

Emergence of an Out-of-Plane Optical Phonon (ZO) Kohn Anomaly in Quasifreestanding Epitaxial Graphene

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In neutral graphene, two prominent cusps known as Kohn anomalies are found in the phonon dispersion of the highest optical phonon at $q = \Gamma$ (LO branch) and $q = K$ (TO branch), reflecting a significant electron-phonon coupling (EPC) to undoped Dirac electrons. In this work, high-resolution electron energy loss spectroscopy is used to measure the phonon dispersion around the Γ point in quasifreestanding graphene epitaxially grown on Pt(111). The Kohn anomaly for the LO phonon is observed at finite momentum $q \sim 2k_F$ from Γ , with a shape in excellent agreement with the theory and consistent with known values of the EPC and the Fermi level. More strikingly, we also observe a Kohn anomaly at the same momentum for the out-of-plane optical phonon (ZO) branch. This observation is the first direct evidence of the coupling of the ZO mode with Dirac electrons, which is forbidden for freestanding graphene but becomes allowed in the presence of a substrate. Moreover, we estimate the EPC to be even greater than that of the LO mode, making graphene on Pt(111) an optimal system to explore the effects of this new coupling in the electronic properties.

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Introduction.—Kohn anomalies are kinks in the phonon dispersion of a material produced by abrupt variations in the screening of atomic vibrations by gapless electrons [1–3]. The properties of these anomalies are completely determined by the electron-phonon coupling (EPC) and the shape of the Fermi surface, and their observation thus offers a window to study the interplay between electronic properties and phonon dynamics.

As a paradigmatic example, in graphite [4–7] and graphene [8–15], Kohn anomalies are realized as linear cusps in the dispersion of the highest optical phonon branches at Γ (the E_{2g} phonon) and at K (the A_1' phonon). The form and position of this cusp is determined by the Dirac fermion dispersion of the electronic π bands around K and the Fermi level $\mu \approx 0$. These two in-plane phonon branches are commonly accepted to be the only ones with a significant EPC in graphene [16]. Within a tight-binding picture, these are the only branches that modify the nearest neighbor hopping integrals, so other in-plane phonons require a different mechanism to couple to electrons.

For the case of out-of-plane phonons, the EPC is strongly constrained by the presence of mirror symmetry with respect to the horizontal plane which forbids a first order coupling to electrons, at least in freestanding graphene. When graphene is supported by a substrate a first order EPC becomes allowed, in principle [17,18], but it has remained unknown whether its strength is large enough to produce any significant effect. In particular, for the out-of-plane optical mode

(the ZO mode), it has been speculated that a finite coupling could be responsible for a Peierls instability to a spontaneous buckling of the lattice [19,20], which has not been observed so far. A coupling of the ZO mode to electrons would influence many physical properties, since the ZO has significantly lower energy than the in-plane branches with strong EPC. The observation of a Kohn anomaly for the ZO phonon [21] would represent a definitive proof of the existence of the EPC for this phonon branch and would allow an estimate of it. Herein, we demonstrate the existence of precisely this Kohn anomaly by means of high-resolution electron energy loss spectroscopy [22] (HREELS) measurements on monolayer graphene grown on Pt(111). In addition, we also present evidence of the expected Kohn anomaly for the E_{2g} phonon branch.

Graphene on Pt(111) is an ideal playground for investigating the possible emergence of a ZO Kohn anomaly, as it is characterized by the weakest graphene-substrate interaction [23]. The graphene-Pt distance (3.31 Å) lies close to the c -axis spacing in graphite. Moreover, the electronic structure of graphene on Pt(111) resembles that of isolated graphene [24], with the Dirac fermion dispersion of π bands preserved. Angle-resolved photoemission spectroscopy (ARPES) experiments [24] do not show any significant hybridization of the graphene π states with Pt d states, which simply superpose in energy with minimal interaction between them. This is in contrast to the case of, for example, graphene on Ni(111), where the hybridization

of the graphene π states with the Ni d bands has a very strong effect on the π bands [25]. The graphene sheet grown on Pt(111) is p doped with a shift by 0.30 ± 0.15 eV of the Fermi level from the Dirac point.

Experimental methods.—Experiments were carried out in an ultrahigh vacuum chamber operating at a base pressure of 5×10^{-9} Pa. The sample was a single crystal of Pt(111). The substrate was cleaned by repeated cycles of ion sputtering and annealing at 1300 K. Surface cleanliness and order were checked using Auger electron spectroscopy and low-energy electron diffraction measurements, respectively. Graphene was attained by dosing ethylene onto the clean Pt(111) substrate held at 1150 K. The completion of the first layer was reached upon an exposure of 3×10^{-8} mbar for 10 min (24 L, $1 L = 1.33 \times 10^{-6}$ mbar). The graphene layer was characterized by Raman spectroscopy, low-energy electron diffraction, and scanning electron microscopy experiments [26,27]. In particular, Raman measurements indicate the unique presence of monolayer graphene domains.

HREELS experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS) with an energy resolution ranging from 1 to 3 meV. The dispersion of the peaks in the energy loss E_{loss} was measured by moving the analyzer while keeping the sample and the monochromator fixed. The phonon in-plane momentum was determined from $\vec{q}_{\parallel} = \vec{k}_i \sin \theta_i - \vec{k}_s \sin \theta_s$ as

$$q_{\parallel} = \sqrt{2mE_p}(\sin \theta_i - \sqrt{1 - E_{\text{loss}}/E_p} \sin \theta_s), \quad (1)$$

where θ_i and θ_s are the incident and scattering angles, and we set $\hbar = 1$. The impinging energy E_p and the incident angle θ_i were chosen so as to obtain the highest signal-to-noise ratio. A primary beam energy of $E_p = 20$ eV provided the best compromise among surface sensitivity, the highest cross section for mode excitation and momentum resolution. The angular acceptance of the apparatus was $\alpha = \pm 0.5^\circ$, which determines the momentum resolution as

$$\Delta q_{\parallel} = \sqrt{2mE_p}(\cos \theta_i + \sqrt{1 - E_{\text{loss}}/E_p} \cos \theta_s)\alpha. \quad (2)$$

For the investigated range of q_{\parallel} , Δq_{\parallel} was found to range from 0.005 near Γ to 0.022 \AA^{-1} at K . To obtain the energies of loss peaks, a polynomial background was subtracted from each spectrum. The resulting spectra were fitted by a Voigt line shape [27]. All measurements were made at room temperature.

Experimental results.—The phonon spectrum in graphene is composed by six phonon branches. Four vibrate in-plane and are labeled transverse and longitudinal acoustic (TA and LA) and optical (TO and LO). The other two are acoustic and optical out-of-plane vibrations (ZA and ZO). Figure 1 shows a map of the HREELS intensity as a

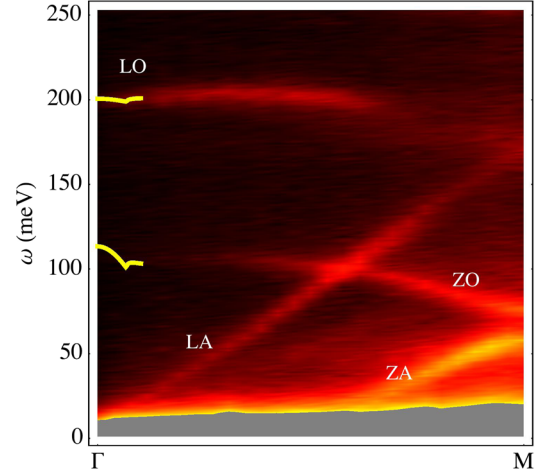


FIG. 1 (color online). HREELS intensity plot for phonon dispersion of graphene/Pt(111). Phonon modes have been recorded in HREELS spectra acquired in off-specular geometry with the sample oriented along the Γ - M direction. The incidence angle is $\theta_i = 80^\circ$ with respect to the surface normal and the primary electron beam energy is $E_p = 20$ eV. To put in evidence only inelastic losses due to phonons, the tail of the elastic peak is grayed out for clarity. The LO, LA, ZO, and ZA branches are clearly identified, while the TO and TA are barely visible due to a selection rule [28]. Note the very low intensity of the ZO mode close to Γ . Yellow lines are fits to the dispersion obtained with higher resolution data, where Kohn anomalies can be appreciated (see text for details).

function of energy and momentum, where four phonon branches (ZA, ZO, LA, and LO) can be clearly observed. Their dispersion is consistent with previous works [25,29,30]. The other two phonon branches (TO and TA) are practically absent because a selection rule that forbids the emission of odd phonons under reflections by the scattering plane [28]. This is also clearly observed in Fig. 2, where the energy loss is plotted for a selected angle, and four peaks are clearly identified. The displacement pattern for each of these four modes is shown as an inset to Fig. 2.

We now focus on the dispersion of the ZO and LO modes around Γ . As usual, the ZO mode is significantly softened compared to the LO mode, due to the higher freedom for atom motion perpendicular to the plane with respect to the in-plane motion. The intensity of the ZO phonon at small momenta has very low weight, as shown in the intensity plot reported in Fig. 1 (see also Ref. [27]). To enhance the signal-to-noise ratio from the ZO phonon in the nearness of Γ , each spectrum was acquired for several days. While this allowed us to resolve the ZO loss peak, the error bars for its frequency are still in general larger than for other branches. A careful fitting procedure [27] was used to extract the experimental frequencies for the LO and ZO phonons for small momenta, which are reported in Fig. 3. The most striking feature in these plots is that they both display a clear cusp at the same momentum $q \sim 0.13 \text{ \AA}^{-1}$. This

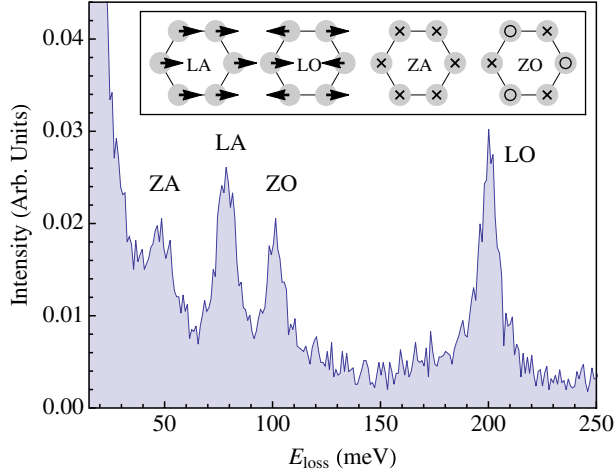


FIG. 2 (color online). Selected phonon spectrum from the data set of Fig. 1 at $\theta_s = 48^\circ$, which corresponds to $q_{\parallel} = 0.56 \text{ \AA}^{-1}$. The TA and TO modes are not observed due to a selection rule. Inset: Phonon displacements for the four phonons observed. Crosses and circles denote displacements in and out of the plane, respectively.

strongly suggests that both cusps are Kohn anomalies at $q = 2k_F$, which originate from the interaction of phonons with electrons. The Fermi wave vector $k_F = E_F/v_F$ can be estimated from ARPES measurements of graphene/Pt(111) [24]. The reported values of the Fermi energy and Fermi velocity are $E_F \approx 0.30 \pm 0.15 \text{ eV}$ and $v_F \approx 6 \text{ eV \AA}$. Thus, $2k_F \approx 0.10 \pm 0.05 \text{ \AA}^{-1}$, in good agreement with the position of the cusp found in this work. The position of the G peak in our Raman measurements [27] can be used to estimate [31,32] $E_F \sim 0.42 \text{ eV}$, also in good agreement. While a Kohn anomaly for the LO mode is known to occur, the presence of the cusp for the ZO mode is unexpected and represents the first evidence of the coupling of the ZO mode to electrons. In hindsight, by carefully inspecting the phonon dispersion recorded for graphene on Pt(111) in a

previous experiment by some of the authors [29], a dip for both LO and ZO at finite momentum is in fact seen but was not noticed or discussed. In Ref. [33], the LO anomaly was incorrectly presented by shifting it to the Γ point due to a misunderstanding, but in fact occurs at finite momentum as well. To substantiate the claim that these cusps are in fact Kohn anomalies, we now compute the self-energies of both LO and ZO phonons following the conventions of Refs. [14,16,34] and compare the predictions to the experimental data.

Theory.—The dispersion of the phonons around Γ is modified because of their coupling to electrons, which at low energies can be modeled with a Dirac Hamiltonian

$$H = \int \frac{d^2k}{(2\pi)^2} \psi^\dagger (v_F \vec{\sigma} \cdot \vec{k} - \mu) \psi, \quad (3)$$

with $\vec{\sigma} = (\sigma_x, \sigma_y)$ are Pauli matrices, v_F is the Fermi velocity and μ is the chemical potential. This effective model is applicable up to energies $\Lambda_E \approx 1.5 \text{ eV}$ or momenta $\Lambda_q = \Lambda_E/v_F = 0.25 \text{ \AA}^{-1}$, beyond which the dispersion is no longer linear. Therefore, our predictions are only valid for phonon momenta within this range as well. The phonon Hamiltonian is

$$H = \sum_i \int \frac{d^2q}{(2\pi)^2} \omega_i(q) b_{i,q}^\dagger b_{i,q}, \quad (4)$$

with creation and destruction operators defined by the effective displacements associated with each phonon mode

$$u_i = \sqrt{\frac{A_c}{4\omega_i M}} \int \frac{d^2q}{(2\pi)^2} (b_{i,q} e^{i\vec{q}\cdot\vec{r}} + b_{i,q}^\dagger e^{-i\vec{q}\cdot\vec{r}}), \quad (5)$$

where $i = \text{LO, TO, and ZO}$ and $A_c = 3\sqrt{3}a^2/2$ is the unit cell area, with $a = 1.42 \text{ \AA}$ the nearest neighbor distance.

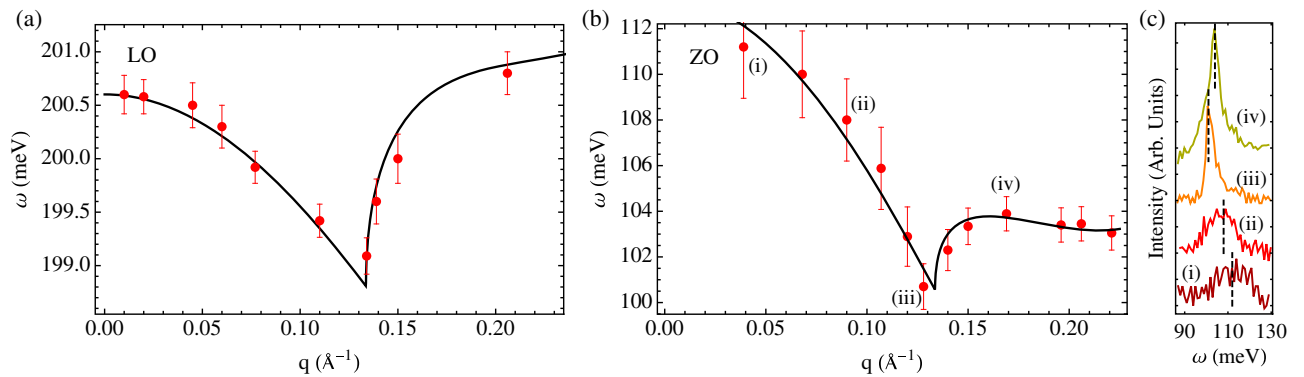


FIG. 3 (color online). Phonon dispersions close to the Γ point, showing cusps around $q_c \sim 0.13 \text{ \AA}^{-1}$. (a) Dispersion of the LO phonon. A fit to Eq. (8) (full line) gives an EPC $\lambda_{\text{LO}} = 0.029$, and parameters $\omega_{\text{LO}}^0 = 200.6 \text{ meV}$, $a_{\text{LO}} = -110 \text{ meV \AA}^2$, $b_{\text{LO}} = 558 \text{ meV \AA}^4$. (b) Dispersion of the ZO phonon. A fit to Eq. (8) (full line) gives an EPC $\lambda_{\text{ZO}} = 0.087$ and $\omega_{\text{ZO}}^0 = 102.3 \text{ meV}$, $a_{\text{ZO}} = -810 \text{ meV \AA}^2$, $b_{\text{ZO}} = 5243 \text{ meV \AA}^4$. (c) Representative spectra used to produce (b). The frequencies are marked with a dashed line. Note the fits in (a) and (b) are also shown in Fig. 1 as yellow lines.

The dispersions of the phonons $\omega_i(q)$ are analytic in the absence of EPC. For momenta close to the Γ point they can be expanded as $\omega_i(q) = \omega_i^0 + a_i q^2 + b_i q^4$, where ω_i^0 , a_i , and b_i are parameters to be fitted from experimental data. The coupling between electrons and phonons is described by

$$H_{e-ph} = F_i \int d^2 r u_i \psi^\dagger \mathcal{M}_i \psi, \quad (6)$$

with F_i the electron-phonon coupling. The matrix \mathcal{M}_i for the different phonons is equal to $\mathcal{M}_{LO} = \hat{q} \times \vec{\sigma}$, $\mathcal{M}_{TO} = \hat{q} \cdot \vec{\sigma}$, $\mathcal{M}_{ZO} = \sigma_3$. Following Ref. [16], it is customary to introduce a dimensionless EPC as

$$\lambda_i = \frac{F_i^2 A_c}{2M\omega_i v_F^2}. \quad (7)$$

The electron-phonon coupling induces a phonon self-energy $\Pi_i(q)$ that corrects the dispersion according to

$$\omega_{R,i} = \omega_i^0 + a_i q^2 + b_i q^4 + \frac{\lambda_i}{2} \Pi_i(q/k_F). \quad (8)$$

In the static approximation, the self-energies for the different phonon branches in terms of the dimensionless variable $x = q/k_F$ are given by [27]

$$\Pi_{LO}(x) = \frac{g_{s,v}\mu}{4\pi} \left(\sqrt{1 - \frac{4}{x^2}} + \frac{x}{2} \arccos(2/x) \right) \theta(2-x), \quad (9)$$

$$\Pi_{TO}(x) = 0, \quad (10)$$

$$\Pi_{ZO}(x) = \frac{g_{s,v}\mu}{4\pi} [2 + x \arccos(2/x) \theta(2-x)]. \quad (11)$$

These expressions can be used to fit the cusps in the experimental curves to obtain an estimate for the different electron-phonon couplings. To do so, we have fitted the dispersion parameters for both curves and determined the optimal Fermi level as $E_F = v_F q_c/2 \approx 0.401$ eV, which corresponds to a cusp momentum of $q_c = 0.133 \text{ \AA}^{-1}$. The fits are shown in Fig. 3 with the experimental dispersion, and the result for the LO EPC is $\lambda_{LO} = 0.029$, in excellent agreement with the estimates obtained from Raman, $\lambda_{LO} = 0.027-0.034$ [16]. The fit for the ZO gives $\lambda_{ZO} = 0.087$, an even greater value.

Discussion.—Since this is the first work to observe the effects of electron-phonon coupling to the ZO mode in graphene, there are no measurements of λ_{ZO} available to compare with. Theoretically, this coupling has only been estimated for a SiO₂ substrate in Ref. [19], giving a maximum value of $F_{ZO} = 7 \text{ eV \AA}$ or $\lambda_{ZO} = 0.011$ [35]. Our significantly higher value reflects the fact that the substrate is metallic and that, while direct hybridization with graphene is small, the surface electric field induces a

stronger breaking of reflection symmetry which is responsible for the EPC.

Our finding that λ_{ZO} has a significant magnitude implies that its effects should also be observable in other experiments. For example, the EPC is visible in the electron dispersion, in the form of a kink at the phonon frequency that is observable by ARPES [9]. The existence of λ_{ZO} would be responsible for an extra kink at ω_{ZO} that could be resolved in future experiments. One could also expect a finite λ_{ZO} to induce new Raman peaks. A peak at ω_{ZO} from a first order Raman process (an analog of the G peak) for the ZO is not allowed because the ZO transforms as B_2 , which is not contained in $E_1 \times E_1$. However, a second order process (analogous to the $2D'$ peak [16]) is, in principle, allowed by symmetry. This process would give a peak at roughly $2\omega_{ZO}$, which unfortunately may be difficult to detect because of its overlap with the G peak. Therefore, either Raman or ARPES could provide an independent confirmation of electron-phonon coupling for the ZO mode.

The finding that the substrate can induce an EPC to the ZO may also have important implications for transport in the high-field regime. The phenomenon of current saturation at high bias originates from inelastic scattering with optical phonons, both intrinsic [36] or from the substrate [37]. Since the energy of the ZO (~ 100 meV) is significantly lower than the known phonons with strong EPC, the effects of the ZO may already be present in current experiments [36–39], and its presence should be accounted for in theory [40–42].

A related system where the standard (LO and TO) Kohn anomalies have been observed is graphene on Ir(111) [30]. According to ARPES [43], the Fermi level in this system is $E_F \approx 0.1$ eV, which corresponds to $2k_F \approx 0.03 \text{ \AA}^{-1}$. Kohn anomalies at such small momentum are probably too difficult to resolve, which is consistent with the observed broadened dip around Γ instead of a cusp. Similarly, if the ZO EPC in this system is significant, such a feature should be observed for the ZO around Γ . The data in Ref. [30] are inconclusive on this matter. Finite momentum Kohn anomalies will be more likely to be found in graphene on metals more similar to Pt(111), with weak hybridization but large charge transfer [44]. In metallic substrates with stronger hybridization such as Ni(111), Kohn anomalies are not present for the LO and TO phonons [45–49] because the coupling of the graphene π bands with the Ni d orbitals completely rearranges the electron bands. A Kohn anomaly for the ZO is therefore not expected in this type of system.

In summary, in this work we have shown that the presence of a substrate induces a significant electron-phonon coupling to ZO phonons in graphene, which is responsible for a strong Kohn anomaly at $q = 2k_F$. This finding paves the way to explore the many implications of the coupling of flexural phonons to Dirac electrons in supported graphene samples and graphene-metal contacts.

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