Anomalous Quasiparticle Lifetime in Graphite: Band Structure Effects

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We report *ab initio* calculations of quasiparticle lifetimes in graphite, as determined from the imaginary part of the self-energy operator within the *GW* approximation. The inverse lifetime in the energy range from 0.5 to 3.5 eV above the Fermi level presents significant deviations from the quadratic behavior *naively* expected from Fermi liquid theory. The deviations are explained in terms of the unique features of the band structure of this material. We also discuss the experimental results from different groups and make some predictions for future experiments.

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The Fermi liquid theory [1] (FLT) has been one of the most successful paradigms to describe the metallic state of condensed matter. According to it, the excitation spectrum in a metal can be understood in terms of the quasiparticle (QP) concept: Quasiparticles are in one-to-one correspondence with the one-electron excitations of a noninteracting Fermi system, but their properties are modified by the interactions. In a Fermi liquid, for energies very near the Fermi level, quasiparticles have a finite lifetime (τ), which is inversely proportional to the square of the excitation energy [1,2], i.e., $\tau \propto (E - E_F)^{-2}$. It is tempting to claim a breakdown of the paradigm when deviation from this behavior is found for a metallic system. Recent experiments by Xu and co-workers [3] on graphite have reported an anomalous behavior of the QP lifetime for $E - E_F$ in the range of 0.4 to 2 eV. These authors observed that $\tau \propto (E - E_F)^{-1}$. In this Letter, we argue that, when the band structure of graphite is taken into account to compute the QP lifetime within FLT, important deviations from $(E - E_F)^{-2}$ behavior are found in the experimentally accessible energy range. We have found the QP lifetime to be strongly dependent on the wave vector direction and that, when averaged over the first Brillouin zone (BZ), the energy dependence of τ cannot be fitted to a simple power law over the considered energy range, from 0.5 to 2.5 eV. All of these features find a simple explanation in terms of the dependence of the electron self-energy on the peculiarities of the band structure of graphite.

In the experiments carried out by Xu *et al.* the sample (in this case, highly oriented pyrolytic graphite, HOPG) is excited by a laser pulse and a second delayed pulse is used to probe the population of the excited states. Varying the delay time between the first (pump) and the second (probe) pulses provides a powerful, though still

poorly understood, spectroscopic technique known as two-photon photoemission (2PPE). Subsequent measurements by Ertel and co-workers [4], using very similar techniques, have partially confirmed these results. They found that $\tau \propto (E - E_F)^{-\alpha}$ with $\alpha \approx 1.2-1.3$ provided a better fit to their 2PPE data, for 0.2 eV $< E - E_F <$ 1.6 eV. It should also be pointed out that the absolute value of τ seems to depend on the method chosen to fit the 2PPE signal as well as the way in which the transport processes at the surface are accounted for [4]. However, in both experiments the deviation from the $(E - E_F)^{-2}$ dependence (found in many simple and noble metals [5–7]) seems clear.

Graphite is a layered semimetal. The coupling between layers (i.e., along the *c* direction) is much weaker than within the layers (i.e., in the *ab* plane), where strong bonds of covalent type keep the atoms arranged in a honeycomb lattice with two atoms per unit cell. This arrangement makes the valence and conduction π-like bands touch at the corners of the hexagonal first BZ. Interlayer coupling in an *ABAB*... stacking sequence, however, enhances this overlap and shifts the Fermi level, thus leading to the formation of electron and hole pockets responsible for the semimetallic character of graphite. González *et al.* [8] have put forward an explanation that relates the apparent linear dependence of the inverse QP lifetime to the structure of the degenerate π bands near E_F and the weak coupling between layers. These two factors result in a small density of states at E_F. As a consequence, the screening length in graphite is very large [8,9], a fact that strongly affects QP lifetimes. However, the theory developed by González and co-workers relies on a simplified model for the band structure of graphite, which assumes that the π bands disperse linearly with the wave vector parallel to

the *ab* plane ($\mathbf{k}_{||}$) up to an energy of $\approx \pm 3$ eV around E_F. Such a simplified band structure is obtained as a low-energy limit of a tight-binding fit of the π bands [10], and completely neglects interlayer hopping. Our and previous band-structure calculations, however, indicate that, along some $\mathbf{k}$ directions, the dispersion is strongly nonlinear already for $E - E_F \approx 1.5$ eV. Moreover, hopping between graphite layers, although smaller than intralayer hopping, is not negligible (≈ 0.25 eV) and leads to a splitting of the π bands at all energies.

Motivated by these findings and the experiments mentioned above, we have evaluated the QP lifetime accounting for the band structure of graphite [11]. The lifetime for a QP with wave vector $\mathbf{k}$ and band index n was obtained from the imaginary part of the electron self-energy $\Sigma(E)$ [5,12]:

$$\frac{1}{\tau_{n\mathbf{k}}} = -2\langle n\mathbf{k}|\mathrm{Im}\Sigma(E_{n\mathbf{k}})|n\mathbf{k}\rangle,$$

where we take the expectation value over the corresponding LDA orbital $|n\mathbf{k}\rangle$ and set $E = E_{n\mathbf{k}}$, the LDA eigenvalue. $\Sigma(E)$ was obtained within the *GW* approximation [13,14]. Since we are interested in a spectral property, namely the QP lifetime, and not the total energy, it is sufficient to stop at this level of approximation (first iteration in the *GW* scheme) [15–17]. Thus the screened electron-electron interaction can be calculated within the random phase approximation (RPA) [18] in terms of the dielectric matrix $\epsilon_{\mathbf{GG'}}(\mathbf{q}, \omega)$ [5,12]. Finally, since the 2PPE experiments can only probe the energy dependence in the relaxation time of the excitations generated by the pump pulse, we have averaged $\tau_{n\mathbf{k}}^{-1}$ over the states with energy $E = E_{n\mathbf{k}}$ to obtain an energy-dependent inverse lifetime $\tau^{-1}(E)$ [5].

The reason that the average QP lifetime cannot be fitted to a simple power law over the considered energy range is because of the smallness of τ^{-1} in the neighborhood of the M and L points of the first BZ, where the π bands exhibit a saddle poin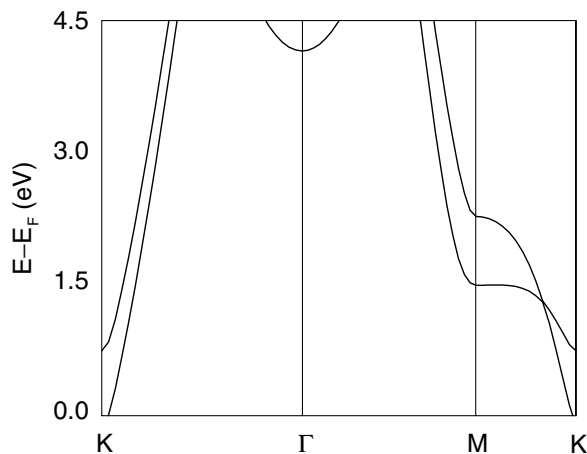t (see Fig. 1). This band topology forces a QP excited near these points to decay into a lower energy state by transferring a relatively large momentum ($\mathbf{q}_{||}$) parallel to the *ab* plane. On the other hand, the large screening length referred to above favors small $\mathbf{q}_{||}$ electron-electron scattering and, at the same time, the band structure below 1.5 eV leads to a small density of low energy excitations available at large momenta. This point is illustrated in quantitative detail by Fig. 2, where it can be seen that the spectral weight of the energy loss function in the low frequency region rapidly decreases with increasing $|\mathbf{q}_{||}|$. This feature is also present in $\mathrm{Im}\epsilon_{00}(\mathbf{q}, \omega)$ (not shown here for simplicity), which exhibits a similar structure, revealing that the low-energy excitations are indeed electron-hole pairs and not plasmons. Thus the main decay channel for QP's is provided by electron-hole pair creation and not by plasmon excitation as speculated in Ref. [3] (see, however, Refs. [8,19]). The coarseness of the grid used in our calculation precludes us from obtaining the lifetime below 0.5 eV where we expect other decay channels such as phonons or low-energy plasmons [20] to be very important as well.

In Fig. 3 our results for $\tau_{n\mathbf{k}}^{-1}$ are plotted vs the LDA energies, $E_{n\mathbf{k}}$, for several $\mathbf{k}$-directions: $K \to \Gamma$ and $M \to \Gamma$. Notice that the value of the QP lifetime depends strongly on $\mathbf{k}$. As discussed above, the unoccupied π bands possess a saddle point near M (cf. Fig. 1), where the QP lifetime increases dramatically. This explains the rapid drop of $\tau_{n\mathbf{k}}^{-1}$ along $M \to \Gamma$, for $E - E_F \approx 1.5$ eV. Above this energy, the states around M become available for a QP to decay and $\tau_{n\mathbf{k}}^{-1}$ becomes appreciable. As $E - E_F$ increases further, more bands come into play and thus the lifetime acquires two values near $E - E_F \approx 2.3$ eV, which correspond to states with similar energies but different band index n. The splitting of the lowest-energy bands along the $K \to \Gamma$ point also has the same effect. This splitting is due to the interlayer hopping, $t_\perp \approx 0.25$ eV, which lifts the degeneracy of the π bands near E_F.

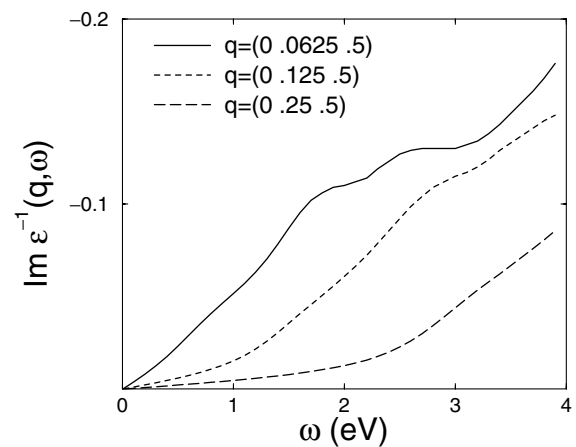FIG. 1. Graphite π-band structure near some relevant points M, Γ, and K in the energy range considered in this work.

FIG. 2. Energy loss function, $\mathrm{Im}\epsilon_{00}^{-1}(\mathbf{q}, \omega)$ vs frequency for different values of $\mathbf{q}$.

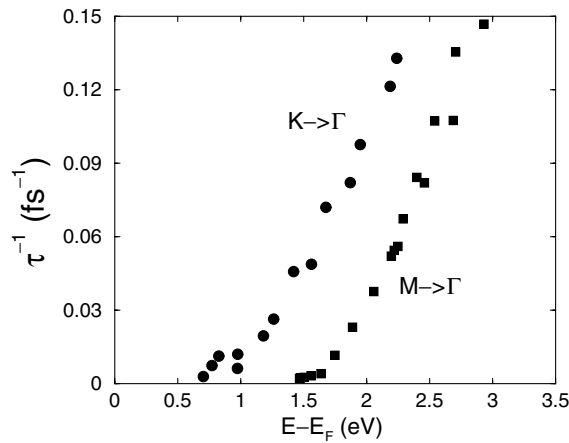

FIG. 3.   Inverse QP lifetime $\tau_{n\mathbf{k}}^{-1}$ vs LDA eigenvalues, for two representative directions $K \rightarrow \Gamma$ (circles) and $M \rightarrow \Gamma$ (squares).

As to the $K \rightarrow \Gamma$ direction, one can regard the behavior of $\tau_{n\mathbf{k}}^{-1}$ as controlled by two parameters: The excitation energy, $\epsilon = E - E_F \approx v_F |\mathbf{k}_{||}|$, where v_F is the Fermi velocity, and the interlayer hopping $t_\perp$. If we focus on the average behavior of the lifetime along this direction, given the small splitting of the bands, we can drop the band index n. Let $\tau^{-1}(\epsilon, t_\perp)$ be the QP inverse lifetime. On dimensional grounds, $\tau^{-1}(\epsilon, t_\perp) = g^2\epsilon f(t_\perp/\epsilon, g)$, where $g \propto e^2/v_F$ is the dimensionless constant "charge" that characterizes the strength of the electron-electron interaction [8,10] and $f(x, g)$ is a scaling function. If $t_\perp = 0$ then the model of Ref. [8] would apply for the QP states along $K \rightarrow \Gamma$. Therefore, $\tau^{-1} \sim g^2\epsilon$, which implies $f(0, g) =$ const. On the other hand, for $t_\perp$ finite the QP lifetime is given by Fermi liquid theory [10] so that $\tau^{-1} \sim g^2\epsilon^2$ as $\epsilon \rightarrow 0$, and therefore $f(x \gg 1, g) \sim 1/x$. This means that we can expect a *crossover* from a regime where τ^{-1} has an approximate linear behavior with ϵ to the quadratic behavior expected from FLT. The latter can be hardly seen in our results, which only extend down to $\epsilon \approx 0.5$ eV, but, since we rely on the QP picture of FLT for our calculations, it should be recovered sufficiently close to E_F. On the other hand, for ϵ well above $t_\perp$, we have approximately $\tau^{-1} \propto \epsilon$ along $K \rightarrow \Gamma$, as seen in Fig. 3. Thus our results for this direction agree qualitatively with the linear dependence found by Gonzalez *et al.* [8] on the assumption that $\epsilon \approx v_F|\mathbf{k}_{||}|$ but using a different approach.

Finally, in Fig. 4 we show the results for the inverse lifetime of all the $\mathbf{k}$ points considered and the resulting average, which shows three different regimes: τ^{-1} increases monotonically between 0.5 and 1.0 eV. From there and up to 1.5 eV, it remains approximately constant and even decreases due to the long QP lifetime found near M and L at $E - E_F \approx 1.5$ eV, which was explained above. Above 1.5 eV τ^{-1} increases rapidly and, as the energy increases, band structure effects should become less and less important. Also, for the sake of comparison we have plotted the experimental results reported in Ref. [3], and new experimental results of Moos *et al.* [21]. Note that nei-
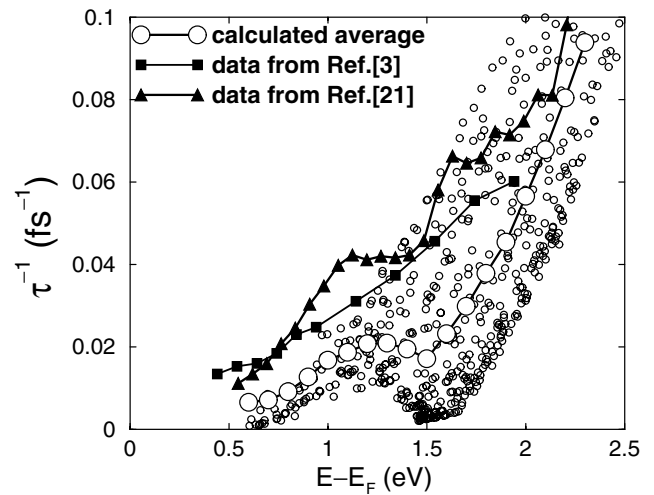

FIG. 4.   Average inverse QP lifetime $\tau^{-1}(E)$ vs QP energy E: present calculation (circles), experimental results from Ref. [3] (squares), and Ref. [21] (triangles).

ther the results in Ref. [3] nor in Ref. [4] show the dip around 1.5 eV that is predicted by our results but instead increase monotonically in the whole energy range. A word of caution is in order as the precise interpretation of what is measured in these experiments in terms of QP lifetime is far from clear [4,5,21]; results from different groups using very similar techniques and interpretations do not always coincide. The most recent and extensive results of Moos *et al.* [21] on pristine HOPG surfaces show a dip in τ^{-1} around 1.5 eV as predicted by the calculations reported here. Furthermore, they also observe a strong dependence on the sample preparation (e.g., disorder induced by defects), which might explain discrepancies with the results from other groups.

Examination of Fig. 4 shows that our calculated average lifetimes are longer than those of either experiment. Discrepancies between theory and experiment could, in principle result from the neglect of phonons, defects and other decay mechanisms, the neglect of photoemission matrix elements, and theoretical inaccuracies resulting from performing a single iteration in the GW approximation. The fact that we do not include phonons, defects and other decay mechanisms in this study, is consistent with the fact that our computed lifetimes are longer than the measured ones. On the other hand, calculations of photoemission matrix elements involving tight-binding wave functions and band energies (which we performed in the spirit of Ref. [22]) indicate that the inclusion of transition matrix elements does not alter the picture shown in Fig. 4. Furthermore, as previous calculations of electron lifetimes using the standard (first iteration scheme) GW approximation have produced excellent results for simple and noble metals [5,7], we expect the approach to have similar quantitative validity for graphite [17].

In conclusion, we have presented the results of a calculation of the lifetime τ, which takes into account the

band structure of graphite. We find important deviations from the $\tau \propto (E - E_F)^{-2}$ naively expected from Fermi liquid theory. The deviations, however, find a natural explanation given the peculiarities of the band structure of graphite. The saddle point near the M point leads to a very large τ (alternatively a very small τ^{-1}), whereas the linearly dispersing bands near along the $K \to \Gamma$ direction lead to $\tau \propto (E - E_F)^{-1}$ for energies well above the interlayer hopping ≈ 0.25 eV, in agreement with previous work [8]. Finally, when averaged over the Brillouin zone, we predict that $\tau^{-1}(E)$ cannot be fitted by a simple power law as it exhibits a dip near 1.5 eV. This behavior has been observed in recent experiments [21].

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