

# Proposal of Partial- $k$ Method for Interpreting the Angle-Integrated Photoelectron Spectrum: A Comparison between First-Principles Calculation and Experiments for Graphite

Shin-ichiro Tanaka<sup>1\*</sup>, Yusaku Takano<sup>2</sup>, Makoto Okusawa<sup>2</sup>, and Kazuhiko Mase<sup>3</sup>

<sup>1</sup>ISIR, Osaka University, Ibaraki 567-0047, Japan

<sup>2</sup>Faculty of Education, Gunma University, Maebashi 371-8510, Japan

<sup>3</sup>Photon Factory, Tsukuba 305-0801, Japan

## 1 Introduction

There are several kinds of apparatuses for analyzing the energy of the photoelectron, and they are categorized into two: the angle-resolved type and the angle-integrated type. The angle-resolved type is superior to the angle-integrated type for a detailed investigation of the valence bands in a crystalline solid because it directly gives information about the band dispersion. For practical usage, however, the angle-integrated type has some advantages; e.g., it is easier to use, the instrumentation requires a lower cost, and it has a greater efficiency (higher count rates). Thus, it is worth investigating what information can be derived from the photoelectron spectrum using an angle-integrated-type electron analyzer.

In the interpretation of the photoelectron spectrum obtained using the angle-integrated type analyzer, a comparison to a calculated density of states (DOS) is often made. However, this introduces some questions regarding the crystals. Even in the angle-integrated type analyzer, the electron entrance angle is usually limited, and thus, the parallel momentum of the electron ( $k_{\parallel}$ ),

whose absolute value is obtained as  $k_{\parallel} = \sqrt{\frac{2m_e E_k}{\hbar^2}} \sin \theta$ ,

where  $m_e$ ,  $E_k$  and  $\theta$  are the mass, the kinetic energy and the emission angle, respectively, of the photoelectron) is limited. Therefore, in order to make a correct comparison, the DOS of the entire  $k$ -space is inappropriate; rather, it seems necessary to perform a calculation of the DOS of the electron that can be detected by the angle-integrated-type analyzer. However, to the best of our knowledge, quantitative calculations to deduce this quantity (hereafter denoted as the partial- $k$  density of states) have not been reported. In the present study[1], we perform first-principles calculations to derive this property for graphite and make a comparison with the experimental results for highly oriented pyrolytic graphite (HOPG).

## 2 Experiment

All experiments were performed in an ultrahigh vacuum chamber at beamline 11D, photon factory, KEK at Tsukuba. The experimental chamber is equipped with a homemade apparatus comprising a coaxially installed double-pass cylindrical mirror analyzer (DCMA) and symmetric mirror analyzer (ASMA), which was originally constructed for electron-electron coincidence spectroscopy. A HOPG sample were cleaved in the air and

cleaned by heating at approximately 1200 K and below  $5 \times 10^{-7}$  Pa.

## 3 Calculation method

The electronic structure of graphite was calculated using a first principles pseudo-potential method within the local density approximation. We used code from the Osaka2k package developed by K. Shirai[2]. In the present condition, the DCMA (ASMA) detects only the electrons whose values of  $k_{\parallel}$  are in the range of

$$\sqrt{\frac{2m_e E_k}{\hbar^2}} \sin 33.7^\circ \quad \text{to} \quad \sqrt{\frac{2m_e E_k}{\hbar^2}} \sin 40.7^\circ \quad (\text{from} \\ \sqrt{\frac{2m_e E_k}{\hbar^2}} \sin 51.0^\circ \quad \text{to} \quad \sqrt{\frac{2m_e E_k}{\hbar^2}} \sin 60.9^\circ),$$

where the emission angle is from the surface normal. These areas, which can be transferred into the first Brillouin zone owing to the translational symmetry, occupy a completely different subspace between the two analyzers. We took all of the  $k$ -points along the  $k_z$  line for which the  $k_{\parallel}$  values satisfied the condition of the detection. The collected sets of the detectable energy-levels were integrated after Gaussian broadening of 0.1 eV to achieve the partial- $k$  DOS.

## 4 Results and Discussion

Figures 1 and 2 show a comparison between the experimental spectra and calculations for the partial- $k$  DOS along with the area of the  $k_{\parallel}$ -space for the DCMA and ASMA for binding energy of 10 eV. The electron of the binding energy near the Fermi level is located only near the K(H) point, and the electron of the binding energy near the valance-band bottom is only near the  $\Gamma$ (A) point. Thus, the partial- $k$  DOS has significantly large intensities at these binding energies when the involved  $k$ -space in the Brillouin zone covers these points. The experimental results are fairly well represented by the calculated partial- $k$  DOS, except for approximately 20% expansion in the binding energy. The discrepancy of the local density approximation (LDA) calculation with the angle-resolved photoelectron spectra is attributed to missing self-energy corrections in the LDA. All of the spectra that we obtained at photon energies in the range of 65 to 180 eV agreed fairly well with the calculated partial- $k$ -space DOS.

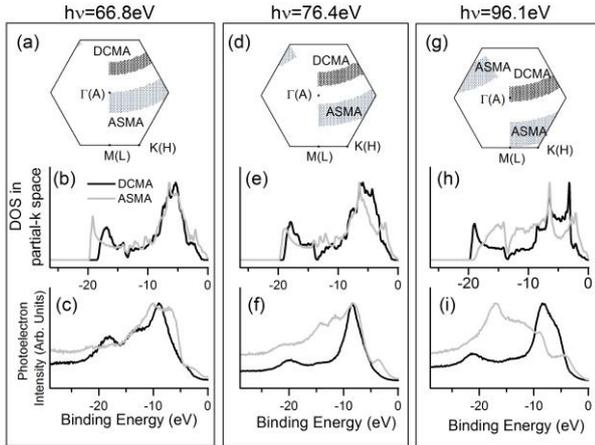


Fig. 1. Comparisons of the DOS in partial- $k$  space and photoelectron spectrum at photon energies of 66.8 ((a)–(c)), 76.4 ((d)–(f)), and 96.1 eV ((g)–(i)). In the upper parts ((a), (d) and (g)), the partial- $k$  spaces in two dimensions that are detectable with the DCMA (black dots) and ASMA (grey dots) at the binding energy of 10 eV are shown. In the middle parts ((b), (e) and (h)) and the bottom parts ((c), (f) and (i)), the calculated partial- $k$  DOS and the photoelectron spectra obtained with DCMA (black lines) and ASMA (grey lines), respectively, are shown. The intensities of the partial- $k$  DOS and the photoelectron spectra are normalized to their maximal intensities for each graph [1].

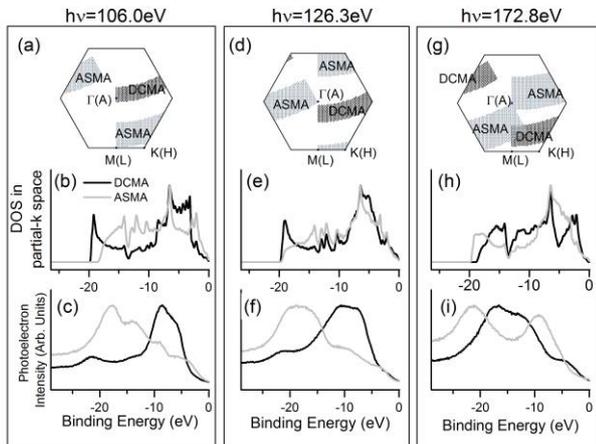


Fig. 2. Similar to Fig. 1, but the photon energies are 106.0 eV ((a), (b), and (c)), 123.6 eV ((d), (e), and (f)), and 172.8 eV ((g), (h), and (i)) [1].

This demonstrates the validity of the partial- $k$  DOS for angle-integrated photoelectron spectroscopy. The difference between the partial- $k$  DOS and the conventional total- $k$  DOS increases a) as the relative size of the partial  $k$ -space decreases with respect to the size of the Brillouin zone and b) as the band dispersion of the material increases. The area size of the partial- $k$  space is larger when the electron kinetic energy is larger. Thus, the partial- $k$  DOS method is more appropriate in photoelectron spectroscopy using lower photon energies (e.g., ultraviolet photoelectron spectroscopy, UPS) than that using higher photon energies (e.g., X-ray photoelectron spectroscopy, XPS), as the relative size of the relevant  $k$ -space is smaller in the former case than the latter case. Moreover, crystals with a smaller unit cell have a larger Brillouin zone, and consequently, the partial- $k$  DOS method is more valid for crystals with a smaller unit cell. Thus, graphite is one of the most suitable materials for demonstrating the validity of the partial- $k$  DOS method.

It should be noted that the peak intensity in the experimental spectra is significantly different from that for the calculated partial- $k$  DOS, even though it reproduces well the peak positions in the experimental spectra (Figs. 1 and 2). The discrepancy may be ascribed to the contribution of the transition probabilities

$$\frac{2\pi}{\hbar} \sum \left| \left\langle f, k' \left| \frac{e}{2mc} \mathbf{A} \cdot \hat{\mathbf{p}} \right| i, k \right\rangle \right|^2 \delta(E_{f, k'} - E_{i, k} - hv)$$

from the initial states to the final state according to Fermi's golden rule. The matrix elements that reflect the dipole-selection rule are involved in calculating the photoelectron intensity; only the excitations that have a surface-normal dipole moment are allowed in the present experimental condition that the incidence angle of the photon is  $84^\circ$ . When the excitation photon energy is changed, the final state of the photoexcitation process changes through the final-state energy. In the present case, only the initial state of the photoexcitation is considered; thus, it is difficult to precisely predict the photoelectron intensity. However, the peak energy positions can be fairly well predicted because the final states are structureless plane waves of free electrons. Calculations of the transition probabilities demand a more detailed analysis.

## References

- [1] S. Tanaka *et al.*, J. Phys. Soc. Jpn., 83, 084705 (2014)  
Figures are permitted to reproduce by the Physical Society of Japan.
  - [2] The source code is available from the following site  
[<http://www.cmp.sanken.osaka-u.ac.jp/~koun/osaka.html>].
- \* stanaka@sanken.osaka-u.ac.jp