Temperature Dependent Resistivity of Single Wall Carbon Nanotubes

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Since their discovery[1], there has been great interest in the electronic properties of carbon nanotubes. These are nanometer scale structures which can be understood as a single layer of graphite wrapped to form a cylindrical tube. This wrapping can be specified by two integers \([M,N]\) which define the superlattice translation corresponding to an elementary orbit around the waist of the cylinder. Theory predicts that a single wall tube can exhibit insulating, semi-metallic or metallic behavior depending on the choice of the integers \(M\) and \(N\). Using double laser ablation of Co- and Ni- doped graphite targets, a new catalytic route to the synthesis of these structures has been discovered which now allows the production of single-wall tubes[2]. This process produces bulk samples in which the \([10,10]\) wrapping is predominant[3]. Tubes produced in this process self organize during deposition in a two dimensional triangular close packed lattice forming ropes (bundles of tubes), and ultimately mats (three dimensional samples of entangled ropes). The \([10,10]\) tubes are predicted to be metallic, and experimental evidence that unoriented bulk samples as well as individual ropes are metallic has been presented in [2] and [4]. Here we study the intrinsic intra-tubule scattering processes responsible for the resistivities of these systems and then present experimental measurements of the temperature dependence of the resistivity. We find that the coupling of the low energy electronic states to thermal shape fluctuations of the tubes leads naturally to a resistivity which scales linearly with temperature even deep into the low temperature regime. This behavior is quite unconventional for a metal, and is actually found experimentally in tubule-derived samples down to a crossover temperature \(\approx 10\text{–}100\text{ K}\). The effects of inter-tube coupling on the electronic and vibrational degrees of freedom responsible for this effect are also briefly discussed below.

Here we will focus on the \([N,N]\) “armchair” tubes, which band theory predicts to be metallic [2]. The low energy electronic structure of a single armchair tube consists of two pairs of one dimensional bands which cross the Fermi energy, and these can be described by the massless Dirac Hamiltonian:

\[
H_e = \int dx \sum_{a,\sigma} \hbar v_F (\psi_{a\sigma}^\dagger \partial_x \psi_{a\sigma} - \psi_{a\sigma} \partial_x \psi_{a\sigma}^\dagger). \tag{1}
\]

Here \(\psi_{a\sigma}\) describes a right (left) moving electron with band index \(a = 1,2\) and spin \(\sigma = \uparrow, \downarrow\). \(v_F\) is the Fermi velocity.

The electrical resistivity is determined by the dominant mechanism for backscattering of electrons. In the presence of short range direct electron electron interactions, the Hamiltonian (1) maps onto a two channel “Hubbard ladder” [5]. The backscattering of electrons due to repulsive electron electron interactions has been studied within this model [6], and one finds that above a crossover temperature it leads to a resistivity which scales linearly with temperature [3]. Here we consider a different and what we believe to be the dominant scattering process, namely the coupling between electrons and elastic deformations of the tubes. Our theory is the tubule analog to the Bloch Gruneisen (BG) theory of the scattering of a Bloch electron by the low energy long wavelength acoustic modes of the lattice [4]. For the tubules one finds that modes which twist the tube around its axis of symmetry locally compress and stretch bonds on the surface of the cylinder. We have found that these elastic deformations couple the right moving and left moving electronic states of (1) [3] and are thus effective at backscattering the electrons. However, the
dispersions of both the electronic and lattice degrees of freedom are unusual for these structures which, as we discuss below, leads one naturally into a regime in which the modes responsible for the backscattering are always heavily thermally populated. We find that this implies a temperature dependent resistivity which is proportional to the absolute temperature even well below the nominal Debye temperature. In this regime, one cannot use the "high temperature" limit for phonon scattering even at temperatures well below the Debye temperature. The coupling constant for an $N,N$ twist provides an efficient backscattering mechanism for a conduction electron [3]. Thus we consider the scattering of electrons by thermally excited long wavelength "twistons", i.e. the acoustic torsional modes of the tubule. The coupling between electrons and twist is given by [3]

$$H_{e-t} = \lambda \int dx \sum_{a,\sigma} \nabla \theta \left( \psi^\dagger_{a\sigma +} \psi_{a\sigma -} + h.c. \right)$$

(2)

where $\theta(x)$ is the angle of the twist at a position $x$ along the tubule. The coupling constant for an $[N,N]$ tube is $\lambda = 3N\beta\hbar v_F/4\pi$, where $\beta = \partial \ln t/\partial \ln d$ describes the change in the bond hopping amplitude $t$ with bond length $d$. The dynamics of long wavelength twistons may be described by the continuum elastic Lagrangian,

$$L_t = \frac{1}{2} \int dx \left[ M_t \dot{\theta}^2 - C_t (\nabla \theta)^2 \right],$$

(3)

where $M_t$ is the moment of inertia per unit length of the tube and $C_t$ is the twist modulus. The twiston dispersion is then $\omega_q = v_t q$ with $v_t = \sqrt{C_t/M_t}$.

The effect of twistons is rather unusual because they are the only long wavelength phonons which couple the right and left moving electrons in the Dirac spectrum for this system [3]. Unlike the phonon scattering in an ordinary metal, which requires a phonon with momentum $2k_F$, backscattering from twistons is not quantum mechanically frozen out at low temperatures. Twiston scattering introduces a single scattering event which scatters an electron from the right to left moving branch, as shown in the inset of Fig. 1. Moreover, since the momentum of a typical electron at temperature $T$ is $k_B T/v_F$, the energy of the relevant twistons are of order $2k_B T v_t/v_F$. Since $v_t << v_F$, these phonons are always heavily thermally populated. The system is thus effectively in the "high temperature" limit for phonon scattering even at temperatures well below the Debye temperature.

The backscattering rate for an electron with momentum $k$ may be computed from Fermi’s golden rule to be

$$\frac{1}{\tau} = 2\pi \lambda^2 \int \frac{dq}{2\pi} C_t \coth \left( \frac{\hbar \omega_q}{2k_B T} \right) \delta (v_F(2k - q)),$$

(4)

where we have ignored the small twiston energy $\hbar v_t q$ in the delta function. This rate is independent of $k$ and linearly proportional to $T$. The one dimensional electrical resistivity is given by $\rho_{1D} = (\hbar/e^2)/(8\pi v_F^2 \tau)$, where for pure backscattering the transport lifetime is $\tau_{tr} = \tau/2$. We thus find

$$\rho_{1D} = \frac{9}{32\pi^2} \frac{h}{C_t k_B T},$$

(5)

where $c_t = C_t/N^3$ is independent of $N$.

While the parameters in our theory have not yet been measured for carbon nanotubes, they can be estimated using the corresponding quantities known for graphite. Based on the in plane shear modulus of graphite we estimate $c_t = 18eVÅ$ [11]. This predicts a velocity $hv_t = 0.09eVÅ$ which is equal to the speed of the in plane transverse acoustic phonon of graphite. In addition, we estimate $h\rho_F = 5.3eVÅ$ and $\beta = 2.3$ [12]. For a rope of triangular close-packed [10,10] tubes with a lattice constant 17 Å, this leads to a temperature dependent contribution to the three dimensional rope resistivity with slope $d\rho_{3D}/dT = 0.005\mu\Omega cm/K$.

Balents and Fisher have recently shown that Umklapp scattering due to electron-electron interactions also leads to a resistivity which is linear in temperature [3]. Whereas the twiston resistivity scales as $1/N$, the Umklapp resistivity is proportional to $1/N^2$. Thus for sufficiently large tubes the lattice effects should dominate. Comparing the prefactors we estimate that for $N = 10$ the two have comparable magnitudes, with the twiston resistivity larger by a factor of 4 [3].

The above discussion has focused on the resistivity of an isolated tube. This ignores three-dimensional effects for the dynamics of both the electrons and the phonons, which may be crucial for the correct interpretation of measurements on bundles (or “ropes”) of tubes. At low frequency, twistons on neighboring tubes should be coupled elastically which leads to a gap in the twiston spectrum as $q \to 0$. This may be described within an Einstein model for the inter-tube twistons, with the dispersion relation $\omega_q = \sqrt{v_t^2 q^2 + \omega_0^2}$. The energy scale $\hbar \omega_0$ may be estimated by considering the corresponding phenomena in graphite and in crystalline $C_{60}$. In graphite the relevant zone boundary phonon has energy 4 meV [13], whereas the energy of librions in crystalline $C_{60}$ span the range 2 - 6 meV [14].

Coherent tunneling of electrons between the tubes also destroys the nesting of the Fermi surface. Given the bandwidth $W$, a phonon with wavevector as large as $q \approx W/v_F$ is needed to backscatter, so that at low temperature, direct backscattering can ultimately be frozen out over a large part of the Fermi surface. $W$ is difficult to estimate, because it will depend on the details of the orientational registry between neighboring tubes. However, it is unlikely that it will be negligible for this system. Solid phases of $C_{60}$ have an interbar electronic bandwidth of order 0.5 eV [15]. In graphite tunneling between neighboring layers leads to two interlayer bandwidths, one of order 1 eV and one with a much narrower...
rameters our one-dimensional model, and recalculated including sistivity as a function of temperature calculated using sistivity due to twiston scattering may be generalized to be slightly narrower.

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within the local density approximation for a three dimen-
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twiston. The upper bold curve is calculated for a one di-

mensional model for which \( \rho \propto T \). Including three di-

mensional intertube effects in both the electron and twiston
degrees of freedom we obtain the lower curve, which shows

that the linear temperature dependence occurs in a three di-

mensional sample above relatively low crossover temperature.
The inset shows the process in which an electron scatters from

the right to left moving branch, emitting a long wavelength

twiston.

FIG. 1. Calculated temperature dependent resistivity due
to twiston scattering. The upper bold curve is calculated for

a one dimensional model for which \( \rho \propto T \). Including three di-

mensional intertube effects in both the electron and twiston
degrees of freedom we obtain the lower curve, which shows

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width of order 10 meV. Electronic structure calculations

within the local density approximation for a three dimen-
sional lattice of [12,12] tubes have estimated a bandwidth

of order 0.5 eV \[10\]. It is possible that because of the frus-

tration of a five-fold symmetric [10,10] tube in a six-fold

coordinated environment, the intertube bandwidth may

be slightly narrower.

Our estimates of the scattering rates, and thus the resis-
tivity due to twiston scattering may be generalized to

include both of these effects. In Fig. 1 we plot the re-
sistivity as a function of temperature calculated using

our one-dimensional model, and recalculated including

these three dimensional effects for the representative pa-

tameters \( \omega_0 = 4 \) meV and \( W = .5 \) eV. We find that

the resistivity of the three dimensional system is then

essentially linear for \( T > 100K \). This is well below the

effective Debye temperature for the twistons which is

of order 1000 K. We find that in this system the one
dimensional behavior can control the resistivity so long as

\( (v_t/v_F)W > \hbar \omega_0 \) as seems likely in this sys-
tem. The dynamics is then essentially one dimensional for

\( k_B T > \max(\hbar \omega_0, (v_t/v_F)W) \). We note that Umklapp

scattering is suppressed for \( k_B T < W \). Due to the small

ratio \( v_t/v_F \approx .02 \), twiston scattering is more robust in

the presence of inter tube coherence.

To test the above theory, it is clearly desirable to mea-

sure the electrical transport through a single isolated

tube. However, to date, single tube transport has only

been measured at very low temperature, where Coulomb

charging effects dominate \[17\]. In Fig. 2 we present 4

different measurements of the temperature dependence

of the electrical resistivity of nanotube ropes and unori-

ented bulk samples, all prepared as described in Ref. 2.
The top curve in Fig. 2(a) is a 4-probe 1 KHz measure-

ment on a bulk sample using silver paint contacts. Above

about 200 K \( \rho \) increases linearly with temperature. This

confirms and extends to 580 K the linear behavior pre-

viously observed up to 470 K \[3\]. The absolute value has

little meaning since the tensor components are not

separable, the material is very porous, and the effect of

inter-rope contacts is unknown. The logarithmic deriva-
tive obtained from a linear fit in the interval 300 K <

\( T < 580 \) K is 0.0008 K\(^{-1}\). The lower curve is derived

from a microwave absorption measurement on a few mi-

crograms of similar material. The absolute value of \( \rho \)

from this technique depends on the depolarization fac-
tor which is very difficult to estimate given the complex

morphology, while the logarithmic derivative, 0.001 K\(^{-1}\)

is comparable to the 4-probe value.

Fig. 2(b) shows a 2-probe measurement of \( \rho_\parallel \) (de-
dscribed previously \[3\]) on several ropes in parallel. Again,

linear behavior is observed over a wide temperature

range, with a somewhat smaller logarithmic derivative,

.0004 K\(^{-1}\). 4-probe absolute \( \rho_\parallel \) measurements were

performed at 300 K on similar samples and span the range

30 - 100 \( \mu \Omega cm \).

Fig. 2(c) shows a 4-probe measurement on a single

7 nm diameter rope with voltage contacts 500 nm apart.
The room temperature resistivity is 90\( \mu \Omega cm \),

which is consistent with the above measurement. The

slope \( d\rho/dT \approx .1 \mu \Omega cm/K \).

These measurements clearly indicate metallic behavior

at high temperatures with \( \rho \) increasing approximately lin-

early with temperature. Taking \( \rho_\parallel (300 \) K = 90\( \mu \Omega cm \),

and assuming the T dependence of the bulk samples is
dominated by \( \rho_\parallel (T) \), we infer the absolute slope from the

first three measurements. For the bulk, microwave and 2-

probe rope measurements we thus find \( d\rho/dT \sim .07...09 \)

and \( .04 \mu \Omega cm/K \). While the four measurements of the

slope agree to within a factor of 2.5, they are a factor

of 8-20 larger than the twiston scattering theory predic-
tion. Part of this discrepancy could arise from the pres-

ence of non-metallic tubes in the ropes. Recent electron

diffraction measurements \[3\] on similar materials have

indicated that more than 50% of the tubes in a rope are

chiral and hence insulating \[3\]. The presence of such

“dead” tubes would lead to an overestimate of the rope’s

intrinsic resistivity. In addition, variations in the elec-

tron tunneling matrix elements between different tubes

in a rope - which depend sensitively on the relative ori-

entation of the tubes - could lead to an additional source

of backscattering which is not present for a single tube.

In order to distinguish such effects from the intrinsic re-

sistivity of a single tube a high temperature transport

measurement on a single tube is clearly desirable.

It is striking that in addition to the high tempera-
ture linear resistivity, all the experimental measurements

show an upturn in the resistivity at low temperature.
The onset of this low temperature behavior depends on

the sample morphology and can be as low as 10K for sin-

gle ropes. It has been suggested that this upturn may

signal a condensation of the system to form a collective

charge- or spin- density wave ground state in the tube \[3\]
However, the observed dependence of this crossover on the sample morphology and quality suggests that disorder or other three dimensional effects may actually control this low temperature behavior. It will be important to carry out further experimental work to understand the origin of this nonconducting low temperature behavior.

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[1] S. Iijima and T. Ichihashi, Nature 363, 603 (1993)
[2] A. Thess et al., Science 273, 483 (1996).
[3] J. M. Cowley, P. Nikolaev, A. Thess and R. E. Smalley, Chem. Phys. Lett. 265, 379 (1997).
[4] J.E. Fischer et al., Phys. Rev. B 55, R4921 (1997).
[5] R. Saito, M. Fujita, G. Dresselhaus and M. Dresselhaus, Appl. Phys. Lett. 60, 2204 (1992); N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. 68 1579 (1992); J.W. Mintmire, D.H. Robertson, and C.T. White, J. Chem. Phys. Sol. 54, 1835 (1993).
[6] C.L. Kane and E.J. Mele, Phys. Rev. Lett. 78, 1932, (1997).
[7] R.M. Noack, S.R. White and D.J. Scalapino, Europhysics Letters, 30 163 (1995).
[8] L. Balents and M.P.A. Fisher, cond-mat preprint 96-11216.
[9] Y.A. Krotov, D.H. Lee and S.G. Louie, cond-mat preprint 96 11073.
[10] J.M. Ziman, Electrons and Phonons, (Oxford, 1962) p 364.
[11] M.S. Dresselhaus and G. Dresselhaus, in Light Scattering in Solids III Vol. 51, p3. (M. Cardona, ed., Springer - Verlag, 1982)
[12] L. Pietronero and S. Strassler, Phys. Rev. Lett. 47, 593 (1981).
[13] The relevant Umklapp matrix element is estimated using the repulsive Ohno potential (Theor. Chim. Acta 2, 219 (1964)) which is believed to describe the bare interelectronic repulsive interactions in these systems.
[14] D.A. Neumann et. al., J. Chem. Phys. 96, 8631 (1992)
[15] S.C. Erwin and W.E. Pickett, Science 254 842 (1991)
[16] J.Charlier, X. Gonze and J. Michenaud, Europhysics Letters 29, 43 (1995)
[17] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs and C. Dekker, Nature 386, 474 (1997).