Anomalous electronic states in graphite studied by angle-resolved photoemission spectroscopy

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Abstract

We report high-resolution angle-resolved photoemission spectroscopy (ARPES) on high quality single crystal of graphite (kish graphite) to elucidate the origin of anomalous physical properties of carbon-based materials. We found an almost flat band in the vicinity of the Fermi level around the K(H) point which is not predicted by the bulk band calculation. We discuss the origin of this anomalous structure in relation to the edge-localized state on the step edges of cleaved surface.

Keywords: Edge-localized state; Angle-resolved photoemission spectroscopy; Graphite

1. Introduction

Graphite-based materials have attracted much attention since they show various interesting physical properties such as superconductivity, metal–insulator transition, and anomalous magnetism. These interesting properties strongly owe to the dimensionality, size, and geometry of a graphite sheet (graphene). Superconductivity with relatively high transition temperature \((T_c = 11.5 \text{ K})\) recently observed in Ca-intercalated graphite [1] suggests a possibility to achieve higher \(T_c\)'s in graphite intercalation compounds and related materials. It has been suggested from the tight-binding calculations [2–6] that the electronic structure near the Fermi level \((E_F)\) of graphite ribbons contains anomalous feature in the vicinity of \(E_F\) which is not expected from the bulk band calculation of graphite. This feature is ascribed to the edge-localized state, and recently observed experimentally by scanning tunneling spectroscopy (STS)/microscope (STM) measurements of graphite [7,8]. To better understand the nature of anomalous properties on carbon-based materials, it is very important to elucidate the basic electronic structure such as the band structure and the Fermi surface (FS) of graphite itself which is essential in understanding the electronic structure of carbon-based materials. Angle-resolved photoemission spectroscopy (ARPES) has a unique capability to determine the momentum \((k)\)-resolved electronic structure. However, the \(k\)-resolved fine electronic structure of graphite in the vicinity of \(E_F\) has not been reported because of the limitation of the crystal quality and the insufficient energy and momentum resolutions of previous ARPES experiments.

In the paper, we report high-resolution ARPES results on high-quality kish graphite. We found that valence band structure along high symmetry directions is fully consistent with the bulk band calculation, while the band structure near \(E_F\) contains anomalous feature which is not predicted by the bulk band calculation. This feature shows small but finite dispersion around 0.1 eV, and is observed only around the K(H) point of the Brillouin zone. Origin of this feature is discussed in relation to theoretical calculations and STM/STS studies.

2. Experiment

ARPES measurements have been performed on kish graphite which is the artificially grown single-crystalline
graphite produced during purification of iron at high temperatures [9]. The high single-crystallinity of kish graphite used in this study was confirmed by the sharp six-fold X-ray Laue diffraction pattern. We used a GAMMADATA-SCIENTA SES-2002 spectrometer with a high-flux discharge lamp and a toroidal grating monochromator at Tohoku University, with the He I \( \alpha \) (\( h\nu = 21.218 \text{ eV} \)) and He IIz (40.814 eV) resonance lines. The energy and angular resolutions were set at 4–10 meV and 0.2°, respectively. Clean surfaces for the ARPES measurement have been obtained by cleaving sample in situ in the ultrahigh vacuum of \( 2 \times 10^{-11} \text{ Torr} \). The Fermi level (\( E_F \)) of samples was referred to that of a gold film evaporated onto the sample substrate.

3. Valence band structure of graphite

Fig. 1 shows valence band ARPES spectra of kish graphite measured at 20 K along: (a) \( \Gamma KM \) (AHL) and (b) \( \Gamma M \) (AL) directions with the He IIz resonance line. We clearly find highly dispersive bands along both directions. For example, along the \( \Gamma KM \) (AHL) direction (Fig. 1(a)), one band has the top of dispersion at the \( \Gamma \) point at 4 eV and disperses toward the higher binding energy on approaching the K(H) point. This band has the bottom at about 12 eV at the K(H) point and then disperses back toward the lower binding energy on approaching the M(L) point. We also find another prominent peak located at about 8 eV at the \( \Gamma \) point. This band rapidly approaches \( E_F \) on moving toward the K(H) point, and the spectrum shows a clear Fermi-edge cutoff indicative of a tiny hole pocket centered at the K(H) point. On the other hand, along the \( \Gamma M \) (AL) direction (Fig. 1(b)), the band does not cross \( E_F \) but stays at 2 eV around the M(L) point, indicative of the absence of FS along this direction. All these features are consistent with previous ARPES results [10,11]. It is also noted that we are able to observe separately the electronic structure along the \( \Gamma KM \) (AHL) and \( \Gamma M \) (AL) directions due to the single-crystal nature of kish graphite, which is not possible on the highly oriented pyrolytic graphite (HOPG) samples. This suggests that to perform the ARPES of high-quality single crystal is essential in establishing the intrinsic electronic structure of graphite.

In order to see more clearly the dispersive features in ARPES spectra, we have mapped out the band structure and show the result in Fig. 2. The experimental band structure was obtained by taking the second derivative of ARPES spectra and plotting the intensity by gradual shading as a function of wave vector and binding energy. Dark areas correspond to experimental bands. Fig. 2 also shows the first-principle band calculation of graphite [12] using JD (Johnson and Dresselhaus) model [13] with AB stacking sequence. It is clear that the experimental band structure and the bulk band calculation show a good agreement along both directions. However, we also note several quantitative differences. For example, the \( \sigma \) band due to the C2\( p \) bonding states is located at about 4 eV at the \( \Gamma \) point in both the experiment and the calculation, while the dispersive feature from the \( \Gamma \) point to the K(H) point shows a quantitative deviation. The lower-lying branch of the \( \sigma \) band (\( \sigma_2 \) band) along the \( \Gamma KM \) direction is located at slightly higher binding energy in the experiment than in the calculation. Similar trend is also seen along the \( \Gamma M \) (AL) direction. The \( \pi \) band is located at a slightly higher binding energy in the experiment than in the calculation at the \( \Gamma \) point, while both perfectly coincide with each other near \( E_F \) at the K(H) point in the energy scale of Fig. 1(b). The finite deviation of the energy position of bands between the experiment and the

![Fig. 1. ARPES spectra of kish graphite at 20 K measured along (a) \( \Gamma KM \) (AHL) and (b) \( \Gamma M \) (AL) directions using He IIz resonance line.](image-url)
calculation may be due to many-body effects and/or final-state effects as reported by previous ARPES works on graphite surface [14,15].

4. Anomalous structure in the vicinity of $E_F$

We found an anomalous feature in the vicinity of $E_F$. Fig. 3(a) shows ARPES spectra measured at 150 K along the cut slightly away from the K(H) point in the first Brillouin zone as shown in the inset, with the He I$z$ resonance line. At first, we find the broad peak located at 0.5 eV around $k_x = 0.1 \text{Å}^{-1}$. This band, which is assigned as a $\pi$ band, gradually moves toward $E_F$, forming a sharp peak at 80 meV around $k_x = 0.0 \text{Å}^{-1}$ and disperses back again toward higher binding energy showing a hole-like dispersion. It is noted that this $\pi$ band does not cross or touch $E_F$ at this momentum region, since the measurement was done outside of the hole pocket. In addition to the $\pi$ band, we clearly find an anomalous feature (band) at about 130 meV around $k_x = 0.0 \text{Å}^{-1}$. This band is almost flat at $k_x = 0.0 - 0.05 \text{Å}^{-1}$ while it shows a small but finite dispersion toward $E_F$ at $k_x = 0.0 - 0.10 \text{Å}^{-1}$. This anomalous band is not clearly observed at momentum area above $k_x = 0.05 \text{Å}^{-1}$, showing an asymmetric intensity distribution. This asymmetric behavior might be due to the matrix-element in the photoelectron exciting process since the polarization of incident light is different between the two cases. It is noted that the intensity of the bulk $\pi$ band shows a smooth variation as a function of momentum, whereas that of anomalous feature shows relatively strong variation, suggesting that these two features may suffer different matrix-element effect. We speculate that anomalous feature may have somewhat different final-state electronic structure, although detailed photon-energy dependent measurement is necessary to elucidate this point. In order to elucidate the origin of this anomalous feature near $E_F$, we have plotted in Fig. 3(b) the ARPES spectral intensity as a function of binding energy and wave vector, together with the projected bulk $\pi$ band onto the (001) plane [16]. As clearly seen in Fig. 3(b), the projected bulk band calculation shows a good agreement with the hole-like $\pi$ band in the experiment, while the anomalous feature is located outside the projected bulk bands. We will discuss this point later in detail.

Fig. 4 shows the ARPES spectral intensity at 150 K as a function of wave vector and binding energy measured at several cuts around the K(H) point as shown in the inset, with the He I$z$ resonance line. ARPES data at cut D is the same as Fig. 3(b), and the cut C corresponds to the momentum cut which crosses the K(H) point. At cut A which is located at slightly away from the K(H) point in the second Brillouin zone, we observe only the $\pi$ band and do not clearly find the anomalous feature. At cut B, which is at the opposite side of cut D with respect to the K(H) point, we clearly identify the anomalous feature at about 0.1 eV. This feature is seen in the right-hand side in contrast to the one at cut D (left-hand side). This certainly suggests that intensity variation of the anomalous feature is essentially symmetric with respect to the K(H) point, suggesting the intrinsic nature of the anomalous feature. As we move further away toward the $I(A)$ point (cut E), we do not find anomalous feature as in the case of cut A. All these experimental results indicate that the anomalous feature appears only at the narrow momentum region around the K(H) point.

We now discuss the origin of the anomalous feature near $E_F$. One of the possibility may be the finite band dispersion along the momentum perpendicular to the graphite layers ($k_z$). As clearly seen in Fig. 3(b), the anomalous feature is located outside the projected bulk bands. Therefore, the dispersion along $k_z$ of the $\pi$ band is not responsible for the anomalous feature. In addition, the anti-bonding
electron-like $\pi^*$ band may not be the origin of the anomalous feature since the $\pi^*$ band is located at well above $E_F$. Another possibility is the angle-integrated-type background caused by the indirect transition, characteristic of the ARPES measurement. However, this background would not show any dispersion so that the finite dispersion of the anomalous feature as seen in Figs. 3 and 4 is inconsistent with this interpretation. The coupling of electrons with a certain bosonic mode as observed in cuprate superconductors [17,18] cannot explain this observation. Because, the band produced by such mode should follow or mimic the original hole-like $\pi$ band [18]

Fig. 3. (a) ARPES spectra at 150 K in the close vicinity of $E_F$ around K(H) point measured at the momentum cut shown in the inset, with the He I$\alpha$ resonance line. Filled circles show the energy position of anomalous feature; (b) experimental band structure near $E_F$ around the K(H) point (bright areas) obtained by plotting the ARPES-spectral intensity as a function of binding energy and wave vector, compared with the projection of calculated $\pi$ band onto the (001) plane (shaded areas) [16]. Black dotted line shows the peak position of a weakly dispersive band near $E_F$ indicated by filled circles on the spectra in (a).

Fig. 4. ARPES intensity plots near $E_F$ as a function of wave vector and binding energy measured along several cuts (A–E) in the Brillouin zone shown in the inset. ARPES spectra were measured at 150 K with the He I$\alpha$ resonance line.
with a considerable renormalization of the bandwidth near $E_F$. However, the observed anomalous band shows the electron-like character in contrast to the hole-like $\pi$ band. Most possible explanation to explain the anomalous feature is the edge-localized state predicted from the calculation for the zigzag edges of graphite ribbons [2–6]. According to the recent calculation, the zigzag edges of graphite ribbons show the characteristic band which is not predicted in the bulk band calculation. It shows an almost flat band below $E_F$ and exists only around the K point [19], which is in good agreement with the present ARPES result. In fact, recent STS/STM studies reported the existence of zigzag steps and resultant edge-localized states on graphite surface [7,8]. The energy position of this state in STS is about 50–100 meV below $E_F$, which is consistent with the present ARPES result. It has been also revealed that the zigzag step affects the electronic structure substantially away from the step since the edge-localized state is observed on the flat surface about 35 Å away from the step [8]. This long-distant effect of the zigzag step may enable the observation of the edge-localized states by ARPES which probes the electronic structure averaged over a wide area of the surface. The small energy dispersion observed in the present ARPES measurement is not reconciled with the localized nature of the states, and needs further theoretical and experimental studies.

5. Conclusion

We reported ultrahigh-resolution ARPES on kish graphite. We have determined the electronic band structure and found anomalous structure in the close vicinity of $E_F$ around the K(H) point. This is not predicted by the bulk band calculation and cannot be explained in terms of the anti-bonding $\pi^*$ band, $k_z$ dispersion, angle-integrated-type background, and coupling of electrons to a bosonic mode. We have concluded that the origin of this anomalous feature is the edge-localized states characteristic of the stepped surfaces.

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