

## Experimental low-temperature heat capacity of one-dimensional xenon adsorbate chains in the grooves of carbon c-SWNT bundles

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The experimental studies of the heat capacity of 1D chains of xenon atoms adsorbed in the outer grooves of bundles of closed single-walled carbon nanotubes  $C_{Xe}$  have been first made at temperature range 2–30 K with the adiabatic calorimeter. The experimental data  $C_{Xe}$  have been compared with theory [A. Šiber, *Phys. Rev. B* **66**, 235414 (2002)]. The experimental and theoretical heat capacity curves are close below 8 K. Above 8 K the experimental curve  $C_{Xe}(T)$  exceeds the theoretical one and excess capacity  $\Delta C_{Xe}(T)$  increases monotonously with temperature. We assume that the  $\Delta C_{Xe}(T)$  caused mainly by the increase of the distance between the neighboring xenon atoms in the chain with increasing temperature.

PACS: 65.40.Ba Heat capacity;

**65.80.-g** Thermal properties of small particles, nanocrystals, nanotubes, and other related systems;

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The unique structure of bundles of the single-walled carbon nanotubes (SWNTs) permits obtaining quasi-one, two and three-dimensional structures formed by adsorbates [1,2]. Technologically, most of the tubes in the prepared bundles have closed ends unless special steps are taken to open them. The possible sites of adsorption of relatively small impurity atoms or molecules in a bundle of closed SWNTs (c-SWNTs) are interstitial channels (IC), grooves at the outer surface (G) and the outer surface (OS) (see Fig. 1). These positions differ in geometrical size and energy of adsorbate binding to c-SWNT bundles [3]. Physical properties (adsorption, thermal and structural) of simple gas admixtures deposited in c-SWNT bundles were investigated in experimental and theoretical works [1–26]. The heat capacity of  $^4\text{He}$  adsorbed on c-SWNT bundles was investigated at temperatures below 6 K [19,20]. It was observed [20] that the heat capacity of the adsorbed helium exhibited the behavior of 1D and 2D structures depending on the technique of sample preparation (laser evaporation or arc discharge).

Structures of  $^4\text{He}$  adsorbates in the grooves and at the outer surface of c-SWNT bundles were measured by the neutron diffraction method [27]. At low coverage, the  $^4\text{He}$  atoms formed a 1D single line lattice along the grooves. As the concentration of the adsorbed helium atoms increased, a 2D mo-

nolayer was formed, which covered the whole c-SWNT bundle surface [27]. Antsygina *et al.* [15–17] suggested a rigorous thermodynamic model describing the multilayered atomic adsorbate in grooves, interstitials and external surface of

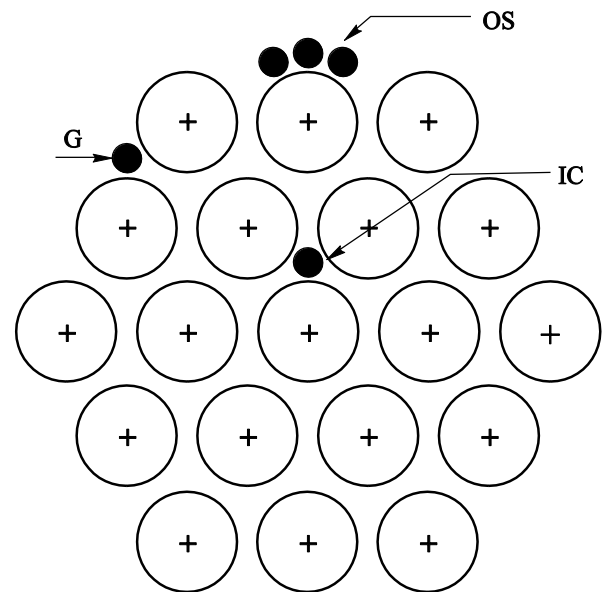


Fig. 1. Possible sites of adsorption of relatively small impurity atoms or molecules in a c-SWNT bundle.

bundles. The model [16,17] based on a proper account of the temperature-dependent adsorbate redistribution between 1D, 2D and 3D subsystems made it possible to explain on a quantitative level the adsorption isotherms and isotheric heat of He deposited on the bundles [15,19]. The thermodynamic research on the neon films adsorbed by HiPco c-SWNT bundles was carried out experimentally in Ref. 28. However, the behavior of the one-dimensional chains of the adsorbed gas in the grooves on the outer surface of the bundles has not been given enough attention in this work. The radial thermal expansion coefficients of c-SWNT bundles saturated with Xe atoms to rather high (1.64 mole/mole, %) concentration were measured in Refs. 18 and 25.

The 1D chains of Xe atoms adsorbed in the grooves at the outer surface of a c-SWNT bundle are shown schematically (one in each groove) in Fig. 2.

Low temperature dynamics of inert gas atoms and methane molecules in c-SWNT bundles was considered in theoretical studies [29–31]. The calculated heat capacities of 1D chains of inert gas atoms and methane molecules adsorbed physically in the grooves of c-SWNT bundles are reported in [29] (Ar, Kr, Xe) and [30] (Ne, CH<sub>4</sub>).

To our knowledge, no experimental investigations of the thermal properties of c-SWNT bundles containing 1D chains of adsorbed classical inert gas atoms (Ar, Kr, Xe) have been reported so far.

Our goal was to investigate the low-temperature heat capacity of the 1D chains of xenon atoms adsorbed in the grooves at the outer surface of c-SWNT bundles. The choice of the adsorbate was dictated by the following reasons. First, physical adsorption of Xe atoms is possible only in the grooves and at the outer surface of c-SWNT bundles. Adsorption in the interstitial channels is prohibited because of the relationship between the geometrical

sizes of channels and Xe atoms [12]. Second, the binding energy of Xe atoms is higher in the grooves than at the outer surface [3,8] and Xe atoms are physically adsorbed primarily in the grooves where they form one-dimensional chains (see Fig. 2).

The heat capacity of 1D chains of Xe atoms adsorbed in the outer grooves of c-SWNT bundles has been first measured in this work at temperature range from 2 K to 30 K using an adiabatic calorimeter [32].

A cylindrical sample of c-SWNT bundles (7.2 mm high, 10 mm in diameter and 1.27 g/cm<sup>3</sup> density) was prepared by compressing c-SWNT plates under the pressure 1.1 GPa. The plates (~0.4 mm thick) were obtained by compacting a c-SWNT powder (“Cheap Tubes”) under  $P=1.1$  GPa [33]. The powder was prepared by chemical catalytic vapor deposition (CVD). It contained over 90 wt% of c-SWNT bundles, other allotropic forms of carbon (fullerite, multiwalled nanotubes and amorphous carbon) and about 2.9 wt% of cobalt catalyst. The average tube diameter in the sample was 1.1 nm; the average length of the c-SWNT bundles was 15  $\mu\text{m}$  [33]. The number of nanotubes in the bundles varied within 100–150 (estimated from high-resolution TEM pictures) and was equal to, on the average, 127. The mass of the c-SWNT bundles sample was equal to  $716.00 \pm 0.05$  mg.

The temperature of the calorimeter was measured with a calibrated CERNOX resistance thermometer (Lake Shore Cryotronics).

First, the addenda heat capacity  $C_{\text{ad}}$  (the heat capacity of calorimeter with an inserted sample of pure c-SWNT bundles) was measured in a separate experiment. Then the calorimeter with sample was warmed to room temperature. The c-SWNT bundles were saturated with Xe directly in the calorimeter cell. The vacuum cavity of the calorimeter was filled with Xe gas:  $3.19 \cdot 10^{-4} \pm 5 \cdot 10^{-6}$  mole. The obtained ratio is  $N_{\text{Xe}}/N_{\text{C}} \approx 0.55\%$ , where  $N_{\text{Xe}}$ ,  $N_{\text{C}}$  is the number of Xe and C atoms in the SWNT sample, respectively. The quantity of Xe was estimated by PVT-method. The chemical purity of xenon was 99.98% (0.01% N<sub>2</sub>, 0.01% Kr).

It was assumed within the employed geometric model that the distance  $a$  between the nearest Xe atoms in the chain is equal to the distance between the nearest neighbors in the FCC lattice of solid Xe  $a = 4.336 \text{ \AA}$  at  $T = 0 \text{ K}$  [34]. In the case of complete occupancy of the grooves by Xe atoms (one chain in each groove) we obtained the ratio  $n_{\text{Xe}}/n_{\text{C}} \approx 0.5\%$  ( $n_{\text{Xe}}$  and  $n_{\text{C}}$  are the number of Xe and C atoms in the c-SWNT bundles, respectively). This value is 10–20% lower than in the experiment.

The calorimeter was cooled from room temperature to 90 K for eight hours. During this period Xe atoms were being adsorbed in the c-SWNT bundles. For the geometrical reasons Xe atoms cannot penetrate into the interstitial channels [12] under low pressure. Since the binding energy of Xe atoms is higher in grooves than at the outer surface [3,8], the Xe atoms are physically adsorbed first of all in the grooves

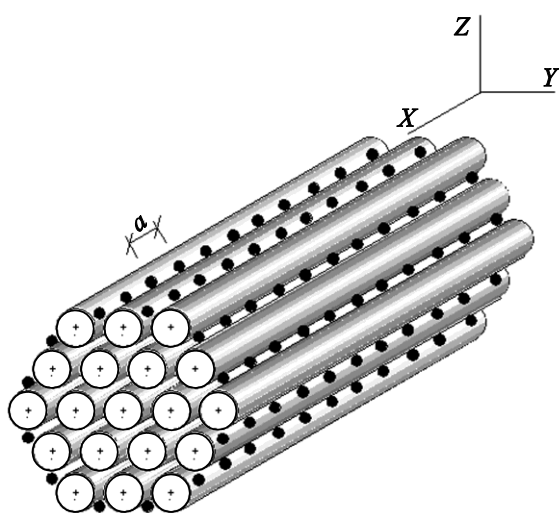


Fig. 2. One-dimensional chains of Xe atoms adsorbed in the grooves at the outer surface of a c-SWNT bundle;  $a$  is the distance between the nearest neighboring Xe atoms in the chain.

where they form 1D chains. After cooling of the calorimeter from 90 K to helium temperatures (during 5–6 h), the sample was thermocycled (about 1 K heating–cooling) several times and then the heat capacity was measured. The heat capacity measurement runs were made from the lowest temperature of the run up to 30 K. After each measurement series up to 30 K the sample was heated to 80 K and then, after a slow cooling down to helium temperature and thermocycling, the measurement was repeated. Several measurement runs were made. The results of different runs coincided within the measurement error. Other experimental features have been reported elsewhere [32,35].

The temperature dependencies of the total heat capacity  $C_{ad+Xe}$  and its addenda component  $C_{ad}$  are shown in Fig. 3 at the temperature range from 2 to 30 K (Insert: the heat capacities below 5 K). It is interesting that the introduction of only 5–6 atoms of xenon per 1000 carbon atoms causes a significant increase in the heat capacity in the whole temperature range of the experiment. For example, ratio  $(C_{ad+Xe}-C_{ad})/C_{ad} \approx 160\%$  and  $\approx 20\%$  at  $T = 2.6$  K and at 30 K, respectively. The contribution  $C_{Xe}$  of xenon atoms to the total heat capacity  $C_{ad+Xe}$  has been separated by subtracting the heat capacity of the addenda from the total heat capacity  $C_{ad+Xe}$ .

Random error in the  $C_{Xe}$  — value is within  $\pm 20\%$  at 2.2 K and  $\pm 5\%$  at the temperature region 10–30 K. The systematic error is mainly contributed by inaccuracies concerning the number of SWNTs.

The  $C_{Xe}(T)$  is shown in Fig. 4 in the coordinates  $C_{Xe}(T)/(\mu R)$ , where  $\mu$  is the number of xenon atoms (in moles),  $R$  is the gas constant. For comparison, Fig. 4 includes a theoretical temperature dependence of the heat capacity of 1D chains of Xe atoms adsorbed physically in the grooves at the outer surface of c-SWNT bundles [29].

It is seen in Fig. 4 that below 8 K the experimental and theoretical [29] curves of heat capacity  $C_{Xe}$  are close. Ac-

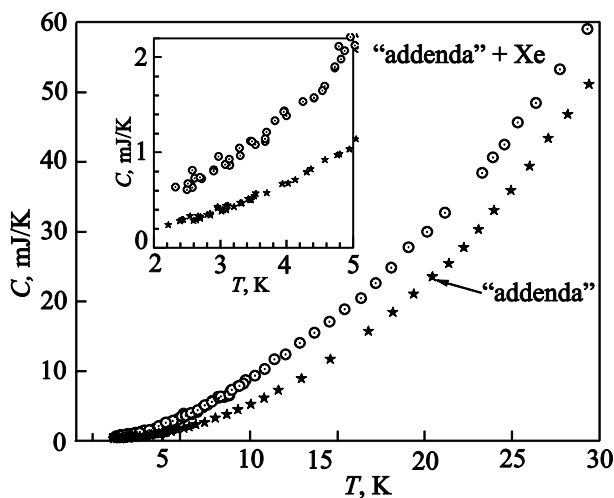


Fig. 3. Experimental temperature dependencies of the total heat capacity  $C_{ad+Xe}$  and its component  $C_{ad}$ .

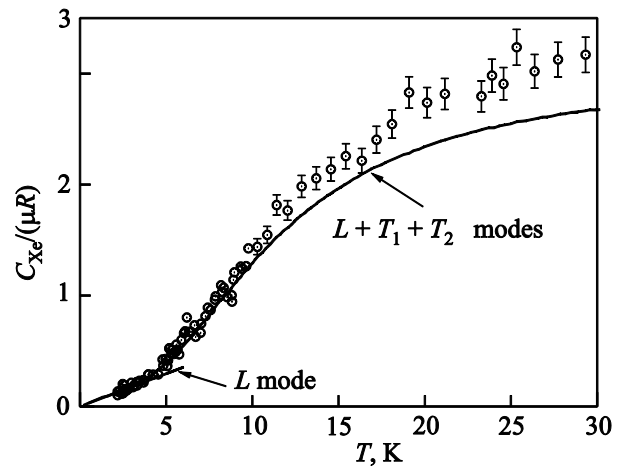


Fig. 4. The heat capacity of 1D chains of Xe atoms adsorbed in the grooves at the outer surface of c-SWNT bundles. Experiment (this work): open circles. Theory [29]: solid curve for the  $L + T_1 + T_2$  modes; solid straight line only for the  $L$  mode.

ording to the Šiber theory [29], at  $T < 4$  K the heat capacity is influenced mainly by the longitudinal mode and is proportional to the temperature. Above 4 K the transverse optical modes begin to take effect. Figure 5 illustrates the low temperature part of heat capacity  $C_{Xe}$  in coordinates  $C_{Xe}/\mu RT$  vs  $T$ . The straight line in the same figure shows the theoretical low-temperature heat capacity of the chain of Xe adatoms caused by the longitudinal mode [29]. It is seen that below  $\approx 4$  K the experimental dependence of  $C_{Xe}$  is close to the predicted straight line characteristic for the low temperature heat capacity of 1D chains. Above 4 K the experimental points start to deviate from this line. Using the formula (13) from Ref. 29, we estimated both the phonon frequency of the longitudinal mode  $\hbar\omega_L \approx 3.1$  meV which is close to the theoretical value 3.06 meV [29] and the Debye temperature  $\Theta_{D,L} \approx 35.7$  K of 1D chains. The Debye temperatures  $\Theta_{D,L}$  of one-dimensional Xe and Ne chains are given in the table. There is good agreement between theoretical and experimental Debye temperatures of 1D Xe chains. The large discrepancy observed for Ne chains is somewhat surprising [28,30].

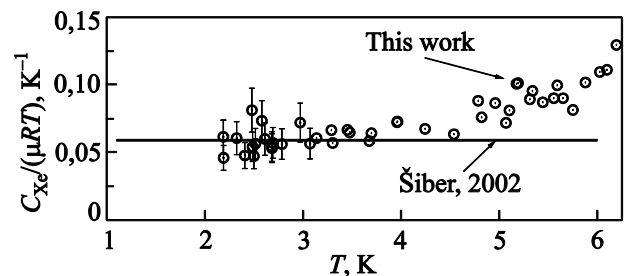


Fig. 5. The dependence of  $C_{Xe}/\mu RT$  vs  $T$ : circles — experiment, the straight line — theoretical low temperature asymptotics of the heat capacity of the longitudinal mode of the chains of Xe adatoms [29].

Table 1. 1D Debye temperatures  $\Theta_{D,L}$

Substance	1D Debye temperature, $\Theta_{D,L}$ , K (nearest neighbor distance, Å)			
	$\Theta_{D,L} \approx 2.095RT/C_v$ after [29]		$\Theta_{D,L} = \pi^2 RT/(3C_v)$ after [30]	
	Experiment	Theory	Experiment	Theory
Xe	35.7 [present work]	35.5 (4.59 Å) [29]	56.5 [present work]	55.8 (4.59 Å)*
Ne	—	—	58 [28]	78 (3.08 Å) [30]

Notes:\* The  $\Theta_{D,L}$  calculation was made according to Ref. 30 using theoretical  $C_v$  for the longitudinal mode of the chains of Xe adatoms from Ref. 29.

At  $T > 8$  K the experimental curve  $C_{Xe}(T)$  starts to exceed the theoretical one [29] and the  $\Delta C_{Xe}(T)$  increases monotonously with the rising temperature. We assume that the excess caused mainly by the increase of the distance between the neighboring xenon atoms in the chain with increasing temperature.

Šiber [29] suggested that the heat capacity of 1D chains of inert gas atoms adsorbed physically in the grooves of c-SWNT bundles could be calculated using a simple model in which for simplicity author assumes that substrate is rigid, ignores the discrete structure of the tubes surrounding a groove and neglects all the interactions between the adsorbates that are not in the same groove. It should be noted, that the absolute minimum (−225 meV) of external potential for Xe atom in the groove [29] is higher, than the experimental binding energy (−282 ± 11 meV) [3]. These values are an order of magnitude smaller than the binding energy of the adsorbate–adsorbate [29]. He calculated the temperature dependencies of one-dimensional chains of inert gas adsorbates (Ar, Kr, Xe) in the interval 2–40 K [29]. Similar results on the heat capacity of the chains of Ne atoms and CH<sub>4</sub> molecules adsorbed physically in the grooves of c-SWNT bundles were obtained in a theoretical study [30].

There is surprisingly good agreement between the theoretical predictions and experimental results despite significant simplification in the theoretical model [29] and possible deviations from the ideal object.

The discrete structure of nanotubes has little effect on the transverse modes of Xe atoms beyond the center of the Brillouin zone [31], but the longitudinal mode is more sensitive to the parameters of the models and the chain density.

In this study the heat capacity of one-dimensional chains of xenon atoms adsorbed in the outer grooves of bundles of single-walled carbon nanotubes with closed ends has been first studied in the temperature interval 2–30 K. The experimental and theoretical [29] results are close below 8 K. Observed at higher temperatures, the discrepancy between the experimental and theoretical heat capacities could be mainly due to the increase of the distance between the nearest

neighboring xenon atoms in the chain with increasing temperature.

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