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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.

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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, substituional 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 $N_B \sim 2$ at.%, compared with other B-MWNTs with different $N_B$ values. Very importantly, we find that only the B-MWNTs with $N_B \geq 2$ 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 $\sim 2$ 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 $T \approx 40$ K for $\alpha \approx 0.7$, while it gradually starts to deviate below $T \approx 12$ K. At $T \lesssim 6$ K, it saturates completely. Subsequently, a small increase in $G_0$ due to the SC correlations appears at $T \lesssim 2.5$ K. However, the trend towards the SC transition is not completed above $T = 1.5$ 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 $v$ 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 $T \approx 7$ 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]:

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

(1)

where $V$ is the applied voltage, $\Gamma(x)$ the Gamma-function, $k$ the Boltzmann constant and $\gamma$ the inverse number of the measured junctions $M$ weighted by their resistance [20]. For $M$ junctions in series, the value of $\gamma$ should be within $\gamma = 1/M$. The best fit gives the parameter $\gamma \approx 0.7$, 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 $T \gtrsim 7$ K [6].

However, we importantly find appearance of a deviation from the universal curve in the low-temperature regime (e.g., at $T \lesssim 6$ 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 $T = 6$ K) in the universal curve at $T \lesssim 6$ K. The inset of fig. 4(b) shows $\Delta E_c$ (width of the saturation region) as a function of temperature in a doubly logarithmic scale. Indeed, we can confirm that $\Delta E_c$ 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 $T \lesssim 6$ 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 $T \lesssim 3$ 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 $3K < T \lesssim 6$ 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 \( eV/kT < \Delta E = \hbar v_F/L \), where \( \Delta E \) is the energy spacing of the quantized electronic orbital formed in the CNTs in the ballistic charge transport regime. 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 \( T = 1.5 \text{K} \). This is very anomalous and, hence, strongly implies a possibility that appearance of the SC regime introduces superconducting gap \( \Delta_{\text{SC}} \) in the system, resulting in \( \Delta E + \Delta_{\text{SC}} \).

Moreover, the inset of fig. 4(a) shows the values of \( \alpha \), which were estimated from the main panel of fig. 4(a), as a function of temperature. It is very important to note that the \( \alpha \) 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 \( T \approx 6 \text{K} \). 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 \( \varepsilon_F \) 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 \( \varepsilon_F \) in \( \sim 0.3 \text{eV} \) [18,19] and a corresponding \( T_c \) of 3–12K. Thus, figs. 3 and 4 are the results when \( \varepsilon_F \) locates at \( \sim 0.3 \text{eV} \) in fig. 5, although we cannot exactly confirm the boron concentration in the MWNTs and also the position of \( \varepsilon_F \) 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 \( T_e \) under a low \( eV \) value, the system undergoes the transition from the TLL to the SC regime as shown in fig. 5.

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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\[ \alpha_{\text{bulk}} = (g^{-2} + g - 2)/8 \] for tunneling from electrode to the bulk of CNTs and 
\[ \alpha_{\text{nm}} = (g^{-1} - 1)/4 \] to the ends of the CNTs are given. The value of \( g \), the Luttinger parameter, is dictated by the strength of the \( e-e \) interaction, with ranges \( g < 1, g > 1 \) reflecting respectively its repulsive or attractive character.


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[6] Takesue I., Haruyama J. et al., Phys. Rev. Lett., 96 (2006) 057001. Power laws have been also discussed from viewpoints of Coulomb blockade coupled with its external electromagnetic environment (i.e., MWNT acts as a LC transmission line connected to tunnel junctions) [1] and also one-dimensional localization. However, the present case does not correspond to these models, because the calculation result of our MWNT as a LC transmission line does not agree with the observed power laws [7] and also the present interplay of power laws with SC cannot be understood by these models.


