Cutting lines near the Fermi energy of single-wall carbon nanotubes

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Analytic expressions for the cutting line number μ of a single-wall carbon nanotube (SWNT) which gives van Hove singularities for optical transitions are found to exist around $\mu = N/3$ for most SWNTs, where N is the number of cutting lines of the SWNT. However, for metal-2 SWNTs, the cutting line number shows an irregular dependence on (n, m). In this paper a classification is proposed for metal-2 nanotubes which are classified as either metal-$2p$ or metal-$2m$ SWNTs. The appearance of metal-1, metal-$2p$, and metal-$2m$ SWNTs in a two-dimensional (n, m) plot is not regular.

I. INTRODUCTION

The physical properties of a single-wall carbon nanotube (SWNT) are inherited from those of graphite, and their unique quantum properties and the chirality dependence of their electronic structure are given by their cylindrical geometry denoted by (n, m). In a SWNT, the wave vector along the circumferential direction is discrete because of periodic boundary conditions[1–3] while the wave vector along the nanotube axis is continuous. The one-dimensional (1D) Brillouin zone (BZ) plotted on the extended two-dimensional (2D) BZ of graphite is known as the cutting lines.[4] Semiconducting nanotubes consist of types I and II SWNTs, depending on whether $\mathrm{mod}(2n+m, 3) = 1$ or 2, respectively.[5–7] Type I semiconducting SWNTs show a similar photoluminescence (PL) energy pattern known as the family pattern[7,8] which differs from the family pattern observed for type II semiconducting SWNTs. The concept of the cutting lines[4] is thus important for understanding the family patterns observed in PL spectroscopy[5,6,9] and resonance Raman spectroscopy (RRS).[10]

We classify metallic nanotubes which include narrow-gap semiconducting nanotubes, as metal-1 and metal-2, depending on whether $d_R = d$ or $d_R = 3d$, respectively.[3,11,12] Here d and d_R are the greatest common divisor (gcd) of two integers, $d = \gcd(n, m)$ and $d_R = \gcd(2n+m, 2m+n)$, respectively. In metal-1 SWNTs, the Fermi energy is located at the Γ points of the 1D BZ, while in metal-2 SWNTs, the Fermi energy is located at a $2/3$ position on the $\Gamma-X$ line[3] (or at a $5/6$ position on a cutting line).

Since there are N [$N = 2(n^2 + m^2 + nm)/d_R$] cutting lines for (n, m) SWNTs, the ordinal number μ of the cutting lines starting from the Γ point ($\mu = 0$) is related to the symmetry of the wave function of the electrons and phonons. The transition energies E_{11}, E_{22} are important to know for practical use in computer programs that describe fundamental physical phenomena, especially for the cutting lines which give the van Hove singularity (vHS) energies. When we try to understand analytic expressions for the cutting lines, we find a different classification for SWNTs, which is very useful for

giving a general description of nanotube physics.

In this paper we present an analytic expression for the ordinal numbers of the cutting lines which give the vHS energies. The derivation of this expression is not so simple and we therefore explain this derivation in the present paper. What we found in this study is that the classification of SWNTs is not a periodic function of n or m. For example, we found that metal-2 SWNTs further consist of two types of tubes, depending on whether $\mathrm{mod}(3m/d_R, 3) = 1$ or 2. We think that this classification for metallic tubes will provide potential significance for understanding nanotube physics.

II. THE μ VALUE FOR THE VAN HOVE SINGULARITY

The $\boldsymbol{k}$ points on the μth cutting line of the (n, m) SWNT in the 2D BZ of graphite is given by

$$\boldsymbol{k} = k \frac{\boldsymbol{K}_2}{|\boldsymbol{K}_2|} + \mu \boldsymbol{K}_1 \quad \left(-\frac{\pi}{T} < k < \frac{\pi}{T}, \quad \mu = 0, \ldots, N-1 \right), \quad (1)$$

where $\boldsymbol{K}_1$ and $\boldsymbol{K}_2$ are the reciprocal lattice vectors of a SWNT, which are, respectively, perpendicular and parallel to the cutting lines (see Fig. 1).[3] Here $\boldsymbol{K}_1$ and $\boldsymbol{K}_2$ are expressed by the reciprocal lattice vectors of 2D graphite $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ as[3]

$$\boldsymbol{K}_1 = \frac{1}{N}(-t_2 \boldsymbol{b}_1 + t_1 \boldsymbol{b}_2), \quad \boldsymbol{K}_2 = \frac{1}{N}(m \boldsymbol{b}_1 - n \boldsymbol{b}_2). \quad (2)$$

Also t_1 and t_2 are components of the translational vectors $\boldsymbol{T} = t_1 \boldsymbol{a}_1 + t_2 \boldsymbol{a}_2 \equiv (t_1, t_2), T = |\boldsymbol{T}|$ which are given by

$$t_1 = \frac{2m+n}{d_R}, \quad t_2 = -\frac{2n+m}{d_R}. \quad (3)$$

We will now obtain the μ value which gives the van Hove singularity E_{ii} ($i = 1, 2, 3, \ldots$) for metallic and semiconducting SWNTs.

A. Metal-1 ($d_R = d$) SWNTs

First we consider the case of metal-1 ($d = d_R$) carbon nanotubes. Since a metal-1 SWNT has a Fermi energy at the
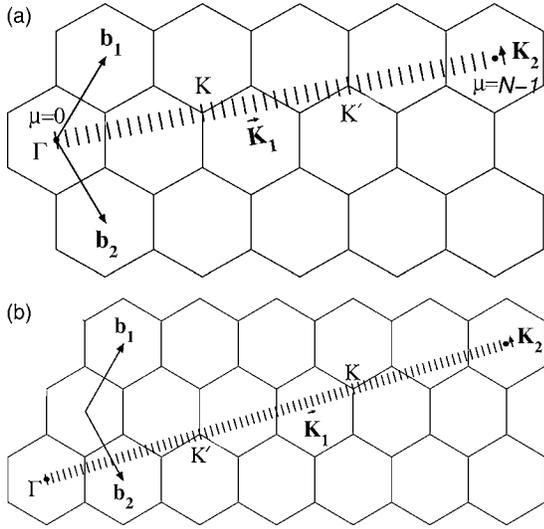
FIG. 1. (a) Cutting lines of (6,3) metal-1 nanotubes on a hexagonal 2D BZ, where $N=42$, $p=q=1$, and $\mu=14,28$. (b) The cutting lines of (9,3) where $N=78$, $p=4$, $q=3$, and $\mu=26,52$. Starting from the Γ point, we meet first K' point prior to K point.

Γ point (center) of the 1D BZ, the K and K' points (inequivalent hexagonal corners of the 2D BZ of graphite) are located at the center of the cutting lines. Starting from the Γ point of the hexagonal 2D BZ of graphite, the 1D Γ point on the μth cutting lines goes on the K and K' points of the 2D BZ of graphite for metallic (n,m) nanotubes (see Fig. 1). As shown in Fig. 1, the K point of the SWNT is not always at the K point of the first BZ for 2D graphite but rather is on an equivalent K point in the extended BZ which differs from it by the reciprocal lattice vectors of graphite, $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$. The condition determining μ for a metallic energy band is given by

$$\mu \boldsymbol{K}_1 = \boldsymbol{\Gamma K} + p\boldsymbol{b}_1 + q\boldsymbol{b}_2, \tag{4}$$

in which p and q are integers. Using the fact $N\boldsymbol{K}_1 = -t_2\boldsymbol{b}_1 + t_1\boldsymbol{b}_2$ and $0 \leq \mu < N$ restricts p and q to

$$0 \leq p < (-t_2), \quad 0 \leq q < t_1. \tag{5}$$

It is noted that $(-t_2)$ and t_1 are positive or zero for $n,m \geq 0$. $\boldsymbol{\Gamma K}$ is the vector which connects Γ to *the K point in the first BZ of 2D graphite*, which is given by

$$\boldsymbol{\Gamma K} = \frac{1}{3}(2\boldsymbol{b}_1 + \boldsymbol{b}_2). \tag{6}$$

By substituting Eqs. (2) and (6) into Eq. (4) and by comparing the coefficients of $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ on both sides of Eq. (6), we get

$$\mu = \frac{2(3p+2)(n^2+m^2+nm)}{3(2n+m)},$$

$$\mu = \frac{2(3q+1)(n^2+m^2+nm)}{3(2m+n)}. \tag{7}$$

From these conditions, we obtain the following equation which determines p and q:

$$(3p+2)t_1 = (3q+1)(-t_2). \tag{8}$$

It is noted that t_1 and $(-t_2)$ are not a multiple of 3 in the case of metal-1 [$d_R=d$ and $d=\gcd(n,m)$]. Since t_1 and $(-t_2)$ do not have a common divisor except for unity by the definition of $\boldsymbol{T}$, the following relations should be satisfied:

$$3p+2 = -xt_2, \quad 3q+1 = xt_1, \tag{9}$$

where x is either 1 or 2 because of Eq. (5). When we set Eq. (9) into Eq. (7), μ becomes either $N/3$ or $2N/3$, respectively, for $x=1$ or 2, which corresponds to the cutting lines that cross the K or K' points first when we start from $\mu=0$.

In Fig. 1(a) we show the cutting lines of a (6,3) nanotube. A (6,3) SWNT is a metal-1 SWNT ($d=d_R=3$), and the results are $\boldsymbol{T}=(4,-5)$, $N=42$, $x=1$, $p=q=1$, and $\mu=14=N/3$ for the K point. The cutting line of $\mu=28$ corresponds to that on the K' point. Thus μ values for E_{11}^M are 13, 15, 27, and 29 for which the van Hove singularities are split by the trigonal warping effect[13] into the two peaks $E_{11}^M(H)$ ($\mu=13,29$) and $E_{11}^M(L)$ ($\mu=15,27$), corresponding to the higher (H) and lower (L) energies, respectively.

Another example of a metal-1 SWNT is (9,3) [Fig. 1(b)]. The values for (9,3) are $\boldsymbol{T}=(5,7)$, $N=78$, $x=2$, $p=4$, $q=3$, and $\mu=52=2N/3$ for the K point. The cutting line of $\mu=26$ goes over the K' point.

When we increase the μ value starting from 0 (the Γ point in Fig. 1), the question about which point, K or K', meets a cutting line first is related to the handedness of the nanotube.[14] Here we propose to denote the handedness of a metal-1 tube by its value of x. In fact, when we change (n,m) to (m,n) or $(-n,-m)$, the value of x is changed from 1 to 2 or from 2 to 1. In a previous paper, we reported that (n,m) and (m,n), which have different handedness (or the K and K' points), cannot be distinguished by optical measurements because of time reversal symmetry.[4,14] Thus we will not classify these two species of metal-1 tubes further.

B. Semiconducting nanotubes

Before discussing metal-2 tubes, we will give results for semiconducting nanotubes since we directly obtain such results from the previous discussion. Since $d_R=d$ is satisfied for all semiconductor SWNTs, the energy gap appears near the Γ points of the 1D BZ if we do not consider the trigonal warping effect. In fact, especially for smaller diameter semiconducting nanotubes, the energy gap is shifted from the Γ points of the 1D BZ in opposite directions for the K and K' points with respect to each other. The condition for the cutting lines which cross the K point is given by

$$\left(\mu \pm \frac{1}{3}\right)\boldsymbol{K}_1 = \boldsymbol{\Gamma K} + p\boldsymbol{b}_1 + q\boldsymbol{b}_2, \tag{10}$$

where $+$ and $-$ are applied for type I and II semiconducting nanotubes, respectively. Equation (10) is obtained from Eq. (4) by substituting μ for $\mu \pm 1/3$, and thus only the left-hand side of Eq. (7) can be modified. Therefore, we get the same results as Eqs. (8) and (9). When we denote the μ values for E_{11} and E_{22} by μ_1 and μ_2, we get the following results, depending on whether $\mathrm{mod}(N,3)=1$ or 2:
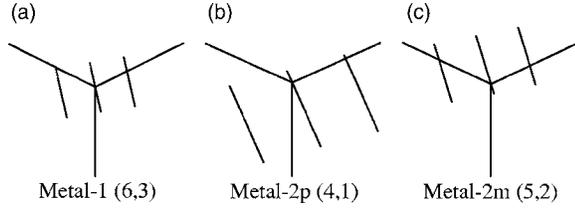
FIG. 2. Three cutting lines around the K points for (a) metal-1 (6,3), (b) metal-2p (4,1), (c) metal-2m (5,2) SWNTs. While the K point is located at the center of the cutting line for metal-1, the K points are located at a 1:5 (or 5:1) position of the cutting line for metal-2p (or metal-2m).

$$\mu_1 = \pm\frac{N-1}{3}, \quad \mu_2 = \pm\frac{N+2}{3} \quad \text{if } \mathrm{mod}(N,3)=1,$$

$$\mu_1 = \pm\frac{N+1}{3}, \quad \mu_2 = \pm\frac{N-2}{3} \quad \text{if } \mathrm{mod}(N,3)=2. \quad (11)$$

Here, the sign $\pm$ denotes the doubly degenerate singularities. To avoid negative μ indices, one needs to add N in the case of a minus sign in Eq. (11). The condition of $\mathrm{mod}(N,3)=1$ (or 2) appears for both type I $[\mathrm{mod}(2n+m,3)=1]$ and type II $[\mathrm{mod}(2n+m,3)=2]$ SWNTs. For example, (6,1) and (6,4) are both type I SWNTs, but the values of N are, respectively, 86 and 76, and thus the values of $\mathrm{mod}(N,3)$ are 2 and 1, respectively.

For example (4,2) is a type I semiconducting SWNT with $N=28$ and therefore $\mathrm{mod}(N,3)=1$, $\mu_1=9$, and $\mu_2=10$. Also $\mu_1=-9$ and $\mu_2=-10$ (equivalently $\mu_1=19$ and $\mu_2=18$), respectively, give E_{11} and E_{22}. Another example of a type I semiconducting SWNT is (6,1) for which the values are $N=86$, $\mathrm{mod}(N,3)=2$, $\mu_1=\pm28$, and $\mu_2=\pm29$.

The two cases of $\mathrm{mod}(N,3)=1$ and $\mathrm{mod}(N,3)=2$ are different according to whether E_{11} and E_{22} first appear either around the K point or around the K' point. Thus the value of $\mathrm{mod}(N,3)$ can be used to obtain the handedness of semiconducting SWNTs, just as we use x in the case of metal-1 tubes.

An important fact for semiconducting nanotubes is that energy gaps open around the K and K' points at different 1D k points because of the trigonal warping effect. When many-body effects mix electronic states with each other to form a localized electronic state such as an exciton, with k around the K and K' points, the relative position of the two energy bands is important for the properties of the exciton.[15]

C. Metal-2 ($d_R=3d$) SWNTs

In the case of metal-2 nanotubes, the Fermi energy appears at $k=\pm K_2/3$ positions. When we increase the number of μ from the Γ point of the 2D BZ, a cutting line will first touch a K point, but there are two possibilities of the K point touching at $k=+K_2/3$ and $k=-K_2/3$ [see Figs. 2(b) and 2(c)]. The corresponding conditions for the metallic cutting lines touching the K point are given by

$$\mu \mathbf{K}_1 \pm \frac{1}{3}\mathbf{K}_2 = \Gamma K + p\mathbf{b}_1 + q\mathbf{b}_2. \quad (12)$$

Using Eqs. (2) and (6), we get the following equation:

$$t_1 p + t_2 q = -\frac{m}{d_R} \pm \frac{1}{3}. \quad (13)$$

Since $d_R=3d$ and m/d is an integer, then m/d_R is not an integer but is a fraction whose denominator is 3. Further, since the right-hand side of Eq. (13) should be an integer, we can reclassify metal-2 tubes according to metal-2p or metal-2m by $\mathrm{mod}(3m/d_R,3)=1$ or $=2$, respectively. For an integer value of the right-hand side of Eq. (13), we can get a unique integer solution of p and q in the region of Eq. (5).

In Fig. 2, we show three different metallic energy bands which touch at the K points for (a) metal-1 (6,3), (b) metal-2p (4,1), and (c) metal-2m (5,2). The values of $\mathrm{mod}(3m/d_R,3)$ are (a) 0, (b) 1, and (c) 2, respectively. Because of the trigonal warping effect around the K point, the cases of metal-2p and metal-2m SWNTs clearly have a different energy dispersion.

The corresponding μ values for metal-2 are not near $N/3$ and $2N/3$. The μ value for Eq. (5), for the unique solution of p and q for Eq. (13), is given by

$$\mu = \frac{(3p+2)N \pm m}{-3t_2}. \quad (14)$$

For example, each (n,n) armchair nanotube is of the metal-2p type and $\mu=n=N/2$. The nanotube (10,1) is of the metal-2p type and μ is 7 for $N=74$ while the nanotube (11,2) is of the metal-2m type and the μ value is 45 with $N=98$. The values of μ for metal-2 SWNTs are far from $N/3$. We could not get an analytic formula for the μ value.
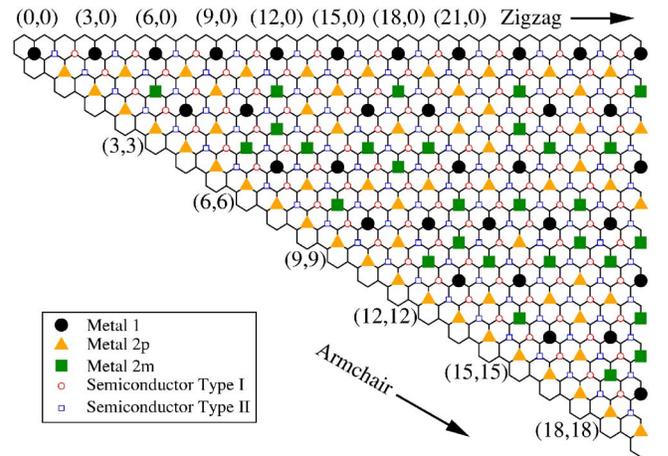

FIG. 3. (Color online) Classification of (n,m) single-wall carbon nanotubes. Small open symbols denote type I (red circle) and type II (blue square) semiconducting nanotubes. Solid symbols denote metal-1 (black circle), metal-2p (yellow triangle), metal-2m (green square). The appearance of the solid symbols is not periodic except for zigzag and armchair SWNTs.

TABLE I. Classification of single-wall carbon nanotubes. μ values for semiconducting SWNTs are common for Types I and II semiconducting SWNTs. gcd is the greatest common divisor. p is given by solving Eq. (13). This table is for (n,m) SWNTs. $N=2(n^2+m^2+nm)/d_R$, $d_R=\gcd(2n+m,2m+n)$, $d_X=\mathrm{mod}[(2n+m)/d,3]$,

Type	Condition	Cutting line near E_F
Semiconducting SWNTs:		
Type I	$\mathrm{mod}(2n+m,3)=1$	
Type II	$\mathrm{mod}(2n+m,3)=2$	
	if $\mathrm{mod}(N,3)=1, \mu_1=\pm(N-1)/3, \mu_2=\pm(N+2)/3$	
	if $\mathrm{mod}(N,3)=2, \mu_1=\pm(N+1)/3, \mu_2=\pm(N-2)/3$	
Metallic SWNTs $\mathrm{mod}(2n+m,3)=0$:		
Metal-1	$\mathrm{mod}(3m/d_R,3)=0$	$\mu=\pm N/3$
	if $d_X=1, \mu_1^{\mathrm{H}}=\pm(N/3+1), \mu_1^{\mathrm{L}}=\pm(N/3-1)$	
	if $d_X=2, \mu_1^{\mathrm{H}}=\pm(N/3-1), \mu_1^{\mathrm{L}}=\pm(N/3+1)$	
Metal-2p	$\mathrm{mod}(3m/d_R,3)=1$	$\mu=[(3p+2)N+m]/(-3t_2)$
Metal-2m	$\mathrm{mod}(3m/d_R,3)=2$	$\mu=[(3p+2)N-m]/(-3t_2)$

III. DISCUSSION AND SUMMARY

In Table I we summarize the results of the present paper. In the table we use a negative sign for μ values in the range of $-N/2 \leqslant \mu < N/2$. Since we have a periodicity on μ such that μ and $\mu+N$ are equivalent to each other, we can use suitable definitions of μ which we can select for computer programs.

For semiconducting SWNTs, the cutting line numbers μ_1 and μ_2 for E_{11} and E_{22} van Hove singularities, respectively, depend not on the type but on $\mathrm{mod}(N,3)$. The van Hove singularity μ values always appear near $\pm N/3$.

For metal-1 SWNTs, the cutting line number for the metallic energy subband is $\pm N/3$. It is natural that $\mathrm{mod}(N,3)$ $=0$ for metal-1 SWNTs. The cutting line numbers μ_1^{H} and μ_1^{L} for the higher and lower split E_{11} van Hove singularities depend on $d_X=\mathrm{mod}[(2n+m)/d,3]$. By comparing Table I with Eq. (9), we obtain $x=3-d_X$. The proof of this statement is not easy but we checked that it is correct for many (n,m) values by a computer program.

The μ values are related to the symmetry of the wave function (angular momentum) around the nanotube axis. Thus if there is not a simple relation between (n,m) and the μ value, such as for the semiconductor types I and II nanotubes and for the metal-1 SWNTs, the metal-2 tubes will show anomalous physical properties that are sensitive to the wave function.

In Fig. 3 we show a map of (n,m) and the classification of semiconductor types I and II, metal-1, -2p, and -2m tubes. The appearance of types I and II semiconductor SWNTs is regular by specifying their $\mathrm{mod}(2n+m,3)$ values. All metallic zigzag $(3n,0)$ and all armchair (n,n) nanotubes are metal-1 and metal-2p SWNTs, respectively. However, the appearance of metal-1, metal-2p, and metal-2m for chiral nanotubes is irregular. The integer function $\mathrm{mod}(3m/d_R,3)$ seems to generate 0, 1, and 2 randomly.

In summary, we have shown that the cutting line number near the K point is around $N/3$ or $2N/3$ for semiconductor nanotubes and metal-1 nanotubes. However, for metal-2 nanotubes, the cutting number strongly depends on (n,m) and we can classify metal-2 further to metal-2p and metal-2m SWNTs, depending on the value of $\mathrm{mod}(3m/d_R,3)$. We think that this information will affect physical properties, especially for the properties which are sensitive to the symmetry of the wave functions.

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