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Interplay of Tomonaga-Luttinger liquids and superconductive phase in carbon nanotubes

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Abstract – We report the observation of the interplay between repulsive and superconducting correlations in boron-doped multi-walled carbon nanotubes (MWNTs) with a small number of conductance channels. NMR measurements ascertain the presence of substitutional boron doping with the optimum concentration for superconductivity (SC) in the MWNTs. We find that a gradual transition from Tomonaga-Luttinger–liquid (TLL) states to a SC regime can start only from low (eV/kT) values at low temperatures, while keeping a constant Luttinger parameter at high eV values, but the development of the SC enhances the regime to a high-(eV/kT) region. The phase diagram obtained from low-energy theory reveals that such a transition is actually possible depending on van Hove singularity in one-dimensional electronic states.

A carbon nanotube (CNT) is a typical one-dimensional (1D) molecular conductor, with a ballistic charge transport regime in which electron scattering takes place only at the leads. A variety of 1D quantum phenomena have been reported in CNTs. The Tomonaga-Luttinger liquid (TLL) provides the relevant theoretical description [1–3], representing a collective electronic state (*e.g.*, showing spin-charge separation) that arises from the repulsive Coulomb interaction between electrons confined in a 1D ballistic conductance regime.

Many previous works have reported TLL features in CNT systems. It is known that the tunneling density of states $\nu(E)$ for the TLLs decreases following a power law dependence on energy, $\nu(E) \propto E^{\alpha}$, where the power α is given by different expressions according to the different tunneling regimes [1,2,4]. Most previous works on CNTs have been dealing with the regime of strong Coulomb interaction.

In contrast, it is well known that the phonon-mediated attractive electron-electron interaction may lead to a superconducting instability in 2D and 3D conductors. This phenomenon corresponds to a regime different to that of the Coulomb repulsion leading to the TLL state. Intrinsic superconductivity (SC) has been reported in the CNTs by several groups, see refs. [5,6] and [8]. This leads naturally to the question of how the SC can develop in the CNTs, with the consequent transition from the TLL [9–14].

The interplay between the TLL state and intrinsic SC has been only reported in our multi-walled CNTs (MWNTs) with a significant number N of shells participating in the conduction [6]. The results were qualitatively consistent with low-energy theories of CNTs [10], which had already predicted the breakdown of the TLL at low temperatures in nanotube bundles with a strong intertube electrostatic coupling between the different 1D conduction channels.

In the MWNTs, however, the interplay of the SC with the TLL and the value of T_c as high as 12 K still had to be quantitatively understood, as the samples were not intentionally doped and the number of 1D conduction channels was unknown. On the other hand, the high T_c value was in approximate agreement with T_c's $\cong$ 10 K of CaC_6 and boron (B)-doped diamond. Indeed, low-energy theories of MWNTs have suggested the importance of

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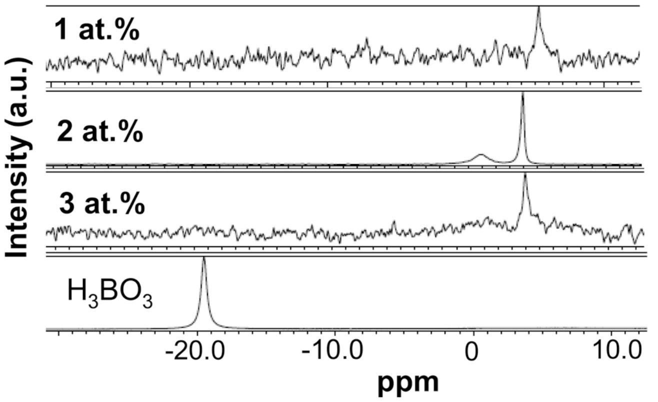

Fig. 1: NMR measurement results of the MWNTs that were synthesized from Fe/Co with different B concentration noted by atomic %, using ^{11}B. The result with H_2BO_3 is a reference. H_2BO_3 was mixed in $FeSO_4$ and $CoSO_4$, and then the Fe/Co catalyst including B was electrochemically deposited into the bottom ends of the nanopores of the alumina template [6,17].

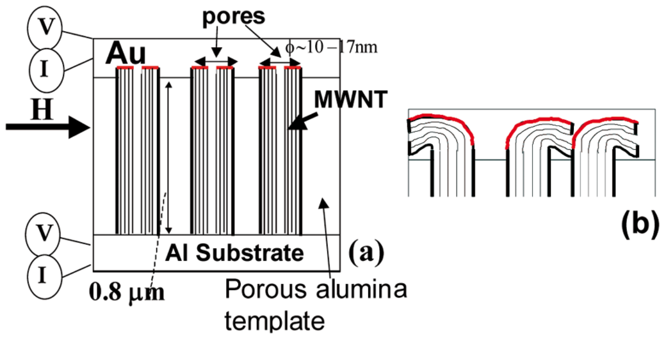

Fig. 2: (Colour on-line) Schematic cross-sections of an array of MWNTs with (a) entirely end-bonded and (b) partially end-bonded junctions between the Au electrode and the top ends of MWNTs. The red lines indicate the interfaces between the MWNTs and the electrodes.

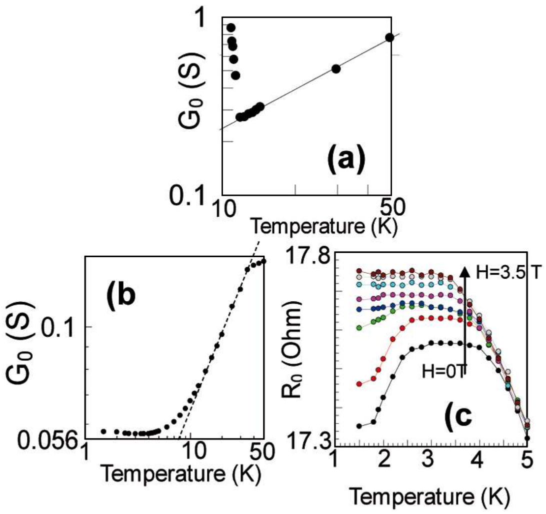

Fig. 3: (Colour on-line) Doubly logarithmic scales of zero-bias conductance G_0 and temperature for (a) entire and (b) partial end junctions. (c) Magnetic-field dependence of the zero-bias resistance R_0 as a function of temperature, corresponding to (b).

having a large number of 1D conduction channels for the development of a SC instability [12]. Therefore, it is crucial to clarify the correlation between the appearance of the SC phase and carrier doping in MWNTs. B-doping has been actually successfully achieved following known methods [15,16].

Based on these reasons, in the present study, we have analyzed the possibility of unintentional B-doping in our MWNTs, which were synthesized by chemical-vapor deposition using Fe/Co catalyst and methanol gas in the nanopores of the alumina template [6,17]. Boron has been intentionally used only for the enhancement of the chemical reaction of the Fe/Co catalyst [6,17]. Figure 1 shows the results of nuclear-magnetic-resonance (NMR) measurements of our MWNTs with three different boron concentrations (N_B) in the catalyst. Evident peaks can be observed at 0–5 ppm in individual samples. The peak position implies the presence of chemical bonds of B-C and, hence, substitutional B-doping in the carbon network of the MWNTs. Moreover, an at least five times higher intensity of the NMR signal peak for the B-C was detected in the B-MWNTs with $N_B \cong 2$ at.%, compared with other B-MWNTs with different N_B values. Very importantly, we find that only the B-MWNTs with $N_B \cong 2$ at.% showed SC with high T_c (fig. 3(a)) and also present signature of SC (fig. 3(b)) with the highest reproducibility. This result implies that the most suitable condition for substitutional B doping into the MWNTs, which leads to appearance of the SC, is ~2 at.%. This is consistent with our recent discovery [18] and a theory [19].

Figure 2 shows the schematic cross-sections of our samples, which include arrays of B-MWNTs with (a) entirely end-bonded ($N = 9$) and (b) partially end-bonded ($1 < N < 9$) junctions to Au electrodes [6].

Figure 3 shows the doubly logarithmic scales of the zero-bias conductance G_0 and temperature for the two different junctions shown in fig. 2. The observed power law behaviors in the different types of junctions ($G_0 \propto T^{\alpha}$; $\alpha = 0.7$ and 0.8 in (a) and (b), respectively) are in excellent agreement with the previous reports of TLL behavior in CNTs [2,6]. As shown in fig. 3(a), the abrupt G_0 increase (*i.e.*, SC regime) appears overcoming the TLL behavior (*i.e.*, the power law at $T > 12$ K) at $T_c = 12$ K in the entirely end-bonded B-MWNTs. The origin of this effect was in the large screening of the Coulomb interaction, arising from the electrostatic coupling between a large number of 1D conduction channels due to boron-doping and also the large N value originating from the entire end-bonding of the B-MWNTs [6,10].

In contrast, in the partially end-bonded B-MWNTs, only a slight and gradual G_0 increase at $T < 2.5$ K (*i.e.*, a signature of SC correlations) can be observed as shown in fig. 3(b). As we implied in ref. [6], the appearance of SC and the correlations of power laws with G_0 increase were strongly correlated with the values of N as shown in fig. 3.

Because we could confirm that the abrupt G_0 increase in fig. 3(a) was attributed to SC as mentioned above [6], it can be concluded that the small G_0 increase observed in fig. 3(b) is also attributed to SC. The gradual G_0 increase corresponds to the slight and gradual resistance drop shown in fig. 3(c). With an increase in the magnetic field, the drop in R_0 disappears rapidly. This behavior actually agrees with that of conventional superconductors.

In fig. 3(b), the power law is observable up to $T \cong 40\,\mathrm{K}$ for $\alpha \cong 0.7$, while it gradually starts to deviate below $T \cong 12\,\mathrm{K}$. At $T \lesssim 6\,\mathrm{K}$, it saturates completely. Subsequently, a small increase in G_0 due to the SC correlations appears at $T \lesssim 2.5\,\mathrm{K}$. However, the trend towards the SC transition is not completed above $T = 1.5\,\mathrm{K}$ in this case. This is consistent with the fact that the SC phase requires the coherent transport of Cooper pairs along the directions transverse to the CNTs, which cannot be established when only part of the shells are electrically active and the number of conductance channels is smaller as in the partially end-bonded B-MWNTs with the small N values [6,10]. This also implies that the Coulomb interaction cannot be sufficiently screened to allow for the development of SC correlations. In fact, B-MWNTs with $N = 1$ exhibited no G_0 increase, consequent with the absence of screening of the Coulomb interaction.

On the other hand, besides the dependence on temperature, the power law behavior of the observables as a function of the bias voltage V provides absolute evidence of the TLL behavior [2,3,20]. Thus, it is crucial to investigate the regime $eV \gg kT$ to discuss in depth the transition from the TLL behavior to the SC phase. In this sense, fig. 4(a) exhibits doubly logarithmic plots of the normalized differential conductance *vs.* eV/kT, which is one of the typical dependences to check the TLL behavior for $eV \gg kT$ [20]. It shows that the entire data collapse suitably onto a single universal curve at $T \gtrsim 7\,\mathrm{K}$. This agrees with the results reported in previous investigations of the TLL behavior [1,2,20]. As shown by the red dotted line, this universal curve can be fitted by the following result for a TLL [20]:

$$\frac{G(V,T)}{G(V=0,T)} = \cosh\left(\gamma \frac{eV}{2kT}\right) \frac{1}{\left|\Gamma(\frac{1+\alpha}{2})\right|^2} \times \left|\Gamma\left(\frac{1+\alpha}{2} + \gamma \frac{ieV}{2\pi kT}\right)\right|^2, \qquad (1)$$

where V is the applied voltage, $\Gamma(x)$ the Gamma-function, k the Boltzmann constant and γ the inverse number of the measured junctions M weighted by their resistance [20]. For M junctions in series, the value of γ should be within $\gamma = 1/M$. The best fit gives the parameter $\gamma \cong 0.7$, which is mostly in good agreement with $\gamma = 1/M = 0.5$ for $M = 2$ of our individual MWNTs with two end junctions. Therefore, we conclude that the universal curve can be actually attributed to TLL behavior at $T \gtrsim 7\,\mathrm{K}$ [6].

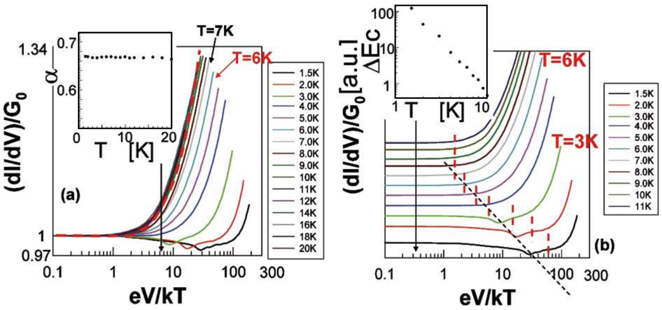

Fig. 4: (Colour on-line) (a) Doubly logarithmic scales on normalized differential conductance *vs.* eV/kT, corresponding to the TLL formula in the $eV \gg kT$ regime [20]. The red dotted line is the best-fitting result by eq. (1). Inset: power value α *vs.* temperature estimated from the main panel (using eq. (1) at $T > 6\,\mathrm{K}$ and directly from data filling to the linear parts in the high-(eV/kT) regions at $T \leqslant 6\,\mathrm{K}$.) (b) The data shown in the Y-axis of (a) was shifted vertically by an arbitrary amount. The long black-dotted line connects the right edges of the conductance peaks. Inset: ΔE_c *vs.* temperature on double-logarithmic scales. $\Delta E_\mathrm{c} = E_\mathrm{c}(T) - E_\mathrm{c}(T = 7\,\mathrm{K})$, where $E_\mathrm{c}(T)$ is the boundary point between the saturation and power law regions, as shown by the short red-dotted lines in the main panel.

However, we importantly find appearance of a deviation from the universal curve in the low-temperature regime (*e.g.*, at $T \leqslant 6\,\mathrm{K}$) in fig. 4. As shown by red lines in fig. 4(b), this deviation originates from a monotonic increase in the width of the low-(eV/kT) saturation region (*i.e.*, $eV/kT \lesssim 2$ at $T = 6\,\mathrm{K}$) in the universal curve at $T \lessapprox 6\,\mathrm{K}$. The inset of fig. 4(b) shows ΔE_c (width of the saturation region) as a function of temperature in a doubly logarithmic scale. Indeed, we can confirm that ΔE_c actually increases with a decrease in temperature, following a power law dependence.

Quite remarkably, it should be noted that the value of the critical temperature of 6 K for the deviation of the universal curve is in excellent agreement with that of the saturation region in fig. 3(b). This agreement strongly suggests that the deviation at $T \lessapprox 6\,\mathrm{K}$ in fig. 4 for $eV \gg kT$ is associated with the appearance of the SC regime. Figure 4(b) supports this argument, because it suggests that the increase in the width of the saturation region is caused by the appearance (insertion) of the conductance peak due to emergence of the SC regime. In particular, this is evident at $T \leqslant 3\,\mathrm{K}$, where G_0 is seen to increase in fig. 3(b)[1]. This implies that the emergence of the SC regime at low eV/kT leads to the deviation from the TLL states[2].

[1] As the critical temperature of 6 K for the appearance of the deviation is in excellent agreement with that from fig. 3(b), the SC regime potentially exists even at $3\,\mathrm{K} < T \leqslant 6\,\mathrm{K}$, though the conductance peak is not seen there due to the obstruction by the TLL regime.

[2] Experimental observation of TLL states and its confirmation by theory requires $\nu(E)$ in CNTs [1], while SC transition may not favor a tunnel junction. However, ref. [4] predicted that even attractive Coulomb interactions could lead to power law behaviors along with

In the conventional theory of a TLL, the width of the low-(eV/kT) saturation region ($\lesssim 1$) reflects the regime of $eV/kT < \Delta E = hv_{\mathrm{F}}/L$, where ΔE is the energy spacing of the quantized electronic orbital formed in the CNTs in the ballistic charge transport regime[3]. This means that the noise from thermal fluctuations smears the effects of the bias voltage (*i.e.*, power laws) out in the low-(eV/kT) regime ($\lesssim 1$). In contrast, one should notice that insertion of the conductance peak in fig. 4(b) enhances this thermal smearing region to the high-(eV/kT) regime ($\sim$100) at $T = 1.5$ K. This is very anomalous and, hence, strongly implies a possibility that appearance of the SC regime introduces superconducting gap Δ_{SC} in the system, resulting in $\Delta E + \Delta_{\mathrm{SC}}$.

Moreover, the inset of fig. 4(a) shows the values of α, which were estimated from the main panel of fig. 4(a), as a function of temperature. It is very important to note that the α value is constant ($\sim$0.67) in all the temperature range, despite the emergence of conductance peak due to the SC regime at the low-(eV/kT) regime below $T = 6$ K. This implies that the transition from the TLL behavior to the SC regime starts to occur only in the low-eV regime, when the values of eV are drastically lowered under constant low kT values. This is because the long-range 1D electron correlation is enhanced by applied voltage energy at high-eV regimes. Only when low eV values are satisfied under low kT values, this 1D electron correlation can be suppressed. This is in agreement with the low-energy theory of TLL states.

Here, in fig. 5, we show that such a transition is actually possible in the light of the low-energy theories of doped MWNTs [12]. The two regimes are represented in the phase diagram of fig. 5, which has been obtained following the approach of ref. [12]. We observe that a minimum N value per shell (10) in a MWNT is needed for the onset of the SC regime, and that subsequent peaks arise in the critical temperature as the Fermi level (ε_{F}) crosses the top of a new subband (*i.e.*, a van Hove singularity). This result is in good agreement with the present experimental results, in which the N_{B} value is below 2 at.% with small N values leading to a shift of ε_{F} in $\sim$0.3 eV [18,19] and a corresponding T_{c} of 3–12 K. Thus, figs. 3 and 4 are the results when ε_{F} locates at $\sim$0.3 eV in fig. 5, although we cannot exactly confirm the boron concentration in the MWNTs and also the position of ε_{F} in the present experiments.

The characterization of doping in the MWNTs provides actually the clue to account for the SC regime. This appears as a consequence of the large screening of the Coulomb interaction, which arises in doped MWNTs, as in the case of CNT ropes [18], from the electrostatic coupling of a large number of 1D conduction channels. The effect is such that the long-range part of the Coulomb potential is largely suppressed, placing the system on the verge of a pairing instability. This takes place as the intertube Cooper-pair tunneling is progressively enhanced at low energies [12]. In this respect, the Cooper pairs do not find the obstruction that single electrons have to tunnel between the incommensurate CNT lattices of a MWNT. When intertube coherence can be established at some low temperature T_{c} under a low eV value, the system undergoes the transition from the TLL to the SC regime as shown in fig. 5.

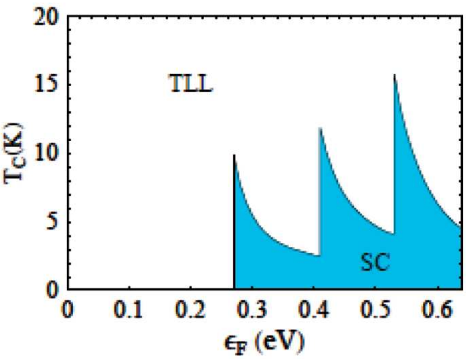

Fig. 5: (Colour on-line) Phase diagram of doped MWNTs (incorporating the average over different geometries of the shells) in terms of the doping level, represented by the shift in the Fermi energy ε_{F} with respect to the charge neutrality point, and the temperature [12].

Although further quantitative investigation is expected, the present phenomena must shed light on the understanding of the interplay of SC with 1D electron correlations in B-CNTs.

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perfect transmission of Cooper pairs via tunnel junction. Thus, the present result is consistent with this theory.

[3] $v_{\mathrm{F}} (= hk_{\mathrm{F}}/m^*)$ and L are the Fermi velocity and the tube length of the 1D conductor, respectively. The previous studies on TLL states in CNTs reported that the saturation regimes fall onto a universal curve in any temperature ranges.

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