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Kinks in the σ Band of Graphene Induced by Electron-Phonon Coupling

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Angle-resolved photoemission spectroscopy reveals pronounced kinks in the dispersion of the σ band of graphene. Such kinks are usually caused by the combination of a strong electron-boson interaction and the cutoff in the Fermi-Dirac distribution. They are therefore not expected for the σ band of graphene that has a binding energy of more than ≈ 3.5 eV. We argue that the observed kinks are indeed caused by the electron-phonon interaction, but the role of the Fermi-Dirac distribution cutoff is assumed by a cutoff in the density of σ states. The existence of the effect suggests a very weak coupling of holes in the σ band not only to the π electrons of graphene but also to the substrate electronic states. This is confirmed by the presence of such kinks for graphene on several different substrates that all show a strong coupling constant of $\lambda \approx 1$.

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Many-body interactions can strongly affect the spectral function of solids, and their presence is frequently heralded by so-called kinks in the dispersion of the electronic states near the Fermi energy, as observed by angle-resolved photoelectron spectroscopy (ARPES). Such kinks are primarily caused by electron-boson interactions and many cases of electron-phonon [1–3] or electron-magnon [4] induced kinks have been reported. In the cuprate high-temperature superconductors, strong kinks have been found near the Fermi energy [5,6], and their origin as well as their significance for the mechanism for high-temperature superconductivity have given reason to some debate [7]. The observed kinks in the spectral function contain a wealth of information about the underlying many-body interactions, such as the strength of the coupling as a function of position on the Fermi surface, as well as the energy of the bosons [8]. Note, however, that the presence of kinks does not necessarily imply the presence of bosonic interactions in correlated materials [9].

The observation of a kink signals a strong change in the real part of the self-energy Σ' that describes the deviation of the observed dispersion from the single-particle picture [10]. The origin of this structure can most easily be understood by considering the imaginary part of the self-energy Σ'' that is inversely proportional to the lifetime of the ARPES photohole and related to Σ' via a Kramers-Kronig transformation. Far away from the Fermi energy E_F , a photohole can be filled by electrons from lower binding energies dropping into the hole, emitting a boson of energy $\hbar\omega_E$ to conserve energy and momentum. For binding energies smaller than $\hbar\omega_E$, this is no longer possible, leading to a marked increase in lifetime. The

corresponding decrease in Σ'' leads to a maximum in Σ' , and this gives rise to the kink [10].

The lack of occupied states above E_F (at low temperature) is thus crucial for the appearance of the kink, and many-body effect related dispersion kinks are only expected near E_F , at least for the coupling to bosonic modes. In this Letter, we report the observation of pronounced kinks near the top of the σ band in graphene or graphite (see Figs. 1 and 2). Since these states are found at a binding energy of >3.5 eV, the presence of such kinks is unexpected. We show that the observed spectral features can still be explained by a strong electron-phonon interaction but the role of the Fermi-Dirac distribution cutoff is assumed by the density of σ states. This novel mechanism suggests that the hole in the σ band primarily decays through electrons from the same band instead of electrons from the π band or the substrate. This is confirmed by the observation of a similarly strong coupling for a large variety of graphene systems.

ARPES data were collected for six different material systems at three different synchrotron radiation beam lines: graphite, epitaxial monolayer (MLG) and bilayer (BLG) graphene on SiC [11] at beam lines I3 [12] and I4 [13] of MAX-III, as well as MLG graphene on Ir(111), oxygen-intercalated quasi-free-standing monolayer graphene (QFMLG) on Ir(111), with and without Rb doping, on the SGM-3 line of ASTRID [14]. Measurements were carried out under ultrahigh vacuum and temperatures which are low compared to those required for the excitation of optical phonon modes (see Table I). The energy and momentum resolutions were better than 35 meV and $0.01 \text{ \AA}^{-1}$, respectively.

FIG. 1 (color online). Noninteracting (tight-binding) band structure of graphene, depicting the σ bands (red lines) and the π band (blue line) [15]. The Brillouin zone is depicted in the inset. The σ band consists of two branches σ_1 and σ_2 meeting at a common maximum at $\bar{K}$, with a binding energy of 3.5 to 4.0 eV. ARPES data for MLG graphene on SiC (gray scale) are superimposed. The detailed dispersion in the vicinity of the σ band maximum in the $\bar{\Gamma}$ - $\bar{K}$ direction is magnified. The measured dispersion deviates from the noninteracting behavior, showing a clear kink accompanied by a band narrowing near the top of the σ band. The photon energy and temperature of data acquisition were $h\nu = 36$ eV and $T = 100$ K, respectively.

Figures 1 and 2 illustrate the strong renormalization of the σ band for different graphene systems. An overview is given in Fig. 1 showing the noninteracting (tight-binding) band structure of graphene [15] together with the ARPES data for MLG graphene on SiC (acquired at 100 K) near the top of the σ band. The general agreement of data and calculated band structure is satisfactory. However, a closer

FIG. 2. ARPES data acquired for (a) quasi-free-standing monolayer graphene on Ir(111), (b) Rb-doped quasi-free-standing monolayer graphene on Ir(111), (c) monolayer graphene on SiC, and (d) bilayer graphene on SiC. The energy scales are plotted relative to the σ band maximum ($E_\sigma \approx 3.5$ eV). The dispersion direction corresponds to the $\bar{\Gamma}$ - $\bar{K}$ for all the three systems. The photon energy of data acquisition was $h\nu = 36$ eV.

inspection shows the formation of a pronounced kink in the dispersion near the top of the band, accompanied by a band narrowing, the characteristic sign of a strong electron-boson interaction. While such kinks are expected and observed for doped graphene near the Fermi energy [8,16,17], their appearance at a high binding energy of ≈ 3.5 eV is unexpected. Results for graphene and bilayer graphene show that the strong renormalization is an ubiquitous feature (see Fig. 2). The energy scale in this figure has been defined relative to the top of the σ band extrapolated from the high energy dispersion of the bands. For these graphene systems, matrix element effects can strongly suppress the photoemission intensity of one or both of the σ bands at the chosen photon energy and experimental geometry [18]. Indeed, near normal emission, either it is only possible to see a single branch of the two forming the σ band or the intensity of one branch is drastically reduced compared to the other (see Fig. 2). Note that the loss of intensity near normal emission is a mere interference effect and should not be confused with the loss of spectral weight near the Fermi energy that is observed in the case of polaron formation [19].

While the electron-phonon coupling appears to be an obvious candidate for the appearance of the kinks, the mechanism must be very different from the situation near the Fermi level where the Fermi-Dirac function cutoff is ultimately responsible for the strong change in the self-energy. Consider the imaginary part of the self-energy Σ'' for the electron-phonon coupling [10,20]:

$$\Sigma''(\epsilon_i, T) = \pi \int_0^{\omega_{\max}} \{ \alpha^2 F^A(\epsilon_i, \omega) [1 + n(\omega) - f(\epsilon_i - \omega)] + \alpha^2 F^E(\epsilon_i, \omega) [n(\omega) + f(\epsilon_i + \omega)] \} d\omega + \Sigma''_0, \quad (1)$$

where $\alpha^2 F^{A(E)}$ are the Eliashberg coupling functions for phonon absorption (emission), ϵ_i is the initial state energy of the hole with respect to the top of the σ band, and ω is the phonon energy. n and f are Bose-Einstein and Fermi-Dirac distributions, respectively, and Σ''_0 accounts for electron-defect and electron-electron scattering, which is assumed to be independent of ϵ_i in the small energy range of interest here. Far from E_F , as in the present situation, we can approximate $f = 1$. If we assume that the electron-phonon interaction is dominated by an optical Einstein mode of $\hbar\omega_E \approx 190$ meV, we further find that $n(\omega_E) \ll 1$. The expression simplifies to

$$\Sigma''(\epsilon_i, T) = \pi \int_0^{\omega_{\max}} \alpha^2 F^E(\epsilon_i, \omega) d\omega + \Sigma''_0. \quad (2)$$

The crucial point now is that the Eliashberg function is strongly energy dependent: if we only consider electron-phonon scattering events within the σ band, a hole that is closer than $\hbar\omega_E$ to the top of the σ band cannot decay by the emission of an optical phonon, but a hole at a slightly larger binding energy can. More precisely, the phase space

for the electron-phonon scattering is given by the density of states in the σ band. For a two-dimensional (nearly) parabolic band, this density of states is well approximated by a step function. Hence, we can write the Eliashberg function as

$$\alpha^2 F^E(\epsilon_i, \omega) = \frac{\omega_E}{2} \lambda \delta(\omega - \omega_E) \Theta(\epsilon_i - \omega_E), \quad (3)$$

where λ is the electron-phonon coupling constant and Θ the Heaviside function. This corresponds to the standard model Eliashberg function for coupling to an Einstein mode but the mechanism is only permitted for $\epsilon_i > \omega_E$.

We test this model by using it to calculate the spectral function and compare it to the experimental data. This is illustrated in Fig. 3 for MLG on SiC at low temperature ($T = 100$ K). The phonon energy for an accurate description of the data can be directly read from the position of the kink to be $\hbar\omega_E \approx 190$ meV. Since the phonon for the intraband scattering needs to have a small wave vector,

this can be identified unambiguously as the E_{2g} optical mode also relevant for the scattering within the π band [8,21]. The only free parameters in the model are then λ , Σ_0'' , and those describing the parabolic bare band dispersion. From Σ_0'' , we obtain Σ' by a Kramers-Kronig transformation. The bare dispersion of the σ band is approximated by two parabolas (one parabola describing each branch).

For the comparison with the calculated spectral function, the measured data undergo a background subtraction and an intensity normalization (such that the measured geometry-induced difference in matrix elements between the $+k_{\parallel}$ and $-k_{\parallel}$ directions is averaged). The region $[-0.08 \leq k_{\parallel} \leq 0.08] \text{ \AA}^{-1}$ is excluded since the matrix elements are so small that the ARPES intensity approaches zero [18]. The simulated spectral function is convolved by experimental energy and momentum resolutions and normalized to the same intensity as the measurement. The agreement between measured and calculated spectral functions shown in Figs. 3(a) and 3(b) is quantified by the sum of the root-mean-square (rms) differences between the pixel values in the data and model. The parameters in the simulation (λ , Σ_0'' , and those describing the bare dispersion) are optimized until the lowest sum of rms differences is reached. Figure 3(c) shows that the difference between model and data is very small, at most a few percent. Figure 3(d) shows the sum of rms differences as a function of λ with all the other parameters optimized for each λ value. For the present case of MLG graphene on SiC, we find $\lambda = 0.96 \pm 0.04$.

The excellent agreement between the spectral function derived from our simple model and the data has several important implications: The observation of kinks is only possible if the density of states cutoff replaces the usual cutoff of the Fermi-Dirac function. This, in turn, implies that holes in the σ band are not filled by electrons from the (degenerate) π band, by electrons from the substrate (SiC, Ir), or from nearby atoms (O, Rb). This is not unexpected: In unperturbed graphene, there is no π - σ interaction and this should not change strongly in the presence of small lattice displacements. Scattering between the σ band and the substrate, or nearby atoms, is not expected to be strong either because the bonding to these is primarily mediated through the π electrons with little involvement of the σ band. The little importance of the substrate is supported further by the fact that the σ band kink is ubiquitous and of similar strength in several other graphene systems investigated here, as illustrated in Table I and already seen in Fig. 2. Indeed, the effect appears to be present independently of the substrate, decoupling by intercalation or electron doping. The coupling strength λ is only slightly smaller for BLG/SiC, indicating that interlayer interactions play a small role.

The values of λ reported in Table I are not only similar, they are also high on an absolute scale, in the same order of

FIG. 3 (color online). (a) ARPES data for the σ band of MLG graphene on SiC along the $\bar{K}$ - Γ - $\bar{K}$ direction and (b) model spectral function derived from Eqs. (2) and (3). The binding energy is shown relative to the σ band maximum ($E_{\sigma} \approx 3.5$ eV). The red parabolas depict the expected dispersion in a noninteracting model. (c) Difference between (a) and (b). (d) Sum of the root-mean-square difference of the pixels in (a) and (b) as a function of λ , optimizing all the other parameters in the model for each λ value. The photon energy of data acquisition was $\hbar\nu = 36$ eV and the temperature 100 K.

TABLE I. Results of the analysis carried out for different graphene systems. The electron-phonon coupling parameter λ and its uncertainty are quoted, together with the sample temperature (T) during acquisition of ARPES data.

System	$\lambda \pm \Delta\lambda$	T (K)
MLG/SiC	0.96 ± 0.04	100
MLG/SiC	0.97 ± 0.04	300
BLG/SiC	0.75 ± 0.05	100
Graphite	0.97 ± 0.04	100
MLG/Ir	0.97 ± 0.05	70
QFMLG/Ir	0.96 ± 0.04	70
QFMLG/Rb/Ir	0.96 ± 0.04	70

magnitude as for a strong coupling BCS superconductor [20]. This is in contrast to the π band where very small λ values have been found near E_F for the weakly p -doped case [22,23] and somewhat stronger coupling upon electron doping [8,16,17]. Note, however, that even though the density of states is zero both at the Dirac point and at the top of the σ band, its energy dependence is very different. It linearly increases for the π band but is a step function for the σ band. This step function is ultimately responsible for the observation of the kink because it instantaneously changes the coupling strength from zero to the high λ observed here. Energy-dependent changes of λ have been observed before [24], but in most (three-dimensional) systems, the changes in the density of states causing them are more gradual than here.

In conclusion, we have observed an electron-phonon coupling-induced kink near the top of the σ band of graphene. The kink is placed far away from the Fermi level and cannot be explained by the cutoff in the Fermi-Dirac function. Instead, its observation is ascribed to the quasi-instantaneous change in the density of states of the σ band. The electron-phonon coupling is found to be strong ($\lambda \approx 1$), and the kink is ubiquitous for graphene systems. Its presence suggests that the σ band is decoupled not only from the π states but also from the electronic states of the substrate. This is not unexpected but it also suggests that the strength of the observed kink can provide information of the interaction between graphene and its surroundings. The mechanism for the observed kink is neither limited to graphene nor to high binding energies. In fact, the only required ingredients are a pronounced change in the density of states combined with electron-boson coupling. The former is typically associated with band edges in (quasi-) two-dimensional systems. Therefore, similar band renormalizations could play a role in a variety of solids. They could even have an effect on transport properties and electronic instabilities when the band edges (almost) coincide with the Fermi energy. This is the case in several classes of materials, such as in iron pnictide superconductors [25,26], transition metal silicides [27], or transition metal dichalcogenites [28].

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