

Giant thermopower in carbon nanotubes: A one-dimensional Kondo system

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The electrical transport properties of single-wall carbon nanotubes are shown to be strongly influenced by the presence of transition-metal impurities derived from the catalyst introduced to stimulate their growth. Data on thermoelectric power and electrical resistance in the temperature range 10–400 K were obtained on a series of samples prepared using M - Y catalysts ($M = \text{Cr, Mn, Co, Fe, Ni}$). The unusual transport behavior observed is tentatively assigned to an interaction between the magnetic moment of the M atom and the spin of the conduction π electrons of the nanotubes, i.e., the Kondo effect. [S0163-1829(99)50240-3]

Small diameter ($d < 2$ nm) single-wall carbon nanotubes (SWNT) have now been prepared in sufficient yield from catalyzed carbon plasmas to allow the widespread study of the chemical and physical properties of these molecular filaments.¹ In this work, we present the results of a systematic study of the transport properties of SWNT mats produced from a series of transition-metal- Y catalysts which show that the identity of the catalyst has a pronounced effect on the electrical transport.

It is known from numerous studies on nonmagnetic metallic hosts (X) that only ~ 10 – 100 ppm magnetic impurity (M) can have a dramatic effect on the electrical transport properties of the host.² A giant peak in the thermopower vs temperature and an associated resistivity minimum were reported in the systems $X:M$, where $X = \text{Au, Ag, Cu}$, and $M = \text{Ti, V, Cr, Mn, Fe, Co, Ni}$.^{2,3} These observations are explained theoretically as the result of an interaction between the magnetic moments of the impurity atoms and the conduction electron spins of the host.^{2,3} This interaction was shown to lead to a new spin-dependent scattering mechanism and a narrow hybridization peak or ‘‘Kondo resonance’’ in the electronic density of states positioned near the Fermi energy E_F .^{3,4} The Kondo temperature can be written approximately as

$$T_K \sim (E_F/k) \exp\{-1/[2|J|D(E_F)]\},$$

where J is the antiferromagnetic ($J < 0$) exchange integral between the localized electrons of impurity atoms (M) and the conduction electrons of the host, and D is the polarized electronic density of states (DOS) of the host (per atom per spin).² T_K is therefore most sensitive to J and $D(E_F)$. The width of the hybridization peak in the electronic DOS at E_F is $\sim kT_K$.²⁻⁴

The first measurements of the thermopower in SWNT mats produced both by pulse laser vaporization, PLV (Ref. 5) (Ni-Co catalyst) and arc discharge, AD (Ref. 6) (Ni-Y catalyst) yielded surprising results: *large* positive values at room temperature, i.e., $S(300 \text{ K}) \sim +40$ to $+60 \mu\text{V/K}$, and a strongly nonlinear T dependence with $dS/dT > 0$.^{7,8} This behavior is in a sharp contrast to that observed for the basal plane of graphite which exhibits a value for $S(300 \text{ K}) = -4 \mu\text{V/K}$ and a nearly linear T dependence. Graphite has a pair of weakly overlapping electron and hole sp^2 or π

bands with near mirror symmetry about the Fermi energy E_F . Approximately equal numbers of electrons and holes in these symmetric π bands are consistent with the small (negative) linear thermopower observed below room temperature. Similarly, the one-dimensional band structures of isolated, defect-free, metallic carbon nanotubes¹ are also found to be quite symmetric about E_F , although, in this case, the conduction- and valence-band overlap by ~ 2 eV. As appreciated earlier,⁷ one should therefore anticipate small values for the room-temperature thermopower of SWNT's as well, contrary to experiment. Tube-tube interactions within a bundle have been proposed as a means to alter the density of states at E_F which should impact the transport properties.^{7,9,10} However, the work presented here suggests that magnetic impurities may be responsible for the anomalously large thermopower of metallic SWNT's and contribute to the upturn of the resistivity at low T .

SWNT mats, a single bundle of SWNT and even a single nanotube, have all been reported to exhibit anomalous resistance $R(T)$ behavior (see Ref. 11 for a recent review). These nanotube systems exhibit a very shallow minimum in R at $T = T^* \sim 40$ – 300 K with $dR/dT < 0$ for $T < T^*$. Various mechanisms have been proposed to explain the anomalous $R(T)$ behavior, i.e., weak localization,^{7,12} contact tunneling resistance between tube bundles in the mat,¹¹ tube-tube interactions within a bundle,^{7,9} and contributions from both semiconducting and metallic tubes in the sample.⁷ In this work, consistent with the model proposed in Ref. 11, the electrical transport properties of mats of SWNT bundles are viewed as dominated by the contribution from bundles of metallic tubes (and interbundle electrical contacts) which allow the formation of percolating metallic pathways throughout the sample. Hereafter, when we refer to the experimental SWNT mat thermopower or resistance, these quantities are discussed in terms of a presumed dominant contribution from an interconnected metallic network of SWNT bundles.

Our transport data were primarily collected on mats of tangled bundles of SWNT's taken directly from an AD apparatus (CarboLex Inc., Lexington, KY; www.carbolex.com). The approximate volumetric yield was estimated on the basis of Raman scattering¹³ to be ~ 20 – 70% , depending on the specific catalyst, i.e., M -Yttrium ($M = \text{Mn, Cr, Fe, Co, Ni}$; $M = 4$ at. %, $Y = 1$ at. %). The bal-

ance of the material in the mats was in the form of $\sim 10\text{--}20$ nm diam carbon nanospheres and carbon-coated catalyst particles which are presumed not to participate in the transport. After the initial transport measurements on the mats, a postsynthesis iodine treatment of the samples was carried out in an attempt to convert the interstitial M into $M\text{-I}$ complexes. The treatment involves the intercalation and subsequent deintercalation of charged polyiodide chains (I_n^-) into the interstitial channels between the tubes in the bundle.⁸

X-ray diffraction (XRD), and scanning and transmission electron microscopy were used to characterize the SWNT materials. All of the SWNT samples exhibited an x-ray diffraction peak in the range $2\theta \sim 5.9^\circ\text{--}6.1^\circ$ ($\text{Cu } K_\alpha$ radiation) associated with the average tube separation in a bundle.^{5,8} The existence of the XRD peak confirms the presence of well-ordered, large bundles of nearly monodispersed tubes in our samples. For the Fe-Y, Co-Y, and Ni-Y derived samples, we estimate the same mean diameter $d \sim 1.3$ nm, midway between the values expected for (9,9) and (10,10) tubes, where the notation (n,m) refers to the SWNT symmetry.¹ However, insufficient material was available for XRD analysis of the Cr-Y and Mn-Y catalyzed samples. Raman-scattering spectra for all samples (including Cr-Y and Mn-Y) taken with a yttrium aluminum garnet laser (1064 nm) excitation were very similar. In particular, the SWNT radial mode band¹⁴ in all the mat samples was found to exhibit an unresolved doublet with peaks at ~ 165 and ~ 178 cm^{-1} , suggesting very small differences in the mean tubule diameter¹⁵ from one sample to the next. In the AD samples, the 165 cm^{-1} peak is the stronger component of the doublet, whereas in the PLV sample the 178 cm^{-1} peak is more dominant. The similarity of the Raman spectra in these AD-derived samples produced with different catalysts probably stems from the fact that the arc conditions (He pressure, current, voltage) were maintained identical; only the catalyst was changed from run to run. The thermopower (S) and four-probe resistance (R) measurements were carried out using freshly prepared SWNT samples under He atmosphere as described elsewhere.^{16,17} It is important to note that these properties were observed to change if the samples were stored in ambient conditions over weeks or months.²²

Figure 1 shows typical thermopower data in the range $10 < T < 400$ K. The data were obtained from “as-prepared” SWNT mats using the $M\text{-Y}$ catalysts indicated in the figure. The thermopower data (Fig. 1) are positive over the entire range of temperature, indicating that the contribution from positive hole carriers dominates the response. The data for mats grown using $M\text{-Y}$ ($M = \text{Fe, Co, Ni}$) can be viewed as a superposition of a broad peak on a positive linear term (aT). Metallic materials normally exhibit this linear term which is associated with the “diffusion” of free carriers. The contribution from the large thermopower *peak* is tentatively assigned to the presence of magnetic impurities within the bundle. This general phenomenon has been studied extensively in many hosts and is known as a manifestation of the “Kondo effect.” For example, as little as 200 ppm Fe impurity in Au (Ref. 18) has been shown to introduce a “giant” thermopower peak similar in form to those shown in Fig. 1. Our data (Fig. 1) clearly demonstrate that the magnitude and position of the broad thermopower peak depends strongly on the identity of the catalyst present in the arc

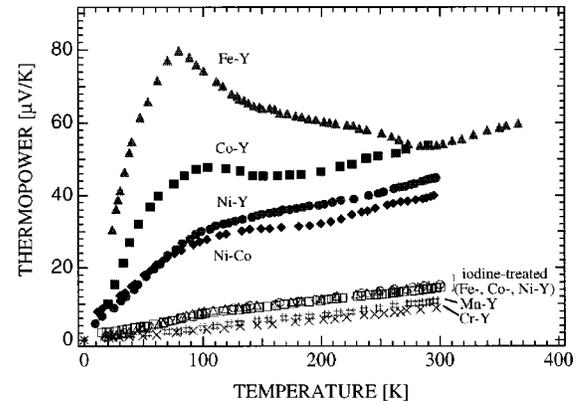


FIG. 1. Temperature dependence of the Seebeck coefficient (S) for the various samples indicated. A postsynthesis “iodine treatment” (see text) on mats produced using Fe-Y, Ni-Y, or Co-Y catalysts strongly suppresses the broad peak in S .

plasma. The thermopower data for the “as-prepared” PLV-produced (Ni-Co) SWNT sample (Fig. 1) is similar to the “as-prepared” AD-produced samples (Ni-Y), evidence that the anomalous thermopower peak is not associated with one nanotube synthesis method or the other. The thermopower data for Cr-Y, Mn-Y derived SWNT’s are nearly identical to each other, much smaller in magnitude than those obtained using Ni-, Co-, or Fe-Y catalyst, and linear vs T . This may be evidence that Mn and Cr are not active Kondo centers in SWNT bundles.

The pronounced effect of the *postsynthesis iodine treatment* on the thermopower data from mats grown using Fe-Y, Co-Y, and Ni-Y catalysts is also evident in Fig. 1. As can be seen, the iodine treatment very nearly suppresses the broad (Kondo) peak, leaving an almost linear thermopower, slightly larger than that obtained with as-synthesized mats grown from Cr-Y and Mn-Y. After iodine treatment, the data for Ni-, Co-, or Fe-Y derived samples are now almost identical. This observation, and a similar response of the mat resistance $R(T)$ to iodine treatment (discussed below), are consistent with our proposal that the intercalated iodine chemically reacts with the interstitial magnetic impurity atoms to form metal iodide complexes. This reaction alters the valence of the interstitial metal (M), suppressing the Kondo effect. Similar chemical effects have been observed, i.e., oxygen in the classic Kondo system Au:Fe, where the Fe is complexed as an oxide suppressing the Kondo anomaly.¹⁹

Metal-Y residue is also present in “as-prepared” mats as carbon-encapsulated $M\text{-Y}$ nanospheres. Fortunately for this study, these nanospheres do not enjoy intimate contact with the nanotube walls, and therefore are not expected to affect the transport properties. Their presence in the sample does, however, interfere with a chemical analysis for the concentration of M in the interstitial channels. Finally, we mention that the fact that the thermopower of the iodine-treated mats is found slightly higher than that found for mats grown from Mn-Y and Cr-Y, suggests that the iodine treatment may have failed to reach all interstitial M within the bundles.

To more quantitatively examine the broad peak in the thermopower, the data $S(T)$ in Fig. 1 were fit to the sum of a metallic diffusion term ($S_d = aT$) and a peak $S_K = S - S_d$, where S_K is the proposed contribution resulting from the

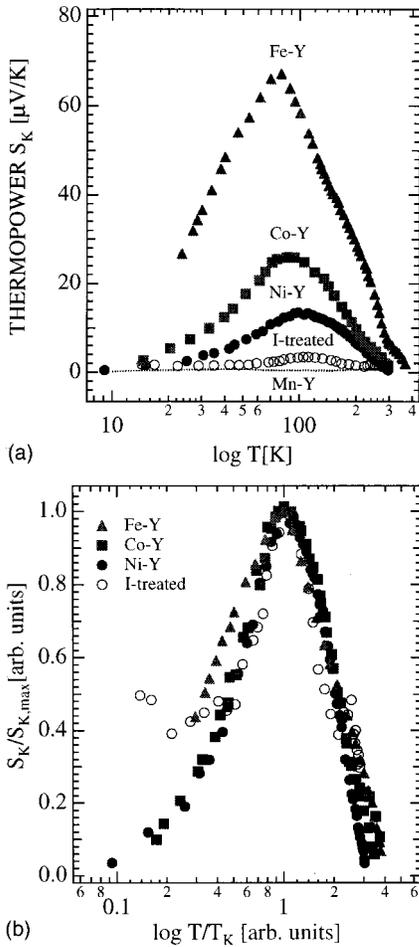


FIG. 2. (a) Temperature dependence ($\log_{10} T$) of the thermopower $S_K = S - S_d$, where a linear contribution $S_d = aT$ has been subtracted from the data. (b) Normalized data are plotted vs $\log_{10}(T/T_K)$; see text.

magnetic impurity. The S_d term was found by measuring $S(T)$ at high temperatures, typically 300 to 500 K, where the data gradually became linear. In Fig. 2, as is usually done in Kondo systems,¹⁰ we plot S_K [Fig. 2(a)] and the normalized thermopower $S_K/S_{K,\text{max}}$ [Fig. 2(b)] on a logarithmic temperature scale. In Fig. 2(a), it can be seen that the Kondo contribution to S decreases as we pass through the end of the 3d transition metal row (Fe, Co, Ni), and is not discernible for the early transition metals (Cr, Mn). On the scale of Fig. 2(a), the small residual Kondo behavior is still evident after iodine treatment. In Fig. 2(b), the normalized thermopower is plotted vs $\ln(T/T_{\text{max}})$, where T_{max} is the temperature at the maximum value of $S_{K,\text{max}}$. It is common to use values of T_{max} as an estimate for the Kondo temperature, i.e., $T_K \sim T_{\text{max}}$.³ For the samples studied here we find T_K in the range $80 < T_K < 100$ K, depending on M . These values for T_K fall about midway in the range discovered so far for Kondo systems, i.e., from a few degrees K to as high as 1000 K.^{2,3} The fact that the normalized thermopower data all fall on the same universal curve [Fig. 2(b)] suggests that the same mechanism dominates the thermopower for all samples. The shape of the universal curve suggests to us that a Kondo effect may be present.^{2,3} If our proposal is correct, SWNT's

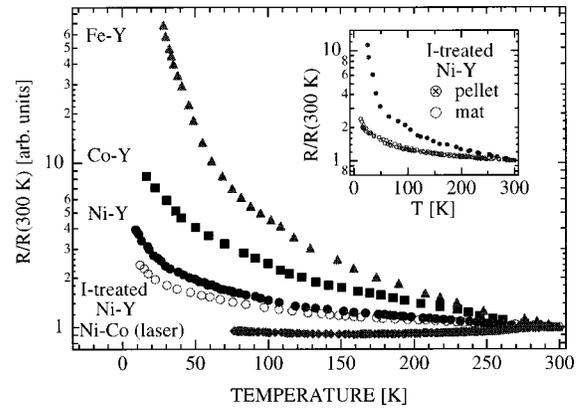


FIG. 3. $\log_{10}[\rho(T)/\rho(300\text{ K})]$ vs $\log_{10} T$. Data were collected on the same mats as used for the thermoelectric power studies (Fig. 1). Inset: effect on $\rho(T)$ of mild pressure to densify the material in the mat. Open (crossed) symbols represent ρ before (after) densification.

provide the first example of a Kondo anomaly in a carbon material. Of further significance may be the quasi-one-dimensional (1D) nature of SWNT's and the recent theoretical advances in 1D Kondo systems.²⁰

In Fig. 3, we plot the logarithm of the *normalized* resistivity²¹ $\rho_N(T) = \rho(T)/\rho(300\text{ K})$ vs T for mats whose $S(T)$ data appear in Figs. 1 and 2. The strong low- T upturn in the ρ_N data is evident, and this anomaly has been the subject of much discussion in the literature on SWNT's.^{11,12} Importantly, our data show that the strength of the ρ_N upturn correlates well with the strength of the broad peak in the thermopower [Fig. 2(a)], suggesting that Kondo scattering may make a substantial contribution to the low- T resistance. We should add here that other mechanisms are probably also contributing to this low- T upturn in ρ_N . It is important to note that the iodine-treated mats all exhibit similar ρ data, with a significantly reduced low- T upturn. The fact that a residual low- T upturn remains after iodine treatment is certainly consistent with an incomplete attempt to complex all the M (with iodine). However, it should be recalled that other mechanisms should remain which also can contribute to the low- T upturn.^{7,9,11,12} All our AD-derived mats exhibited negative $d\rho_N/dT$ over the entire range of temperature, in contrast to the behavior of the PLV (Ni-Co) SWNT sample which exhibited weakly positive $d\rho_N/dT$ for $T > 150$ K, in agreement with previous work on other PLV material.^{5,12} In fact, the weakly negative $d\rho_N/dT$ for AD-derived mats surviving up to room temperature may well stem from *inter-bundle* contact resistance, as proposed in Ref. 11 (see the inset to Fig. 3). As the thermopower is measured at zero current, the effect of interbundle contacts on S is observed here to be very small.

The data obtained for $M = \text{Mn, Cr}$ are tentatively interpreted as “intrinsic” behavior, yielding a diffusion coefficient $0.0314\ \mu\text{V/K}^2$ and a $S(300\text{ K}) \sim +9\ \mu\text{V/K}$ for a typical metallic nanotube bundle. This result is still a factor of 2–3 times larger than those measured in the basal plane of graphite. Although the “intrinsic” linear thermopower we obtain is much smaller than the total thermopower observed in “as-

prepared'' mats, it is still an open question as to whether or not the magnitude and sign of this ''intrinsic'' diffusion thermopower can be supported by theory.

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¹⁵The radial mode frequency ω_r is inversely proportional to tube diameter d , i.e., $\omega_r = 223.75 \text{ (cm}^{-1} \text{ nm)}/d$ (see Ref. 14 for details).

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²¹We have measured the four-probe resistance of nanotube mats using two current and two voltage leads. By plotting the normalized resistivity we avoid the estimation of the geometrical factor linking the four-probe resistance to the resistivity.

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