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Tight-binding parameters of graphite determined with angle-resolved photoemission spectra

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ABSTRACT

An exfoliated Kish graphite sample on a heavily *n*-doped Si substrate covered with native oxide was prepared with a conventional micromechanical cleavage method. From angle-resolved photoemission spectra (ARPES), we measured the band structure of graphite over photon energies from 28 eV to 116 eV. The inner potential V_0 = 17.25 eV is determined with a period from the band dispersion in the *KH* direction. A set of parameters in the tight-binding method and the SWMcC model for graphite is extracted from the fitted results. A comparison of constant-energy mapping results at large binding energy indicates the reliability of the tight-binding parameters extracted from the ARPES results.

1. Introduction

Graphite comprises weakly coupled layers of carbon atoms with a honeycomb structure in two-dimensional sheets. Graphite is a semi-metal because the charge carriers occupy small regions along the edges of the Brillouin zone. For an understanding of the electronic structure of graphite, the tight-binding approach provides direct insight into the interactions between individual carbon atoms. Wallace proposed the first tight-binding model for graphite [1]; soon after, the band structure of graphite was calculated with perturbation methods by Slonzewski and Weiss, and McClure [2,3]. Seven parameters that define the interaction energy of various carbon atoms in graphite lattices were introduced and are referred to as the SWMcC model [4–6]. This model described successfully the band structure of graphite; its seven parameters were evaluated in many experiments, such as the de Haas–van Alphen effect [7–9], SdH oscillation [10–12], infrared spectra [13–16], transport properties [17], high-field magnetoreflectance [18] and angle-resolved photoemission spectra [19,20]. In that SWMcC model, the content of the trigonal warping effect indicated by the value of γ_3 is insensitive to the shape of the Fermi surface, but in many experiments the parameters of the SWMcC model are extracted from the behavior of electron and hole carriers at the Fermi surface, which creates an uncertainty of the determined γ_3 value. In contrast, the trigonal warping effect can affect strongly the shape of contours of constant energy in the region of large binding energy. Angle-resolved photoemission spectra (ARPES) provide a general tool to probe the band structure of solids. In this work, we recorded, at high resolution, ARPES of Kish graphite on a heavily *n*-doped Si substrate over an energy range 28–116 eV. The parameters of the SWMcC model are extracted from the band mapping results. With the tight-binding method we simulated the constant mapping contours in satisfactory agreement with experimental results.

2. Methods

With a conventional micromechanical cleavage method we prepared exfoliated Kish graphite samples on a heavily *n*-doped Si substrate covered with native oxide. Because the spot size of the synchrotron beam can be larger than the size of exfoliated graphite, the advantage of a heavily *n*-doped Si substrate is the presence of a thin native oxide layer that insures negligible charging effects during ARPES measurements and provides a featureless background below 4 eV of the Fermi level. The preparation of an exfoliated Kish sample *ex situ* involved annealing at 500 °C in a UHV environment for 12 h before ARPES measurements. The ARPES experiment

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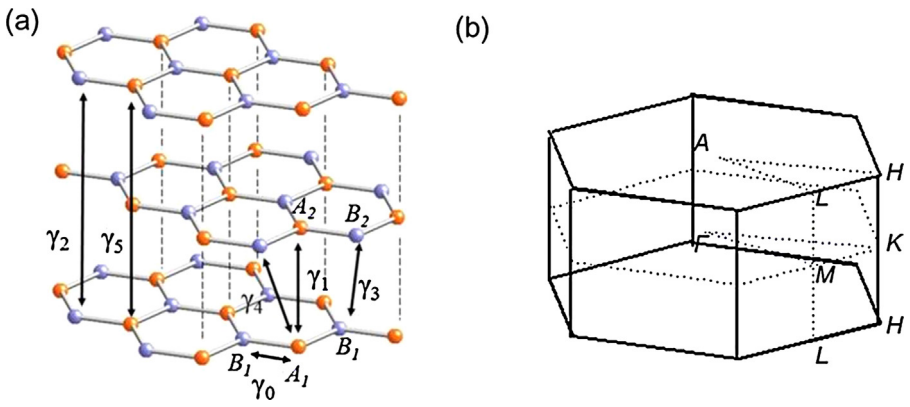

Fig. 1. (a) Crystal structure of graphite; the correspondence denotes the relation between the interactions of individual carbon atoms and the tight-binding parameters γ_i. (b) The Brillouin zone of graphite with the high symmetry points.

was performed at National Synchrotron Radiation Research Center (NSRRC) in Taiwan at beamline BL21B1. The photoemission spectra were collected in an UHV chamber equipped with a hemispherical analyzer (Scienta R4000) at 45 K and base pressure 5×10^{-11} Torr. The total energy resolution is better than 30 meV; the angular resolution is 0.2° over the entire range of photon energy.

3. Tight-binding calculations of graphite

The form of graphite comprises many coupled graphene sheets with Bernal or AB stacking order. A graphene sheet comprises carbon atoms in two sets in a single layer with a honeycomb structure. Two carbon atoms with atoms of basis A and B form a hexagonal structure with a periodic unit cell. A Bernal stacking order has two coupled graphene layers with inequivalent sites A_1 and B_1 on the lower sheets and A_2 and B_2 on the upper sheets. Fig. 1(a) displays the crystal structure of graphite; lattice vectors are described as $\vec{a}_1 = a_0(1/2, \sqrt{3}/2, 0)$, $\vec{a}_2 = a_0(-1/2, \sqrt{3}/2, 0)$ and $\vec{a}_3 = (0, 0, 2c_0)$ in which $a_0 = 2.46$ Å is the lattice parameter and $c_0 = 3.35$ Å is the distance between two adjacent graphene sheets. To understand the electronic structure of graphite, the tight-binding method gives direct insight to sketch its energy band. The tight-binding Hamiltonian of graphite is expressed as [20,21].

$$H\left(\vec{k}\right) = \begin{pmatrix} E_0 + \Delta + \gamma_5(\Gamma^2 - 2) & \gamma_0 f(\vec{k}) & \gamma_1 \Gamma & \gamma_4 \Gamma f^*\left(\vec{k}\right) \\ \gamma_0 f^*(\vec{k}) & E_0 + \gamma_2(\Gamma^2 - 2) & \gamma_4 \Gamma f^*\left(\vec{k}\right) & \gamma_3 \Gamma f(\vec{k}) \\ \gamma_1 \Gamma & \gamma_4 \Gamma f(\vec{k}) & E_0 + \Delta + \gamma_5(\Gamma^2 - 2) & \gamma_0 f^*(\vec{k}) \\ \gamma_4 \Gamma f(\vec{k}) & \gamma_3 \Gamma f^*(\vec{k}) & \gamma_0 f\left(\vec{k}\right) & E_0 + \gamma_2(\Gamma^2 - 2) \end{pmatrix}$$

in which the tight-binding hopping parameters γ_0, γ_1, γ_2, γ_3, γ_4, γ_5, Δ are described in Fig. 1(b); $f\left(\vec{k}\right) = \exp(ik_x a_0/2\sqrt{3}) + 2\exp(-ik_x a_0/2\sqrt{3})\cos(k_y/2)$ for $\vec{k} = (k_x, k_y)$; $\Gamma = 2\cos(k_z c_0)$. The SWMcC model provides a treatment of the electron energy band near the Fermi level of graphite according to the $(k \cdot p)$ method based on the crystal symmetry. Parameters $\left(\gamma'_0, \gamma'_1, \gamma'_2, \gamma'_3, \gamma'_4, \gamma'_5, \Delta'\right)$ in the SWMcC model can correspond to the tight-binding hopping parameters individually [4,21]. In this work, the band structure of graphite along ΓKM (AHL) direction was measured over an energy range 28–116 eV by using ARPES. The band dispersion of graphite around the K point for each incident photon energy was sketched correctly from the fitted results of energy distribution curves (EDCs) and momentum distribution curves (MDCs) in photoemission intensity mapping results. To find the tight-binding hopping parameters in graphite, the inner potential V_0 in ARPES results was determined from the period of band dispersion for two π bands in KHK direction. Then the band structure of graphite sketched with the tight-binding method was compared with the band structure determined from the ARPES results at photon energies 49.91 eV and 84.08 eV to extract a set of tight-binding parameters. The band dispersion at other photon energies and the constant energy mapping results simulated with the extracted parameters were compared with ARPES result to examine the precision of fitted results. The parameters in this SWMcC model are obtained from the correspondence relation between the two methods. Fig. 2(a) shows the band structure of graphite in plane along ΓKM directions. We used reported SWMcC parameters [4] $E'_0 = -0.024$ eV, $\gamma'_0 = 3.16$ eV, $\gamma'_1 = 0.39$ eV, $\gamma'_2 = -0.02$ eV, $\gamma'_3 = 0.315$ eV, $\gamma'_4 = 0.044$ eV, $\gamma'_5 = 0.038$ eV, $\Delta = -0.008$ eV in our calculations. The results are consistent with previous calculations [5,20]. Fig. 2(b) is an enlarged plot of Fig. 2(a) near the K point. Two touching points along the ΓKM direction are shown in Fig. 2(b): one is located in the $K\Gamma$ direction and another at the K point. Around the K point, there are four touching points between the valence and conduction bands. Three touching points are located at 0°, 120° and 240° deviating from the $K\Gamma$ line; a fourth point is located at the K point. A clear trigonal warping effect is visible in the contours of constant energy at the K point. Fig. 2(c) displays the simulated result of band dispersion along the KH direction. The π bands are most separated at the K point, but almost merge at the H point. Fig. 2(d) and (e) shows the simulated constant energy contours in plane at H ($k_z = 0.47$ Å^{-1}) and K ($k_z = 0$ Å^{-1}), respectively. Each contour separated by 0.1 eV is plotted from 0.1 eV to 0.7 eV in both pictures. A strong trigonal warping effect at the K point is visible. Because the trigonal warping effect is strongly affected by the value of γ_3, a larger $\gamma_3 = 0.443$ eV suggested recently from the de Haas–van Alphen effect implies that there exists a trigonal warping effect stronger than that proposed by preceding authors [9]. Fig. 2(f) shows contours of constant energy at 0.1, 0.5, 1.0 and 1.5 eV at the K point simulated with two proposed parameters of the SWMcC model; the set of parameters in solid blue lines is currently used in Fig. 2(a), and another contour set labeled with solid red lines uses the recently reported parameters

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