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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 $C(T)$.

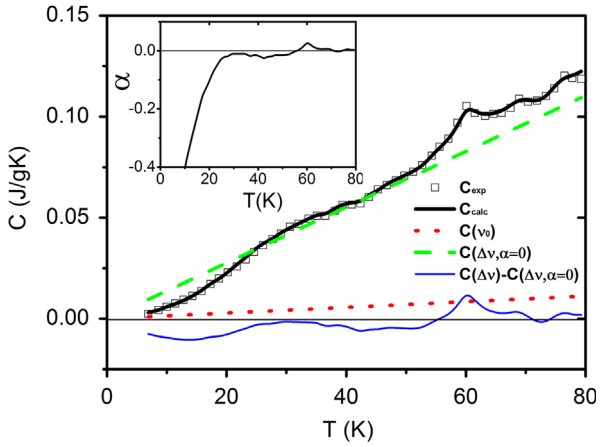

Fig. 1. Experimental C_{exp} [3] (squares) and calculated data C_{calc} (thick solid line) for specific heat with the fitted dependence $\alpha(T)$ (inset).

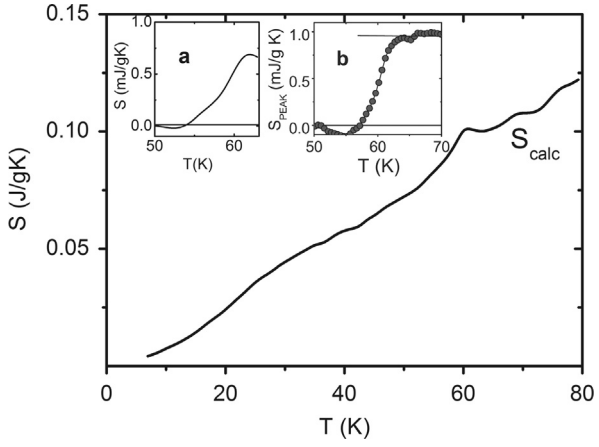

Fig. 2. Temperature dependence of entropy S_{calc} calculated using Eq. (4) and peak entropy calculated in the frame of our model (inset a) and in [3] (inset b).

The dotted line $C(\nu_0)$ in Fig. 1 is a linear contribution to $C(T)$ determined by DOS in a defect-free tube, it is an order of magnitude smaller than the experimental data [3]. The dashed line $C(\Delta\nu,\ \alpha=0)$ corresponds to a contribution from electrons scattered on point defects (impurities and vacancies) and determines the linear growth of $C(T)$ and quantitative agreement of our results with the experimental data, which is achieved due to a proper number of electronic states $\Delta\nu(T)$ at $\alpha=0$. All peculiarities in $C(T)$ and $\Delta\nu(T)$ at $\alpha\neq 0$ follow the singularities of $\alpha(T)$ (see inset in Fig. 1).

Finally, the contribution to electronic specific heat from electrons involved in the short-range order atomic reconstruction of the "phase separation-ordering" type is shown in Fig. 1 by the solid thin line. This contribution requires a separate discussion. The following should be pointed out:

1. This contribution is small and ΔC ($\alpha=0$) is the main contribution. This indicates an electronic nature of the low-temperature specific heat in CNTs.
2. This contribution determines the deviation from the linear temperature dependence of specific heat at $\alpha>0$ (the case of local phase separation), it increases and at $\alpha<0$ (the case of local ordering) it decreases specific heat.
3. A well-pronounced peak in $C(T)$ appears at a sharp activation of phase separation with a subsequent transition to a locally ordered structure, when the sign of the short-range order parameter changes from plus to minus.
4. In the latter case, the density of formation (ordering) energy passes through zero and changes its sign as well.
5. The contribution to $C(T)$ under ordering ($\alpha<0$) is negative, i.e. specific heat associated with the restructuring is also negative. This suggests that as the temperature decreases, the interaction potential energy (negative ordering energy) increases faster than the kinetic energy of electrons decreases. This results in an increase in this contribution to the internal energy, when the temperature is increased. The negative contribution to specific heat implies that the ordering may be treated as a certain condensation in the course of chemical localization of electrons.

In [3], the so-called "peak entropy" (which has the local maximum in the temperature dependence) is calculated by integrating of $\Delta C(T)/T$ over temperature. Quantity $\Delta C(T)$ is the difference between the experimental curve for $C(T)$ and the linear contribution to specific heat. We also have calculated entropy using Eqs. (4) and (5) (Fig. 2), and obtained the peak entropy (inset in Fig. 2) by the same method as in [3]. At $T\sim 60$ K, this contribution becomes negative as is the case in our investigation [3].

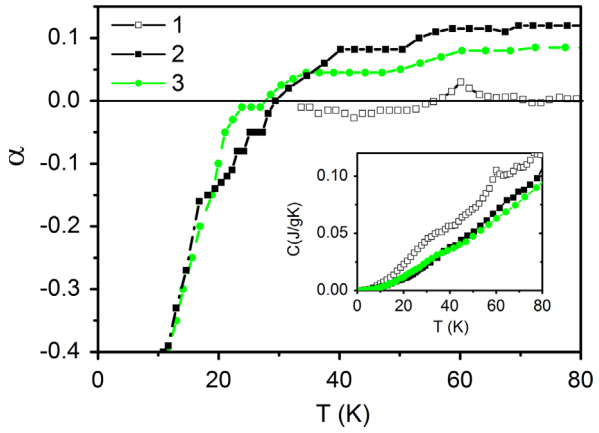

Fig. 3. $\alpha(T)$ plots calculated for [3] (curve 1), [12] (curve 2) and [11] (curve 3), and experimental data on specific heat [3,11,12] (inset).

The authors of Ref. [3] associate this phenomenon with the orientation phase transition. In our calculation, the change of entropy sign results from that of short-range order parameter, which could take place under conditions of the local phase separation – ordering structural transition. The entropy peak corresponds to that in the specific heat plot, when α has a maximum value. Above 65 K, parameter α varies but slightly near zero, and entropy is linear function of temperature.

In Fig. 3 the calculated data on short-range order parameters $\alpha(T)$ are presented (in inset – the corresponding experimental data of the specific heat $C(T)$ [3,11,12]). All of them, except the peak at $T\sim 60$ K in curve 1 (in inset), have a singularity at $T\sim 30$–40 K. All relevant short-range order parameters pass through zero at this temperature, i.e. all the peculiarities of the low-temperature specific heat can be generated by the electrons involved in the "ordering-phase separation" rearrangement, when the temperature increases.

When the alien atom concentration in a CNT increases, the temperature of structural restructuring increases as well (curve $\alpha(T)$ intersects the temperature axis at higher T (Fig. 4)).

3. Discussion

In Ref. [20], we considered the local atomic ordering in a disordered system, which is due to the interrelated processes of

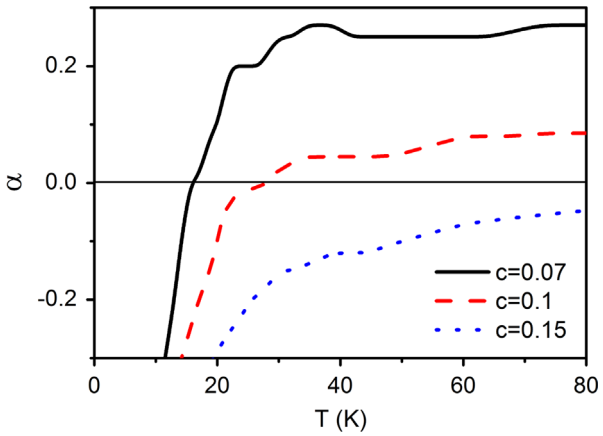

Fig. 4. Dependence $\alpha(T)$ for different concentrations of alien atoms in a CNTs calculated from the data on specific heat [11].

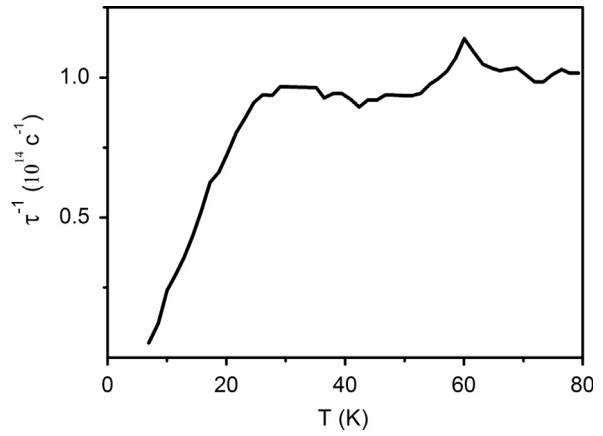

Fig. 5. Reversed relaxation time $(\Gamma_q = \hbar/\tau)$ for samples [3].

electron relaxation, the changes in population of decaying electronic states and polarization exciting a change in atomic configurations, which forms the region with a new short-range order.

Using the method of equations of motion, it was shown in Ref. [20] that during the formation of new chemical bonds, atoms or molecules (in the absence of dissociation) the structure of disordered systems exhibits a kind of local ordering and forms islands with a short-range order, which are composed of hydrides, oxides, etc. Under certain conditions, new structures can form and decay. In particular, ordering takes place when

1) the resonance condition is fulfilled

$$\omega_q = 2c(1-c)W(q) - \mu, \tag{8}$$

where $\omega(q) = \varepsilon_{k+q} - \varepsilon_k$, ε_k is the electron energy in the absence of ordering, k is the wave vector, q is the vector that determines the structure of a new order, $W(q)$ is the energy of ordering, and μ is the chemical potential of atomic pairs that determine the new short-range order (new chemical bonds).

2) the condition of the formation of a coherent standing wave in an atomic system is fulfilled

$$\Gamma_q > \omega_q, \quad \Gamma_q \geq W(q), \tag{9}$$

where $\Gamma_q = \hbar/\tau$ is damping of the electronic states in a disordered system. At $\Gamma_q < W(q)$, the ordering process is the beating with the period equal to $2\pi/\omega_q$, i.e. a new structure is either formed and broken during $t = \pi/\omega_q$, and no coherent atomic structures appear. At $\Gamma_q \geq W(q)$, the ordered structures become stable and hence $\partial W(q)/\partial q = 0$. In the course of formation of stable ordered structures, the electrons from the flat bands or those with wave vectors q in the extremums of the ε_q plot are involved. So-called bamboo structures [3] can represent examples of such structures in CNTs.

Moreover, apart from the case described above, conditions (8) and (9) can be fulfilled for a different case. At $\varepsilon_{k+q} = \varepsilon_k$, i.e. when the electron susceptibility has a singularity and $W(q)$ passes through zero changing its sign from positive to negative (from phase separation to ordering), equality $\mu = 0$ is automatically guaranteed under resonance. Vanishing of the chemical potential of configurational excitations (bosons) corresponds to the local "resonance" Bose condensation of atomic pairs in the short-range order at the temperature for which the $W(q)$ (or $a(T)$) curves cross zero. In this case, condition (9) is also satisfied (Fig. 5).

The maximum in Fig. 5 corresponds to $T \sim 60$ K, a sharp drop in Γ_q starts at $T \sim 30$ K. The formation of stable structures and resonance condensate is likely to be a common mechanism of electronic domain formation under diffusion phase transformations of the "phase separation -ordering" type [21], the high-temperature transitions in the alloys do not allow the role of electrons to be identifies in such an evident form as is the case with CNTs.

4. Conclusion

Thus, in this paper we have shown that low-temperature anomalies of specific heat in CNTs might have electronic nature rather than be associated with a change in dimension of atomic vibrations. We have demonstrated that they are determined by electrons scattered on point defects and participating in the formation of a new short-range order at low temperatures. The persistence of this ordering during the "phase separation - ordering transition" can occur as a resonance condensation, and the contribution to electronic specific heat and entropy in this case will be negative. Moreover, within the frame of our model it is possible to calculate the short-range order parameters and their temperature behavior using the experimental specific heat data in disordered carbon nanotubes.

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