Thermal properties of single-walled carbon nanotube crystal*

Hu Li-Jun(胡丽君)[a)b)], Liu Ji(刘 基)[a)], Liu Zheng(刘 政)[a)],
Qiu Cai-Yu(邱彩玉)[a)b)], Zhou Hai-Qing(周海青)[a)b)], and Sun Lian-Feng(孙连峰)[a)†]

[a)] *National Center for Nanoscience and Technology, Beijing* 100190, *China*
[b)] *Graduate University of Chinese Academy of Sciences, Beijing* 100049, *China*

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In this work, the thermal properties of a single-walled carbon nanotube (SWCNT) crystal are studied. The thermal conductivity of the SWCNT crystal is found to have a linear dependence on temperature in the temperature range from 1.9 K to 100.0 K. In addition, a peak (658 W/mK) is found at a temperature of about 100.0 K. The thermal conductivity decreases gradually to a value of 480 W/mK and keeps almost a constant in the temperature range from 100.0 K to 300.0 K. Meanwhile, the specific heat shows an obvious linear relationship with temperature in the temperature range from 1.9 K to 300.0 K. We discuss the possible mechanisms for these unique thermal properties of the single-walled carbon nanotube crystal.

Keywords: single-walled carbon nanotube，SWCNT crystal，thermal conductivity, specific heat

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1. Introduction

Since their discovery by Iijima and Ichihashi,[1] single-walled carbon nanotubes (SWCNTs) have attracted much attention and have been extensively studied for nearly 20 years due to their unique properties and potential applications. Among these studies, electrical and mechanical properties as well as relevant applications have been particularly investigated.[2−5] Compared with these intense and thorough studies, the thermal properties of the SWNTs, especially for applications as highly efficient thermal conducting materials, need further investigation, since the other form of the carbon sp^3 bonds, monocrystalline diamond, is shown to be one of the best thermal conductors.[6] A molecular dynamics simulation performed by Berber's group predicted unusually high thermal conductivity ($K \approx 6600$ W/mk) for an isolated (10,10) carbon nanotube at room temperature.[7] However, for SWNT mats and SWNT bundles, the measured thermal conductivity is found to be one or two orders of magnitude lower.[8] Recent reports show that the alignment of the SWNTs dominates the thermal conductivity for the fiber-liked SWNT composite. For example, the thermal conductivity is about 35 W/(m·K) and 210 W/(m·K) for the SWNTs before and after the processing for orientation at room temperature, respectively,[9] which is similar to that of highly oriented pyrolytic graphite (HOPG). Limited SWNT length, poor continuity and many connections between individual nanotubes in bundles or ropes generally result in small thermal conductivity compared with that of a single SWNT or that of a long SWNT bundle with good continuity. In this work, based on a newly fabricated SWNT condensed material, which is formed from highly dense and perfectly aligned (HDPA) SWNTs[10] and named SWNT crystal, the thermal conductivity and the specific heat are reported. We find the metal-like thermal conductivity and the linear specific heat in a temperature range from 1.9 K to 300 K.

2. Experiment

SWNT films were grown by floating catalytic chemical vapour deposition (CVD), as reported previously.[11] After about 6 h growth, SWNT films with dimensions of 100 mm×50 mm could be carefully peeled off the quartz tube with a hook. There was no obvious level of orientation found in the SWNT films after the removal process. In order to align the

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†Corresponding author. E-mail: slf@nanoctr.cn
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SWNTs, a series of diamond wire drawing dies were used. The drawing was carried out using the diamond dies with decreasing pore diameters in sequence (from 1.2 mm to 0.2 mm). Before being drawn, the as-grown SWNT films were black. During each drawing, the SWNTs formed a bundle with the same diameter as that of the die used. Finally, the surface of the SWNT bundle became gray with a metallic luster, which is quite different from that of as-grown nanotube films.

Figure 1(a) shows a typical scanning electron microscopy (SEM) image of the as-grown SWNT film. It is found that the individual SWNTs interconnect with each other without an obvious growth direction. Individual SWNTs can hardly be seen in the image of the as-grown film, because they tend to gather together due to the van der Waals interaction in the course of growth. The entangled SWNT bundles pile up with no obvious direction of alignment and their diameters are determined by the number of the SWNTs included. In Fig. 1(b), very few catalytic particles (white dots) can be seen on the smooth surface of the SWNT crystal, indicating the high quality of the SWNTs. There is a great difference between the as-grown SWNT films and the SWNT crystal from the viewpoint of the surface morphology. The SWNT crystal is composed of regularly packed SWNTs and the number of the SWNTs is estimated to be as high as 10^6.

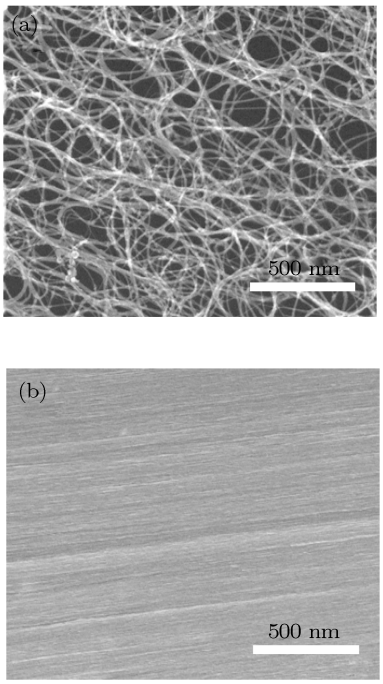


Fig. 1. (a) Scanning electron microscopy images of as-grown SWNT film. (b) The aligned and highly dense SWNTs in SWNT crystal.

It has an ideal two-dimensional triangular lattice with a lattice constant of 19.62 Å and a d spacing of 3.39 Å, which arises from the van der Waals interaction and the graphitic packing of the individual SWNTs. Compared with the SWNT film, the SWNT crystal has a large length of orientation, good continuity and small connections between nanotubes.[12]

The thermal properties of the SWNT crystal were investigated by using a physical property measurement system (PPMS, from Quantum Design Corporation). The custom-built stage designed for the PPMS was used to measure the specific heat (C) and the thermal conductivity (K), which are the main thermal properties of a material. Figure 2 shows the instrument with four supporters for the thermal measurement. The thermal conducting measurement was carried out in a cylindrical chamber and four polished oxygen-free high-conductivity (OFHC) copper plates were suspended as the supporters to locate the sample. After the sample was fixed without any contact to the wall of the chamber, it was put into a high vacuum ($\sim 10^{-4}$ Pa) chamber. Then the measurement was carried out as shown in Fig. 2(b). If a voltage is applied between electrodes 1 and 4, the Joule heat will be generated and then dissipated along the SWNT crystal, which was used as the thermal conductor during the measurement. Two thermometers monitored the temperature of the two in-between plates (copper plates 2 and 3 with temperature T_0 and T_1, respectively), and the thermal conductivity could be obtained through a software calculation.

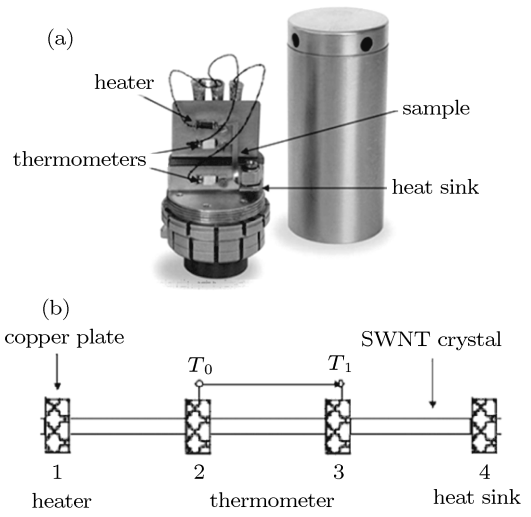


Fig. 2. (a) Custom-built stage used for thermal property study. (b) Schematic diagram for thermal conductivity measurement.

The geometry of the sample used for the thermal conductivity measurement is limited by the chamber,

which was about 10.0 mm (length)×0.3 mm (diameter). In Fig. 2(b), the distance between copper plates 2 and 3 is ∼2.0 mm, and the contact length with the copper plate is ∼1.0 mm. During the measurement, the sample was suspended, a little Apiezon N-grease was used to enhance the thermal contact between the suspended SWNT crystal and the copper plate. The high vacuum chamber was used to reduce thermal losses due to radiation and convection. The thermal isolation of the SWNT crystal ensured that the heat produced by the Joule self-heating was conducted along the sample itself.

3. Results and discussion

In Fig. 3, the measured thermal conductivity $K(T)$ is plotted as a function of temperature T in a temperature range from 1.9 K to 300 K. From 1.9 K to 100 K, the thermal conductivity increases linearly with the increasing temperature, which shows a similar temperature dependence to that of unoriented SWNTs. At about 100 K, a clear peak of the thermal conductivity ∼658 W/mK is observed. The thermal conductivity gradually decreases with the increasing temperature in the temperature range from 100 K to 200 K, and becomes a constant with a value ∼470 W/mK in the temperature range from 200 K to 300 K.

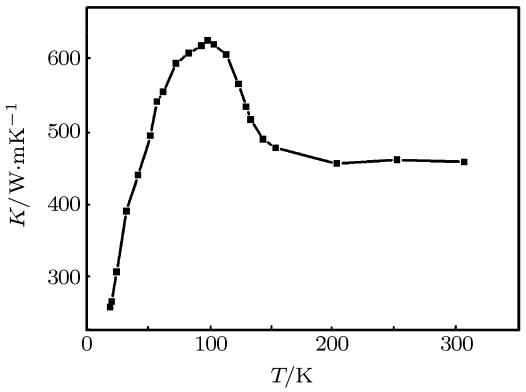


Fig. 3. Variation of the thermal conductivity of SWNT crystal with temperature.

To understand the physical mechanism of the above observation of the thermal conductivity, we neglect the sample surface and approximate the crystal by an infinite lattice. It is usually assumed that at low temperature the thermal conductivity is dominated by phonons at least down to 10 K. So when discussing the thermal conductivity in the range from 1.9 K to 100 K, we will only pay attention to the phonon contribution. The phonon thermal conductivity can be described by the following equation:

$$K = \sum_p C_p V_p L_p, \tag{1}$$

where C_p is the specific heat capacity, V_p the phonon group velocity and L_p the mean free path. Generally, the mean free path of the phonon is expected to be extraordinarily long due to the long wavelength acoustic phonons (especially at low temperature). An ideal and infinitely long nanotube has four phonon modes: a longitudinal acoustic mode, two transverse acoustic modes and a twist mode. The longitudinal acoustic and twist modes involve atoms moving along the cylindrical surface of the undistorted tube. Considering the significant phonon population in a wide range of phonon branches at room temperature, we expect that contributions to the heat conduction at low temperature will come from phonons with wide range of wave numbers and frequencies, including optical phonons with sufficiently large group velocity. The sound velocity has been calculated for tubes in the size range of interest with a reliable tight-binding molecular-dynamics scheme.[13] According to the calculation, the phonon velocities estimated at low temperature are as follows: $V_{\rm la} \sim 10^6$ cm/s and $V_{\rm ta} \sim 10^5$ cm/s. The mean free path is taken to be several hundred micrometers. Therefore, the thermal conductivity can be estimated to be about several hundreds of W/mK, which is in very good agreement with our experimental value for the temperature range from 1.9 K to 100 K (Fig. 3). The $K(T)$ follows a linear tendency until the temperature reaches about 100 K.

To explain the interesting and novel maximum thermal conductivity at the temperature of about 100 K, we propose that the structural properties of the SWNT crystal may play a dominating role here. It was theoretically predicted that in the SWNT crystal a clear transition of its structure exists, which depends on the nanotube diameters.[14] Nanotubes with sizes smaller than 10 Å behave as rigid cylinders, while nanotubes with sizes larger than 25 Å flatten against each other due to van der Waals attraction, forming a honeycomb structure. These results indicate that there will be a crossover of the structural properties of the SWNT crystal and the distortion along the circumference of each SWNT takes place in a direction perpendicular to their axes. The average diameter of the SWNTs in our sample is about 16 Å, which is within the range of the predicted diameter for the nanotubes. Moreover, the band repulsion from the

tube–tube contact is expected to occur by the interaction in the crystal.[15] The phonon scattering or the phonon dispersion, especially caused by the structural torsion, plays a main role in reducing the thermal conductivity as the temperature increases. From 1.9 K to 100 K, the phonon thermal transference dominates and the mean free path increases as the temperature goes up. As the effect from the decreasing mean free path is equal to that from the temperature contribution, a peak value of the thermal conductivity is found. It should be noted that the thermal conduction is an integration of the longitudinal and the the transverse modes. For isolated and individual SWNTs, the thermal conductivity along the tube has a much higher value than that across the axis.[16] However, in the case of the SWNT crystal, the heat can be conducted primarily in both directions. The SWNT crystal is likely to conduct the heat flow following a tortuous path in the perpendicular direction.

When the temperature is above 100 K, the thermal conductivity decreases quickly with the increasing temperature and becomes almost a constant (with a value $\sim$ 480 W/mK) around room temperature. The mechanism for these observations can be related to the temperature-dependent properties of phonons. We consider two kinds of mechanisms for phonon relaxation, which are applicable at low and at high temperatures, respectively.[17,18] At low temperature (100 K to 150 K), the relaxation time is shown to be inversely proportional to the temperature, which makes the thermal conductivity decrease with the increasing temperature. At high temperatures (150 K to 300 K), especially near room temperature, phonon–phonon scattering is expected to contribute significantly to the phonon decay.[19] The mechanism for the phonon decay is the competition between the boundary and the defects scattering, which makes the phonon relaxation time show no temperature dependence. The molecular dynamics study on the thermal conduction of carbon nanotubes and graphite also shows that the thermal conductivity increases and then converges to a constant as the temperature increases, which is consistent with our result.[20] Besides the above discussion, the large surface area, impurities, defects, the neighbouring tubes and the small nanotube length may also contribute to the thermal conductivity in some way.

The measured specific heat $C(T)$ versus temperature is shown in Fig. 4. It can be seen clearly that the specific heat shows a linear dependence on temperature in the temperature range from 15 K to 300 K, which is different from that of the graphite and the multi-wall carbon nanotubes.[21,22] Meanwhile, there is a turning point at about 15 K, which can be seen clearly from the inset of Fig. 4.

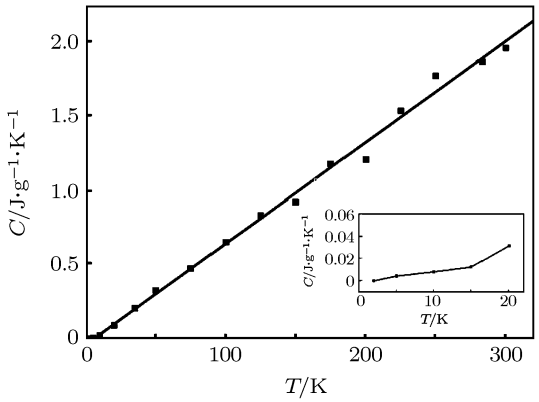


Fig. 4. Specific heat of SWNT crystal in the temperature range from 1.9 K to 300 K. The inset shows the low temperature specific heat.

Generally speaking, the individual SWNTs in the SWNT crystal have different diameters with a very narrow distribution. For simplicity, we take the (10, 10) SWNT as an estimation example. The modeling of the band structure for a (10, 10) SWNT shows that the lowest energy of the subband is about 2.5 meV and the energy level of the subband in the sample can be estimated by

$$\Delta E \approx h\nu/R, \tag{2}$$

where h is the Plank's constant, ν is the velocity of the corresponding mode and R is the radius of the SWNT.[23] Considering the composition of the SWNT film prepared by the CVD,[24] the temperature corresponding to the lowest energy is about 15 K. Thus the turning point at 15 K of the above C–T curve should result from the only occupation of the phonon subband.[25] Since the electron contribution is negligible in the temperature range of the measurement,[26] the nearly linear C–T provides information about the low-energy excited states of the SWNT crystal, which is dominated by the phonon contribution at temperatures above 15 K.

The $\rho(\omega)$ is the phonon spectrum determined by using the phonon energy dispersion $\omega(k)$ of different modes and the occupational dimensionality of the phonon excitations in k space. For the SWNT of $\sim$1.6 nm diameter, $\rho(\omega)$ and $\omega(k)$ have been calculated and shown to have a linear phonon dispersion

and one-dimensional behaviour.[27] From the following equation:

$$C_p = \int_0^{\omega_{\max}} \kappa_{\rm B} \left(\frac{\hbar\omega}{\kappa_{\rm B}T}\right)^2 \frac{{\rm e}^{\hbar\omega/\kappa_{\rm B}T}\rho(\omega){\rm d}\omega}{({\rm e}^{\hbar\omega/\kappa_{\rm B}T}-1)^2}, \qquad (3)$$

it can be seen that if there is a constant $\rho(\omega)$, the linear temperature dependence of C_p will be concluded when $T \ll \Theta_{\rm D} = h\omega_{\max}/k_{\rm B}$, where $\Theta_{\rm D}$ is the Debye temperature. Considering the graphitic nature of the SWNT crystal, we propose reasonably that the $\Theta_{\rm D}$ for the SWNT crystal has a value similar to that of the graphite, which is as high as 2400 K. Therefore, the linear T-dependence of the C_p reflects a constant $\rho(\omega)$ for the phonon states excitable in the temperature range of our experiment. Furthermore, the surface C–C bond breaking and the evaporation of carbon atoms caused by the vibration of Stone–Wales defects at high temperature seem to illustrate the stable existence of the SWNT crystal.[28]

4. Conclusion

We fabricate an SWNT crystal and measure its thermal conductivity and its specific heat. The thermal conductivity of the SWNT crystal is found to have a linear dependence on temperature in the temperature range from 1.9 K to 100.0 K. A peak is found at the temperature around 100.0 K and the thermal conductivity is a constant in the temperature range from 100.0 K to 300.0 K. Meanwhile, the specific heat shows an obvious linear relationship with the temperature in the temperature range from 1.9 K to 300.0 K. This indicates a constant $\rho(\omega)$ for the phonon states of the SWNT crystal excitable in the temperature range of our experiment.

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