Thermal conductivity of zigzag single-walled carbon nanotubes: Role of the umklapp process

J. X. Cao,[1,2] X. H. Yan,[1,*] Y. Xiao,[1] and J. W. Ding[1,2]
[1]*Faculty of Material and Photoelectronic Physics, Xiangtan University, Xiangtan 411105, Hunan, China*
[2]*Institute of Mechanics and Material Engineering, Xiangtan University, Xiangtan 411105, Hunan, China*
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Considering the three-phonon process, we calculate the thermal conductivity of zigzag tubes. It is found that thermal conductivity of an isolated (6, 0) single-walled carbon nanotube increases with the increase of temperature at low temperature, and would show a peak behavior at about 85 K before falling off at high temperature. Moreover, thermal conductivity is high for single-walled carbon nanotubes with small diameters as compared to the tubes with large diameters. The thermal conductivity at 300 K is approximately inversely proportional to the tube's diameter.

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Potential applications of carbon-nanotube-based devices, such as diodes,[1] field-effect transistors,[2] single-electron transistors,[3] as well as elementary logic circuits[4] rely on an effective way of removing high density of excess heat from the device active regime.[5–7] Removal of heat, actually, depends on the thermal conductivity of carbon nanotubes and the related compounds.[8] Thermal conductivity of single-walled carbon nanotubes (SWCN's) is predicted to be unusually high by molecular-dynamics simulations at room temperature.[9–11] The measurement on ropes of SWCN's indicates a linear temperature dependence up to 30 K and an upward bend near 30 K on the curve of thermal conductivity $\kappa(T)$.[12] In contrast to that of SWCN's, κ for multiwall carbon nanotube (MWNT) ropes increases with temperature in a parabolic fashion at low temperature up to ~ 120 K.[13] In order to reveal temperature dependence behavior of κ, Kim[14] performed scanning electron microscopy technique on individual MWNT. It is found that at low temperature ($8 \text{ K} < T < 50$ K), κ increases following a power law with an exponent 2.50, and then increases quadratically when $T < 150$ K. Although there is a vast literature concerning thermal transport in SWCN's, it is necessary to describe phonon characteristics for understanding the physical essence of the various experimental observations. In this paper, considering the three-phonon umklapp process, we analyze the physical mechanics of the thermal transport in a perfect isolated SWCN.

As heat in SWCN's is mostly carried by acoustic phonons, it is reasonable to neglect the electronic component of thermal conductivity. The expression for lattice thermal conductivity κ at a given temperature T can be written as[15,16]

$$\kappa(T) = \sum_{\lambda} \tau_\lambda(T) C_\lambda(T) V_\lambda^2, \tag{1}$$

where τ_λ, C_λ, and V_λ are phonon relaxation time, specific heat, and phonon group velocity of phonon mode λ, respectively. In a perfect isolated SWCN, phonon relaxation time is mainly controlled by boundary scattering and three-phonon umklapp scattering process. So, the total phonon relaxation time τ is usually given by the Matthiessen rule as[17]

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_U} \tag{2}$$

with the relaxation-time parameters for boundary scattering τ_B and for three-phonon umklapp scattering process τ_U. Here, we choose $\tau_B = 50$ ps to be independent of temperature and phonon energy.[12,14,19–21] From the first-order perturbation theory, the relaxation time τ_U in the three-phonon umklapp process for thermal modes q is given by[18]

$$\frac{1}{\tau_U} = \sum_{q'} \frac{8\gamma^2 \hbar \omega \omega' \omega''}{3 n_a V_g^2 M} \pi \delta(\omega + \omega' - \omega'')(N_0' - N_0''), \tag{3}$$

where γ is the Gruneisen parameter, $\hbar$ is the Planck constant, M is atomic mass, V_g is phonon group velocity, and n_a is the number of atoms per unit volume. N_0' and N_0'' are, respectively, phonon equilibrium occupancies of modes q' and q''.

In order to obtain the relaxation rate for the three-phonon umklapp process that goes through all possible channels, it is necessary to substitute dispersion relation and V_g calculated for the relevant range of q for SWCN's into Eq. (3), and then sum all together. As a typical example, we take account of the first four acoustic modes to investigate the influence of umklapp process on relaxation time for a phonon in SWCN's. The phonon dispersion relations are obtained by lattice dynamics theory within force constant model described in Ref. 15 first. Here, we replot in Fig. 1(a) the four acoustic modes which include the doubly degenerated transverse acoustic modes (TA), a longitudinal acoustic mode (LA), and a torsional acoustic mode (TW) for $(n,0)$ SWCN's $(n = 6,7,\ldots,14)$. It furnishes a roughly linear phonon dispersion relation curve for these four phonon branches of all zigzag tubes at low frequency. The linear relations of the phonon frequency versus wave vector q would be kept same for all zigzag tubes with different diameters. However, as the phonon frequency increases further, TA and LA might be driven down. Our results illustrate that the magnitude of depressing increases as the tube diameter increases. However, TW would still remain linear and have same slope for all these tubes which results in the increases of the band gaps between LA and TA (ω_{LT}) and between TW and TA (ω_{ST}) with the increases of tube diameter. As shown in Fig. 1(b), V_g of TA for zigzag tubes $(n = 6,7,\ldots,14)$ increases slowly

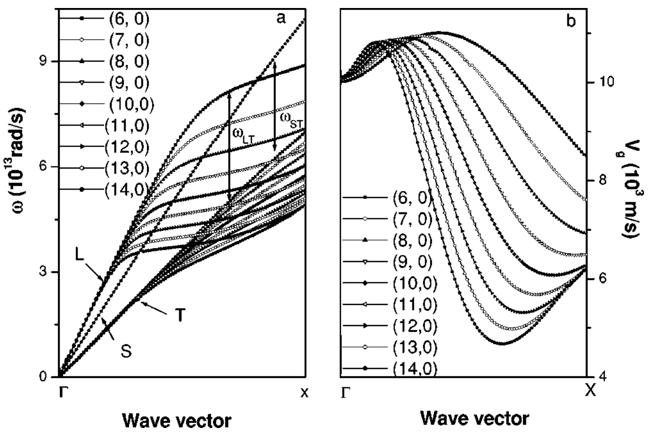

FIG. 1. Phonon dispersive relations of acoustic modes (a) and group velocity (b) of zigzag $(n,0)$ SWCN's $(n=6-14)$.

from the Γ point, after it reaches a maximum it decreases rapidly. In contrast to the zigzag SWCN's $(n=6-9)$ with small diameter, V_g of $(n,0)$ SWCN's $(n=10-14)$ with large diameter would reach a minimum at high frequency and increase smoothly to reach approximately the same value at X point. Additionally, one can find that V_g of small diameter tubes is greater than that of the tubes with large diameter near the Γ point. On the contrary, when wave vector $q > \pi/3a$, V_g of the larger diameter would be greater than that of the small diameter tubes. Considering elastic collision of phonon, we predict that V_g would have an important effect on the phonon process in SWCN's.

Due to the energy and quasimomentum conservation laws, the interaction among the phonons for the three umklapp processes is restricted.[18] For an isotropic medium, the restriction suggested that the three participating phonons should not belong to the same polarization branch, whereas the frequency of the final phonons should be higher than that of the initial phonons.[17,18,21] However, the higher-frequency phonon modes in SWCN's could, in principle, decay with the help of the lower acoustic branches.[22] As the phase space will be so restricted by the energy and momentum conservation, detailed calculations show that such decay rate will be very small. Consequently, the mainly possible three-phonon anharmonic decay processes in SWCN's include the following six modes

$$TA+TA \Leftrightarrow LA, TA+TA \Leftrightarrow TW, TA+LA \Leftrightarrow LA,$$

$$TA+LA \Leftrightarrow TW, TA+TW \Leftrightarrow LA, TA+TW \Leftrightarrow LA. \quad (4)$$

Herein, we calculate the relaxation rates τ_U^{-1} of zigzag tubes (6,0) according to Eq. (3) at $T=100$, 200, 300, 400 K, as shown in Fig. 2(a). It is found that τ_U^{-1} would be zero at low frequency under different temperature. When $T=200$ K, 300 K, and 400 K, τ_U^{-1} increase rapidly as the phonon frequency increases. However, τ_U^{-1} remain zero for the phonon frequency lower than 40 THz at 100 K and then increase slowly with the increase of the frequency. Those results suggest that phonons with low frequency would transfer comparatively freely in the SWCNs without any contribution to τ_U^{-1} except surface scattering.[8] With the increases of temperature,

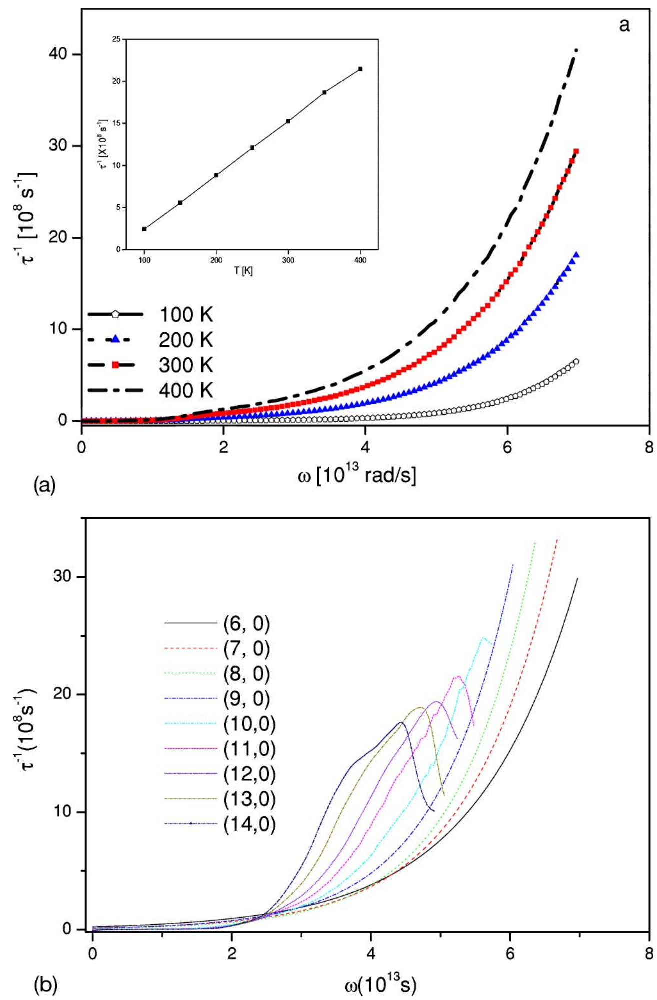

FIG. 2. (a) Relaxation rates of umklapp process of (6, 0) SWCN at $T=100$, 200, 300, 400 K. The inset shows that the relaxation rates of (6, 0) SWCN increase linearly as temperature increase at phonon frequency $\omega=6\times10^{13}$ rad/s. (b) Relaxation rates of umklapp process of $(n,0)$ SWCN's $(n=6-14)$ at $T=300$ K.

phonons with high frequency are thermally populated to dominate umklapp process, which leads to increases of τ_U^{-1}. In addition, we found that τ_U^{-1} increase linearly with increases of temperature at phonon frequency $\omega=6\times10^{13}$ rad/s as shown in the inset of Fig. 2(a). By virtue of simple numeric analysis technique, relaxation rates τ_U^{-1} would approximate to be $BT\omega^2\exp(-\hbar\omega_c/k_BT)$ with fitting parameters B and cutoff frequency ω_c. Our results are in fair agreement with analysis for the quantum wires by Khitun and Wang.[18] τ_U^{-1} for different diameter zigzag tubes would increase with increasing the phonon frequency as presented in Fig. 2(b). However, τ_U^{-1} for (10,0)–(14,0) tubes would reach a maximum and then decrease rapidly compared to those of (6,0)–(9,0) tubes. Such a phenomenon maybe attributed to the decrease of the group velocity for (10,0)–(14,0) tubes at high frequency as shown in Fig. 1(b). Moreover, the calculations show that the tube with smaller diameter has larger τ_U^{-1} for the phonon frequency lower than about 2.5×10^{13} rad/s. However, for the phonon frequency above 2.5×10^{13} rad/s, the reverse situation would occur. It

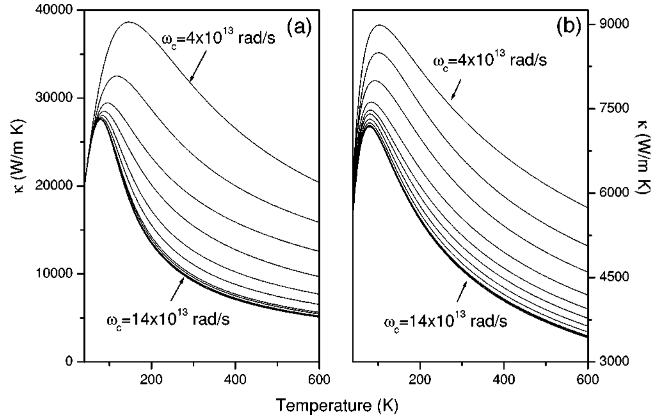

FIG. 3. Thermal conductivity of (6, 0) SWCN's (a) and (14, 0) SWCN's (b) with different cutoff frequency from 4×10^{13} to 16×10^{13} rad/s with step frequency 1×10^{13} rad/s.

may be caused by V_g and the energy gap between phonon modes. The increase of V_g would lead to the increase of the probability of the three-phonon process. Moreover, the energy gap would also restrict the phonon-phonon scattering according to the selection rules as described in Eq. (4). The increases of energy gap would reduce the probability of umklapp process. Furthermore, the equilibrium occupancy of phonon modes is another factor to have an influence on umklapp process. The equilibrium occupancies of the two nearest modes N_n, N_{n+1} are related to the Planck formula $N_{n+1}/N_n = \exp[-\hbar\omega_g/k_BT]$, where ω_g is the energy gap. An increase of the energy gap between modes results in a decrease of the final number of states, which would reduce the probability of the umklapp process. As shown in Fig. 1(a), the increasing of energy gap ω_{LT} and the decreasing of energy gap ω_{ST} with increasing diameters would lead to a change of dominant umklapp processes from $TA+A\Leftrightarrow LA$ to $TA+A\Leftrightarrow TW$ $(A=TA,LA,TW)$.[23]

It should be noted that there are more very low lying folded phonon branches as the tube's diameter increases. These low-lying folded phonon branches, especially the first and the second optical phonon modes of large-diameter tubes, would contribute to the thermal conduction.[24] Consequently, calculation of the umklapp relaxation rate at some phonon frequency requires integration over all possible phonon modes. It is a quite complicated procedure that requires detailed consideration of special information of all phonon modes. However, the modes with high frequency would contribute little to the thermal conductivity κ because of the small phonon equilibrium occupancies below room temperature. (At 300 K, the phonon equilibrium occupancies $\tilde{n}=0.15$ for a phonon with $\omega=8\times10^{13}$ rad/s.) In Fig. 3, we show κ for (6, 0) SWCN and (14, 0) SWCN with cutoff frequency ω_c from 4×10^{13} rad/s to 14×10^{13} rad/s with frequency step 1.0×10^{13} rad/s. It is shown that κ of (6, 0) SWCN's would decrease with increase of cutoff frequency ω_c. One can find that the modification of κ would decrease as the cutoff frequency ω_c increases. It should be noted that the deviation for κ is lower than 1% when the phonon modes with frequency $\omega>10\times10^{13}$ rad/s are added to the three-phonon umklapp process. The results are believed to hold in our case, referring to the fact that as the cutoff frequency increases, more and more phonons participate in umklapp process and contribute to relaxation rate. However, the phonon modes with higher frequency contribute little to κ because of the small decay rate and the small phonon equilibrium occupancies. Compared to the umklapp process in (6,0) SWCN, the collision of phonons in (14,0) nanotubes becomes more complicated. As the tube's diameter increases, the frequencies of the folded branches decrease, which would increase the probability of the umklapp process. Luckily, κ of (14,0) SWCN would be convergent until $\omega_c=12\times10^{13}$ rad/s. Herein, it would be reasonable to calculate κ for zigzag $(n,0)$ SWCN's $(6\leqslant n\leqslant14)$ while taking account of the cutoff frequency $\omega_c=14\times10^{13}$ rad/s.

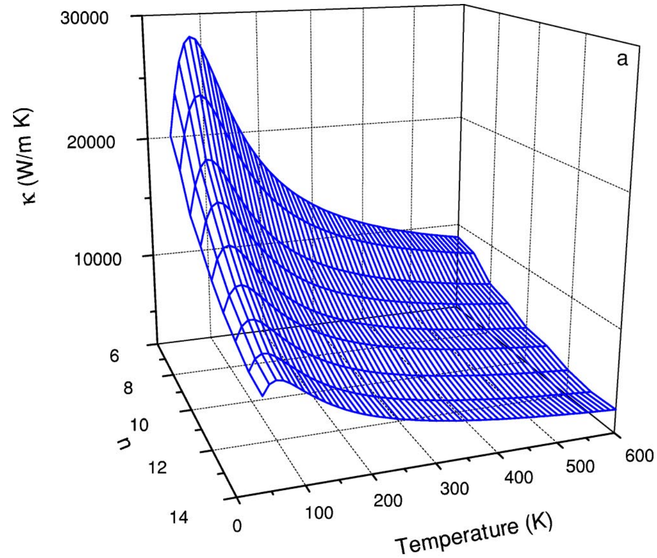

FIG. 4. Thermal conductivity of $(n,0)$ SWCN's $(n=6-14)$ as a function of temperature. (b) Thermal conductivity of zigzag tubes at 300 K.

With cutoff frequency $\omega_c=14\times10^{13}$ rad/s, we calculated κ of zigzag $(n,0)$ SWCN's $(n=6-14)$ over a temperature range of 40–600 K as shown in Fig. 4. At low temperature $(40<T<80$ K), the κ of an isolated SWCN would increase almost quadratically with the increases of temperature. Above this temperature range, $\kappa(T)$ versus temperature curve shows a downward bend and has a peak at about 85 K for (6,0) SWCN. The peak position shifts to lower temperatures for the tubes with larger diameters. Beyond this peak, $\kappa(T)$ decreases rapidly. The behavior of $\kappa(T)$ for SWCN can be understood by the aforementioned three-phonon umklapp process. At low temperature, the umklapp scattering freezes out as shown in Fig. 2(a). The phonon process is dominated by the boundary scattering, and $\kappa(T)$ simply follows the temperature dependence of specific heat.[14] As T increases, the strong umklapp scattering becomes more effective as higher-energy phonons are thermally populated. As the umklapp scattering becomes comparable to the boundary scattering, κ reaches maximum. As T increases further, the umklapp process dominates the phonon process in a SWCN and the relaxation rates for the umklapp process increases rapidly with temperature, resulting in the decrease in κ. In addition, it is demonstrated that the smaller diameter SWCN shows higher thermal conductivity. As shown in Figs. 4(b), κ at 300 K is approximately inversely proportional to the diameter of SWCN. It may be caused by the group velocity and the umklapp process. The average group velocity would decrease as the diameters of SWCN's increase.[15] Furthermore, at any given temperature, the probability of the umklapp process is higher in SWCN's with larger diameter as compared to tubes with smaller diameter. Since the umklapp process and the group velocity would reduce the thermal conductivity in SWCN, κ would decrease with the increase of the tube's diameter.

In summary, we presented a theoretical model to calculate the thermal conductivity of SWCN's considering the three-phonon umklapp process. It is shown that thermal conductivity of an isolated SWCN increases with the increase of temperature at low temperature, and would show a peak behavior at about 85 K before falling off at higher temperature. It is found that the behavior of temperature dependence of thermal conductivity can attribute to the boundary scattering and the umklapp scattering process in SWCN's. At low temperature, thermal transport in SWCN's is dominated by the phonon boundary scattering. As temperature increases, umklapp scattering process becomes strong to make the main contribution to the heat transfer. In addition, we find that thermal conductivity is higher for SWCN's with smaller diameters as compared to the tubes with large diameters. The thermal conductivity at 300 K is approximately inversely proportional to the diameter of SWCN.

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*Corresponding author. Email address: xhyan@xtu.edu.cn

[1] G.P. Collins, A. Zettl, H. Bando, A. Thess, and R.E. Smalley, Science **278**, 100 (1997).

[2] J.M. Bonard, H. Kind, T. Stockli, and L.-O. Nilsson, Solid-State Electron. **45**, 893 (2001).

[3] H.W.C. Postma, T. Teepen, Z. Yao, M. Grifoni, and C. Dekker, Nature (London) **293**, 76 (2001).

[4] A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, Science **294**, 1317 (2001).

[5] S. Frank, P. Poncharal, Z.L. Wang, and W.A. De Heer, Science **280**, 1744 (1998).

[6] P.M. Ajayan, M. Terrones, A. de la Guardia, V. Huc, N. Grobert, B.Q. Wei, H. Lezec, G. Ramanath, and T.W. Ebbesen, Science **296**, 705 (2002).

[7] M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).

[8] B.A. Glavin, Phys. Rev. Lett. **86**, 4318 (2001).

[9] S. Berber, Y.K. Kwon, and D. Tomanek, Phys. Rev. Lett. **84**, 4613 (2000).

[10] M.A. Osman, and D. Srivastava, Nanotechnology **12**, 21 (2001).

[11] J.W. Che, T. Cagin, and W.A. Goddard III, Nanotechnology **11**, 65 (2000).

[12] J. Hone, M. Whitney, C. Piskoti, and A. Zettl, Phys. Rev. B **59**, R2514 (1999).

[13] W. Yi, L. Lu, Z. Dian-lin, Z.W. Pan, and S.S. Xie, Phys. Rev. B **59**, R9015 (1999).

[14] P. Kim, L. Shi, A. Majumdar, and P.L. McEuen, Phys. Rev. Lett. **87**, 215502 (2001).

[15] J.X. Cao, X.H. Yan, Y. Xiao, Y. Tang, and J.W. Ding, Phys. Rev. B **67**, 045413 (2003).

[16] S.I. Tamura, Y. Tanaka, and H.J. Maris, Phys. Rev. B **60**, 2627 (1999).

[17] J. Zou and A. Balandin, J. Appl. Phys. **89**, 2932 (2001).

[18] A. Khitun, and K.L. Wang, Appl. Phys. Lett. **79**, 851 (2001).

[19] J. Hone, B. Batlogg, Z. Benes, A.T. Johnson, and J.E. Fischer, Science **289**, 1730 (2000).

[20] G.C.R. Luis and K. George, Phys. Rev. Lett. **81**, 232 (1998).

[21] H.B.G. Casimir, Physica **5**, 495 (1938).

[22] M. Lax, P. Hu, and V. Narayanamuti, Phys. Rev. B **23**, 3095 (1981).

[23] Y. Xiao, X.H. Yan, J.X. Cao, and J.W. Ding, J. Phys.: Condens. Matter **15**, L341 (2003).

[24] Carbon nanotubes have very low-lying folded acoustic branches, especially for large-diameter tubes. For example, tube (14, 0) has an optical phonon at $\sim 30\ \mathrm{cm}^{-1}$. The low-frequency phonon branches would give contribution to the thermal conductivity.