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Low temperature behavior of the heat capacity of MWCNTs with Ø9.4 nm: component of flexural dispersion for phonons

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Low-temperature specific heat C(T) of multi-walled carbon nanotubes (MWCNTs) was studied. Two sets of modified, milled and milled-oxidized MWCNTs with an average outer diameter of 9.4 nm were used to measure specific heat in the temperature range of 1.8 to 275 K. The experimental results were compared with literature data for different carbon systems: bundles of single-walled carbon nanotubes (SWCNTs), graphite and other MWCNTs.
The initial MWCNTs were obtained by the CVD method. The length of MWCNTs and parameters of defects (number and types) in MWCNTs were changed: 1) grinding of the initial nanotubes in a ball mill; 2) the initial nanotubes were first oxidized and then milled. The figure shows low-temperature experimental heat capacity curves of ground (Sm), ground-oxidized (Sm-o) MWCNTs with outer diameters of Ø9.4 nm, as well as, for comparison, original nanotubes (Si), bundles of SWNCTs (Ø1.1 nm) and graphite. The analysis of the low-temperature behavior of the heat capacity of carbon materials below 3 K was carried out under the assumption that C(T) is determined primarily by phonons with sufficiently long wavelengths (deformation waves). The specific heat C(T), described by the equation C(T) = AT + BT3+ D*T5. The coefficients A, B and D were calculated and analyzed. The decrease in the length of nanotubes and the appearance of defects as a result of both grinding and oxidation with subsequent grinding lead to an increase in heat capacity in the low-temperature region. The obtained negative D parameter indicated flexural dispersion for phonons. It was found that the magnitudes of the Debye (B) and flexural dispersive components (D) depend on the structural parameters of nanotubes: such as the diameter of individual nanotubes, the average diameter of the bundle and the size of agglomerates.

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