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Are carbon nanotubes with impurities and structure disorder metals or semiconductors?

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HIGHLIGHTS

- The ideal nanotubes become metallic at diameter $d > 10^{-9}$–10^{-8} m. This is possible only for multiwalled CNTs or bundles of nanotubes.
- Change in impurity concentration does not result in appearance (or disappearance) of gap in DOS but moves the Fermi level.
- The metallic or semiconducting type of conductivity depends on structure imperfection of nanotubes more than on their electron structure.

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ABSTRACT

Electron relaxation time and density of states near the Fermi level were calculated for 'dirty' carbon nanotubes taking into account multiple elastic electrons scattering on impurities and structural inhomogeneities of a short-range order type. A possible explanation of low-temperature behavior of density of states and electrical conductivity depending on defect structure, impurities and diameter of nanotube is presented.

1. Introduction

Extraordinary electrical properties of carbon nanotubes (CNTs) together with their excellent mechanical stability make them very attractive for nanoelectronic applications. That is why the theoretical and experimental study of electronic structure and density of states (DOS) $\nu(\varepsilon)$ of CNTs is important [1–12].

One of the most interesting characteristics of CNTs is that they can possess metallic or semiconducting properties, depending on the tube structure defined by chirality [5]. Their metallic or semiconducting nature is also determined by the local atomic arrangement. CNTs include impurities of catalysts used during their synthesis, amorphous carbon, adsorbed gas, attached radicals (OH, CO, etc.), and structure defects. Concentration of different structure defects can be on the order of 1–20% [13,14], resulting in local short-range ordering regions in the structure of CNTs, which change their properties.

A useful analysis of the available data on electronic structure and electron transport properties of CNTs is given in [15]. In [16] it was shown that a metallic CNT becomes semiconducting when the BN pairs of stoichiometric concentration are incorporated into an ordered atomic arrangement ($BC_{10}N$ nanotubes). An introduction of disorder, however, restores the finite DOS at the Fermi level. In other words disorder effectively restores the symmetry of nanotubes, returning the CNT to its original metallic state [16].

The effect of impurities on electronic properties of single-walled CNTs was studied in [17]. The electronic band structure and DOS of (4,4) and (7,0) carbon nanotubes were calculated in the presence of different amounts of B and N impurities. It was shown that a metallic (4,4) nanotube retains its conducting metallic properties after being doped with either type of impurities. A semiconducting (7,0) nanotube also remains to be semiconductor after doping. At the Fermi level however, DOS $\nu(\varepsilon_F)$ shows a dependence on the concentration of impurities.

In [18], the effect of the Ti chain adsorption on the semiconducting (14,0) and metallic (8,8) tubes was investigated. It was shown that when the Ti chain is adsorbed on a CNT, a (14,0) zigzag

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nanotube becomes metallic and an (8,8) armchair tube transforms from metal into semiconductor. The results of DOS calculation for pure and Ti adsorbed CNTs [18] are the following: in a (14,0) tube the original gap is closed due to introduction of a Ti chain and new states are generated below and above the Fermi level. For a (8,8) nanotube, the changes are completely reversed— the states near the Fermi level in a pure tube are pushed below and above the Fermi level, opening a small gap in the Ti adsorbed tube. There is no pseudogap.

In [19], the data on narrowing of the DOS near the Fermi level were reported for metallic CNTs for chirality changing from (8,8) to (20,20).

In [1–6,12,13], the electronic structure of CNTs was investigated by the methods of resonant Raman scattering, fluorescence, tunneling spectroscopy, etc. The peak structure of DOS near the Fermi level is found to depend on temperature and chirality of CNTs. Single-walled 'metallic' zigzag and armchair CNTs (both isolated tubes and bundles) were studied in [20]. A gap-like feature at the Fermi level was found in the bundle of tubes, which was not present in the spectra of an isolated tube.

To investigate single-walled zigzag and armchair nanotubes, both thought to be metallic, low-temperature atomically resolved scanning tunneling microscopy was used in [20]. Isolated 'metallic' zigzag nanotubes were found to have energy gaps with their values depending on the squared tube radius. The isolated armchair CNTs do not have any energy gaps, while the armchair nanotubes packed in bundles do have pseudogaps exhibiting an inverse dependence on the tube radius [20].

In an experimental investigation of DOS of single-walled CNTs grown on a metal tip apex [6] the authors observed that the substrate-to-tube charge transfer can also change DOS and shift ε_F.

Due to a direct observation of conductivity electrons in multi-walled CNTs performed in [3] at low temperatures, it was found that the depth of the DOS minimum at the Fermi level and the tilt angle of $\nu(\varepsilon)$ decrease, while the value of $\nu(\varepsilon_F)$ increases when the temperature is increased. A similar feature of low-temperature behavior of $\nu(\varepsilon)$ was observed in [12], where disordered multiwalled carbon nanotubes were analyzed using tunneling spectroscopy.

Thus we can argue that the above-listed factors (defect structure, impurities and diameter) strongly affect the electronic structure, density of states and the temperature behavior of conductivity of CNTs. That is why their experimental and theoretical investigations have to be continued. In the present paper electron relaxation time and DOS near the Fermi level were calculated for 'dirty' CNTs with armchair type of chirality. We took into account multiple elastic electrons scattering on impurities and structural inhomogeneities of a short-range order type. A possible explanation of the low-temperature behavior of DOS is presented.

2. Calculation

2.1. Relaxation time and contribution to DOS $\Delta\nu(\varepsilon,\alpha,T,C_h)$

In order to describe 'dirty' CNTs as systems with impurities and structural inhomogeneities of the short-range order type, we shall consider a solid with randomly distributed defects such as catalyst impurities, retained atoms, etc. (irrespective of their origin).

For simplicity, let us introduce a random field of adsorbed atoms of one and the same sort.

$$V(\vec{R}) = \sum_i c(\vec{R})U(\vec{R}_i - \vec{R}) \tag{1}$$

where $c(R_i)$ are the filling numbers and U is the site potential in a tube. In the absence of long-range ordering the representation $c(R_i) = c + \delta c(R_i)$ allows us to introduce a new quantity $\langle \delta c(R_i)\delta c(R_i)\rangle$ which defines either new chemical bonds or new short-range ordering [21] in a system with defects via fluctuations of concentration $\delta c(R_i)$ in site R_i and averaged (macro-) concentration $c = \langle c(R_i)\rangle$. The angle brackets mean averaging over a random field. The Fourier image $\langle \delta c(R_i)\delta c(R_j)\rangle = \left\langle |c_k|^2 \right\rangle$ determines the structure of short-range order, so $\left\langle |c_k|^2 \right\rangle = \frac{c(1-c)}{N}\sum_{i=1}^{N}\alpha_i \cos kR_i$ [22]. Here α_i are the short-range order coefficients ($\alpha_0 = 1$), and N is the number of atoms inside the structure inhomogeneity of the short-range order type. For all $\alpha_{i\neq 0} = 0$ and $c \to 0$, $\langle |c_K|^2 \rangle = \frac{c(1-c)}{N}$ determines the input system impurities.

To calculate single-particle properties such as electron relaxation time, DOS, etc., let us represent the single-particle Green function in the following form:

$$G = G_0 + \sum_i G_i^{(1)} + \sum_{ij} G_{ij}^{(2)} + \cdots, \tag{2}$$

where G_0 is the electron Green function in a pure CNT and $G_i^{(1)} = c(R_i)\int G_0(\vec{r}, R)U(R-R_i)G_0(R, \vec{r}')dR$ (the detailed expression for $G_{ij}^{(2)}$ is given in [21]). In a p-representation after averaging over disorder we have [21]

$$\langle G\rangle = G_0 + G_0^2\Sigma,$$

where Σ is the self-energy part which includes multiple elastic scattering of electrons on impurities and structural inhomogeneities of the short-range order type given by

$$\Sigma = cU_0^2\delta(p-p')\int G_0(p_1)\frac{dp_1}{(2\pi)^3} + U_0^2\int \left\langle |c(p-p')|^2 \right\rangle G_0(p_1)\frac{dp_1}{(2\pi)^3}. \tag{3}$$

Here, for simplicity, we have assumed that $U(R-R_i) = U_0\delta(R-R_i)$ because the radius of its action is small in comparison with the distance between the atoms (disperse system). In this case instead of the site potential we may go to the site t-matrix representing amplitude of multiple scattering on a site. Hence U_0 is considered to be the effective potential t_0. Furthermore, we assume U_0 to be low, which allows us to use only the first orders of the perturbation theory for the scattering amplitude.

The first term in Eq. (3) corresponds to the scattering on impurities and the second one describes the multiple elastic scattering of electrons on structural inhomogeneities of the short-range order type.

Now let us calculate the relaxation time $\frac{1}{\tau} = -\mathrm{Im}\Sigma$, and the contribution to DOS $\Delta\nu = -\frac{1}{\pi}\mathrm{Im}Sp(\langle G\rangle - G_0)$, using the self-energy part Σ(3) and the Green function $G_0 = \frac{1}{\varepsilon - \varepsilon_p + i0}$, where ε_p is the electron spectrum in an ideal CNT, which may be represented near the Fermi level as follows [15]:

$$\varepsilon_p = \frac{\sqrt{3}a\gamma_0}{2}\sqrt{\left(\frac{2\hbar}{3d}\right)^2 + p^2}, \tag{4}$$

where $d = \frac{C_h}{\pi}$ is the diameter of nanotube, $C_h = a\sqrt{n^2+mn+m^2}$ is the chirality, (n,m) are the chirality indexes, a is the lattice constant, and γ_0 is the transfer integral between the first neighbor p_z orbitals.

As a result we have

$$\frac{1}{2\tau} = cU_0^2\nu_0\pi\left(1 + \left\langle |c(p)|^2 \right\rangle\right), \tag{5}$$

where the original DOS at the Fermi level ν_0 strongly depends on the nanotube diameter and the Fermi momentum p_0 in an