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Temperature-dependent resistivity of single-wall carbon nanotubes

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Abstract. – Samples of single-wall carbon nanotubes containing tubes with an "armchair" wrapping have been produced and exhibit metallic behavior with an intrinsic resistivity which increases approximately linearly with temperature over a wide temperature range. Here we study the coupling of the conduction electrons to long-wavelength torsional shape fluctuations, or twistons. A one-dimensional theory of the scattering of electrons by twistons is presented which predicts an intrinsic resistivity proportional to the absolute temperature. Experimental measurements of the temperature dependence of the resistivity are reported and compared with the predictions of the twiston theory.

Since the discovery of carbon nanotubes in 1993 [1], [2] there has been interest in these structures as prototypical molecular wires. Research in this direction has been given additional impetus by the recent discovery of a new catalytic route to the synthesis of single-wall carbon nanotubes (SWNTs) [3]. In this process the tubes self-organize during deposition in a two-dimensional triangular lattice forming ropes (bundles of tubes), and ultimately mats (three-dimensional samples of entangled ropes). Transmission electron microscopy indicates that up to 40% of the nanotubes have the $[10, 10]$ "armchair" wrapping, which is predicted by band theory to be metallic. Indeed, metallic behavior has been observed in unoriented bulk samples as well as individual ropes [3], [4]. A thorough understanding to the electronic properties of the nanotubes is thus essential.

In this letter we study the intrinsic scattering processes responsible for the electrical resistivity in nanotubes. Remarkably, we find that the coupling of the low-energy electronic states to thermal *shape fluctuations* of the tubes leads to a resistivity which scales *linearly*

with temperature even at temperatures well below the Debye temperature of the phonons unlike in an ordinary metal. We then present a wide range of experimental evidence for this temperature dependence, measured in both bulk samples as well as individual ropes. The effects of inter-tube coupling on the electronic and vibrational degrees of freedom responsible for this effect are also considered. We find that the one-dimensional physics controls the transport properties of nanoropes over a wide parameter range relevant to the experimental measurements.

Here we will focus on the $[N, N]$ "armchair" tubes, which band theory predicts to be metallic [5], [6]. 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

$$H_{\rm e} = \int {\rm d}x \sum_{a,\sigma} i\hbar v_{\rm F} (\psi^{\dagger}_{a\sigma+} \partial_x \psi_{a\sigma+} - \psi^{\dagger}_{a\sigma-} \partial_x \psi_{a\sigma-}). \tag{1}$$

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

The electrical resistivity is determined by the dominant mechanism for backscattering of electrons. The backscattering of electrons due to repulsive electron-electron interactions has been studied within a model for a two-channel Hubbard "ladder" [7]-[9], and one finds that above a crossover temperature it leads to a resistivity which scales linearly with temperature [8]. 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 [10]. 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 and are effective at backscattering electrons [6]. However, the dispersions of both the electronic and lattice degrees of freedom are unusual for these structures, which leads one naturally into a regime in which the modes responsible for the backscattering are always heavily thermally populated. This implies a temperature-dependent resistivity which is proportional to the absolute temperature even well below the nominal Debye temperature for this system, as observed experimentally, and in contrast to the usual BG theory of a conductor.

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 [6]

$$H_{\rm e-t} = \lambda \int {\rm d}x \sum_{a,\sigma} \nabla\theta \ \left(\psi^{\dagger}_{a\sigma+} \psi_{a\sigma-} + {\rm h.c.} \right), \tag{2}$$

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 $\lambda = 3N\beta\hbar v_{\rm F}/4\pi$, 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,

$$L_{\rm t} = \frac{1}{2} \int {\rm d}x \left[M_{\rm t} \dot{\theta}^2 - C_{\rm t} (\nabla\theta)^2 \right], \tag{3}$$

where $M_{\rm t}$ is the moment of inertia per unit length of the tube and $C_{\rm t}$ is the twist modulus. The twiston dispersion is then $\omega_q = v_{\rm t} q$ with $v_{\rm t} = \sqrt{C_{\rm t}/M_{\rm t}}$.

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 [6].

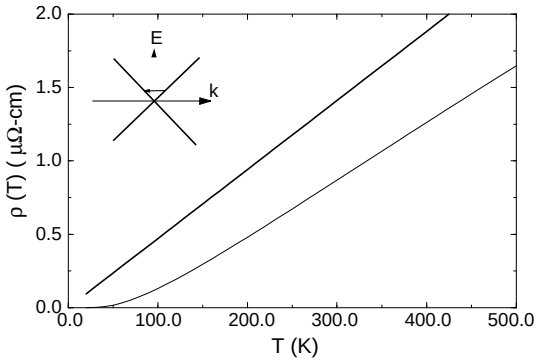

Fig. 1. – Calculated temperature-dependent resistivity due to twiston scattering. The upper bold curve is calculated for a one-dimensional model for which $\rho \propto T$. Including three-dimensional intertube effects in both the electron and twiston degrees of freedom we obtain the lower curve, which shows that the linear-temperature dependence occurs in a three-dimensional 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.

Unlike the phonon scattering in an ordinary metal twiston scattering introduces a *single* low-temperature scattering event which backscatters conduction electrons, as shown in the inset of fig. 1. Since the momentum of a typical electron at temperature T is $k_{\rm B}T/v_{\rm F}$, the energy of the relevant twistons is of order $2k_{\rm B}Tv_{\rm t}/v_{\rm F}$. Since $v_{\rm t} \ll v_{\rm F}$, these phonons are always heavily thermally populated. For this reason the system is effectively in the "high temperature" limit for phonon scattering even at physical temperatures well below the Debye temperature.

To quantify this result we study the backscattering rate for an electron with momentum k which can be computed from Fermi's golden rule:

$$\frac{1}{\tau} = 2\pi\lambda^2 \int \frac{{\rm d}q}{2\pi} \frac{v_{\rm t}q}{C_{\rm t}} \coth(\frac{\hbar\omega_q}{2k_{\rm B}T}) \delta\left(v_{\rm F}(2k-q)\right) , \tag{4}$$

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

$$\rho_{\rm 1D} = \frac{9}{32\pi^2} \frac{h}{e^2} \frac{\beta^2}{Nc_{\rm t}} k_{\rm B}T, \tag{5}$$

where $c_{\rm t} = C_{\rm t}/N^3$ is independent of N.

The parameters in our theory can be estimated from corresponding quantities for graphite. Using the in-plane shear modulus modulus, $C_{66} = 44 \times 10^{11}$ dyn/cm^3 [11] we estimate $c_{\rm t} = 18$ eVÅ. This predicts a velocity $\hbar v_{\rm t} = 0.09$ eVÅ $= 1.4 \times 10^4$ m/s which is equal to the speed of the in plane transverse acoustic phonon of graphite. In addition, we estimate $\hbar v_{\rm F} = 5.3$eVÅ 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 ${\rm d}\rho_{3D}/{\rm d}T = 0.005$ μΩcm/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 [8]. 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 [13]. We also note that for an isolated graphite sheet, scattering of the π electrons from the transverse acoustic phonons (the analog of the twistons of the tubule) also leads to a resistivity proportional to the absolute temperature, as we find in eq. (5) [14].

The above discussion has focused on the resistivity of an isolated tube and 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. We now generalize the model to include these effects. At low frequency, twistons on neighboring tubes should be coupled elastically, which leads to a librational gap in the twiston spectrum 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 [11], whereas the energy of librons in crystalline C_{60} span the range 2–6 meV [15].

Coherent tunneling of electrons between the tubes also introduces a transverse bandwidth in the problem and destroys the nesting of the Fermi surface. For a transverse bandwidth W, a phonon with wavevector as large as $q \approx W/v_F$ is needed 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 interball electronic bandwidth of order 0.5 eV [16]. In graphite tunneling between neighboring layers leads to two interlayer bandwidths, one of order 1 eV and one with a much narrower width of order 10 meV [17]. Electronic structure calculations within the local density approximation for a three-dimensional lattice of [6, 6] tubes have estimated a bandwidth of order 0.5 eV [18].

Our estimates of the scattering rates, and thus the resistivity due to twiston scattering may be generalized to include both of these effects. In fig. 1 we plot the resistivity as a function of temperature calculated using our one-dimensional model, and recalculated including these three-dimensional effects for the representative parameters $\omega_0 = 4$ meV and $W = 0.5$ eV. We find that the resistivity of the three-dimensional system is then essentially linear for $T > 100$ K, which 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 will control the resistivity so long as $(v_t/v_F)W > \hbar\omega_0$ as seems likely in this system. 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 $v_t/v_F \approx 0.02$, twiston scattering is more robust in the presence of inter-tube coherence.

To test the above theory, it is clearly desirable to measure 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 [19], [20]. In fig. 2 we present 4 different measurements of the temperature dependence of the electrical resistivity of nanotube ropes and unoriented bulk samples, all prepared as described in ref. [2]. The top curve in fig. 2(a) is a 4-probe 1 KHz measurement on a bulk sample using silver paint contacts. Above about 200 K ρ increases linearly with temperature, which confirms and extends to 580 K the linear behavior previously observed up to 470 K [4]. The logarithmic derivative 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 micrograms of similar material [21]. Its logarithmic derivative, 0.001 K^{-1}, is comparable to the 4-probe value. Figure 2(b) shows a 2-probe measurement of $\rho_\parallel$ (described previously [4]) on several ropes in parallel. Again, linear behavior is observed over a wide temperature range, with a somewhat smaller logarithmic derivative, 0.0004 K^{-1}. 4-probe absolute $\rho_\parallel$ measurements were performed

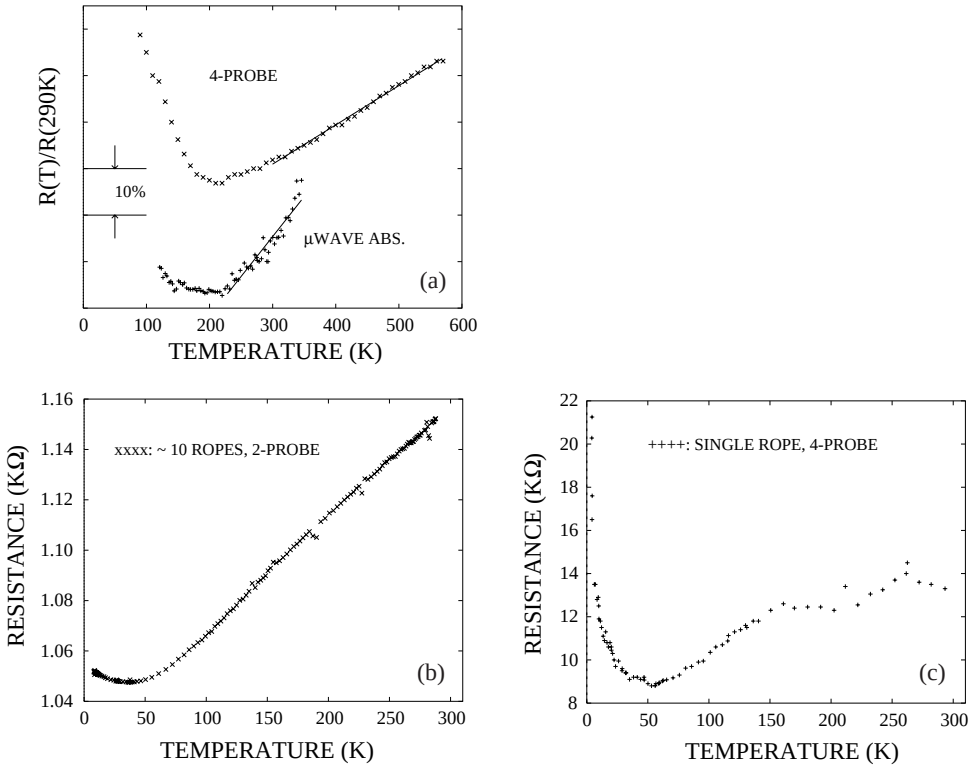

Fig. 2. – Measured resistivities of samples of carbon nanotubes. (a) Bulk material: The top curve is a 4-probe measurement. The lower curve is measured by microwave absorption. (b) 2-probe measurement on several ropes in parallel. (c) 4-terminal measurement of a single rope.

at 300 K on similar samples and span the range 30–100 μΩcm. Figure 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 μΩcm, which is consistent with the above measurement. The slope $\mathrm{d}\rho/\mathrm{d}T \approx 0.1$ μΩcm/K.

These measurements clearly indicate metallic behavior at high temperatures with ρ increasing approximately linearly with temperature. Taking $\rho_{\|}(300\ \mathrm{K}) = 90$ μΩcm, and assuming the T-dependence of the bulk samples is dominated by $\rho_{\|}(\mathrm{T})$, we infer the absolute slope from the first three measurements: $\mathrm{d}\rho/\mathrm{d}T \sim 0.07, 0.09$ and 0.04 μΩcm/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 prediction. Part of this discrepancy could arise from the presence of non-metallic tubes in the ropes. Recent electron diffraction measurements [22] on similar materials have indicated that more than 50% of the tubes in a rope are chiral and hence insulating [5], [6]. The presence of such "dead" tubes would lead to an overestimate of the rope's intrinsic resistivity. In addition, variations in the electron tunneling matrix elements between different tubes in a rope —which depend sensitively on the relative orientation 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 resistivity 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-temperature 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 10 K for single ropes. Other authors have 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 [8], [9]. 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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