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Thermoelectric power of a single-walled carbon nanotubes strand

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Abstract
We have investigated the thermoelectric power (TEP) and the electrical conductance of single-walled carbon nanotube (SWNT) strands containing large numbers of aligned crystalline ropes. A linear temperature dependence of TEP and a power-law behaviour of conductance were observed at low temperatures. The TEP increases with temperature at a very large slope of $\sim 1\ \mu\text{V K}^{-2}$ below $\sim$50 K, peaks around 100–150 K depending on the treatment of high temperature annealing, then decreases with the further increase of temperature. The large slope at low temperatures is interpreted as a property of the Luttinger liquid in the presence of defects.

(Some figures in this article are in colour only in the electronic version)

It has been found through tunnelling measurements that the single quasiparticle density of states of a metallic SWNT follows a power law at low energies, showing the characteristic of a Luttinger liquid (LL) [1, 2]. For an LL, recent theories predict that its thermoelectric power (TEP) is linear in temperature in a form similar to Mott's formula for conventional diffusive metals [3, 4]. Experimentally, a linear or nearly linear TEP at low temperatures has been observed on SWNT bundles and mat-like samples by a number of groups [5, 6], but the observation of a strict power law of conductance on the same samples has not been reported. With the further increase of temperature a knee-like or a peak-like structure emerges, and this is explained as a Kondo effect [7] or a phonon drag effect [8, 9]. However, since the TEP increases at an unusually large slope at temperatures below the knee or peak structure, an alternative possibility exists as well that the structure is just a consequence of eventual departure or saturation of the TEP to the large-slope trend[4]. More complicated behaviour of the TEP has recently been observed by Small and co-workers on a mesoscopic system involving only one individual SWNT. They find that with the variation of the gate voltage the TEP oscillates at a very large amplitude at low temperatures [10]. The result also implies on average a large absolute value of the TEP at most given gate voltages. A general picture of the TEP for SWNTs should be able to explain the unusual large value of the TEP at low temperatures. In the present paper we report our investigation of this issue on a strand form of SWNTs which contains aligned crystalline ropes of SWNTs. Both a linear TEP and a power law of conductance have been observed at low temperatures. The results confirm that the large value of TEP comes from the LL state, and we find it consistent with the recent theories of TEP enhancement in an LL with impurity scattering.

The samples used in this experiment are SWNT strands synthesized by chemical vapour deposition (CVD) [11]. High-resolution transmission electron microscopy (HRTEM) shows that the SWNTs in the strand form crystalline ropes, and the ropes align in parallel to form the strand. Most of the SWNTs are metallic (11, 5) tubes with a diameter of 1.1 nm, as suggested by Raman spectroscopy studies [12]. We picked up those strands of $\sim$5 μm in diameter and cut them to $\sim$1 mm in length, then had them annealed in two different ways. Sample type A was first heated to 450 °C in air and kept there for half an hour, then mounted on a TEP and resistivity measurements stage and reheated to $\sim$127 °C (400 K) in a vacuum of 6.5×10^{-3} Pa for 20 min. This vacuum was maintained during the TEP and resistance measurements. Sample type B was first annealed at 1100 °C in a vacuum of 2×10^{-3} Pa for 10 min, re-exposed to air after being cooled down, then mounted on the TEP stage and retreated and measured following the same procedures as for sample type A. Silver paste was used to attach the two ends of the strand to the hot and cold plates 0.5 mm apart. The TEP signal was measured in the presence of an ac temperature modulation of <0.5 K and the resolution of the measurement was $\sim$20 nV K^{-1} [13, 14]. The two-probe sample resistance was measured in the absence of temperature modulation.

Figure 1 shows the temperature dependence of the TEP of the two types of samples. The TEP of both type A and B samples (hereafter referred to as samples A and B, since the results of each type are reproducible) is positive, showing a linear temperature dependence at low temperatures. It gradually deviates from linearity above $\sim$30 K, peaks around 150 or 100 K for sample A or B, respectively, then decreases with further increasing temperature.

It is noticed that at low temperatures the TEP of both samples grows with temperature at a very large slope of $\sim$1 μV K^{-2}, much larger than that of the ordinary metals, and several times larger even than that of thermoelectric materials such as constantan. A large slope at low temperatures has also been observed in film or mat-like SWNTs [5, 7, 8]. The huge value of TEP ($\sim$400 μV K^{-1}) found in the mesoscopic configuration at finite temperatures [10] also implies the existence of a large slope in its temperature variation, since the TEP has to be zero at zero temperature. As we already mentioned, it would be interesting to ask if this large slope is a precursor of some peak or knee structure at higher temperature, or whether the peak or knee structure is just a by-product when the TEP naturally flattens out from the large slope trend (as a measure of the entropy carried by each carrier, the absolute value of the TEP should not grow with temperature without limitation).

In order to explain the peak or knee structure, a number of pictures involving a phonon drag effect or Kondo effect have previously been examined, but disagreement remains. Vavro and co-workers [9] believed that the phonon drag effect is important in doped SWNTs when

[4] Some rope or mat-like samples reported in the literature show a much smaller value of TEP, but still having a knee structure. Whereas phonon drag could be the mechanism responsible for the structure, the possibility exists as well that a part of the SWNTs feels TEP saturation but other parts do not.

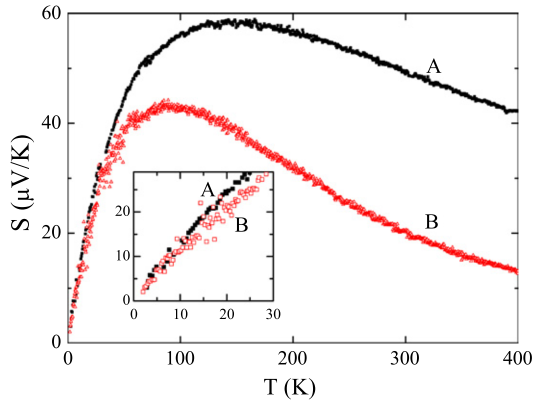

Figure 1. The temperature dependence of the TEP of SWNT strands. Sample B differs from sample A in that it is annealed at 1100 °C for purification. The TEP of both samples shows a linear temperature dependence below ~30 K (magnified in the inset). It gradually deviates from linearity with increasing temperature and peaks around 150 or 100 K for sample A or B, respectively.

electron–phonon scattering is the dominant decay mechanism for the phonons. Similarly, owing to the phonon drag effect Scarola *et al* predicted a large value and a broad peak of the TEP from 40 to 150 K [15]. However, in these theories the TEP should decrease much faster than linearly below the peak temperature, which is in contradiction to the experimental findings. Based on the electron–phonon effects, Kaiser *et al* also predicted a large TEP in SWNTs [8], including a large increase above 250 K, which is again in contradiction to the experimental findings. Grigorian and co-workers believed that the magnetic impurities coming from the catalyst particles during the synthesis could result in a TEP peak via the Kondo effect [7]. In our case the HRTEM image indicated that the carbon encapsulated Fe catalyst particles are laid at the interstitial position [11], which should not affect the electron transport properties of the samples, including the TEP. In fact, the temperature dependence of the conductance remains as a power law, just as for magnetic impurity-free samples (figure 2).

In figure 2 the conductance G of the same samples used in the TEP measurement is plotted against temperature T in a double logarithmic scales, demonstrating a power-law temperature dependence $G \sim T^{0.34}$. We have also measured on sample A the bias voltage dependence of the differential conductance below 20 K, and found that $\mathrm{d}I/\mathrm{d}V \sim V^{0.34}$. For SWNT samples the power-law behaviour of the conductance is believed to be a characteristic of a Luttinger liquid [2, 16, 17]. In our experiment this behaviour should mainly reflect the single quasiparticle tunnelling processes at some blockade sites along the strand. The carriers in between two adjacent blockade sites can be regarded as finite-length LL. It is speculated that the blockade sites correspond to certain kinds of defects, impurities, or tube–tube side contacts that cause strong back scattering to the electrons [3, 18].

The energy scale of our differential conductance data is about 25 times larger than that measured on single tube or single rope samples [1, 2]. Therefore, we conclude that there are about 25 effective tunnelling junctions, hence 25 effective blockade sites, along the 0.5 mm length of each SWNT. Because the previous investigation [11] indicates that our SWNTs in the strand are unbroken in the whole sample length, the tunnelling processes would then take place at some impurity or defect sites which are about ~20 μm apart along the SWNTs (i.e., the amount of impurities or defects effectively causing backscattering is about 1 ppm, one every million carbon atoms). Due to the large spatial separation between the tunnelling sites,

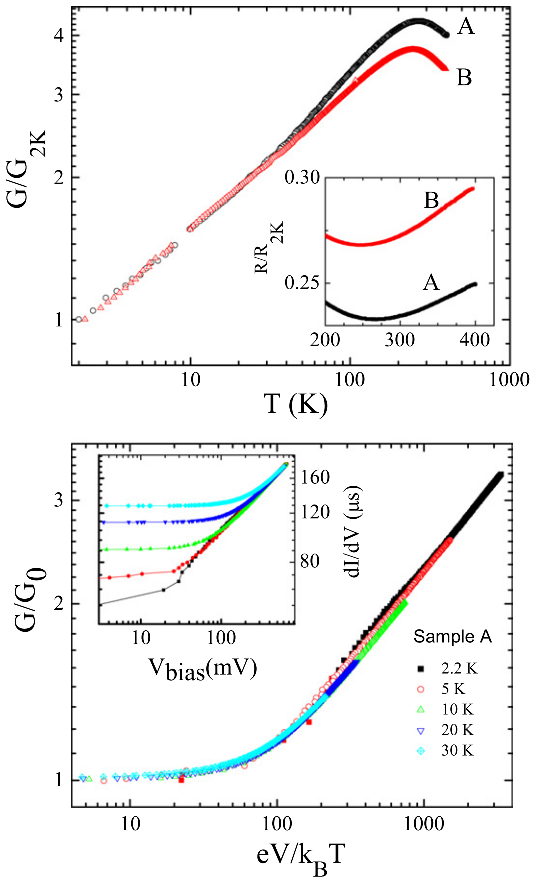

Figure 2. The temperature (upper panel) and bias voltage (lower panel) dependences of the conductance of the same samples as used in the TEP measurement. Both samples A and B show a power law behaviour with a same power exponent at low temperatures. At high temperatures, a linear temperature dependence of resistance is restored, as shown in the upper inset. The bias voltage dependence of the differential conductance also follows a power law at low temperatures, with the same power exponent as found in the temperature dependence. The lower panel shows the data measured on sample A at different temperatures, which can be scaled onto a universal functional form as expected for a Luttinger liquid. With increasing temperature, the power-law behaviour gradually gives way to the ohmic law, implying the establishment of a diffusive transport process.

we believe that the tunnelling processes happening at each site are largely independent, so that those theories dealing with one impurity or defect in an LL are applicable to our data [19].

For single quasiparticle tunnelling from one LL to another with a similar value of Luttinger parameter, the conductance is proportional to $T^{2\alpha}$ or $V^{2\alpha}$. Fitting these forms to our data we have $\alpha \approx 0.17$, which corresponds to a Luttinger parameter $g = 0.6$ using the relation $\alpha_{\text{end}} = (g^{-1} - 1)/4$. Therefore, the TEP signal will be enhanced by a factor of $g^{-1} = 1.68$ according to Krive's theory. This may contribute to the observed large slope at low temperatures.

With increasing temperature, the mechanism of electron transport gradually switches from a tunnelling-like process to a diffusive process, as is shown in the insets of figure 2 where the $\mathrm{d}I/\mathrm{d}V$ versus V curves become increasingly flatter (approaching Ohm's law) and the resistance becomes proportional to the temperature at high temperatures; the latter behaviour is attributed to electron–twiston phonon scattering [20]. As a consequence, the g^{-1} enhancement mechanism gradually fades away. We believe that this is the reason for the resulting TEP peak around 100–150 K.

Now let us discuss the annealing dependence of the TEP. It is believed that in defect-free SWNTs the electron–hole symmetry is kept so that the TEP should vanish. The existence of defects, including lattice deformations and impurities, will mediate interactions between the bonding and anti-bonding band electrons near the Dirac point, resulting in band bending and the occurrence of a small energy gap [21]. With such a band structure and with a certain level of carrier doping, the electron–hole symmetry in SWNTs will be broken, yielding the observed TEP signals. For CVD-synthesized SWNTs which usually contain a certain amount of defects such as the contamination of amorphous carbon and catalyst particles on the walls, high-temperature annealing is likely to reduce these defects and also to release the adsorbed gas molecules, especially the oxygen molecules which cause hole doping. Both processes are likely to reduce the TEP. In our experiment, the main difference between samples A and B is that sample B may contain fewer defects as it was annealed at $\sim$1100 °C in vacuum. The situation of gas adsorption would be roughly the same because sample B was re-exposed to air after the annealing (if one believes that the situation of gas adsorption does not sensitively depend on the amount of defects). Therefore, the difference in TEP above the peak temperature could mainly reflect the difference in the amount of defects between the two samples.

It is interesting to see that although the TEP of samples A and B differs significantly at high temperatures, below the peak temperature the values are rather close to each other. The reason is not clear. According to our previous analysis, the electrons form an LL below the peak temperature. Therefore the experimental data seem to indicate that in the LL regime the TEP is insensitive to the degree of defects—it only depends on the band term (i.e., on the energy derivative of the density of states). Above the peak temperature, as the LL picture gradually fades away and the conduction mechanism switches to diffusive transport, the scattering term (namely the energy derivative of the scattering rate) might become important, resulting in the difference in TEP between the two samples. Further study is needed to clarify the above assumption.

To summarize, our TEP measurement on SWNT strands confirms the previously reported behaviours observed on SWNT film and mat-like samples. In addition to the linear TEP at low temperatures, we also observed a power-law conductance on the same samples. The large slope of the TEP at low temperatures is tentatively interpreted as a characteristic of Luttinger liquids.

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