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Reducing the thermal conductivity of carbon nanotubes below the random isotope limit

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We find that introducing segmented isotopic disorder patterns may considerably reduce the thermal conductivity of pristine carbon nanotubes below the uncorrelated disorder value. This is a result of the interplay between different length scales in the phonon scattering process. We use *ab initio* atomistic Green's function calculations to quantify the effect of various types of segmentation similar to that experimentally produced by coalescence of isotope-engineered fullerenes.

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I. INTRODUCTION

Recent experimental and theoretical works have shown that introducing lattice matched nanocrystals into an alloy can further reduce its thermal conductivity, in what has been termed "beating the alloy limit."[1–3] This has a very important practical application in the field of thermoelectric materials, in which a major goal is to obtain low thermal conductivities without affecting electronic properties. The fact that clusters of scatterers can scatter phonons more efficiently than they would if they acted separately has been known for some time.[4,5] However, combining atomic and cluster scattering effects in order to minimize the thermal conductivity had not been clearly achieved until recently, and only for three dimensional systems.[1]

In confined systems, such as nanowires or nanotubes, there appear to be no experimental reports on this approach. The case of isotopic scattering in carbon nanotubes is especially interesting in this respect. First, it represents a well-defined system, where theory[6–8] has been successful in explaining measurements.[9,10] In addition, the use of isotopic disorder means that electron transport will not be affected at all. This means that the thermal conductivity could be tailored independently of the electrical properties of the system, which is especially attractive to nanoelectronics. In contrast, we do not think carbon nanotubes may be used for thermoelectric applications, due to their still too large thermal conductivity.

One problem is how to create nanostructures with isotopes. Isotopes of different masses are chemically identical, so thermodynamically speaking it is in principle not possible to arrange them inside the solid into anything other than an uncorrelated alloy. Nevertheless, there are ways to achieve nanotubes where the isotopic concentration is distributed in a segmented way. One of them consists in synthesizing nanotubes from C_{60} peapods.[11,12] In particular, C_{60} buckyballs can be synthesized with different isotopic concentrations. For example, pure ^{13}C buckyballs, pure ^{12}C buckyballs, and $^{12}C_{0.5}\,^{13}C_{0.5}$ buckyballs could be produced separately. These different buckyball types can then be mixed together and get to form nanopeapods, with the buckyballs encapsulated into nanotubes. Once there, they can be heated up until they coalesce to form an inner nanotube. In absence of carbon diffusion, the isotope concentration of the inner tube keeps a segmented distribution in accordance with the distribution of the original buckyball types. A detailed comparison between the measured and simulated Raman spectra of heated nanopeapods has clearly demonstrated that it is indeed possible to obtain segmented isotope distributions.[12] The outer nanotube that has been used to hold the buckyballs can subsequently be removed by, e.g., burning the outer tube with an electrical current.[13–15] A possible alternative route that may enable the growth of isotopically segmented carbon nanotubes is via chemical vapor deposition techniques.[16]

In this work we study thermal transport in isotope engineered carbon nanotubes. We show that the thermal conductivity can be significantly reduced below the random isotope alloy limit in nanotubes produced from buckyball nanopeapods in which the isotopic disorder is nanostructured.

II. TYPES OF DISORDER

We consider (5,5) armchair nanotubes, that have a diameter of 0.68 nm, close to that observed experimentally for the inner tubes produced by the coalescence of buckyball peapods.[12] The unit cell of (5,5) tubes contains 20 atoms. We consider three kinds of isotopic disorder, see Fig. 1. In all the three cases we consider a 50% mixture of ^{12}C or of ^{13}C atoms. In the random *alloy* case the two isotopes are randomly distributed throughout atomic sites. *Sliced* disorder corresponds to choosing at random whether a region of 60 consecutive atoms (three tube cells) will be composed of either ^{12}C or of ^{13}C atoms. *Mixed* disorder is a combination of both disorders, each 60-atom section being either homogeneously composed of ^{12}C or ^{13}C atoms, or of alloy type, mixing ^{12}C and ^{13}C in a random fashion. In the latter case we assume that the probability to have an isotopically pure or a

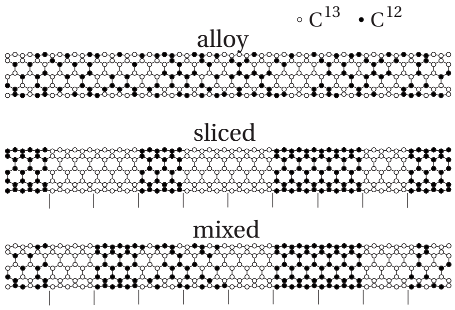

FIG. 1. Types of disorder. In the alloy case the isotopes are randomly distributed. In the other two cases the isotope distribution is nanostructured. The separation of homogeneous 60-atom sections is indicated by vertical ticks.

mixed section is the same. Finally, for sliced disorder, we also addressed the effect of section size (20, 60, 120, and 240 atoms) on the mean free paths.

III. COMPUTATIONS

To compute the phonon-transport properties, we use interatomic force constants obtained from density-functional theory calculations, as described in Ref. 7. The transmission functions $T_L(\omega)$ for a given length L of the nanotube and a phonon pulsation ω are computed using nonequilibrium Green's functions.[7] In this model, a disordered region is attached to two semi-infinite perfect leads, which are kept at different temperatures, so that there is a net energy flow from one end of the chain to the other. The ballistic transmission $T_{\text{ballistic}}(\omega)$, obtained in the case when there is no mass disorder, does not depend on the system length.

The phonon mean-free-paths $l_{\text{isotope}}(\omega)$ are obtained as described in Ref. 8, by computing short tube length transmissions and assuming a diffusive behavior, i.e.,

$$T_L(\omega) = T_{\text{ballistic}}(\omega)\frac{1}{1 + L/l_{\text{isotope}}(\omega)}. \tag{1}$$

Therefore,

$$l_{\text{isotope}}(\omega) = \left(\frac{T_{\text{ballistic}}(\omega)}{T_L(\omega)} - 1\right)^{-1} L. \tag{2}$$

We estimated l_{isotope} by computing the transmission (averaged over 60 independent realizations of the mass disorder) as a function of the length, for short tubes of lengths $L = 7.5, 15, \ldots, 75$ nm, and performing a least-square fit based on Eq. (2). The estimated mean free paths are presented in Fig. 2. As a consistency check, we verified that the mean free paths obtained for the lowest-frequency modes are independent of the contact, by comparing results obtained for ^{13}C atoms randomly inserted in an otherwise perfect ^{12}C tube, and ^{12}C atoms randomly inserted in an otherwise perfect ^{13}C tube. In general, random disorder scatters short wavelengths (high frequencies) quite efficiently, but it does not affect long wavelengths (low frequencies) as strongly. On the other hand, larger inhomogeneities comparable in size to the wavelength are much more effective in scattering the low frequency phonons. This can be seen in the plot of the mean free paths in Fig. 2. At low frequency, sliced disorder yields shorter mean free paths than the other disorder types. On the other hand, at high frequency it has longer mean free paths than the other two types. In the sliced case, the figure also shows two clearly differentiated dependences with cluster size: at the lower frequencies, the larger the

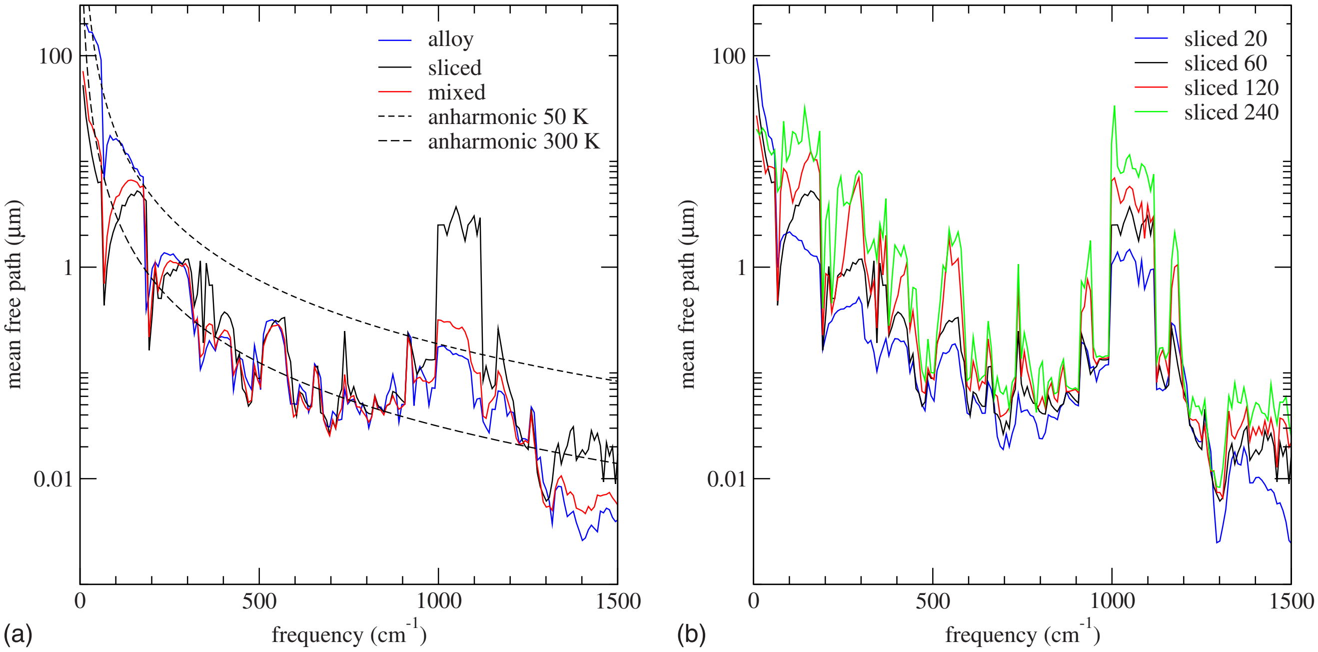

FIG. 2. (Color online) (a) Mean free paths $l_{\text{isotope}}(\omega)$ for different types of isotopic disorder. The segments in the sliced case comprise 60 atoms. Dashed lines: anharmonic mean free path, $l_{\text{anh}}(\omega)$, of pure nanotubes at 50 and 300 K. (b) Mean free path in the sliced case for different sizes (number of atoms) of the segments. See explanations in main text.

slice, the shorter the mean free path; for higher frequencies on the other hand, the shorter the slices, the shorter the mean free path. The latter behavior is a result of the larger density of interfaces when the slices are small. The low-frequency phonons carry most of the heat, due to their much longer mean-free paths. Therefore, by employing sliced disorder, it is possible to decrease the thermal conductance of the nanotube below the random disorder value.

Figure 2 also shows an enhanced mean free path at a frequency window around 1100 cm^{-1} for the segmented case. This is the result of angular momentum conservation which forbids many scattering processes. We verified that such resonance decreases dramatically if the symmetry of the segments is broken by making their edges irregular. This feature turns out to give a negligible contribution to the thermal conductance. We have checked that its presence or absence makes no difference in the final thermal conductance, which is determined by the much longer mean free paths of the lowest frequencies.

In order to estimate the temperatures at which the disorder pattern has an influence, we combine, by Mathiessen's rule, the mean-free paths computed above, and a rough estimate of anharmonic relaxation length in graphite materials:[17] $l_{\mathrm{anh}}(\omega)=BT^{-1}\omega^{-2}$, with $B=9.38$ K cm^{-2} m. We show this relaxation length as the dashed lines in Fig. 2(a). The total relaxation length is therefore $l_{\mathrm{diff}}(\omega)=[l_{\mathrm{anh}}(\omega)^{-1}+l_{\mathrm{isotope}}(\omega)^{-1}]^{-1}$, and an estimate of the transmission function for a Carbon Nano Tube (CNT) of length L is obtained as

$$T_L(\omega)=T_{\mathrm{ballistic}}(\omega)\frac{1}{1+L/l_{\mathrm{diff}}(\omega)}. \tag{3}$$

Once the transmission is known, the thermal conductance can be computed as[18]

$$g(L,T)=\int_0^{+\infty}\frac{\hbar\omega}{2\pi}T_L(\omega)\frac{\partial f_T(\omega)}{\partial T}d\omega,$$

where $f_T(\omega)=\{\exp[\hbar\omega/(k_{\mathrm{B}}T)]-1\}^{-1}$ is the Bose-Einstein distribution.

Figure 3 compares the conductance computed with mixed or sliced disorder, to the conductance obtained with random mass disorder, as a function of temperature, for different lengths of the tube, with and without the contribution of anharmonic scattering. The segments in the sliced case considered are 60 atoms in size. Nanostructured disorder can reduce the thermal conductivity of the nanotubes as much as 50% below the isotope alloy limit for low enough temperatures. Therefore, it is possible to obtain thermal conductivities clearly lower than those of the random disorder nanotube.

The observed reductions depend on the temperature and also on the nanotube length. At temperatures high enough to have important anharmonic scattering, isotope scattering becomes of secondary importance, and nanostructured disorder has a smaller influence. Similarly, if the nanotubes are very short, transport becomes ballistic, and the effect of isotopes on the thermal conductance becomes less apparent. Lowering the temperature increases the impact of nanostructuring, down to a certain minimum at a particular temperature. Below this temperature, the reduction decreases because heat is increasingly carried by low frequency modes, which have very long mean-free paths. A general conclusion is that the effects should be maximized for longer nanotubes at low temperatures.

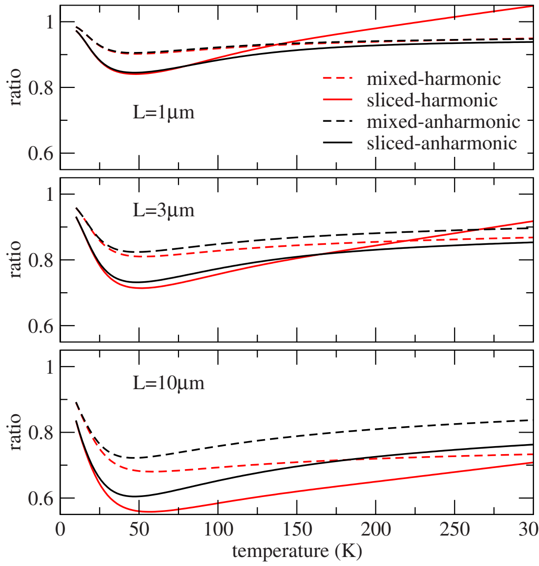

FIG. 3. (Color online) Ratios of the thermal conductance of CNTs with mixed or sliced (60 atom segments) disorder, divided by the thermal conductance of CNTs with alloy disorder, as a function of the temperature, for different disorder patterns, and for tubes of lengths $L=1,3,10$ μm. Red lines represent results in the case when anharmonicity is not taken into account [using only Eq. (1)], and the black lines gives the ratio when anharmonicity is present [using Eq. (3)].

IV. DISCUSSION

It should be possible to experimentally verify the predicted effects, by synthesizing segmented disordered nanotubes in the way we proposed earlier. Such nanostructured-disordered nanotubes could then be suspended and contacted, and their thermal conductivity could be measured using direct methods.[19,20] Our calculations show that the effects should be clearly noticeable in nanotubes 3 µm long at low temperature. Thermal conductivity reductions of 50% have been reported for boron nitride (BN) nanotubes in a wide range of temperatures. The phonon structures of BN and C nanotubes are rather similar, and the isotope effect at the same concentrations affects them in a similar way.[6] Thus, carbon nanotubes with sliced disorder at 50% isotope concentration can display even larger reductions than those reported for BN. The additional effect of segmentation reported here implies that it might be possible to reduce the low temperature (50 K) thermal conductivity of long (10 μm) pristine carbon nanotubes to less than 30% of the isotopically pure value. Such strong effects are also suggested by the theoretical mean-free paths in Fig. 2.

V. CONCLUSIONS

In conclusion, nanostructured disorder leads to an important reduction in thermal conductivity in carbon nanotubes.

Reductions 40% below the random disorder case can be obtained for $^{12}C_{0.5}\,^{13}C_{0.5}$ nanotubes a few micrometers long. Mixed disorder alternating alloy and pure sections is less effective than pure sliced disorder. The relative reduction increases with the nanotube length. For a given length, there is a temperature that minimizes the thermal conductivity. For nanotubes a few micrometers long, this minimum occurs at cryogenic temperatures in the 20–100 K range. We have described a feasible way to produce isotopic segmented nanotubes, which should allow for the experimental verification of the results predicted here. The physical phenomenon described here is not restricted to carbon nanotubes, and can be expected to be a general phenomenon observable also in BN nanotubes and many other isotopically disordered confined systems.

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[1] W. Kim, J. Zide, A. Gossard, D. Klenov, S. Stemmer, A. Shakouri, and A. Majumdar, Phys. Rev. Lett. **96**, 045901 (2006).

[2] W. Kim and A. Majumdar, J. Appl. Phys. **99**, 084306 (2006).

[3] N. Mingo, D. Hauser, N. P. Kobayashi, M. Plissonnier, and A. Shakouri, Nano Lett. **9**, 711 (2009).

[4] L. A. Turk and P. G. Klemens, Phys. Rev. B **9**, 4422 (1974).

[5] G. A. Slack and M. A. Hussain, J. Appl. Phys. **70**, 2694 (1991).

[6] I. Savic, N. Mingo, and D. A. Stewart, Phys. Rev. Lett. **101**, 165502 (2008).

[7] G. Stoltz, M. Lazzeri, and F. Mauri, J. Phys.: Condens. Matter **21**, 245302 (2009).

[8] D. A. Stewart, I. Savic, and N. Mingo, Nano Lett. **9**, 81 (2009).

[9] C. W. Chang, A. M. Fennimore, A. Afanasiev, D. Okawa, T. Ikuno, H. Garcia, D. Li, A. Majumdar, and A. Zettl, Phys. Rev. Lett. **97**, 085901 (2006).

[10] C. W. Chang, D. Okawa, H. Garcia, A. Majumdar, and A. Zettl, Phys. Rev. Lett. **101**, 075903 (2008).

[11] F. Simon, C. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zólyomi, J. Kürti, P. M. Singer, and H. Alloul, Phys. Rev. Lett. **95**, 017401 (2005).

[12] V. Zólyomi, F. Simon, A. Rusznyak, R. Pfeiffer, H. Peterlik, H. Kuzmany, and J. Kurti, Phys. Rev. B **75**, 195419 (2007).

[13] P. G. Collins, M. S. Arnold, and Ph. Avouris, Science **292**, 706 (2001).

[14] P. G. Collins, M. Hersam, M. Arnold, R. Martel, and P. Avouris, Phys. Rev. Lett. **86**, 3128 (2001).

[15] S. Moon, Woon Song, Nam Kim, Joon Sung Lee, Pil Sun Na, Soon-Gul Lee, Jongwan Park, Myung-Hwa Jung, Hyun-Woo Lee, Kicheon Kang, Cheol Jin Lee, and Jinhee Kim, Nanotechnology **18**, 235201 (2007).

[16] R. Xiang, Z. Zhang, K. Ogura, J. Okawa, E. Einarsson, Y. Miyauchi, J. Shiomi, and S. Maruyama, Jpn. J. Appl. Phys. **47**, 1971 (2008).

[17] P. G. Klemens and D. F. Pedraza, Carbon **32**, 735 (1994).

[18] N. Mingo and D. A. Broido, Phys. Rev. Lett. **95**, 096105 (2005).

[19] L. Shi, D. Li, C. H. Yu, W. Jang, Z. Yao, P. Kim, and A. Majumdar, ASME J. Heat Transfer **125**, 881 (2003).

[20] E. Pop, D. Mann, Q. Wang, K. Goodson, and H. Dai, Nano Lett. **6**, 96 (2006).