Raman spectroscopic evidence for superconductivity at 645 K in single-walled carbon nanotubes

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The temperature dependent frequency shifts of the Raman active G-band have recently been measured by R. Walter et al. for single-walled carbon nanotubes containing different concentrations of the magnetic impurity Ni:Co. These Raman data can be quantitatively explained by magnetic pair-breaking effect on a superconductor with a mean-field transition temperature \( T_c \) of 645 K, in excellent agreement with independent electrical transport and single-particle tunneling data. We suggest that such high-\( T_c \) superconductivity might arise from the pairing interaction mediated mainly by undamped acoustic plasmons in a quasi-one-dimensional electronic system.

The measurements of magnetic and electrical properties in multi-walled carbon nanotube (MWNT) ropes suggest superconductivity above 600 K. This claim is buttressed by our recent works [2,3] where we have made detailed analyses on a great number of existing data in literature. We can consistently explain the temperature dependencies of the Hall coefficient, the magnetoresistance effect, the remnant magnetization, the diamagnetic susceptibility, the conductance, and the field dependence of the Hall voltage in terms of the coexistence of physically separated tubes and Josephson-coupled superconducting tubes with superconductivity above room temperature. A great number of the existing data for electrical transport, the Altshuler Aronov Spivak (AAS) and Aharonov Bohm (AB) effects, as well as the tunneling spectra of individual single-walled nanotubes (SWNTs) and MWNTs have been well explained by theories of the quantum phase slips (QPS) in quasi-one-dimensional superconductors [3]. From the single-particle tunneling spectra of SWNTs, we find the superconducting gap \( \Delta \simeq 100 \text{ meV} \). Using a simple BCS relation, one obtains a mean-field transition temperature \( T_c \simeq 660 \text{ K} \).

We also show that, as observed in ultrathin wires of conventional superconductors such as PbIn and MoGe [6], the non-zero resistance state below \( T_c \) in some individual nanotubes is similarly caused by quantum phase slips inherent in quasi-one-dimensional superconductors [3]. The temperature dependence of the resistance in a single SWNT or MWNT is very similar to that in the ultrathin wires of MoGe and can be naturally explained by the QPS theory [6]. The resistance saturation at low temperatures observed in a single MWNT is a natural consequence of the QPS in quasi-one-dimensional superconductors [3]. Other theoretical models seem to give contradictory explanations to the electrical transport properties [3]. Furthermore, the AAS effect observed in several MWNTs is in quantitative agreement with weak localization of Cooper pairs due to the large QPS [3]. In order for the observed AAS effect to be consistent with weak localization of single particles, one must assume that only the outermost layer of a MWNT is conducting [3], in contradiction with other experiments that show about 14 conducting layers in a MWNT with a diameter of 14 nm [7], and 27 conducting layers in a MWNT with a diameter of 40 nm [8].

Here we analyze the data of the temperature dependent frequency shifts of the Raman active G-band in single-walled carbon nanotubes containing different concentrations of the magnetic impurity Ni:Co. These data have been recently taken by Walter et al. at the University of North Carolina [9]. We show that these data can be quantitatively explained by the magnetic pair-breaking effect on a superconductor with \( T_c \simeq 645 \text{ K} \). The Raman data also suggest that the gap size is about 100 meV, in excellent agreement with independent single-particle tunneling data. From the deduced magnitudes of the gap and \( T_c \), we find that \( 2\Delta/k_B T_c \simeq 3.6 \), in good agreement with the BCS prediction.

It is known that Raman scattering has provided essential information about the electron-phonon coupling and the electronic pair excitation energy in the high-\( T_c \) cuprate superconductors [11,12]. The anomalous temperature-dependent broadening of the Raman active \( B_{1g} \)-like mode of 90 K superconductors RBa\(_2\)Cu\(_3\)O\(_{7-y}\) (R is a rare-earth element) allows one to precisely determine a superconducting gap at \( 2\Delta = 40.0\pm0.8 \text{ meV} \) [11]. Moreover, it was found that the threshold temperature marking the softening of the \( B_{1g} \) mode with \( 2\Delta < \hbar \omega \leq 2.2\Delta \) coincides with \( T_c \), and the mode softens further for lower temperatures. The pronounced softening observed only for the \( B_{1g} \) mode is due to the fact that the phonon energy of the \( B_{1g} \) mode is very close to \( 2\Delta \) and the mode is strongly coupled to electrons [11,12]. We emphasize that such a softening effect is observable only for those phonon modes with their energies very close to \( 2\Delta \).

In Fig. 1a, we reproduce the temperature dependence of the frequency for the Raman-active \( B_{1g} \) mode of a 90
K superconductor YBa$_2$Cu$_3$O$_{7-y}$, which was reported in Ref. [10]. It is apparent that the frequency decreases linearly with increasing temperature above $T_c \simeq 90$ K, and that the mode starts to soften below $T_c$. The temperature dependence of the frequency above $T_c$ is caused by thermal expansion. The temperature dependence of the frequency will become more pronounced at higher temperatures since the magnitude of the slope $-d\ln\omega/dT$ is essentially proportional to the lattice heat capacity that increases monotonically with temperature. The significant softening of the mode below $T_c$ occurs only if the energy of the Raman mode is very close to $2\Delta$ and the electron-phonon coupling is substantial [13], as it is the case in the 90 K superconductor YBa$_2$Cu$_3$O$_{7-y}$ [10,11,12]. In order to see more clearly the softening of the mode, we show in Fig. 1b the difference of the measured frequency and the linearly fitted curve above $T_c$. It is clear that the softening starts at $T_c$ and the frequency of the mode decreases by about 9 cm$^{-1}$ at 5 K.

In order to see more clearly the softening of the mode, we show in Fig. 3 the difference between the measured frequency and the linearly fitted curve above the kink temperatures (e.g., above 630 K for the sample containing 0.2% Ni:Co). It is striking that the results shown in Fig. 3 are similar to that shown in Fig. 1b. This suggests that the softening of the Raman active $G$-band in the SWNTs may have the same microscopic origin as the softening of the Raman active $B_{1g}$ mode in YBa$_2$Cu$_3$O$_{7-y}$. This explanation is plausible only if the phonon energy of the $G$-band is very close to $2\Delta$. Indeed, the phonon energy of the $G$-band is 200 meV, very close to $2\Delta = 200$ meV deduced from the tunneling spectrum [3]. Therefore, it is very likely that the softening of the Raman active $G$-band in the SWNTs is related to a superconducting phase transition.

From Fig. 3, we can clearly see that the softening starts at about 632 K for the sample containing 0.2% Ni:Co, at

![FIG. 2. Temperature dependence of the frequency for the Raman active $G$-band of single-walled carbon nanotubes containing different concentrations of the magnetic impurity Ni:Co. The curves are reproduced from the original plot of Ref. [4].](image)

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From Fig. 3, we can clearly see that the softening starts at about 632 K for the sample containing 0.2% Ni:Co, at
about 617 K for the sample containing 0.45% Ni:Co, and
at about 554 K for the sample containing 1.3% Ni:Co.
By analogy to the result shown in Fig. 1b, we can assign
the mean-field transition temperature $T_{c0} = 632$ K, 617
K, and 554 K for the samples containing 0.2%, 0.45%,
and 1.3% Ni:Co, respectively.

In Fig. 4, we show $T_{c0}$ as a function of the magnetic im-
purity (Ni:Co) concentration. It is known that the resistance of quasi-one-
dimensional (quasi-1D) superconductors is finite below
the mean-field superconducting transition temperature $T_{c0}$ due to quantum phase slips [3,15]. In the smallest
diameter SWNT with $d = 0.42$ nm, the mean-field super-
conducting transition temperature $T_{c0}$ was found to be
about 15 K [16]. The temperature dependence of the res-
sistance for this 1D superconductor is in good agreement
with the theoretical calculation [16]. In Fig. 5a, we plot
the resistance as a function of $T/T_{c0}$ for the smallest di-
ameter SWNT. These data are extracted from Ref. [16].
It is apparent that the resistance increases more rapidly
above $0.5T_{c0}$ and flattens out towards $T_{c0}$. The resis-
tance at $T_{c0}$ appears to be about four times larger than
that at $0.5T_{c0}$. Below $0.5T_{c0}$, the temperature depen-
dence of the resistance can be well fitted by a power law:
$$R(T) = R_0 + AT^\beta,$$
as demonstrated in Fig. 5b. Here $R_0$ is contrib-
uted from the contact resistance and the intrinsic on-tube resistance that arises from the quantum phase
slips. From the fit, we find that $\beta = 1.77 \pm 0.18$. The the-
ory of quantum phase slips in quasi-1D superconductors
decreases with increasing magnetic concentration. The
observed $T_{c0}$ dependence on the magnetic concentration is very similar to the theoretically predicted curve based
on the magnetic pair-breaking effect on superconductiv-
ity [14]. This gives further support that the softening of
the Raman active $G$-band in the SWNTs is related to
a superconducting transition at around 600 K. Extrapo-
lating to zero magnetic-impurity concentration, we find
$T_{c0} = 645$ K. Using $\Delta = 100$ meV and $T_{c0} = 645$ K, we
calculate $2\Delta/k_B T_{c0} = 3.6$, very close to that expected
from the weak-coupling BCS theory. It is also remark-
able that the magnitude of the gap deduced from the
Raman data is in excellent agreement with that inferred
from a tunneling spectrum [3].
predicted that $\beta = 2\mu - 3$, where $\mu$ is a quantity that characterizes the ground state. The on-tube resistance at zero temperature can approach zero when $\mu > 2$, but is finite when $\mu < 2$. Disorder can lead to weak localization of Cooper pairs and thus make $\mu < 2$ \cite{15,3}. 

![Graph](image1)

**FIG. 5.** a) The resistance data as a function of $T/T_0$ for the smallest diameter SWNT with $d = 0.42$ nm. The data are extracted from Ref. \cite{16}. b) The temperature dependence of the resistance below 0.5$T_0$. The data can be well fitted by $R(T) = R_o + AT^\beta$ with $\beta = 1.77\pm0.18$.

In Fig. 6, we show the temperature dependence of the resistivity for a SWNT rope. These data are extracted from Ref. \cite{17}. Below 200 K, the resistivity is nearly temperature independent, which suggests that the measured resistance is contributed only from superconducting SWNTs with metallic chiralities. Since the resistance for semiconducting chirality tubes is larger than that for the metallic chirality tubes by several orders of magnitude \cite{18}, any current paths which include semiconducting chirality tubes are “shorted” by current paths which consist of only superconducting tubes. Considering the fact that two thirds of the tubes have semiconducting chiralities, the intrinsic resistivity of the metallic chirality tubes must be much smaller than that shown in Fig. 6. The contact barriers among the metallic chirality tubes may contribute to the resistance that increases weakly with decreasing temperature \cite{19}. The nearly temperature independent resistance observed below 200 K might be due to the competing contributions of the barrier resistance and on-tube metal-like resistance below $T_{c0}$ (due to quantum phase slips). Above 200 K, the resistivity increases suddenly and starts to flatten out above 550 K. Such a resistive temperature dependence is similar to that shown in Fig. 5a, and is consistent with quasi-1D superconductivity with $T_{c0} \approx 600$ K.

![Graph](image2)

**FIG. 6.** Temperature dependence of the resistivity for a SWNT rope. The data are extracted from Ref. \cite{17}.

We would like to mention that only armchair tubes have zero gap while other metallic chirality tubes have small semiconducting gaps due to a finite curvature \cite{20}. These metallic chirality tubes will superconduct when the doping lever is sufficient to move the Fermi level away from the small gap range. In most cases, the intrinsic defect-mediated doping is enough to drive the metallic chirality tubes to superconduct at a temperature well above room temperature. If the semiconducting chirality tubes could become superconducting by sufficient doping, the resistivity below $T_{c0}$ would be still very large because the quantum phase slips are very significant due to a small number of transverse channels and a large normal-state resistivity \cite{15,3}. The semiconducting chirality tubes would also act to separate and weaken the Josephson coupling between the superconducting tubes. The temperature dependence of the resistance for a single-walled nanotube with $d = 1.5$ nm is shown in Fig. 7. These data are extracted from Ref. \cite{21}. The distance between the two contacts is about 200 nm and the contacts are nearly ideal with the transmission probability of about 1 \cite{21}. It is remarkable that the temperature dependence of the resistance can be fitted by a power
that $R(T) = R_0 + AT^\beta$ with $\beta = 1.71 \pm 0.23$. The power $\beta$ for the 1.5 nm SWNT is nearly the same as that for the 0.4 nm SWNT, which has been proved to be superconducting. Comparing Fig. 7 with Fig. 5, we could infer the 0.4 nm SWNT, which has been proved to be superconducting [15], the theory of quantum phase slips in quasi-1D superconductors [1], $\beta = 2\mu - 3$, so we have $\mu = 2.36 \pm 0.12$ with $\beta = 1.71 \pm 0.23$. The value of $\mu > 2$ implies zero on-tube resistance at zero temperature from the theory [5], in good agreement with the experimental result [2].

![Figure 7](Image)

**FIG. 7.** Temperature dependence of the resistance for a single-walled nanotube with $d = 1.5$ nm. The data are extracted from Fig. 1a of Ref. [2] at zero gate voltage where the Fermi level is at least 0.2 eV from the band center.

It is also interesting to note that the data shown in Fig. 6 and Fig. 7 are not compatible with Luttinger-liquid behavior. Phonon backscattering in Luttinger liquid leads to semiconductor-like electrical transport at low temperatures and to metal-like electrical transport with $0.5 < \beta < 1$ at high temperatures [22,23]. This is in contrast with the data shown in Fig. 6 and Fig. 7, which suggest $\beta > 1$. Furthermore, the resistance at zero gate voltage is even temperature independent from 2 K to 270 K for a SWNT with a length of about 1 $\mu$m (see the inset of Fig. 1b of Ref. [21]). This implies that $\beta = 0$ over the wide temperature region of 2-270 K. Such an unusual temperature dependence of the on-tube resistance cannot be explained by Luttinger liquid theories, but can be naturally explained by the theory of quantum phase slips in quasi-1D superconductors which predicts $\beta = 0$ in the case of $\mu = 1.5$. In addition, the scanning tunneling microscopy on individual undoped armchair SWNTs shows no pseudo-gap feature in electronic density of states at the Fermi level [24]. This experimental result is in contrast with the Luttinger-liquid theory by Kane et al. [22] where the Luttinger parameter $g$ is predicted to be 0.2-0.3, but may be consistent with the Luttinger theory by Konik et al. [25] where the Luttinger parameter is predicted to be close to 1 at any doping levels.

On the other hand, tunneling spectra for SWNT bundles [26] and individual MWNTs [27] indicate that $\alpha_{\text{bulk}}$ and $\alpha_{\text{end}}$ (i.e., $\alpha_{\text{end}} \approx 2.7 \alpha_{\text{bulk}}$) for an individual SWNT are consistent with the Luttinger liquid model. There are several problems with the claim. First of all, they deduced values of $\alpha_{\text{bulk}}$ and $\alpha_{\text{end}}$ from the high-temperature data (above 120 K), while the Luttinger liquid theory [24] predicts that $\alpha_{\text{end}} \approx 2\alpha_{\text{bulk}}$ in this high temperature regime. Second, the experimental data appear to indicate that $\alpha_{\text{end}}$ is temperature independent above 120 K, in contrast with the theoretical prediction [24]. Third, the experimental data suggest that $\alpha_{\text{bulk}}$ is temperature dependent [25], while the authors of Ref. [24] approximated with a single exponent in the whole temperature range of 120-300 K. If one corrects the Coulomb blockade contribution for the data at low temperatures as the authors of Ref. [26] did, one may find from the data of Ref. [25] that $\alpha_{\text{end}} \approx 2\alpha_{\text{bulk}}$ at low temperatures, which is actually inconsistent with the Luttinger liquid theory.

If the Luttinger liquid behavior is not relevant to carbon nanotubes, the mechanism for the non-Luttinger liquid behavior may be a strong nonretarded electron-phonon interaction which would lead to an effectively attractive interaction between two electrons. In doped C60, the phonon energy is comparable with the Fermi energy, the electron-phonon interaction is essentially non-retarded. High-temperature superconductivity may arise from the strong non-retarded electron-phonon interaction that is large enough to overcome the direct Coulomb repulsive interaction. For doped carbon nanotubes, the phonon energy of the G-band is larger than or comparable with the Fermi energy in low doping range so that a strong nonretarded electron-phonon interaction may give rise to an effectively attractive interaction between two electrons. This electron-phonon interaction alone would not lead to high-temperature superconductivity due to a low density of states at the Fermi level.

Now a question arises: What is the pairing mechanism responsible for such high superconductivity in car-
bon nanotubes, and why does the smallest SWNT have a much lower $T_{c0}$? A theoretical calculation showed that superconductivity as high as 500 K can be reached through the pairing interaction mediated by acoustic plasmon modes in a quasi-one-dimensional electronic system \[29\]. The calculated $T_c$ as a function of the areal carrier density for InSb wires of the cross sections of 50 nm×10 nm and 80 nm×10 nm is reproduced in Fig. 8. This calculation indicates that the highest $T_c$ occurs at a doping level where the first 1D subband is nearly occupied, and that superconductivity decreases rapidly with increasing carrier density. This is because an increase of the carrier density raises the Fermi level so that more transverse levels are involved, diminishing the quasi-1D character of the system. For a metallic single-walled nanotube with $d > 1$ nm, two degenerate 1D subbands are partially occupied by hole carriers with the carrier concentration in the order of $10^{19}/\text{cm}^3$. This is the most favorable condition for achieving high-temperature superconductivity within the plasmon-mediated mechanism \[24\]. On the other hand, the smallest SWNT has a carrier density of $3.4 \times 10^{23}/\text{cm}^3$, as estimated from the measured penetration depth (3.9 nm) and the effective mass of supercarriers (0.36 $m_e$) \[1\]. One can easily show that 8 transverse subbands cross the Fermi level in the smallest SWNT, which makes the plasmon-mediated mechanism very ineffective. This can naturally explain why the $T_{c0}$ in the smallest SWNT is only 15 K. Interestingly, the value $2\Delta/k_B T_{c0} = 3.6$ deduced for SWNTs is in remarkably good agreement with the theoretical prediction \[24\].

In summary, we have analyzed the data of the temperature dependent frequency shifts of the Raman active G-band in single-walled carbon nanotubes containing different concentrations of the magnetic impurity Ni:Co. The data can be quantitatively explained by the magnetic pair-breaking effect on superconductivity with a mean-field transition temperature of 645 K and $2\Delta/k_B T_{c0} = 3.6$. We suggest that such high temperature superconductivity might arise from the pairing interaction mediated mainly by acoustic plasmons in quasi-one-dimensional electronic system.

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