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On the low-temperature anomalies of specific heat in disordered carbon nanotubes

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HIGHLIGHTS

- Low-temperature anomalies of specific heat in CNTs might have electronic nature.
- These anomalies cannot be associated with a change in dimension of atomic vibrations.
- Electronic nature is determined by electrons scattered on point defects.
- These electrons participate in the formation of a new short-range order.
- Within our model it is possible to calculate the short-range order parameters.

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ABSTRACT

The low-temperature behavior of the specific heat in disordered nanotubes strongly depends on structure changes and is not explained by the phonon contribution. Expression for electronic specific heat is carried out taking into account the multiple elastic electron scattering on impurities and structural inhomogeneities of short-range order type. The calculated electronic specific heat depends on diameter of nanotube, concentration of impurities, parameters of short-range order (structural heterogeneity) and describes the peculiarities of low-temperature behavior of specific heat observed in disordered CNT.

1. Introduction.

Specific heat of single- and multi-walled carbon nanotubes (CNTs) has been well studied. At temperatures above 100 K, specific heat $C(T)$ is shown to be satisfactorily described by the phonon contribution [1,2]. At low temperatures, below 100 K, $C(T)$ depends nonlinearly on temperature, and has kinks and jumps for tubes with different structures [3–7]. These low-temperature anomalies of specific heat are not described by the phonon contribution to $C(T)$, while a qualitative agreement of theoretical and experimental data could be achieved by an assumption of a change in the dimension of oscillations [6].

Conventionally obtained electronic contribution to specific heat in nanotubes at low temperatures is several orders of magnitude smaller than that of the measured $C(T)$. However, the authors of Ref. [8] note that in the doped tube the electronic specific heat can be much higher, if the Fermi level lies near the band edge.

Experimental studies of $C(T)$ in the doped CNTs were carried out in Refs. [6,9,10]. In Ref. [6] it was found that at $T < 20$ K specific heat in CNTs with He dramatically increases in comparison with $C(T)$ in a clean tube (without He), this growth, however, disappears at higher temperatures. The authors attribute this change to the high heat capacity of helium adsorbed below 20 K and desorbed above 20 K [6]. An increase of specific heat is also found in tubes doped with nitrogen and xenon [9,10].

In [3], the dependence of specific heat on structure and diameter of nanotube bundles is investigated. At $T < 20$ K, $C(T)$ is found to be weakly dependent on diameter, but at higher temperatures in bundles with diameter $d = 5$ nm there is an inflection point in the $C(T)$ plot; in bundles with $d > 20$ nm, in addition to the inflection point, there is a peak in the curve (the "excessive" specific heat).This peak is attributed to a possible orientation order-disorder transition [3]. Similar low-temperature anomalies of specific heat have been also found in other studies [11,12].

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Our investigations of the low-temperature transport properties of disordered metallic CNTs showed that the appearance of a gap in the electronic density of states (DOS) on the Fermi level [13], the inverse temperature dependence of electrical conductivity [14], and the nonlinear thermopower [15] could be associated with the short-range-order atomic reconstruction of the "phase separation-ordering" in CNTs. The results of our investigations [13–15] of DOS and electron transport properties depending on temperature and different types of atomic short-range-order structures in CNTs with different diameters are in good agreement with experimental data. That is why we are going to use our approach to describe the low-temperature behavior of specific heat in the disordered CNTs and show that the anomalies in $C(T)$ at low temperatures may have electronic nature and could be associated with the electrons participating in structure reconstruction of nanotubes.

2. Calculation

To calculate electronic specific heat, let us write the general form of thermodynamic potential

$$\Omega = T\sum_n \int \frac{d\vec{p}}{(2\pi)^3} \ln G\left(i\varepsilon_n, \vec{p}\right) e^{i\varepsilon_n \gamma}, \tag{1}$$

where $\gamma \to 0$, $\varepsilon_n = \pi T(2n+1)$ and $G(i\varepsilon_n, \vec{p})$ is the Matsubara Green function of electrons in a system with impurities and structural short-range order given by [16]

$$G\left(i\varepsilon, \vec{p}\right) = \frac{1}{i\varepsilon - \varepsilon_{\vec{p}} + (i/2\tau)\mathrm{sign}\varepsilon}. \tag{2}$$

Here $1/\tau = 1/\tau_0\left(1+BT^{1/2}\right)$ is the inverse relaxation time of electrons scattered on impurities $(1/\tau_0)$ and structures with different short-range orders $\left(BT^{1/2}/\tau_0\right)$, where $B = (2\sqrt{2\pi}(1-c)m^{3/2}V/\nu_0 N\hbar^3)\alpha$, $\tau_0 = \hbar/4\pi^2 u_0^2 c\nu_0$ and $\nu_0 = \left(p_0/(\pi^2\sqrt{3}a\gamma_0\hbar^2)\right)\sqrt{p_0^2 - (2\hbar/3d)^2}$ is DOS at the Fermi level in a clean nanotube (without defects) [13], α is the short-range-order parameter [17], d is the nanotube diameter, c is the concentration of alien atoms in a tube, m is the electron mass, V is the unit cell volume, N is the number of atoms inside the structure inhomogeneity of the short-range order type, and u_0 is the effective potential of multiple elastic scattering of electrons on defects [18].

Passing from summation to integration on the contour in (1), we obtain the following expression for entropy $S = -\partial\Omega/\partial T$

$$S = \int \frac{d\vec{p}}{(2\pi)^3} \oint \left\{ \frac{z}{2ch^2\frac{z}{2T}} \ln G(z, \vec{p}) + \frac{iB}{2\tau_0 T^{1/2}} th\frac{z}{2T} G(z, \vec{p}) \right\} e^{z\gamma} \frac{dz}{4\pi i}, \tag{3}$$

where $G\left(z, \vec{p}\right)$ is the analytic extension of the Matsubara Green function in the range $\mathrm{Im}z > 0$, $\mathrm{Im}z < 0$, and the contour corresponds to the poles $th(z/2T)$ at $z = i\pi T(2n+1)$. Let us represent Eq. (3) in the form of integrals along the real axis ε and pass from integration over momentum to integration over mass surface. As a result we have

$$S = \frac{\nu}{2} \int_{-\infty}^{\infty} \frac{\varepsilon^2 d\varepsilon}{2T^2 ch^2\frac{\varepsilon}{2T}} = \frac{2}{3}\pi^2 k^2 \nu T. \tag{4}$$

The integrals over ε containing $\mathrm{arctg}(1/2\tau(\varepsilon_p - \varepsilon))$ and imaginary part of the retarded Green function, after the transition to the mass surface and the integration over the momentum, will vanish because of oddness of the integrand.

Expression (4) has a standard form for electronic entropy, but contains DOS at the Fermi level in the disordered nanotube, which depends on temperature, short-range order parameter, concentration of alien atoms and tube diameter [13].

$$\nu = \frac{p_0}{\pi^2\sqrt{3}a\gamma_0\hbar^2}\sqrt{p_0^2 - \left(\frac{2\hbar}{3d}\right)^2} + \frac{8\hbar}{d(a\gamma_0)^2\tau}\sqrt{1+\left(\frac{\beta}{\tau}\right)^2}. \tag{5}$$

Here $\beta = (\sqrt{3}\pi\hbar d/a\gamma_0)$, $a = 2.46 \times 10^{-10}$ m is the lattice constant, $\gamma_0 = 2.9$ eV is the transfer integral between the first neighbor p_z orbitals [19], and p_0 is the Fermi momentum in a defect-free CNT. The first term in Eq. (5) is DOS (ν_0) in a clean tube, and the second one is determined by electron scattering on impurities and structural short-range order in a real tube.

Using the well-known expression for the specific heat $C = T(\partial S/\partial T)$, from Eqs. (4) and (5) we obtain

$$C = \frac{2\pi^2 k^2 T}{3}\left(\nu_0 + \frac{8\hbar\left(1+1.5BT^{1/2}\right)}{d(a\gamma_0)^2\tau_0}\sqrt{1+\frac{\beta^2}{\tau_0^2}\left(1+BT^{1/2}\right)^2}\right). \tag{6}$$

In fact, this expression consists of two linear and one nonlinear contributions. The linear contribution is determined by DOS in a defect-free tube (the first term) and scattering of electrons on impurities (the second term at $B=0$, which is possible if the short-range order parameters is equal to zero). Nonlinear temperature dependence of specific heat at low temperature is defined by the nonlinear DOS in a disordered tube. DOS also explicitly depends on concentration of alien atoms, short-range order parameter, tube diameter and the Fermi momentum (p_0), determining the relevant dependences of electronic specific heat. On the other hand, if specific heat is independent of diameter (dependence on diameter is observed only in tubes with very small diameters, $d \sim 1$ nm), the momentum p_0 has a significant influence on the value of specific heat. For instance, at $p_0 \sim 10^{-25}$ kg m/s the calculated specific heat is two orders of magnitude lower than the measured $C(T)$, while at $p_0 \sim 10^{-24}$ kg m/s the calculated electronic specific heat is already comparable to the experimental data. The maximum value of specific heat is determined by the linear temperature "impurity" contribution:

$$\Delta C = \frac{2\pi^2 k^2}{3} T \frac{8\hbar}{d(a\gamma_0)^2\tau_0}\sqrt{1+\frac{\beta^2}{\tau_0^2}}. \tag{7}$$

Thus, we have found out that the linear impurity contribution to specific heat determines the quantitative agreement with experimental data, while the nonlinear contribution from structural disorder describes the low-temperature behavior of $C(T)$ in disordered CNTs.

From Eq. (6) it is evident that electronic specific heat is a monotonic function of temperature, and does not have any singularities, if all the quantities in Eq. (6) do not depend on temperature. Actually, the short-range order parameter can depend on temperature $\alpha = \alpha(T)$ [17].

In our previous investigations we have shown that the gap in DOS [13], the negative temperature coefficient of electrical resistivity [14], the high value of thermopower S and its derivative $\partial S/\partial T$ in the metallized carbon nanotubes [15] are due to the temperature dependence $\alpha(T)$, when the sign of the short-range order parameter changes from positive to negative as the temperature decreases and the ordering of adsorbed atoms takes place. Thus, to describe the singularities in the temperature plot of specific heat we should assume that short-range order parameter undergoes temperature changes, defining peculiarities of CNT temperature characteristics.

Fig. 1 presents the experimental [3] (squares) and calculated data (thick solid line) for specific heat with the fitted plot $\alpha(T)$ (inset), which allows us to achieve the coincidence of peaks in the calculated and measured $C(T)$.