Conductance and thermoelectric power in carbon nanotubes with magnetic impurities

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By introducing a normal self-energy to incorporate the effects of magnetic impurities, Kondo effects in single-walled metallic carbon nanotubes are investigated within the Anderson model and Landauer formula. Magnetic impurities induce Kondo resonance and bring a valley of conductance function near the Fermi level. The conductance of the nanotube increases with the temperature in the low temperature range. Thermoelectric power induced by magnetic impurities is gotten from Mott relation, and the calculations indicate its dependence on the temperature could interpret the experiment well.

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I. INTRODUCTION

Research on the carbon nanotubes has attracted much interest due to their unique properties and great application potentials. A single-walled carbon nanotube (SWNT) can be metallic or semiconducting depending on its radius and chirality. The properties of carbon nanotubes can be greatly modified by defects or impurities, which may be introduced in the production of nanotubes or be doped artificially. The role of magnetic atoms or clusters in the carbon nanotubes is interesting and may have significant effects on the electronic transport properties. The earlier thermoelectric power (TEP) measurements on single walled carbon nanotube mats suggest that the observed giant TEP comes from the contributions of Kondo state induced by magnetic transition-metal catalysts. In addition, low-temperature scanning tunnelling microscopy (STM) spectroscopy is probed for isolated nanometer ferromagnetic cobalt clusters on surface of metallic single-walled carbon nanotubes. The results clearly indicates the appearance of Kondo resonance.

Magnetic impurities in non-magnetic metallic host, which are called Kondo impurities, have been explored in bulk systems for many years. The most attracting features are that they bring a series of anomalies on the physical properties of the host, including conductance, specific heat and thermoelectric power (TEP) and so on. They are generally called Kondo effects. Recently, the Kondo effects in mesoscopic systems, such as quantum dots and carbon nanotubes, arouse many attentions for their unique properties. In a semiconductor quantum dot or a carbon nanotube quantum dot, the conductance shows different behavior depending on whether the number of electrons confined in the dot is even or odd. By introducing magnetic impurities into a carbon nanotube, an one-dimensional Kondo system is formed and may lead to some important applications. The schemes by employing this magnetic impurities/SWNT systems to generate quantum entanglement states for quantum information processing, a potential field in the future, have been proposed.

A theoretical study on magnetic clusters in carbon nanotubes has given STM spectra and the dependence of Kondo temperature on the size of magnetic clusters. Besides that, the density of states (DOS) for metallic carbon nanotubes with a magnetic impurity is investigated by utilizing the perturbation theory, and give results which agree well with the experiments. However, the transport properties of metallic SWNT with magnetic impurities have not been investigated systematically so far. In this paper, Anderson model is used to describe the system and the transport properties are studied within the Landauer formula. The conductance and the TEP at finite temperature are explored. The relation between the temperature and the Kondo effect is found to interpret the experiment well.

II. MODEL AND FORMULA

The magnetic impurities/SWNT system can be assumed that it gets the contribution from the sum of the isolated impurities, if the impurity density is dilute and the interaction among them can be neglected. Then it can be described by a single-orbital Anderson model. The Hamiltonian of the whole system can be written as:

\[ H = \sum_{k,\sigma} \varepsilon_k C_{k,\sigma}^\dagger C_{k,\sigma} + \sum_{\sigma} \varepsilon_d C_{d,\sigma}^\dagger C_{d,\sigma} + \sum_{k,\sigma} (V_k C_{k,\sigma}^\dagger C_{d,\sigma} + V_k^* C_{d,\sigma}^\dagger C_{k,\sigma}) + U n_{d,\uparrow} n_{d,\downarrow} \]  

(1)

where the first term describes the conduction electrons of nanotubes in a frame of tight-binding model. \( C_{k,\sigma}^\dagger \) and \( C_{k,\sigma} \) are creation and annihilation operators for Bloch states of wave vector \( k \) and spin component \( \sigma \), corresponding to energy \( \varepsilon_k \). In the second term, \( \varepsilon_d \) is the energy of the localized d level of the impurity, and \( C_{d,\sigma}^\dagger \) and \( C_{d,\sigma} \) are creation and annihilation operators for an electron in this state. Here we ignore the orbital degeneracy of the d level and treat it as a state with spin \( \uparrow \) and spin \( \downarrow \) degeneracy only. The third term describes overlap of localized level with the wavefunction of conduction
electrons in carbon nanotubes, and $V_k$ is the hybridization matrix element. For the last term, $U$ is the onsite Coulomb repulsive interaction between electrons in localized state, and $n_{d,\sigma} = G_{d,\sigma}^0 G_{d,\sigma}^\ast$.

The route to work on this Hamiltonian can be based on equations-of-motion method for the double-particle imaginary-time Green function. Applying this method to the above Hamiltonian, we get

$$G_{s}(\varepsilon) = G_{s}^0(\varepsilon) + G_{s}^0(\varepsilon) \left( \sum_{k} V_{k} G_{d}(\varepsilon)V_{k}^\ast \right) G_{s}^0(\varepsilon)$$

$$G_{d}(\varepsilon) = \left( \varepsilon - \varepsilon_{d} - \sum_{k} V_{k} \frac{1}{\varepsilon - \varepsilon_{k}} V_{k}^\ast - \Sigma_{d} \right)^{-1}$$

Comparing the $G_{s}$ with perturbation expansion $G = G_{0} + G_{0}\Sigma' G_{0}$, we get the self-energy of conduction electron, $\Sigma'_{s} = \sum_{k} V_{k} G_{d} V_{k}^\ast$. Therefore, how to get $G_{d}$ is the key to implement calculation. A rapidly convergent perturbation method was firstly proposed and developed in a series papers by Yamada and Yosida. Zlatić and Horvatić extended this method to calculate the DOS of localized electrons for the asymmetric non-degenerate Anderson model. It has been verified that the DOS calculated according to the above method of Zlatić et al. agrees well with the Bethe ansatz results in the dilute magnetic alloy region. We apply their method to calculate the self-energy at finite temperature up to the second-order correction.

The retarded second-order self-energy is obtained as

$$\Sigma_{d}^{R}(\omega) = \frac{\Delta}{2} u^2 \left\{ \int_{-\infty}^{+\infty} \tanh(\frac{\beta \Delta \varepsilon}{2}) \text{Im}[\tilde{G}_{0}^{R}(\varepsilon)] \tilde{\chi}_{0}(\omega - \varepsilon) d\varepsilon \right\}$$

where

$$\tilde{G}_{0}^{R}(\varepsilon) = (\varepsilon - \frac{E_{d}}{\Delta} + i)^{-1},$$

$$\tilde{\chi}_{0}(\varepsilon) = \frac{-1}{\varepsilon(\varepsilon + 2i)} \left\{ \Psi \left[ \frac{1}{2} + \frac{\beta \Delta}{2\pi}(1 + i \frac{E_{d}}{\Delta} - i \varepsilon) \right] \right. + \left. \Psi \left[ \frac{1}{2} + \frac{\beta \Delta}{2\pi}(1 - i \frac{E_{d}}{\Delta} - i \varepsilon) \right] \right.$$  

$$- \left. \Psi \left[ \frac{1}{2} + \frac{\beta \Delta}{2\pi}(1 + i \frac{E_{d}}{\Delta}) \right] \right.$$  

$$- \left. \Psi \left[ \frac{1}{2} + \frac{\beta \Delta}{2\pi}(1 - i \frac{E_{d}}{\Delta}) \right] \right\}.$$

Three parameters have been taken to describe the model: $u = \sqrt{\frac{\pi}{\Delta}}$, $E_{d} = \varepsilon_{d} + \frac{1}{2}\langle n_{d} \rangle$, and $\Delta = \frac{\pi}{2} \rho(0) V^2$. $\rho(0)$ the DOS near the $E_F$ for the nanotube.

The self-energy $\Sigma_{d}(\omega)$ and the Green function $G_{d}(\omega)$ depend on temperature both explicitly, through $\beta$, and implicitly, through the temperature dependence of $E_d$. So for the case of finite temperature, the iteration is needed to reach the self-consistent results.

$$n_{d} = -\frac{2}{\pi} \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon/k_{B}T) \text{Im}\tilde{G}_{d}^{R}(\varepsilon)$$

$$G_{d}^{R}(\varepsilon) = \{ \varepsilon - \Delta \frac{E_{0}}{\Delta} + u \tan^{-1} \frac{E_{0}}{\Delta} \frac{1}{2} \pi u (1 - n_{d})$$

$$+ \Sigma_{d}^{R}(\varepsilon, T, \varepsilon_{d}, \frac{E_{0}}{\Delta}) \}$$

Here $E_{0}$ is taken as initial input, the initial $n_{d}^{0}$ can be judged from solve the transcendental equation.

$$\cot \left( \frac{\pi}{2} n_{d}^{0} \right) + \frac{\pi}{2} u (1 - n_{d}^{0}) = (E_{d}^{0}/\Delta) + \left[ u \tan^{-1} (E_{d}^{0}/\Delta) + \Sigma_{d}^{R}(\varepsilon = 0, T = 0, E_{d}^{0}/\Delta) \right].$$

In order to investigate the transport properties, we take the whole system as a two-terminal device. A long (10, 10) armchair nanotubes with magnetic impurities is investigated, and two semi-infinite (10, 10) armchair nanotubes connected the are taken as ideal leads.

### III. RESULTS AND DISCUSSION

#### A. Resistivity

The transport through mesoscopic system can be calculated within the Landauer formula:

$$G(E, T) = G_{0}\Gamma^{L} G^{R} \Gamma^{L} G_{a}$$

where $G_{0} = 2e^{2}/h$ is the conductance unit, $\Gamma^{L(R)}$ is the coupling matrix between the left (right) lead and the conductor. $G^{R}$ is the retarded Green’s function which can be written as

$$G^{R} = \frac{1}{E - H_{0} - \Sigma_{L} - \Sigma_{R} - \Sigma_{m}}$$

Here $H_{0}$ is the Hamiltonian of the conductor that represents the interaction between the atoms in the carbon nanotubes, and $\Sigma_{L(R)}$ is the self-energy function that describes the effect of the left (right) lead, computed by using the surface Green’s function matching theory. $\Sigma_{m}$ is the normal self-energy function that incorporate the effects of magnetic impurities, and relates to the self-energy $\Sigma'$ through

$$\Sigma_{m} = \frac{\Sigma'_{m}}{1 + G_{0}^{R} \Sigma'_{m}}.$$

As stated above, $\Sigma'_{m}$ can be gotten by comparing with the results with the perturbation expansion of Green’s function.
Kondo resonance and enhance the conductance at $E_F$. The results are given in Fig. 2 for different parameters. The conductance increases with the increasing temperature, and then get saturated. Increasing temperature enhances the conductance $G$, which is clear the evidence of Kondo effects. The transport is ballistic and contributes to $2G_0$ at any temperature as no impurities appear in a nanotube. When the magnetic impurity emerges, the electrons suffer scattering when passing through the conductive channel. In Fig. 2(a), the Coulomb strength $u = 1.5$, the conductance changes smaller and gets saturated at lower value. The Coulomb strength $u = 2.0$ in Fig. 2(b). For different $E_d$, the conductance behaves differently. For small $E_d$, the conductance starts at a higher value and changes relatively smaller with respect to the bigger $E_d$.

B. Thermoelectric power

Thermoelectric power (TEP) is an important transport coefficient, because it is related to the energy derivative of electrical conductivity at the $E_F$. The contribution of magnetic impurities to the low-temperature diffusion TEP $S$ is calculated by Mott relation:

$$S(T) = -\frac{\pi^2 k_B^2}{3e} T \left( \frac{d\ln\sigma(E)}{dE} \right)_{E_F}$$

(12)

It is valid in one-dimensional system by incorporating the Landauer formula for the conductance.$^{24}$

TEP is sensitive to the position of Kondo resonance peak, which determine the sign of TEP. TEP of an individual SWNT has been measured, and gate electric field dependent TEP modulation is found. The effects of defects cause the valley of conductance, and then TEP will change the sigh when changing gate voltage $V_g$. We give the results of $G$ and at $T_K = 0.001\Delta$ for a $(10, 10)$ nanotube. But here the Kondo resonance make the structure different. For the symmetric Anderson model at low temperature, the TEP changes its sign, as shown in Fig. 3.

For symmetric model, which keep the electron-hole symmetry, the TEP always equals to 0. But for asymmetric model in Kondo regime, TEP increases and then
decreases which can interpret the observed phenomenon for the system of nanotubes with transition metal catalyst. Fig. 4 gives the TEP as a function of $K$ for the system of nanotubes with transition metal catalyst. It is clear shown that the TEP gets an increase then decrease process. It is the evidence of Kondo effects. Comparing the two figures, we find that for bigger $u=2.0$, the TEP will need higher temperature to reach the peak value. It is the same for smaller $u$.

Since the $u$ and $E_d^0$ relates to the Kondo temperature $T_k$, here we study the TEP in the scale of $T_k$. At low bias, the $E_F$ can be assumed that it does not shift when the density of impurities is small. Fig. 6 gives the results for different TEP versus $K_BT_k/\Delta$, $T_k$ is given by

$$K_BT_k = U\frac{\Delta}{2U^{3/2}}e^{\frac{\pi\Delta}{2U}}$$

We adjust the x scale according the $T_k$, and give results consistent with the experimental measurements.

![FIG. 3: TEP for $u=1.5$ and $u=2.0$ for different $E_d$](image)

![FIG. 4: TEP versus $K_BT$ for with $E_d=0, 0.25\Delta, 0.5\Delta, 0.25\Delta$ for $u=1.5$ and $u=2.0$](image)

![FIG. 5: TEP versus $T$ in the absolute unit, the dot is the experimental data for Ref.??](image)

IV. SUMMARY

By introducing the normal self-energy contributed by the magnetic impurities in the single-walled metallic carbon nanotubes, we have studied the electric transport properties at finite temperature within the Anderson model and Landauer formula. The magnetic impurities induce Kondo resonance near the $E_F$, and hence the conductance valley appeared. As the temperature increases, the Kondo resonance and the conductance valley fade out for both the symmetric and asymmetric case. For bigger radius nanotubes, the width of resonant peak and the conductance valley at low temperature is suppressed. With the increasing temperature, the conductance of the nanotube increases in the low temperature range.

Based on the Mott relation, the TEP of carbon nanotubes with magnetic impurities has been also investigated. It changes the sign near the $E_F$ due to the Kondo resonance. At low temperature TEP increases with the increasing temperature, and then it decreases after reaching a peak value. The stronger Coulomb strength or the bigger $E_d$ is, the earlier the TEP reaches the peak value. When scaled according to the Kondo temperature, the dependence of TEP on the temperature is found to interpret the experiment well.

Our studies on the magnetic impurities in metallic carbon nanotubes gives Kondo characters of electric transport properties in mesoscopic system. Further experiments would be expected to explore the roles of magnetic impurities in the carbon nanotubes.

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