ to the hole-doped G^+ and G_{IP} to fit the particle-hole asymmetric features in the data. This asymmetry might be due to the asymmetric band structure of the bilayer graphene (Refs. 7 and 8), as well as different changes in the lattice constant with electron or hole doping (Ref. 18).

[28] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1990).