Anomalous Quasiparticle Lifetime and Strong Electron-Phonon Coupling in Graphite

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We have performed ultrahigh-resolution angle-resolved photoemission spectroscopy on high-quality single crystals of graphite to elucidate the character of low-energy excitations. We found evidence for a well-defined quasiparticle (QP) peak in the close vicinity of the Fermi level comparable to the nodal QP in high-T_c cuprates, together with the mass renormalization of the band at an extremely narrow momentum region around the $K(H)$ point. Analysis of the QP lifetime demonstrates the presence of strong electron-phonon coupling and linear energy dependence of the QP scattering rate indicative of a marked deviation from the conventional Fermi-liquid theory.

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It is generally accepted that Landau's Fermi-liquid theory [1] gives an excellent description on the electronic interactions near the Fermi surface (FS) of metals. In the language of Fermi liquid, one-particle excitations modified by the Coulomb interaction among the electrons characterize the low-energy excitation properties. These excitations are called quasiparticles (QPs) and have one-to-one correspondence with the noninteracting electrons. The QP scattering rate $1/\tau$ in a 3D Fermi liquid shows a quadratic dependence ($1/\tau \propto \omega^2$) on the QP energy $\omega = E - E_F$, where τ and E_F are the QP lifetime and the Fermi energy, respectively, and this describes the character of electron-electron (e-e) scattering in the vicinity of E_F in conventional 3D metals. On the other hand, the applicability of Fermi-liquid theory in lower-dimensional systems with a periodic potential is still a subject of intensive debate. There have been long discussions on high-T_c cuprates whether the normal-state QP behaves as a Fermi liquid or not, but it has been recognized that the electron correlation, the magnetic scattering, and the pseudogap opening complicate the QP lifetime [2,3]. In this regard, to investigate the QP dynamics in graphite is promising, since it is free from these complications so that QP features in a more ideal 2D case can be effectively extracted. So far, the QP lifetime in graphite has been intensively studied by ultrafast time-resolved photoemission spectroscopy (TRPES) [4,5], which probes the QP lifetime in the *unoccupied* side by observing the relaxation of *photoelectrons* excited above E_F lower than the vacuum level. The $1/\tau$ value estimated from TRPES shows a linear ω dependence [4,5] and a characteristic anomaly at 1–1.5 eV [5,6], showing a substantial deviation from the ω^2 behavior, sparking intensive debates on its explanation [4–7].

Angle-resolved photoemission spectroscopy (ARPES) is a strong experimental technique to elucidate the scattering process of electrons in solids. It can be regarded as a counterpart of TRPES since it proves the QP lifetime in the *occupied* side by observing the decay of *photoholes* created by photoexcitation. The unique capability to resolve momentum further supplies the k dependence of the QP lifetime. Recent observation of mass renormalization in the band dispersion near E_F, the so-called dispersion kink in high-T_c cuprates [8] and metal surfaces [9,10], together with the discovery of superconductivity in Ca(Yb)-intercalated graphite [11,12] reminds us of the importance to clarify the role of electron-mode coupling responsible for the anomalous physical properties. Hence, the elucidation of low-energy one-particle properties in graphite by high-resolution ARPES is indispensable for establishing the nature of QP dynamics in the 2D limit.

In this Letter, we report high-resolution ARPES results on kish graphite (artificial single crystal graphite). We found that the spectral peak of the π band around the $K(H)$ point sharpens up dramatically at a binding energy below 0.2 eV, indicative of a strong electron-phonon (e-ph) coupling. The linear energy dependence of the QP scattering rate at higher energies provides evidence for the deviation from the conventional Fermi-liquid theory. By use of thermal excitation of electrons at high temperatures, we determine the QP lifetime of the antibonding π^* band above E_F. We compare these results with previous TRPES experiments and theoretical calculations and discuss these implications in terms of the e-e scattering, the e-ph coupling, and the electron-plasmon interaction.

ARPES measurement of high-quality kish graphite was performed using a VG-SCIENTA SES-2002 spectrometer with a high-flux discharge lamp and a toroidal grating monochromator. We used the He I α (21.218 eV) resonance line to excite photoelectrons. The energy and angular resolutions were set at 4–10 meV and 0.2°, respectively. Crystals were cleaved *in situ* in an ultrahigh vacuum of 2×10^{-11} Torr to obtain a clean surface.

Figure 1(a) shows the ARPES spectra of kish graphite near E_F measured at 7 K along a cut which includes the $K(H)$ point [the red line at the $K(H)$ point in the inset in Fig. 1(c)]. To obtain ARPES spectra around the $K(H)$ point, we at first tilted the sample along the ΓK direction by 54.5° with respect to the analyzer and then measured the

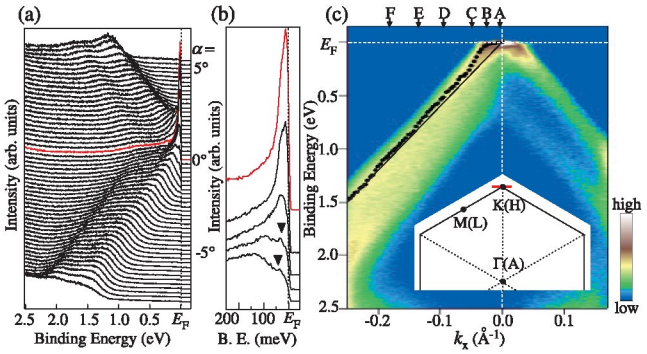

FIG. 1 (color). (a) ARPES spectra of kish graphite measured at 7 K along a cut which includes the $K(H)$ point [red line at the $K(H)$ point in the inset in (c)]. A red curve shows the spectrum at $\alpha = 0°$. (b) Expansion of the ARPES spectra near E_F around $\alpha = 0°$. (c) ARPES intensity plot of (a) as a function of the wave vector and binding energy. The peak position of the upper π band determined by fitting the EDC is shown by dots. We assume linear dispersion of the bare band (solid line).

ARPES spectra along the cut perpendicular to the ΓK direction by simultaneous collection of photoelectrons with a finite angular range ($\Delta\alpha \sim 13°$), where α is the emission angle with respect to the sample-to-analyzer direction. Figure 1(b) shows the expansion of ARPES spectra in the vicinity of E_F around the $K(H)$ point. Figure 1(c) shows the intensity plot as a function of the wave vector and binding energy. We clearly identify in Fig. 1(a) a couple of holelike bonding π bands separated by 0.6 eV, which disperse toward E_F with approaching $\alpha = 0°$. The splitting of π bands is consistent with the previous ARPES reports [13,14] and is created by the AB stacking sequence of kish graphite [15–17]. We also find that the upper π band appears to cross E_F, creating an extremely small hole pocket at the $K(H)$ point. An anomalously sharp QP peak appears in the upper π band at a narrow angle region centered at $\alpha = 0°$, while the peak becomes significantly broad and does not show prominent energy dependence when the position of the peak exceeds $\sim$0.2 eV. As indicated by triangles in Fig. 1(b), we also find a tiny peak slightly away from $\alpha = 0°$ in the close vicinity of E_F, which shows remarkable resemblance to the spectral line shape of the surface band near E_F in a Be surface [9]. The marked sharpening of the spectral line shape as well as the appearance of an additional peak indicates that electrons are coupled to certain collective excitations. It is noted that the observed QP peak in graphite is as sharp as the QP peak along the nodal cut in hole-doped high-T_c cuprates at the superconducting state [18]. Both cases can be explained by the presence of similar electronic states at low temperature [19]; in graphite, the extremely small FS limits the phase space available for the scattering, while in the d-wave superconductors, the scattering among point nodes causes a similar effect and reduces the scattering rate dramatically.

To elucidate quantitatively the character of low-energy excitations, we fit energy distribution curves (EDCs) by two peaks corresponding to the upper and lower π bands. We simulate an ARPES spectrum by two weakly asymmetric Lorentzian peaks together with a broad background multiplied by the Fermi-Dirac distribution (FD) function at 7 K, and they are convoluted with a Gaussian having an energy width of instrumental resolution (4 meV). Figure 2 shows the result of fitting for representative k points as denoted by arrows A–E in Fig. 1(c). It is evident that the calculated spectral functions (blue curve) reproduce satisfactorily the experimental data (red open circles) in the whole energy region up to 2.5 eV. To clarify the QP scattering rate $1/\tau$, we plot in the inset in Fig. 2 the imaginary part of the electron self-energy $\mathrm{Im}\Sigma(\omega)$, obtained by plotting the half width at half maximum of the peak at the upper π band. Interestingly, we find an almost linear behavior of $\mathrm{Im}\Sigma(\omega)$ at $\omega > 0.18$ eV, in remarkable similarity with the nodal QP scattering rate in high-T_c cuprates [2,3]. $\mathrm{Im}\Sigma(\omega)$ shows a sudden drop below 0.18 eV, in accordance with the sharpening of the QP peak in Fig. 1(a). This sudden drop has not been clearly observed in previous TRPES experiments [5–7], possibly

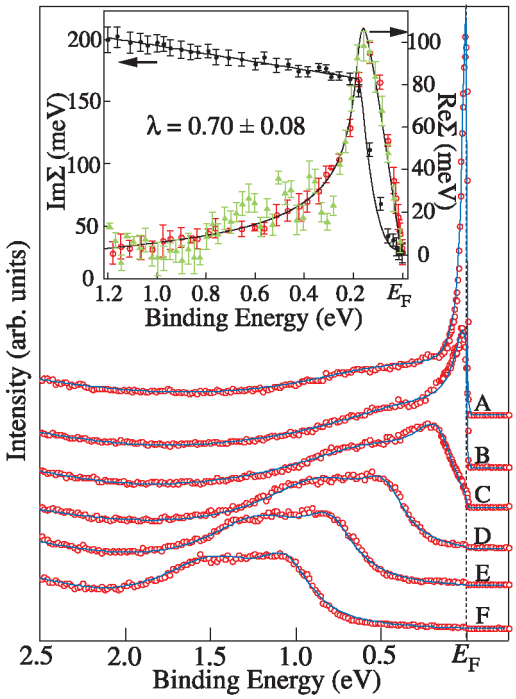

FIG. 2 (color). ARPES spectra of kish graphite measured at representative k points shown by arrows in Fig. 1(c). The result of fitting is shown by blue curves. The inset shows the real and imaginary parts of self-energy $\mathrm{Re}\Sigma(\omega)$ (black circles) and $\mathrm{Im}\Sigma(\omega)$ (red circles), for the upper π band, determined from the dispersion of the EDC peak and its width, respectively. $\mathrm{Re}\Sigma(\omega)$ obtained by a Kramers-Kronig transformation of $\mathrm{Im}\Sigma(\omega)$ is also shown by green triangles. The solid lines show the result of fitting by the 3D Debye model. Note that to apply the fitting of momentum distribution curves is difficult around the $K(H)$ point because of the close momentum separation of the bands.

because of insufficient energy resolution. The sudden drop in $\mathrm{Im}\Sigma(\omega)$ is caused by the coupling between electrons and a collective mode. In the inset in Fig. 2, we also plot the real part of the self-energy $\mathrm{Re}\Sigma(\omega)$ which represents the energy deviation from the dispersion of noninteracting bare band. We defined $\mathrm{Re}\Sigma(\omega)$ as the energy difference between the obtained peak position of EDC and the linear bare band that passes two points at E_F and 1.5 eV in the experimental dispersion [see Fig. 1(c)]. As indicated by red circles in the inset in Fig. 2, $\mathrm{Re}\Sigma(\omega)$ shows a distinct enhancement at the binding energy of 0.16 eV, which indicates the mass renormalization of band. The energy position of the peak maximum in $\mathrm{Re}\Sigma(\omega)$ is close to the energy position of the sudden drop in $\mathrm{Im}\Sigma(\omega)$. We also obtained $\mathrm{Re}\Sigma(\omega)$ by Kramers-Kronig transformation of $\mathrm{Im}\Sigma(\omega)$ (green triangles) and found a reasonable agreement with $\mathrm{Re}\Sigma(\omega)$ determined from the fitting of EDC, demonstrating that the appearance of QP and the renormalization of the band are directly connected to each other. To elucidate the character of the mode quantitatively, we apply the Debye model to reproduce the obtained self-energy, on an assumption of a linear scattering rate higher than the Debye energy ω_D to account for the energy dependence of $\mathrm{Im}\Sigma(\omega)$. The bulk 3D model with $\omega_D = 0.175$ eV and the coupling constant $\lambda = 0.70 \pm 0.08$, and also the 2D model with the same ω_D value and $\lambda = 1.0 \pm 0.1$, well reproduce the experimentally obtained self-energy. The estimated ω_D is similar to the known Debye energy in graphite ($\omega_D =$ 0.2 eV) [20], suggesting that electrons are strongly coupled to phonons. It is remarked here that a proper calculation would involve the actual phonon dispersion into the Eliashberg coupling function $\alpha^2F(\omega)$, but even the oversimplified analysis by using the Debye model reasonably reproduces the obtained self-energy.

We note here that it is possible to attribute the sharp QP peak to the electronlike antibonding π^* band but not the upper π band, since the theoretical band calculations [15–17] have predicted that the top of the π band and the bottom of the π^* band are quite close and actually overlap around the $K(H)$ point. Hence, the π^* band may complicate the ARPES line shape and may also affect the QP scattering rate. In order to examine this possibility, we measured ARPES spectra at 260 K to observe the electronic states above E_F. The result after removing the effect of the FD function is shown in Fig. 3(a). In addition to the peak which originates in the holelike π band, we find another sharp peak above E_F having an electronlike dispersion. This above-E_F band is attributed to the π^* band, and, to our surprise, it is separated from the top of the π band by 25 meV at $\alpha = 0°$. This is unexpected, since the previous theoretical calculations have predicted the point overlap of these bands at a fixed k_z value [15–17]. The observation of band splitting suggests that the interlayer hopping is considerably large in the actual graphite surface. Since the π^* band is well separable at high temperatures, it is possible to evaluate the QP scattering rate by considering both the π and the π^* bands. In Fig. 3(b), we

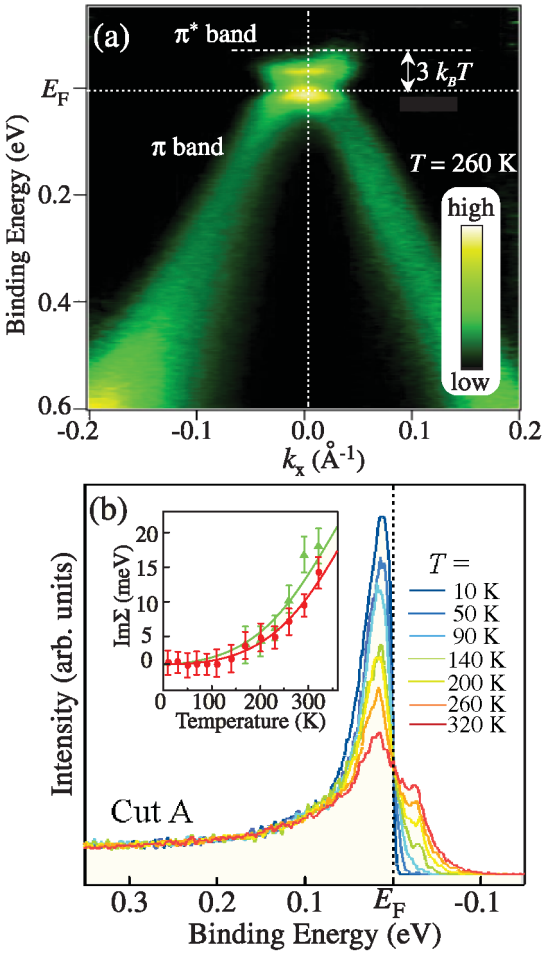

FIG. 3 (color). (a) ARPES intensity plot as a function of wave vector and binding energy measured at 260 K divided by the FD function convoluted with the Gaussian with the instrumental resolution (4 meV). (b) Temperature dependence of ARPES spectra measured at cut A in Fig. 1(c). The inset shows the temperature dependence of $\mathrm{Im}\Sigma(\omega)$ for the below-E_F peak (red circles) and the above-E_F peak (green triangles) after subtracting the impurity term (20 and 5 meV, for the π and π^* bands, respectively). The solid lines show the result of fitting by the Debye model.

plot the temperature dependence of ARPES spectrum at the $K(H)$ point. The above-E_F peak is observed at $T >$ 140 K owing to the thermal excitation up to 3–$5k_BT$ so that the energy width of the peak can be estimated by taking into account two peaks corresponding to the π and π^* bands. The estimated $\mathrm{Im}\Sigma(\omega)$ values as a function of temperature for the π band (red circles) and the π^* band (green triangles) are plotted in the inset in Fig. 3(b). $\mathrm{Im}\Sigma(\omega)$ for both bands shows a monotonic increase with heating the sample. The observed temperature dependence of $\mathrm{Im}\Sigma(\omega)$ is reasonably reproduced by the 3D Debye model (solid curves) with the same ω_D and λ values as in Fig. 2.

We now discuss the origin of the QP peak and dispersion kink in Figs. 1 and 2 in more detail. The coupling of electrons with the low-energy plasmons characteristic of layered graphite, as seen in tunneling [21] and electron-

energy loss spectroscopy [22] experiments, would be unlikely to account for the sudden drop in $\mathrm{Im}\Sigma(\omega)$ at 0.18 eV, since the experimentally determined plasmon energy (30–125 meV) is much smaller. On the other hand, the estimated ω_D value (0.175 eV) is similar to the highest phonon energy at 0.2 eV determined from the tunneling [21] and the Raman scattering [23] experiments. According to the theoretical calculation of phonon dispersion [22], the highest branch is attributed to the longitudinal optical (LO) phonon, which is essentially nondispersive at 0.2 eV around the zone center. The acoustic shear (SH) phonon also produces a pronounced density of states (DOS) at 0.18 eV. We think that the sudden drop in $\mathrm{Im}\Sigma(\omega)$ could be explained by the coupling of electrons with the SH phonon and/or the LO phonon. The obtained coupling constant ($\lambda = 0.7$–1.1) is classified into the strong-coupling regime and is also consistent with the observation of the fine modulation structure in the tunneling DOS [21] and the electric specific heat coefficient γ as twice high as that of the band calculation [17]. It is also inferred that unexpectedly large λ and high ω_D values in pristine graphite should be taken into account in microscopic theories to explain the origin of superconductivity in graphite-intercalation compounds.

Next, we discuss the ω dependence of the QP lifetime, in relation to the previous TRPES and theoretical studies. The absolute value of $\mathrm{Im}\Sigma(\omega)$ at $\omega = 0.5$ eV is about 175 meV in the present ARPES experiment (see Fig. 2), which corresponds to $1/\tau = 0.27$ fs^{-1}. This value is much larger than the value obtained from the TRPES measurement (0.01 fs^{-1}) [5], indicating a considerably shorter QP lifetime in ARPES. This would be possibly because of the broadening of ARPES spectra due to finite energy and momentum resolutions and k_z dispersion and/or the high surface-sensitive nature of ARPES measurement with the He Iα resonance line, where the QP lifetime is much influenced by the surface disorder/defects. Nevertheless, the energy dependence of the QP lifetime higher than 0.18 eV can be directly compared between two experiments because the effect of the e-ph coupling and the impurity scattering can be excluded, since both give the constant offset to $\mathrm{Im}\Sigma(\omega)$ at $\omega > 0.18$ eV. As seen from Fig. 2, $\mathrm{Im}\Sigma(\omega)$ shows a fairly linear behavior up to 1.2 eV [24] without any anomalies, suggesting a small contribution from the saddle point of DOS which would alter the ω dependence of $1/\tau$ by reflecting the shape of DOS near the saddle point [5]. We think that this DOS effect in $1/\tau$, if it exists, was not observed in the ARPES experiment since the saddle point of the π band along the ΓM direction is located at 2 eV, much higher than the present energy scale. We have estimated the damping rate of $1/\tau$ from the slope of the straight line in the $\mathrm{Im}\Sigma(\omega)$ plot to be 0.048 ± 0.012 fs^{-1} eV^{-1}, which is similar to the value estimated from the TRPES measurement (0.03–0.05 fs^{-1} eV^{-1}) [4,7], implying that the particle-hole symmetry essentially holds in the scattering process on a graphite surface. As for the origin of ω-linear behavior, it has been theoretically suggested that both the plasmon excitation [25] and the electron-hole pair creation based on the e-e scattering picture [6,7] can give a linearlike behavior in $1/\tau$. Although we do not have convincing proof to distinguish the two possibilities, a similar damping parameter between the present ARPES and the theory based on the e-e scattering (0.049 fs^{-1} eV^{-1}) [7], rather than the plasmon excitation scenario (0.026–0.029 fs^{-1} eV^{-1}) [4], would favor the e-e scattering picture.

In summary, we reported high-resolution ARPES results on single crystal graphite. We found a QP peak together with the mass renormalization of band in the vicinity of E_F and an unconventional ω-linear dependence of the QP lifetime. We concluded that low-energy excitations lower than 0.18 eV are dominated by phonons, while those for higher energies are characterized by the electron-hole pair creation. Comparison of the scattering rate with previous TRPES experiments suggests that the ω dependence of the scattering rate is essentially symmetric between the particle and the hole side in the graphite.

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