

Absorption spectra of trilayer rhombohedral graphite

Chi-Lang Lu, Hong-Chang Lin, and Chi-Chuan Hwang^{a)}

Department of Engineering Science, National Cheng Kung University, 701 Tainan, Taiwan

Jei Wang and Min-Fa Lin

Department of Physics, National Cheng Kung University, 701 Tainan, Taiwan

Cheng-Peng Chang

Center for General Education, Tainan University of Technology, 710 Tainan, Taiwan

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Absorption spectra of trilayer rhombohedral graphite are studied with the tight-binding model. The interlayer interactions cause a tiny energy gap and band-edge states in electronic structures. The band-edge states exhibit logarithmic divergences and discontinuities in the density of states. The frequencies of the absorption peaks correspond to the vertical transition energies of the band-edge states. Optical spectra of trilayer simple hexagonal and orthorhombic graphites are also investigated. The stacking effects on the density of states and absorption spectra are presented and discussed in detail. © 2006 American Institute of Physics. [DOI: 10.1063/1.2396898]

Graphite, a prototypical layered material, has been the subject of many experimental and theoretical studies for more than a century. The graphite sheets, which are composed of hexagonal carbon rings, are characterized by the strong intralayer sp^2 bonding and the weak interlayer π bonding. Three different stacking modes of graphite layers include simple hexagonal, orthorhombic, and rhombohedral systems (AA-, AB-, and ABC-stacked graphites).^{1–6} They would determine the low energy properties, including carrier density,^{1–4} optical properties,^{7–9} and many other physical properties. Nanographite ribbon^{10,11} is a stripe of graphite sheet, while multiribbon^{12,13} is a stack of graphite stripes. The edge effects,^{12,13} the number of ribbons,^{12,13} and the stacking sequence^{12,13} all play important roles in electronic properties,¹² optical properties,¹³ and magnetic properties¹⁴ of nanographite ribbons. The edge effects have been observed by scanning tunneling microscopy,^{15–17} scanning tunneling spectroscopy,^{16,17} and Raman spectra.¹⁸ Few-layer graphite^{19–21} (FLG) is a stack of graphite sheets with thickness less than 50 nm.¹⁹ FLG is a semimetal in which tiny overlaps between the conduction bands and the valence bands occur near the Fermi level. The fractional quantum Hall effect and the Berry phase of FLG were measured by Novoselov *et al.*²⁰ and Zhang *et al.*²¹ Magnetic properties,²² quantum Hall effect,^{22,23} phonon spectra,¹³ electronic properties,²⁴ and optical excitations²⁵ have been studied extensively by using the theoretical approaches.

This study focuses on the low energy manifested by the π electrons and uses tight-binding model to calculate the absorption spectra of the trilayer ABC-stacked graphite. To compare the three stacking modes, we discuss the density of states (DOS) and absorption spectra of three types of trilayer graphites.

The trilayer ABC-stacked graphite is formed by the alternating stacking of three graphite sheets,¹ as shown in Fig. 1. The hexagonal rings in each layer have a displacement b (C–C bond length) relative to the hexagons in the neighboring layers. Therefore, along the z direction, atoms in different layers alternate in a mosaic line. Thus, atoms A_1 (A_2) and B_2

(B_3) have the same projections. The projections of atoms B_1 (B_2) correspond to the center of the hexagonal rings in layer 2 (layer 3). The hopping integrals, as shown in Fig. 1, are the intralayer and interlayer transfer integrals. And the values of β_i (Ref. 3) are 3.16, 0.36, -0.02 , 0.32, -0.03 , and 0.013 eV. Note that the subscript $i=0-5$.³ Each unit cell contains six atoms. Hence, the Hamiltonian matrix is a 6×6 matrix composed of nine 2×2 matrices, i.e.,

$$H = \begin{pmatrix} H_1 & H_{12} & H_{13} \\ H_{12}^* & H_2 & H_{23} \\ H_{13}^* & H_{23}^* & H_3 \end{pmatrix}, \quad (1)$$

where the index denotes the layer number. Here, the diagonal matrices

$$H_1 = H_2 = H_3 = \begin{pmatrix} 0 & \beta_0 f(\mathbf{k}) \\ \beta_0 f^*(\mathbf{k}) & 0 \end{pmatrix} \quad (2)$$

express the intralayer elements, where $f(\mathbf{k}) = e^{ik_y b} + 2e^{-ik_y b/2} \cos(k_x \sqrt{3}b/2)$. The off-diagonal matrices

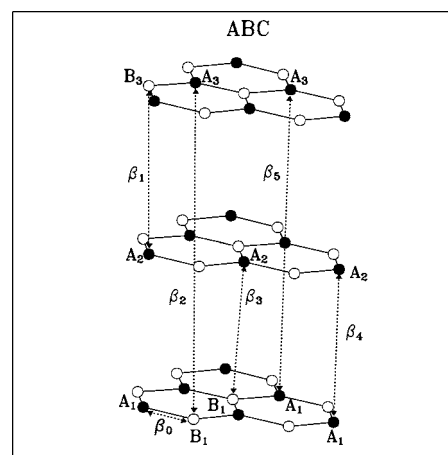


FIG. 1. Geometric structure of trilayer ABC-stacked graphite, parameter β_i is the hopping integral, A_j (B_j) is carbon atom, and index j indicates layer number.

^{a)}Electronic mail: chchwang@mail.ncku.edu.tw

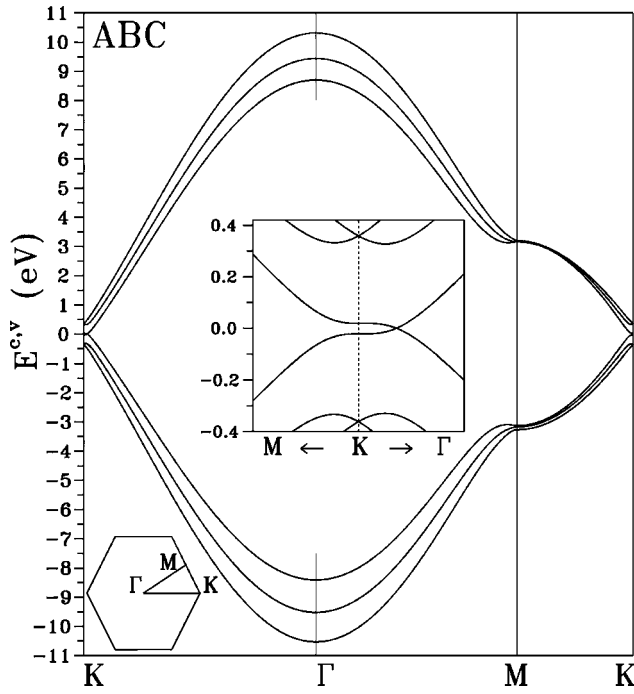


FIG. 2. Energy dispersions of the trilayer ABC-stacked graphite for three symmetric points, K , Γ , and M , in the hexagonal first Brillouin zone. Inset shows the detailed energy structures near the Fermi energy.

$$H_{12} = H_{23} = \begin{pmatrix} \beta_4 f^*(\mathbf{k}) & \beta_1 \\ \beta_3 f(\mathbf{k}) & \beta_4 f^*(\mathbf{k}) \end{pmatrix} \quad (3)$$

are the interlayer elements between layer 1 and layer 2, and between layer 2 and layer 3. The matrix

$$H_{13} = \begin{pmatrix} \beta_5 f(\mathbf{k}) & \beta_5 f^*(\mathbf{k}) \\ \beta_2 & \beta_5 f(\mathbf{k}) \end{pmatrix} \quad (4)$$

is an element between layer 1 and layer 3.

The Hamiltonian equation $H|\Psi(\mathbf{k})\rangle = E(\mathbf{k})|\Psi(\mathbf{k})\rangle$, where $|\Psi(\mathbf{k})\rangle$ is the wave function and $E(\mathbf{k})$ is the energy dispersions. Energy dispersions along the symmetric points K (zone corner), Γ (zone center), and M (zone edge) in the hexagonal first Brillouin zone (inset) are shown in Fig. 2. Previous work²⁴ shows that if we turn off the interlayer interactions, energy dispersions would be the same as those of a monolayer graphite. The interlayer interactions do not destroy the isotropic energy dispersions along k_x and k_y , while they cause asymmetry between occupied and unoccupied energy bands. At the Γ point, energy bands then turn into six states and the energy bandwidth becomes 20.84 eV, i.e., greater than the 15.59 eV bandwidth of a graphite sheet. At the M point, the effects of the interlayer interactions make saddle point structures distribute over 3.13–3.2 eV in conduction bands and –3.26 to –3.09 eV in valence bands. These also cause band-edge states at 3.13 eV (local minimum), 3.18 eV (local minimum), and –3.09 eV (local maximum) along the $M\Gamma$ line. At low energy, the interlayer interaction would make the linear bands curve, causing two intersections at ± 0.36 eV ($\pm\beta_1$; the interlayer interaction between neighboring layers). And the two localized bands will have an energy spacing of 0.04 eV ($2\beta_2$; the interlayer interaction between layer 1 and layer 3) and a tiny energy gap in the $K\Gamma$ line. The trilayer ABC-stacked graphite is therefore a narrow-gap semiconductor.

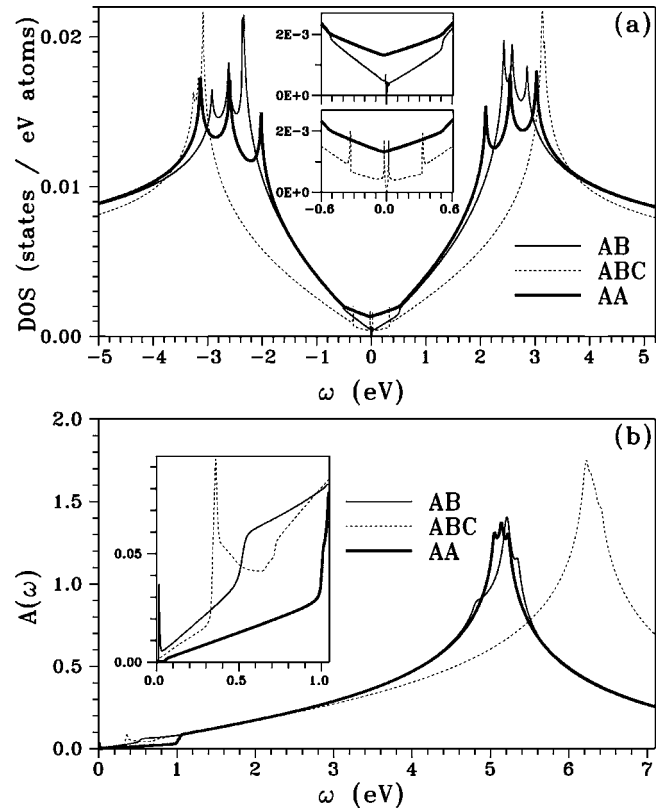


FIG. 3. (a) Density of states and (b) absorption spectra of the ABC-, AB-, and AA-stacked graphites.

The DOS is defined as

$$D(\omega) = \frac{2}{\pi} \sum_{h=c,v} \int_{1st \text{ BZ}} \frac{d^2\mathbf{k}}{(2\pi)^2} \frac{\Gamma}{(E^h(\mathbf{k}) - \omega)^2 + \Gamma^2}, \quad (5)$$

where $h=c,v$ represents the unoccupied or occupied states. The DOS provides a useful meaning to understand the essential physical properties of graphite. The broadening energy width Γ is set as $2.6 \text{ meV} = 8 \times 10^{-4} \beta_0$ ($7 \times 10^{-3} \beta_1$). The special structures in the DOS, namely, logarithmic divergences and square-root divergences, directly reflect the main features of the energy dispersions. In Fig. 3(a), the thin dotted line represents the DOS of the ABC-stacked graphite. The DOS has logarithmic peaks between 3.13 to 3.2 eV and –3.26 to –3.09 eV, which correspond to the separated saddle points near the M point. Low curvature bands near ± 0.36 eV presented as one-dimensional (1D)-like concave-upward (concave-downward) parabolic bands lead to square-root divergences. The logarithmic divergences at ± 0.02 eV correspond to the effect of β_2 . The zero DOS on the Fermi energy indicates that it is a semiconductor.

The optical absorption function of FLG is obtained from

$$A(\omega) \propto \sum_{h,h',J,J'} \int_{1st \text{ BZ}} \frac{d^2\mathbf{k}}{(2\pi)^2} \left| \langle \Psi^{h'}(\mathbf{k},J') | \frac{\hat{\mathbf{E}} \cdot \mathbf{p}}{m_e} | \Psi^h(\mathbf{k},J) \rangle \right|^2 \times \text{Im} \left[\frac{f(E^{h'}(\mathbf{k},J')) - f(E^h(\mathbf{k},J))}{E^{h'}(\mathbf{k},J') - E^h(\mathbf{k},J) - \omega - i\Gamma} \right], \quad (6)$$

where $f(E^h(\mathbf{k},J))$ is the Fermi-Dirac distribution function. The indices $J=\pm 1, \pm 2, \dots$ are set for subbands away from E_F , and $\pm$ indicates unoccupied π^* or occupied π states. Electrons in the presence of an electromagnetic field with

$\hat{E}_x \parallel \hat{x}$ ($\hat{E}_y \parallel \hat{y}$) are excited from occupied π states to unoccupied π^* states. At $T=0$, only interband excitation occurs. The excitation energy is $\omega_{ex}=E^c(\mathbf{k})-E^v(\mathbf{k})$. The photon's momentum is almost zero, and hence the selection rule of optical absorption is vertical transition, $\Delta\mathbf{k}=0$.

In Fig. 3(b), the thin dotted line indicates the absorption spectra of the ABC-stacked graphite. In the frequency region of 6.21–6.46 eV, absorption peaks exhibit several different structures. The absorption peak at $\omega=6.21$ eV comes from the vertical transition between the local minimum of subband $J=1$ and the local maximum of subband $J=-1$. At frequency of 6.28 eV, a shoulder structure is formed, corresponding to the transition between the saddle points of subbands $J=1$ and $J=-1$ on the $M\Gamma$ line. A 6.46 eV shoulder structure is produced, equal to the transition between the saddle points of subbands $J=3$ and $J=-3$ at the M point. The characteristic peak, at frequency $2\beta_0$, is due to the transition between the local minimum of subband $J=1$ and saddle point of subband $J=-2$. At low energy, vertical transitions between the localized subbands $J=\pm 1$ at the K point induce a small structure at frequency of 0.04 eV. The transition between the saddle points of subbands $J=2$ and $J=-1$ ($J=-2$ and $J=1$) results in the absorption peak at 0.36 eV. Two gibbous structures are evident at 0.67 and 0.72 eV, respectively. The former structure arises as a result of the transition between the local minima of subbands $J=2$ and $J=-2$. The second structure is the result of a transition between the intersections of subbands $J=2, 3$ and $J=-2, -3$ at the K point.

To compare the three stacking modes (three kinds of the interlayer interactions) of the trilayer graphite, we focus on band structures around the M (around $\pm\beta_0$ of stacking mode) and the K points (low energy). In the AA-stacked graphite, six nondegenerate saddle points are at the M point around ± 2.569 eV. However, in the AB-stacked graphite, one of the six nondegenerate saddle points has been slightly changed away from the M point. In the ABC-stacked graphite, three saddle points have been changed by the interlayer interactions. Thus, β_3 and β_5 of the AB and ABC modes directly reflect the changes in distributions of the logarithmic DOS peaks around $\pm\beta_0$ and absorption peaks near $2\beta_0$. Due to the changes in the interlayer interactions, the three absorption peaks in the AA-stacked graphite are replaced by one shoulder and two peaks in the AB-stacked graphite. Moreover, in the ABC-stacked mode, the absorption peaks have been turned into one peak and two shoulder structures. The low frequency DOS and absorption spectra cohere with the energy structures near the K point, which are affected by the interlayer interactions β_1 and β_2 . In the AA-stacked graphite, the interlayer interactions have turned energy bands into three separated monolayerlike band structures. Three linear bands have band overlaps and generate free carriers. Band-overlap states above the Fermi level are free holes' states while the others are free electrons' states. The DOS valley structures correspond to the free carriers. A finite value at $\omega=0$ means that the AA-stacked graphite is a semimetal [inset in Fig. 3(a)]. In the AB and ABC modes, the interlayer interactions β_1 and β_2 curve linear bands as well as create band-edge states and energy gap. These states exhibit shoulders, peaks, and zero DOS at $\omega=0$ [insets in Fig. 3(a)]. The low curvature parabolic bands in the ABC-stacked graphite exhibit 1D-like square-root divergences [lower inset in Fig. 3(a)]. In the AB-stacked graphite, the transition between two saddle points generates one absorption peak at frequency of

0.02 eV. The shoulder structure is similar to that of the ABC mode, which results from transition between the local minimum (maximum) of subband $J=2$ ($J=-2$) and that of subband $J=-1$ ($J=1$).

This study examines the absorption spectra of the ABC-stacked trilayer graphite using the tight-binding model. The interlayer interactions cause a tiny energy gap and band-edge states. The density of states exhibits logarithmic divergences and square-root divergences. The frequencies of absorption peaks cohere with the vertical transition energies between the band-edge states. Compared with the different stacking modes, the logarithmic divergences of DOS reveal important differences near $\pm\beta_0$. The low energy DOS also exhibits structural changes. According to the changes in DOS, these stacking effects are also demonstrated in absorption spectra. The main differences among the three modes of graphites include the spectrum structures near $2\beta_0$ and the threshold absorption peak at low frequency. Also note that the threshold absorption peak only exists in ABC- and AB-stacked graphites.

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