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Transverse-field and defect-azimuth effects in achiral carbon nanotubes

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Abstract

The effects of transverse field and a single defect on the conductance of an achiral carbon nanotube have been investigated. It is found that armchair nanotubes under the transverse field are always metallic, and that field-induced metal–semiconductor (MS) and semiconductor–metal (SM) transitions are shown for zigzag nanotubes. MS transition fields are independent of the defect while SM transition fields are sensitive to the field-defect azimuth, defect type and its strength. Most importantly, the field-defect azimuth is a new freedom and can be used to tailor and control the electronic behaviour. The experimental confirmation of the prediction may be possible.

Single-walled carbon nanotubes (SWNTs) have attracted much attention because of their remarkable electronic properties and great potential applications for nanoscale devices. A variety of electronic devices based on SWNTs with use of gate and bias voltages, for instance, single-electron transistors [1], field-effect transistors [2], and diodes [3], have been built experimentally. It is well known that magnetic field [4] and mechanical deformation such as squashing, bending, and stretching [5, 6] can modulate the electronic properties of SWNTs.

Recently, effects of a transverse electric field, which is easy to control in practical applications, on the electronic structures of perfect SWNTs have been investigated [7–10]. It has been found that the transverse field uniformly changes the bands along the tube axis and substantially modifies transport properties of SWNTs, such as the metal–semiconductor (MS) and semiconductor–metal (SM) transitions [8, 10]. However, the tubes are rarely as perfect as they were once thought to be. Various types of defects such as topological defects, impurities, and vacancies substantially modify the electronic properties of SWNTs [11–17]. The presence of defects locally alters the band structures of SWNTs. This has been confirmed by several experiments. For example, scanning tunnelling microscope (STM) measurements on bulk

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nanotube 'mats' suggest that the defects can locally alter electronic properties [16]. Current rectification in a molecular diode consisting of a semiconducting SWNT and an impurity results from the local effect of the impurity on the tube's band structures [17].

An interesting question arises. How do a few defects, in particular a single defect which can induce a local field, modulate the electronic and transport properties of SWNTs combined with the transverse field effects? Two cases, we believe, can appear under the resultant field of the transverse and local fields. One is that a local defect cannot make the density of states at the Fermi level E_F zero and the defective tube is still metallic as the perfect tube under the field is in a metallic state. The other is that the local band change induced by the defect can make the valence band touch the conduction band as the perfect tube under the field is in a semiconducting state with a small gap. In that case, the conduction band is filled by electrons, namely, the local density of states (LDOS) at E_F is finite, and then the defective tube can change from a semiconducting to a metallic state. Moreover, for the tube under the field, a single defect can introduce a new freedom, i.e., the defect azimuth related to the field direction. Therefore, it is interesting and important to study the transverse-field and field-defect azimuth effects on the conductance.

In this paper, the conductance and LDOS of perfect and defective achiral SWNTs with the chiral angle $\theta = 0°$ (zigzag) and $\theta = 30°$ (armchair) under a transverse field are studied by a tight-binding (TB) Green function method, which is effective and suitable for the studies compared with the others [8, 10, 14]. Some new phenomena, such as the chiral-angle dependence of the MS transitions and the field-defect azimuth effects on the SM transitions, are found. The device archetype is as follows: an achiral SWNT without or with a single defect is placed in between two parallel plate electrodes. These plate electrodes can produce a uniform transverse field. In order to better study field-defect azimuth effects on the SM transitions, we rotate the electrodes or the SWNT continuously around the tube axis so that field-defect azimuth can be continuously changed. On the other hand, the uniform transverse field can also simply represent the effects of gate voltage in the field-effect transistors [7, 8].

A π-band TB model is used to describe the electronic properties of SWNTs close to E_F. Within this one-band scheme the energies are usually written in terms of the overlap integral γ_0, which is set to 2.6 eV as determined by experiments [18]. The Hamiltonian of the whole system can be written as

$$H(F, \phi_F, \phi_D) = H_0 + H_1(F, \phi_F) + wH_2(F, \phi_F, \phi_D), \tag{1}$$

where F, ϕ_F and ϕ_D are, respectively, the transverse field strength, the transverse field azimuth and the defect azimuth. $w = 0$ ($w = 1$) corresponds to the perfect (defective) SWNT. H_0 is for the perfect SWNT without the transverse field, which is described by the TB model with one π electron per atom as

$$H_0 = -\gamma_0 \sum_{\langle i,j \rangle} a_i^+ a_j + \text{c.c.} \tag{2}$$

where the sum in i, j is restricted to nearest-neighbour atoms. The transverse field changes the electrostatic potential of carbon atoms in the cylindrical surface of the SWNT, and the on-site energies of carbon atoms can be written as

$$(H_1)_{i,i} = -eRF\cos(\phi_i - \phi_F), \tag{3}$$

where e is the electron charge, R is the tube radius, and ϕ_i is the azimuth of the ith carbon atom. The off-diagonal terms of H_1 can be neglected [7]. H_2 is for a single defect,

$$H_2 = H_2^0 - eRF\cos(\phi_D - \phi_F), \tag{4}$$

where the first term H_2^0 represents the defect term without the field, and the second term is for the defect in the transverse field. The defects studied here include a Stone–Wales defect (pentagon–heptagon-pair defect), a substitutional impurity such as boron and nitrogen, and a vacancy. The Stone–Wales defect can be obtained by rotating one of the C–C bonds by $\pi/2$, resulting in the transformation of four nearby hexagons into a pair of heptagons having a common side and separating two pentagons [13]. A substitutional impurity can be simulated by a parameter: the impurity strength U [13, 15], i.e., $H_2^0 = U a_0^+ a_0$. Here, we set $U = 3\gamma_0$ ($-5\gamma_0$) to simulate a boron (nitrogen) substitutional impurity by fitting the conductance and LDOS which were obtained by a type of *ab initio* calculations [14]. For a vacancy, a carbon atom is taken from the SWNT and the bonds related to the carbon atom are interrupted.

In order to calculate the conductance and LDOS, the whole system can be considered as a left-lead–conductor–right-lead configuration. The left and right leads are semi-infinite perfect achiral SWNTs, and the conductor is a finite region without or with a single defect. Within the Landauer formalism [19], the conductance $G(E)$ can be calculated as a function of the incident energy E,

$$G(E) = G_0 \,\mathrm{Tr}(\Gamma_\mathrm{L} \mathcal{G}^\mathrm{r} \Gamma_\mathrm{R} \mathcal{G}^{\mathrm{r}+}), \tag{5}$$

where G_0 ($=2e^2/h$) is the conductance quantum and $\Gamma_{\mathrm{L(R)}}$ is the coupling matrix between the left (right) lead and the conductor. $\mathcal{G}^\mathrm{r}$ is the retarded Green function which can be written as [19]

$$\mathcal{G}^\mathrm{r} = (E - H_\mathrm{C} - \Sigma_\mathrm{L} - \Sigma_\mathrm{R})^{-1}. \tag{6}$$

Here H_C is the Hamiltonian matrix of the conductor that represents the interaction between the atoms in the conductor, and $\Sigma_{\mathrm{L(R)}}$ is the self-energy function that describes the effect of the left (right) lead, which can be calculated from a surface Green function matching technique as shown in [15]. Once $\Sigma_{\mathrm{L(R)}}$ is known, $\Gamma_{\mathrm{L(R)}}$ is easily obtained as [19]

$$\Gamma_{\mathrm{L(R)}} = \mathrm{i}[\Sigma_{\mathrm{L(R)}} - \Sigma^+_{\mathrm{L(R)}}]. \tag{7}$$

Finally, the averaged LDOS for the jth unit cell from the left boundary of the conductor is calculated from the relation

$$\mathrm{LDOS}_j(E) = -\frac{1}{N\pi}\,\mathrm{Im}[\mathrm{Tr}(\mathcal{G}^\mathrm{r}_{j,j}(E))], \tag{8}$$

where N is the number of carbon atoms per unit cell, and $\mathcal{G}^\mathrm{r}_{j,j}$ is the Green function of the jth unit cell.

First, the conductance at the Fermi level $G(E_\mathrm{F})$ ($E_\mathrm{F} = 0$) for perfect and defective achiral SWNTs under the field has been calculated and compared. The defects studied here include a Stone–Wales defect (pentagon–heptagon-pair defect), a substitutional impurity such as boron and nitrogen, and a vacancy, placed on the surface of SWNTs under the field with $\phi = \phi_\mathrm{D} - \phi_\mathrm{F} = 0°$. As shown in figure 1, the variation of the conductance with the field for the armchair (10, 10) tube shows a significant difference from that for the zigzag (18, 0) and (28, 0) tubes. The conductance of the perfect (10, 10) tube increases with $|F|$ by the step of $4G_0$ while that of the defective (10, 10) tube shows some dips due to the defects, but the drop is not so large that the tube is still metallic. For the zigzag SWNTs, however, the conductance oscillations can appear. With increasing field, the MS and SM transitions, and then the SM and MS transitions, appear for the (18, 0) and (28, 0) tubes, respectively.

The reason why the (10, 10) tube is still metallic under the field can be understood as follows. For the perfect (10, 10) tube under the transverse field, the π and π^* bands remain having opposite parities and then accidentally degenerate at E_F. As $|F| < 0.15$ V Å^{-1}, $G(E_\mathrm{F})$ is always equal to $2G_0$. As $|F| > 0.15$ V Å^{-1}, the other degenerate bands without the certain

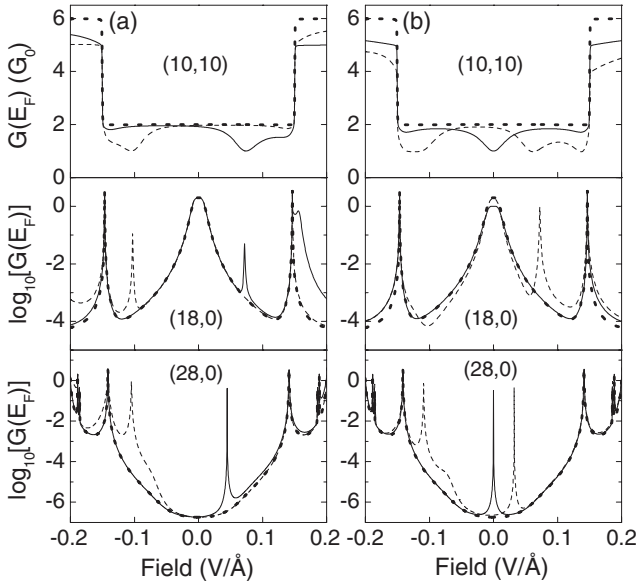

Figure 1. The transverse-field and defect effects on the conductance $G(E_F)$ for the (10, 10), (18, 0), and (28, 0) SWNTs. The thick dotted line corresponds to perfect SWNTs. The solid and dashed lines respectively correspond to SWNTs with a nitrogen impurity and a boron impurity in (a), and to SWNTs with a vacancy and a Stone–Wales defect in (b).

parity can mix and cross at E_F, and then this contributes $4G_0$ to the conductance. Even though the presence of a single defect under the field results in the mixture of the π and π^* bands [15], one of two eigenchannels with $F < 0.15$ V Å^{-1} is completely transmitted while the other is affected by the defect, and thus the minimal conductance is $1G_0$. As $F > 0.15$ V Å^{-1}, the influence of the defect is similar.

For a metallic $(3n, 0)$ tube, the perturbation of the field opens a gap $E_g \propto (eRF)^2/\gamma_0$ in two degenerate bands without the parity. Here we should note that there is a small gap induced by the curvature in the $(3n, 0)$ tube [20]. However, it is much smaller than the maximum gap induced by the transverse electric field obtained in our calculation. Therefore, our π-electron tight binding calculation is still suitable to give a qualitative insight of the transverse field induced gap oscillation. As shown in figure 2(a), the gap of perfect $(3n, 0)$ tubes oscillates with increasing F and strongly depends on R. As $F < F_{1,\max}$ where the gap reaches the first local maximum, the calculated results can be fitted by the scaling relation

$$E_g = 0.177(eRF)^2/\gamma_0. \tag{9}$$

For the sake of convenience, we denote the first SM transition field for metallic (semiconducting) perfect and defective zigzag tubes as F_{MP} and F_{MD} (F_{SP} and F_{SD}), respectively. In the inset of figure 2(a), it is clearly shown that F_{MD} and F_{MP} decrease with increasing R.

Moreover, E_g of the perfect $(3n \pm 1, 0)$ tubes, as shown in figure 2(b), decreases with increasing F and approaches zero at $F = F_{SP}$, and it is in good agreement with the results for E_g and $F_{SP} = 0.21$ V Å^{-1} for the (17, 0) tube obtained by first principle calculations [8]. However, the small oscillations of E_g do appear as $F > F_{SP}$. F_{SP} is respectively equal to 0.636 V Å^{-1} and 0.141 V Å^{-1} for the (10, 0) and (28, 0) tubes. F_{SD} and F_{SP} also decrease with increasing R as shown in the inset of figure 2(b).

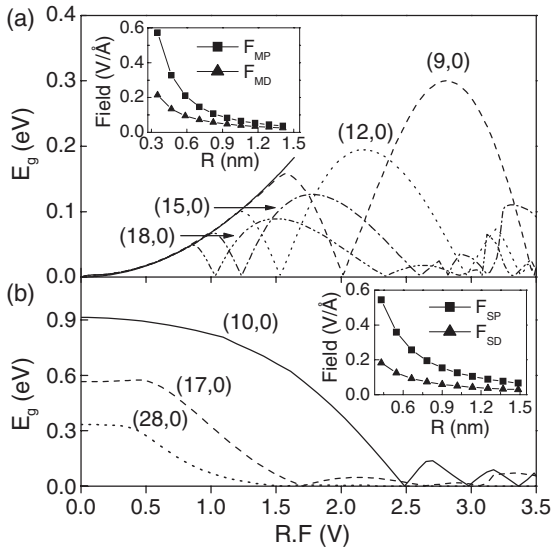

Figure 2. E_g as a function of RF for perfect (a) $(3n, 0)$ and (b) $(3n \pm 1, 0)$ zigzag SWNTs. The solid line in (a) corresponds to a fit of $0.177(eRF)^2/\gamma_0$. F_{MP} (F_{MD}) and F_{SP} (F_{SD}) as a function of R for perfect zigzag tubes (defective ones with a nitrogen impurity) shown in the insets of (a) and (b), respectively.

As shown in figure 1, the additional defect does not affect the MS transition fields when the tubes are in a metallic state; however, the defect under the field can induce new SM transitions when the tubes are in a semiconducting state. In the perfect (18, 0) tube, [F_{MP} (V Å^{-1}), $G(E_F)$ (G_0)] is [0.146, 4.0]. In the defective (18, 0) tube, [F_{MD} (V Å^{-1}), $G(E_F)$ (G_0)] is [0.072, 0.05], [−0.103, 0.13], [0.072, 0.94], and [0.146, 3.2] for a nitrogen impurity, a boron impurity, a Stone–Wales defect, and a vacancy, respectively. In the (28, 0) tube, [F_{SP} (V Å^{-1}), $G(E_F)$ (G_0)] is [0.141, 4.0] while the corresponding [F_{SD} (V Å^{-1}), $G(E_F)(G_0)$] is [0.045, 0.41], [−0.105, 0.90], [0.032, 0.44], and [0, 0.32]. It is clearly shown that the first SM transition field and the corresponding conductance of defective zigzag tubes are smaller than those of the corresponding perfect ones and strongly dependent on the defect type and strength. Furthermore, F_{SD} (F_{MD}) for a impurity with U is exactly equal to $-F_{SD}$ ($-F_{MD}$) for a impurity with $-U$, and then the larger $|U|$ is, the smaller $|F_{MD}|$ and $|F_{SD}|$ are.

To better understand the effects of the resultant field of the transverse and local fields on the local band change related to the conductance of zigzag SWNTs, the LDOS at several typical fields has been calculated for the perfect (28, 0) tube, the defective (28, 0) tube with a nitrogen impurity and that with a boron impurity, respectively. In figure 3, the gap of the perfect (28, 0) tube decreases with $|F|$ and reaches zero at $F_{SP} = 0.141$ V Å^{-1}. For the defective (28, 0) tube, the LDOS curves become asymmetric with respect to $E_F = 0$. The LDOS peaks induced by the defect reach E_F at F_{SD}, and then the SM transitions appear. As F changes from F_{SD}, these peaks move away from E_F. Because the LDOS peaks are very narrow, the range of the field for the metallic state is small as shown in figure 1.

Now, we explore how the field-defect azimuth ϕ affects the first SM transition field and the corresponding conductance. Noting that

$$H(F, \phi_F, \phi_D) = H(F, \phi) = H(F, 360^\circ - \phi), \tag{10}$$

we only consider the case of $0^\circ \leqslant \phi \leqslant 180^\circ$. The field-defect azimuth effects are clearly

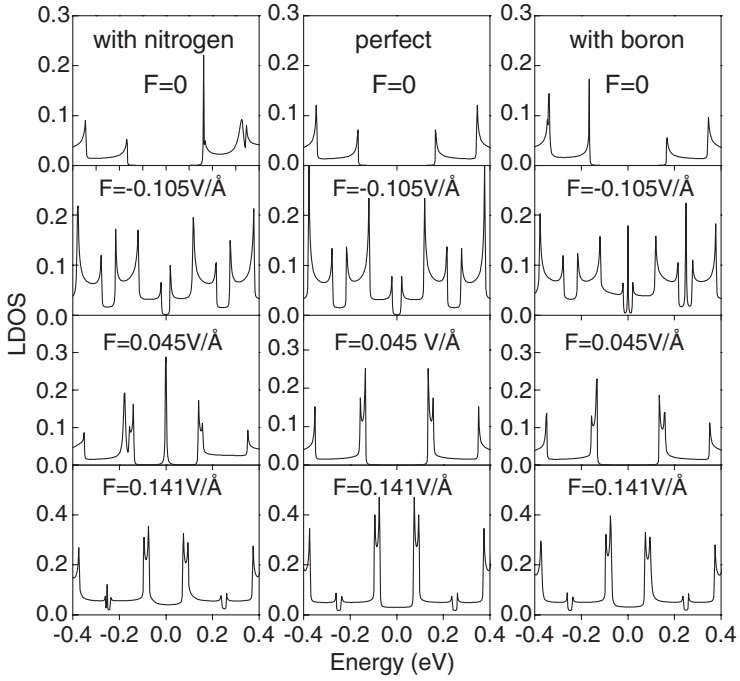

Figure 3. The LDOS as a function of the energy for the (28, 0) tube with a nitrogen impurity (left), without impurities (middle) and with a boron impurity (right) at several typical field strengths.

shown in figure 4(a). $F_{\rm MD}$ and $F_{\rm SD}$ at ϕ are respectively exactly equal to $-F_{\rm MD}$ and $-F_{\rm SD}$ at $180^\circ - \phi$ because of $H(F, \phi) = H(-F, 180^\circ - \phi)$. For the sake of clarity, we have plotted the $F_{\rm MD}$ and $F_{\rm SD}$ respectively for the (18, 0) and (28, 0) tubes with a nitrogen impurity as a function of ϕ in the range $[0^\circ, 90^\circ]$ in figure 4(b), and plotted the corresponding $G(E_{\rm F})$ in the same range in figure 4(c). Some unusual features are clearly shown. $F_{\rm MD}$ ($F_{\rm SD}$) and the corresponding $G(E_{\rm F})$ increase monotonically with increasing ϕ, and reach a maximal value at $\phi = 90^\circ$. The maximal changes of SM transition fields induced by a defect are at $\phi = 0^\circ$ and are defined as $\Delta F_{\rm max} = F_{\rm MP} - F_{\rm MD}(\phi = 0^\circ)$ and $\Delta F_{\rm max} = F_{\rm SP} - F_{\rm SD}(\phi = 0^\circ)$ for $(3n, 0)$ and $(3n \pm 1)$ tubes, respectively. It is found that for the zigzag tubes, the changes $\Delta F(\phi)$ of SM transition fields induced by the defect approach

$$\Delta F(\phi) \simeq \Delta F_{\rm max} \cos\phi \qquad \text{with } \phi < 40^\circ. \tag{11}$$

Moreover, the $G(E_{\rm F})$ at $F_{\rm MD}$ ($F_{\rm SD}$) increases with R. For zigzag tubes including a nitrogen impurity with $\phi = 30^\circ$, for example, [$F_{\rm MD}$ (V Å^{-1}), $G(E_{\rm F})$ (G_0)] are [0.082, 0.454] and [0.025, 0.736] for the (18, 0) and (39, 0) tubes, and [$F_{\rm SD}$ (V Å^{-1}), $G(E_{\rm F})$ (G_0)] are [0.058, 0.518] and [0.037, 0.719] for the (28, 0) and (38, 0) tubes. In fact, our further calculations indicate that the field-defect azimuth effects on the conductance of zigzag SWNTs with two defects (and even more) do exist. For the zigzag tubes with the two same defects on the opposite positions, i.e., $\phi = 0^\circ$ and 180°, the conductance curve is symmetric with respect to $E_{\rm F} = 0$, and the SM transition fields and the corresponding $G(E_{\rm F})$ are independent of the sign of U. We have also calculated the changes of SM transition fields induced by multiple defects with a fixed distribution and found the similar relations

$$\Delta F(\phi_m) \simeq \Delta F_{\rm max} \cos\phi_m \qquad \text{with } \phi_m < 40^\circ \tag{12}$$

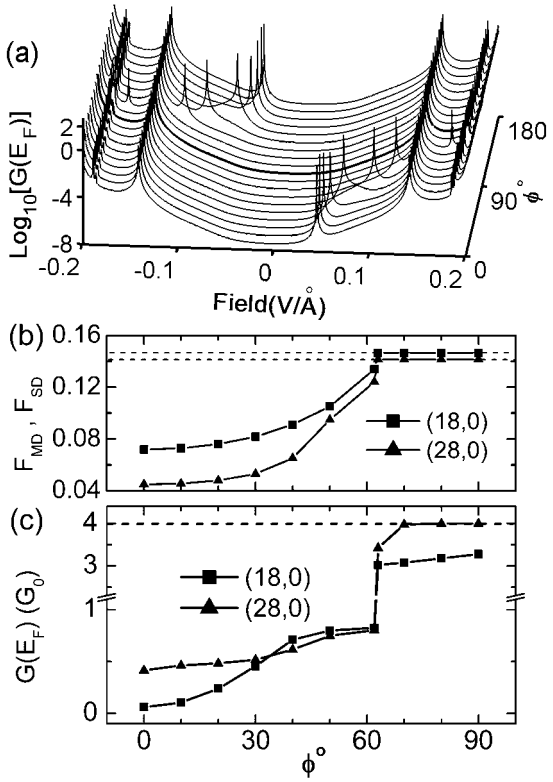

Figure 4. (a) The conductance $G(E_F)$ of the (28, 0) tube with a nitrogen impurity as a function of the field for $\phi = 0°, 10°, 20°, \ldots, 180°$. The thick solid line corresponds to $\phi = 90°$. (b), (c) F_{MD} (F_{SD}) and the corresponding $G(E_F)$ for the (18, 0) ((28, 0)) tube with a nitrogen impurity as a function of ϕ. The dashed lines in (b) and (c) represent the corresponding values of perfect ones.

where we set up $\phi_m = 0°$ for the azimuth at which the changes are equal to ΔF_{max}. Therefore, we conclude that the resultant field of the transverse field and the local field induced by multiple defects with some distribution can uniquely determine the azimuth dependence of $G(E_F)$ and SM transitions.

Compared with the results obtained by first principle calculations [8], the present calculated results and related phenomena are quite reasonable in the range of $F < 0.2$ V Å^{-1} even though the simulation method is not completely accurate within the TB model. Furthermore, the first SM transition fields of perfect SWNTs decrease with the increasing R and are much larger than those of the corresponding defective SWNTs. This makes the method used here more suitable for the studies of larger defective SWNTs. For the SWNTs with and without vacancies under strong transverse fields ($F \gg 0.2$ V Å^{-1}), however, it is interesting to use the *ab initio* approaches to determine a more precise LDOS and how large structure relaxation effects are on the conductance. It may, we believe, be possible to choose defective zigzag tubes to experimentally confirm the present prediction and to check both the TB model calculations and *ab initio* approaches.

In summary, we have shown the transverse-field and field-defect azimuth effects in achiral SWNTs, and arrived at the following conclusions. (1) MS transitions are dependent on the chiral angel θ. Armchair SWNTs ($\theta = 30°$) are still metallic under a transverse field while

metallic zigzag tubes ($\theta = 0°$) can become semiconducting under the field. (2) The energy gaps of zigzag SWNTs oscillate with the field and can be modulated by the defect. (3) The field-induced MS and SM transitions are shown for zigzag SWNTs. The first SM transition field and the corresponding conductance can be greatly changed by the defect and both of them are very sensitive to the tube radius, the defect type and its azimuth. Finally, it is worthwhile to point out that a defective zigzag SWNT introduces a new freedom ϕ, and the electronic structures and transport properties can be tailored and controlled by using the field-defect azimuth effects. The unique behaviour of defective SWNTs under the field is useful for potential applications in novel nanodevices. It is also important to experimentally confirm the prediction and to further study the θ- and ϕ-dependence of MS and SM transitions obtained by different models and calculation methods. This is an open subject.

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