Superconductivity in Ropes of Single-Walled Carbon Nanotubes

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We report measurements on ropes of single-walled carbon nanotubes (SWNT) in low-resistance contact to nonsuperconducting (normal) metallic pads, at low voltage and at temperatures down to 70 mK. In one sample, we find a 2 orders of magnitude resistance drop below 0.55 K, which is destroyed by a magnetic field of the order of 1 T, or by a dc current greater than 2.5 μA. These features strongly suggest the existence of superconductivity in ropes of SWNT.

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Metallic carbon nanotubes are known to be model systems for the study of 1D electronic transport [1–3]. Electronic correlations are expected to lead to a breakdown of the Fermi liquid state. Nanotubes should then be described by Luttinger Liquid (LL) theories [4,5], with collective low energy excitations and no long range order. Proof of the validity of LL description in ropes was given by the measurement of a resistance diverging as a power law with temperature down to 10 K [6]. However, this measurement was done on nanotubes separated from measuring leads by tunnel junctions. Because of Coulomb blockade [7], the low temperature and voltage regime were not explored. In contrast, we have developed a technique in which measuring pads are connected through low contact resistance to suspended nanotubes [8]. We previously showed that when the contact pads are superconducting, a large supercurrent can flow through nanotubes [9]. In this letter, we report experimental evidence of intrinsinc superconductivity below 0.55 K in ropes of carbon nanotubes connected to normal contacts.

The samples are ropes of single-walled carbon nanotubes (SWNT) suspended between normal metal contacts (Pt/Au bilayers). The SWNT are prepared by an electrical arc method with a mixture of nickel and yttrium as a catalyst [10,11]. SWNT with diameters of the order of 1.4 nm are obtained. They are purified by the cross-flow filtration method [11]. The tubes are usually assembled in ropes of a few hundred parallel tubes. Isolation of an individual rope and connection to measuring pads are performed according to the procedure we previously used [8], where ropes are soldered to melted contacts. The contact resistance is low and the tubes can be structurally characterized with a transmission electron microscope (TEM). For the three samples presented here, the contacts were trilayers of sputtered Al_2O_3/Pt/Au of respective thicknesses 5, 3, and 200 nm. This procedure ensures that the tubes do not contain any chemical dopants such as alkalis or halogens. The contacts showed no sign of superconductivity down to 50 mK. The samples were measured in a dilution

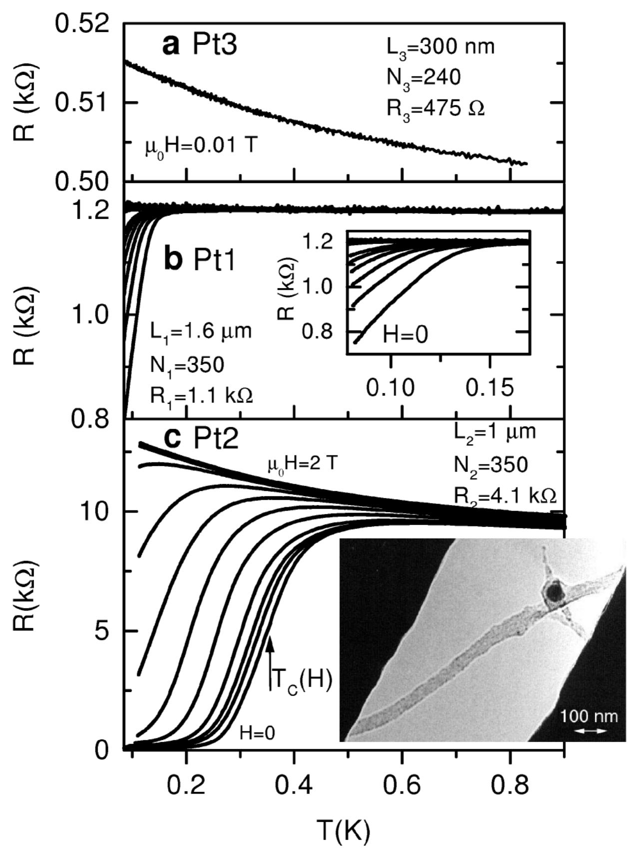

FIG. 1. Resistance as a function of temperature for the three samples. The length L, number of tubes N, and room temperature resistance R of each sample are given in the corresponding panel. (a) Sample Pt3. (b) Resistance of Pt1 in applied magnetic fields of $\mu_0 H = 0$, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 T from bottom to top. The inset is a zoom of the low temperature region. (c) Resistance of Pt2 at $\mu_0 H = 0$, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.25, 1.5, 1.75, 2, and 2.5 T from bottom to top. Inset: TEM micrograph of sample Pt2, from which we deduce L_2 and N_2. N_2 is estimated from the measured diameter D_2, through $N_2 = [D_2/(d + e)]^2$, where d is the diameter of a single tube ($d = 1.4$ nm), and e is the typical distance between tubes in a rope ($e = 0.2$ nm). The dark spot is a Ni/Y catalyst particle.

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refrigerator, at temperatures ranging from 1 to 0.05 K, through filtered lines [12]. Magnetic fields up to 5 T could be applied perpendicularly to the contacts and the tubes. The resistance was measured by applying a small (1 to 10 nA, 30 Hz) ac current though the sample and measuring the ac voltage using lock-in detection.

We select samples with a room temperature (RT) resistance less than 10 kΩ. As is generally observed, we find that the resistance increases as the temperature is lowered between 300 and 1 K. Things change, however, below 1 K, as shown in Fig. 1 for the three samples Pt1, Pt2, and Pt3, measured in magnetic fields ranging from 0 to 2.5 T. At zero field, the zero-bias resistance of Pt3 increases as T is reduced, whereas the resistances of Pt1 and Pt2 decrease drastically below $T_1^* = 140$ mK for Pt1 and $T_2^* = 550$ mK for Pt2. The resistance of Pt1 is reduced by 30% at 70 mK. That of Pt2 decreases by more than 2 orders of magnitude, and saturates below 100 mK at a value $R_r = 74\ \Omega$. We define a transition temperature T_{C_2} by the inflection point of $R(T)$. T_{C_2} is 370 mK at zero field, decreases at higher magnetic fields, and extrapolates to zero at 1.35 T (Fig. 4c below). At fields above 1.25 T, the resistance increases with decreasing temperature, similar to Pt3, and becomes independent of magnetic field. The resistance of Pt1 follows qualitatively the same trend, but the full transition does not occur down to 70 mK. Figures 2 and 3 show that, in the temperature and field range where the zero-bias resistance drops, the differential resistance is strongly bias dependent, with lower resistance at low bias. These data suggest that the rope Pt2 (and, to a lesser extent, Pt1) is intrinsically superconducting. Although the experimental data of Pt2 seem similar to those of SWNT connected to superconducting contacts [9], there are major differences. In particular the $V(I)$, $dV/dI(I)$ do not show any supercurrent because of the existence of a finite residual resistance.

We now analyze the superconductivity in these systems, taking into account several features: the large normal contacts, the coupling between tubes within the rope, the 1D character of each tube, and their finite length compared to relevant mesoscopic and superconducting scales. The resistance of any superconducting wire measured through normal contacts [a normal-superconductor-normal (NSN) junction] cannot be zero because the number of channels in the wire is much smaller than in the contacts [13]: a metallic SWNT, with 2 conducting channels, has a contact resistance of half the resistance quantum, $R_Q/2$ [where $R_Q = h/(2e^2) = 12.9$ kΩ], even if it is superconducting. A rope of N_m parallel metallic SWNT will have a minimum resistance of $R_Q/(2N_m)$. Therefore we use the residual resistance $R_r = 74\ \Omega$ of Pt2 to deduce that Pt2 has at least $N_m = R_Q/2R_r \approx 90$ metallic tubes. This is approximately one-fourth of the number of tubes in the rope, measured by TEM (Fig. 1c). Similarly, R_Q is also the maximum resistance of any phase coherent metallic wire [14]. As a consequence, the high value (9.2 kΩ) of the resistance at 1 K [which corresponds to an average resistance per metallic tube of (9.2 kΩ) $\times N_m = 830$ k$\Omega = 130 R_Q$] cannot be understood if the nanotubes are independent, unless considering a very short (unphysical) phase coherence length $L_\varphi(1\ \text{K}) = L/130 = 8$ nm. On the other hand, if the electrons are free to move from

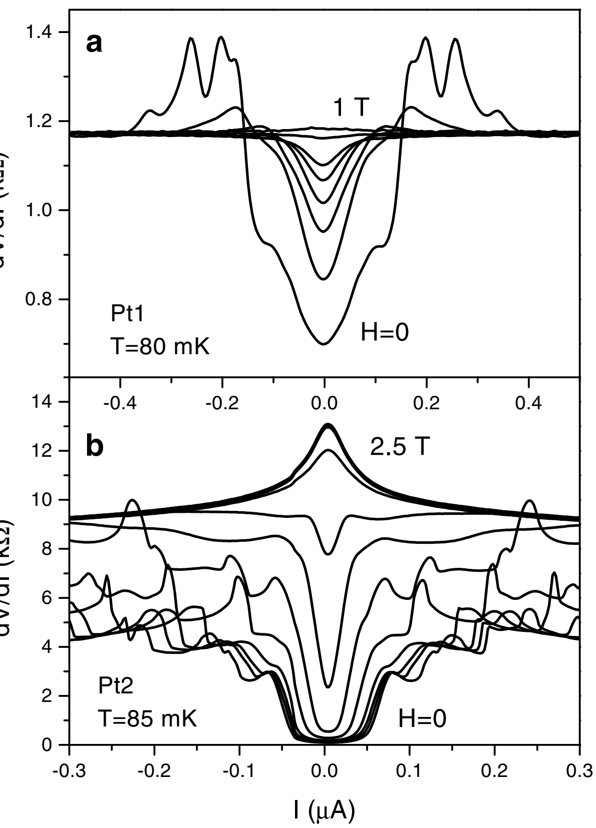

FIG. 2. Differential resistance as a function of current for samples Pt1 and Pt2, in different applied fields. (a) Sample Pt1. Fields are 0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, and 1 T. (b) Sample Pt2. Fields are 0, 0.2, 0.4, 0.6, 0.8, 1, 1.25, 1.5, 1.75, 2, and 2.5 T.

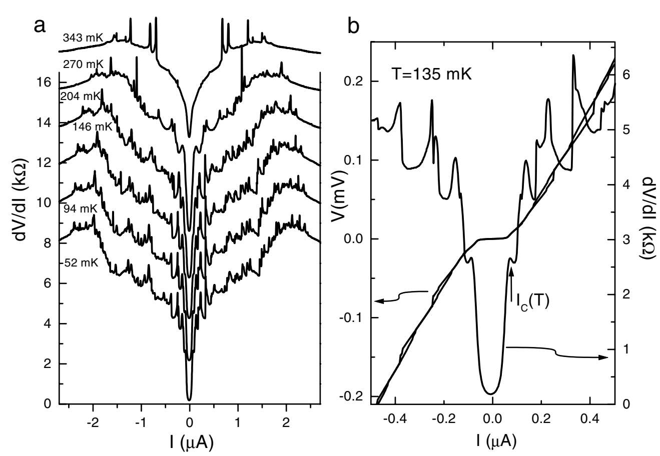

FIG. 3. (a) Differential resistance of Pt2 vs current for a larger current amplitude than in Fig. 2, at different temperatures. Curves are offset vertically for clarity. (b) $V(I)$ and $\frac{dV}{dI}(I)$ curves showing the hysteretic behavior in $V(I)$ at each point in the $\frac{dV}{dI}(I)$ curve.

tube to tube [15], the resistance is simply explained by the presence of disorder. The mean-free path is deduced from the RT resistance $R_2 = 4.1\ \text{k}\Omega$ through [16] $l_{e2} \approx \frac{L}{R_2}\frac{R_Q}{N_m} \approx 18$ nm. We conclude that Pt2 is a diffusive conductor with a few hundred conduction channels.

With such a small number of channels, we expect the superconductivity to differ from 3D superconductivity. In particular, we expect to observe a broad resistance drop starting at the 3D transition temperature T^* [17] and going eventually to R_r at zero temperature. This is what is observed in Pt2 (see Fig. 1c). We estimate the gap through the Bardeen-Cooper-Schrieffer relation $\Delta = 1.76 k_B T^*$: $\Delta \approx 85\ \mu$eV for Pt2. We can then deduce the superconducting coherence length along the tube in the diffusive limit $\xi_2 = \sqrt{\hbar v_f l_{e2}/\Delta} \approx 0.3\ \mu$m, where v_f is the longitudinal Fermi velocity 8×10^5 m/s [18]. Consistent with 1D superconductivity, ξ_2 is 10 times larger than the diameter of the rope.

Finally, reminiscent of measurements of narrow superconducting metal wires [17], we find jumps in the differential resistance as the current is increased (Figs. 2 and 3). For Pt2 the differential resistance at low currents remains equal to R_r up to 50 nA, where it strongly rises but does not recover its normal state value until 2.5 μA (Fig. 3a). The jump in resistance at the first step corresponds approximately to the normal state resistance of a length ξ_2 of Pt2. Each peak corresponds to a hysteretic feature in the V-I curve (Fig. 3b). Above 1 T the differential resistance is peaked at zero current. This is also the case for Pt3 (data not shown). The variations of the differential resistance of Pt1 are similar to those of Pt2 close to its transition temperature. These jumps are identified as phase slips [17,19,20], which are the occurrences of normal regions located around defects in the sample. Such phase slips can be thermally activated (TAPS), leading to an exponential decrease of the resistance instead of a sharp transition, in qualitative agreement with our experimental observation (Fig. 4a). At a sufficiently low temperature, TAPS are replaced by quantum phase slips (QPS), which, when tunneling through the sample, contribute an additional resistance to the zero temperature resistance. Moreover, QPS are predicted to suppress the transition when the normal state resistance of the sample on the phase coherence scale is larger than $R_Q/2$ [21] (as confirmed by recent experiments [22]). Our data on Pt2 show no evidence of such an effect, even though the normal state resistance, measured above T^*, is 40% larger than $R_Q/2$. The current above which the jumps disappear, 2.5 μA, is close to the critical current $I_C = \Delta/R_r e \approx 1\ \mu$A of a superconducting wire without disorder and with the same number of conducting channels [20]. This large value of critical current would also be the maximum supercurrent in a structure with this same wire placed between superconducting contacts (with gap Δ_S), and is much larger than the Ambegaokar-Baratoff prediction $R_N I_C = \Delta_S/e$. This

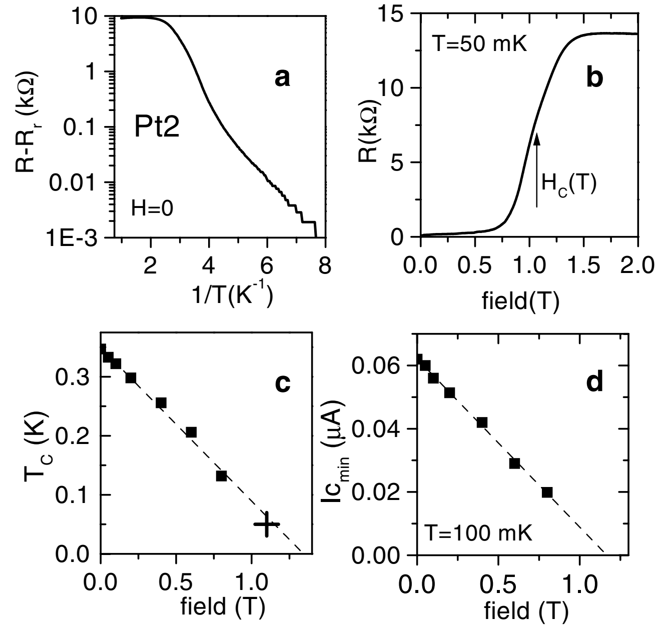

FIG. 4. (a) Resistance of Pt2 plotted on a log scale as a function of the inverse temperature at $H = 0$. We have subtracted the low temperature residual resistance (contact resistance). The slope yields an approximation activation energy of 0.8 K. (b) Magnetoresistance of Pt2 at 50 mK. We define the critical field as the inflection point of $R(H)$: $\mu_0 H_C(T = 50\ \text{mK}) = 1.1$ T. (c) Transition line of Pt2 defined in the H, T plane by the inflection point of $R(T)$ or, equivalently, by the inflection point of $R(H)$. (d) Field dependence of the critical current of Pt2 defined as the current at which the first resistance jump occurs in the dV/dI curves of Fig. 2. $I_C(H)$ extrapolates to a critical field of 1.2 T, in agreement with the linear extrapolation 1.3 T of $T_C(H)$.

might explain the anomalously large supercurrent measured in a previous experiment [9], where nanotubes were connected to superconducting contacts.

We now discuss the effect of the magnetic field. The field at which the resistance saturates to its normal value and at which the critical current vanishes, 1.25 T, coincides with the field obtained by extrapolation of $T_C(H)$ to zero temperature (Fig. 4b). It is difficult to say what causes the disappearance of superconductivity. The value of $Hc(0)$ should be compared to the depairing field in a confined geometry [23], and corresponds to a flux quantum Φ_0 through a length ξ of an individual SWNT of diameter d, $\mu_0 H_C = \Phi_0/(2\sqrt{\pi} d \xi) = 1.35$ T. But $H_C(0)$ is also close to the field $\mu_0 H_p = \Delta/\mu_B = 1.43$ T at which a paramagnetic state becomes more favorable than the superconducting state [24,25]. Note that this value is of the same order as the critical field that was measured on SWNT connected between superconducting contacts, i.e., much higher than the critical field of the contacts.

We now estimate the superconducting coherence length of the two other samples, to explain the extent or absence of observed transition. Indeed, investigation of the proximity effect at high-transparency NS interfaces has shown that superconductivity resists the presence of normal contacts only if the length of the superconductor is much greater than ξ [26], i.e., if the wire contains a superconducting reservoir. This condition is nearly fulfilled in Pt2 ($\xi_2 \approx L_2/3$). By using the high temperature resistance values of Pt1 and Pt3, and by assuming a gap Δ and a number of metallic tubes equal to those of Pt2, we find $\xi_1 \approx L_1/2$ and $\xi_3 \approx 2L_3$. These values explain qualitatively a reduced transition temperature for Pt1 and the absence of a transition for Pt3. Moreover we can argue that the superconducting transitions we see are not due to a hidden proximity effect: if the $Al_2O_3/Pt/Au$ contacts were made superconducting by the laser pulse, the shortest nanotube (Pt3) would become superconducting at temperatures higher than the longer tubes (Pt1 and Pt2). The main result, i.e., no visible transition with a short rope, and a visible transition with a long rope, are confirmed by measurements on two other samples which are not presented here.

We now consider the possible mechanism of superconductivity. It has been suggested that coupling with low energy phonons can turn repulsive interactions in a Luttinger liquid into attractive ones and drive the system towards a superconducting phase [27]. Such low energy phonons have been experimentally observed in the form of mechanical bending modes of a suspended SWNT rope [28]. It was also shown that superconducting fluctuations can dominate at low temperature in ladders such as tubes [4]. In this case the system must be away from half-filling, a condition probably fulfilled in our experimental situation, due to hole doping from the contacts [29,30]. Finally, the superconductivity reported here recalls that of graphite intercalated with alkalis (Cs, K), which also occurs between 0.2 and 0.5 K [31]. Much higher temperatures were observed in alkali doped fullerenes [32] because of the coupling to higher energy phonons. This suggests the possibility of increasing the transition temperature by chemically doping the nanotubes.

We have shown that ropes of carbon nanotubes are intrinsically superconducting. This is the first observation of superconductivity in a system with such a small number of conduction channels. The understanding of this superconductivity calls for future experimental and theoretical work and motivates in particular a search of superconducting fluctuations in a single SWNT.

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