Even-Odd Effect in Andreev Transport through a Carbon Nanotube Quantum Dot

A. Eichler, M. Weiss, S. Oberholzer, and C. Schönenberger*

Institut für Physik, Universität Basel, Klingelbergstr. 82, CH-4056 Basel, Switzerland

A. Levy Yeyati, J. C. Cuevas, and A. Martín-Rodero

Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma de Madrid, E-28049 Madrid, Spain

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We have measured the current (I)-voltage (V) characteristics of a single-wall carbon nanotube quantum dot coupled to superconducting source and drain contacts in the intermediate coupling regime. Whereas the enhanced differential conductance dI/dV due to the Kondo resonance is observed in the normal state, this feature around zero-bias voltage is absent in the superconducting state. Nonetheless, a pronounced even-odd effect appears at finite bias in the dI/dV subgap structure caused by Andreev reflection. The first-order Andreev peak appearing around $V = \Delta/e$ is markedly enhanced in gate-voltage regions, in which the charge state of the quantum dot is odd. This enhancement is explained by a "hidden" Kondo resonance, pinned to one contact only. A comparison with a single-impurity Anderson model, which is solved numerically in a slave-boson mean-field approach, yields good agreement with the experiment.

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There is a growing interest in the exploration of correlated charge transport through nanoscaled low-dimensional systems involving both superconductors and normal metals [1–6]. The penetration of the pair amplitude Δ from a superconductor (S) into a normal metal (N), the proximity effect, is a manifestation of correlated charge transport mediated by Andreev processes taking place at the S-N interface [7] and leading in S-N-S junctions to the Josephson effect [8] and sup-gap current peaks due to multiple Andreev reflection (MAR) [9]. Andreev transport through a low-dimensional region, in the ultimate case through a zero-dimensional quantum dot, is a new emerging field [3,5,10–14]. In a quantum dot (QD) transport occurs through discrete levels. Since the level energies $E_{\{i\}}$, and sometimes also the coupling strengths of the levels to the (normal) leads $\Gamma_{1,2}$, can be tuned through gate voltages, a physically tunable model system of the Anderson "impurity problem" is realized. With one electron on the QD (half-filling), a many-electron ground-state forms, involving both the dot state and conduction electrons from the leads in an energy window given by the Kondo temperature T_K [15,16]. In this Kondo regime, which can be observed if $\Gamma_{1,2}$ is not too small, a resonance pinned at the Fermi energy of the leads forms (Kondo resonance). If superconducting contacts are used instead of normal ones, the additional pair correlation in the leads competes with the Kondo correlations on the QD [1,2,17–20]. Recently, an interesting crossover occurring at $k_BT_K \approx \Delta$ has been found [2,10]: if $\Delta > k_BT_K$, the Kondo correlations are suppressed, whereas they persist in the opposite regime, opening a highly conducting channel for the Josephson effect. CNTs are ideally suited for the realization of such systems, because CNTs can act as well controlled QDs in different transport regimes [21], including the Kondo regime [22], and superconducting contacts can be realized [4,6,10–13]. Similar physics can be addressed in semiconducting nanowires [23].

We report here on finite-bias transport through a single-wall carbon nanotube (SWNT) QD with S contacts in the most interesting regime of intermediate coupling, where Kondo correlations are of similar magnitude as superconducting ones. We have found a new pronounced even-odd effect in the MAR structure.

SWNTs were grown by chemical vapor deposition on Si wafers [24]. Individual SWNTs were localized with a scanning electron microscope and contacted to superconducting electrodes using e-beam lithography; see Fig. 1. The evaporated contacts consist of a Ti(5 nm)/Al(100 nm)/Ti(10 nm) trilayer. Al is the actual superconductor with a bulk critical temperature of $T_c = 1.2$ K. In the trilayer form we rather measure a T_c of 0.9 K, which corresponds to a BCS gap parameter $\Delta_0 = 1.76k_BT_c$ of 0.135 meV. We drive the Al contacts into the normal state by applying a small perpendicular magnetic field of $B = 0.1$ T. The substrate is contacted to a third terminal in order to establish a backgate. We measure the differential source(1)-drain(2) conductance $G := dI/dV$ as a function of source-drain V and gate-voltage V_g. This is achieved by superposing an ac voltage $V_{ac} = 10\ \mu$V on V and measuring the corresponding ac current. Several devices were fabricated and tested at room temperature and at 4.2 K. Here, we focus on a particular interesting device which we selected and measured in a dilution refrigerator. This device has been studied over a large V_g window and displays single-electron charging with addition energies in the range of 2–5 meV. In the following we will focus on a confined gate-voltage regime.

Figure 2 summarizes the main results we will be discussing in the following. It shows in (a) a dI/dV plot in the normal state (n state) and in (b) the corresponding one in

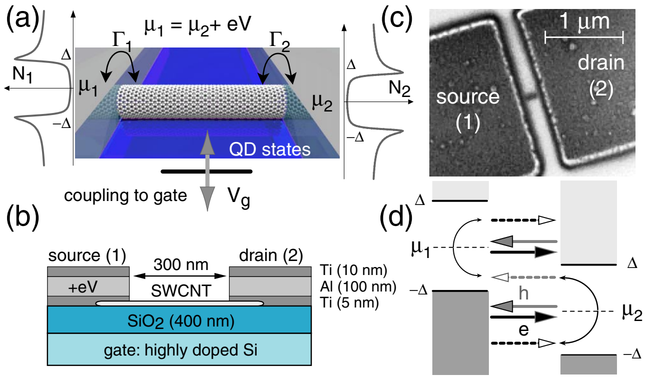

FIG. 1 (color online). (a) Illustration of a SWNT QD contacted by superconducting source (1) and drain (2) electrodes. $\mu_{1,2}$ denote the electrochemical potentials, $N_{1,2}$ the density of states, $\Gamma_{1,2}$ the lifetime broadenings, Δ the superconducting gap parameter, V the applied source-drain voltage, and V_g the gate voltage. (b) Device geometry, showing the evaporated trilayer. (c) shows an actual device and (d) illustrates possible processes that lead to a subgap current. Shown in solid is a first-order Andreev process and dashed a second-order one. In the first (second), two (three) quasiparticles (electrons e and holes h) are involved.

the superconducting state (s state). In the n state a sequence of larger and smaller Coulomb blockade (CB) diamonds are seen (dashed lines), corresponding to a sequence of nearly equidistantly spaced levels on the SWNT QD, which are filled sequentially. The number of electrons on the dot therefore alternates between odd and even [25]. It is also seen that the conductance $G = dI/dV$ around zero bias is suppressed and featureless in the even valleys, but is

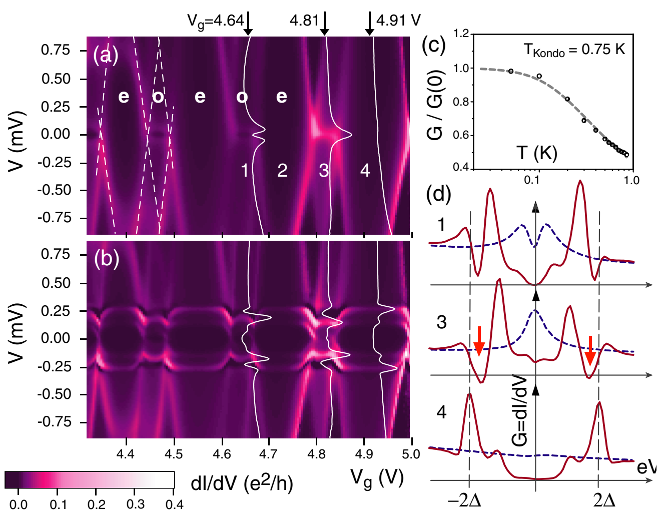

FIG. 2 (color online). Differential conductance $dI/dV(V, V_g)$ plot as a function of bias V and gate voltage V_g of a SWNT QD with superconducting contacts in the normal (a) and superconducting state (b). In (c) we show the linear conductance $G(T)$ measured as a function of temperature T in the middle of charge state 3. The curves in (d) correspond to the one overlaid on the $dI/dV(V, V_g)$ plots.

increased assuming structure in the odd ones. In the CB diamond labeled 3, there is a pronounced peak at $V = 0$, suggesting the appearance of a Kondo resonance. Indeed, the dependence of the linear $G(T)$ on temperature T [Fig. 2(c)] follows the expected dependence [26] with a Kondo temperature of $T_K = 0.75$ K. In the other odd valleys, the Kondo resonances are split by ≈ 0.1 meV [27]. The origin of this splitting is at present not known, but could be due to exchange with ferromagnetic catalyst particles or another tube [28].

The n-state data can be used to deduce a number of parameters. The source, drain, and gate capacitances are $C_{1,2} \sim 50$, 100 aF and $C_g \sim 4$ aF, leading to a gate coupling $\alpha = C_g/C_\Sigma$ of ~ 0.026, where $C_\Sigma = C_1 + C_2 + C_g$. The charging energy $U = e^2/C_\Sigma$ and the level spacing δE are in the range of 0.7–1 meV and 1.4–1.8 meV, respectively. Whereas this SWNT QD is nearly symmetric in its electrostatic coupling, it is quite asymmetric in its electronic one. The total level broadening amounts to $\Gamma = \Gamma_1 + \Gamma_2 \approx 0.2$ meV with an asymmetry of $\Gamma_1/\Gamma_2 \approx 50$. This asymmetry is deduced from the measured current peaks in dI/dV at the border of the CB diamonds at finite bias and is in agreement with the reduced low temperature zero bias $G(0)$ of the Kondo ridge 3, amounting to $G(0) \sim 0.1e^2/h$.

Looking next at the s state, we see that the major changes in the dI/dV are confined to a voltage band of -0.26 meV $< V <$ 0.26 meV, corresponding to $\pm 2\Delta$. Above 2Δ, i.e., $|V| > 2\Delta/e$, quasiparticle current is possible and the main modification is caused by the peak in the superconducting density of state (DOS) [3,5], leading to a peaklike feature in dI/dV. Below the 2Δ gap, first-order charge transfer processes are forbidden and charge has to be carried by higher order Andreev processes [5,11,14]. The first Andreev process, which is of second order, results in a peaklike structure in the vicinity of Δ. Because of the higher order, this peak and all subsequent ones should be smaller than the quasiparticle peak. The suppressed G in the s state is observed together with the dominant 2Δ and the smaller Δ peak in the middle of an even charge state (even valley), see, e.g., the curve labeled 4 in Fig. 2(d). In contrast, in the odd charge states, the 2Δ feature is not present or does not appear at 2Δ. Starting to view the data from large bias voltage, the first peak appears closer to Δ rather than 2Δ, with a preceding negative dI/dV (NDR); see curve labeled 3 in Fig. 2(d). Hence, there is a striking even-odd asymmetry in the finite-bias dI/dV features in the s state. The even-odd alteration of the MAR structure suggest a relation to Kondo physics. To model this, we first extract important parameters from an analysis of the data in the middle of an even valley where Kondo correlations are absent.

Figures 3(a)–3(c) present the temperature dependence of dI/dV in the middle of the even charge state, (a) shows the measurement taken in valley 4 of Fig. 2,

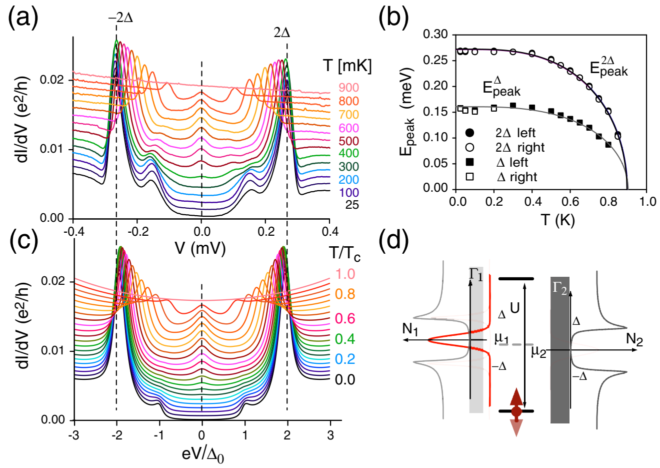

FIG. 3 (color online). (a) measured dI/dV versus temperature T in the even valley 4 of Fig. 2(a). The curves are shifted upwards by $10^{-3}e^2/h$ for clarity. The 2Δ and Δ peak positions $E_{\rm peak}(T)$ are shown in (b) together with a BCS T dependence of Δ. In (c) we show the result of a model calculation based on resonant tunneling [5]. The illustration in (d) is our proposal to understand the appearance of the strong Δ feature in the odd valleys. A Kondo resonance persists on one electrode side only. Because it is pinned to that chemical potential, it will strongly enhance the Δ feature in Andreev tunneling.

and (c) is a model calculation. The experiment displays pronounced quasiparticle current peaks at $E_{\rm peak} = \pm 2\Delta$, and weaker MAR peaks at $\pm\Delta$. The evolution of $E^{j\Delta}_{\rm peak}(T)$ with temperature T is shown in Fig. 3(b) together with an approximate BCS gap function $E^{j\Delta}_{\rm peak} = K_{j\Delta}\Delta_0 \tanh(1.74\sqrt{T_c/T - 1})$, where we used the BCS value for $\Delta_0 = 1.76k_BT_c$, which amounts to 0.135 meV for a T_c of 0.9 K. We then obtain $K_{2\Delta} = 2.0$ and $K_\Delta = 1.15$ for the two peaks. The relevant parameters expressed in units of Δ_0 are: $U = 5$–8, $\delta E = 10$–14, $\Gamma \approx 1.5$ and $T_K \approx 0.5$.

The good agreement with the BCS relation of the peak-positions motivates the modelling of the dI/dV using the BCS DOS in the leads. We use Andreev tunneling through a single resonant level positioned at energy ϵ and follow the work of Levy Yeyati *et al.* [5]. The following parameters in units of Δ_0 were used: $\Gamma_1 = 1.0$, $\Gamma_2 = 0.03$ and $\epsilon = 7$. The BCS DOS was broadened by $0.1\Delta_0$, accounting for the averaging in the experiment due to the "small" ac bias. A remarkably good agreement is found.

We now turn our attention to the odd charge states. We point out, that the zero-bias high-G Kondo "ridge", which is associated with the Kondo resonance and visible in the n state, is not seen in the s state. This is in contrast with the results of Refs. [10,11], which corresponded to a larger value of T_K compared to Δ. Although the Kondo resonance is not visible at zero bias in the s state, we nevertheless suspect it to be responsible for the even-odd asymmetry of the Δ-feature in the s state.

In the Kondo regime, the single spin on the QD in the odd state is screened by exchange with conductance electrons from the leads. Because of the asymmetry in the coupling, it may happen that a Kondo resonance with a reduced width forms on the contact with the larger Γ, whereas on the other contact the Kondo resonance is suppressed. This is illustrated in Fig. 3(d) and at a bias of $V \approx \Delta$ in Fig. 4(e). We modeled this scenario considering a single-level Anderson Hamiltonian with interaction $U = (5$–$10)\Delta_0$ coupled to source and drain contacts. The experimentally deduced Γ's, including the strong asymmetry were used. To deal with the interaction term we use a finite U slave-boson mean-field approach which accounts reasonably well for the low energy spectral density in the Kondo regime [29]. The approach yields renormalized parameters $\tilde{\epsilon}$, $\tilde{\Gamma}_{1,2}$ which depend both on the gate and on the bias voltage. These parameters are obtained in the normal state and introduced into the calculation of the subgap current as in Ref. [5]. The result of the comparison is shown in Fig. 4: (a) corresponds to the n state and (b) and (c) to the s state. Despite this simple model, the agreement is surprisingly good. It is remarkably good in the normal state, shown in Fig. 4(a). In the s state, the dominance of the Δ-like feature in the odd valley is clearly present, as is a similar crossover from odd to even filling. There are also some differences: in the experiment the Δ feature bends to larger V values in the middle of the odd state, whereas this feature is rather flat in the calculation.

In conclusion, we have discovered a pronounced even-odd effect in the Andreev structure in transport through a

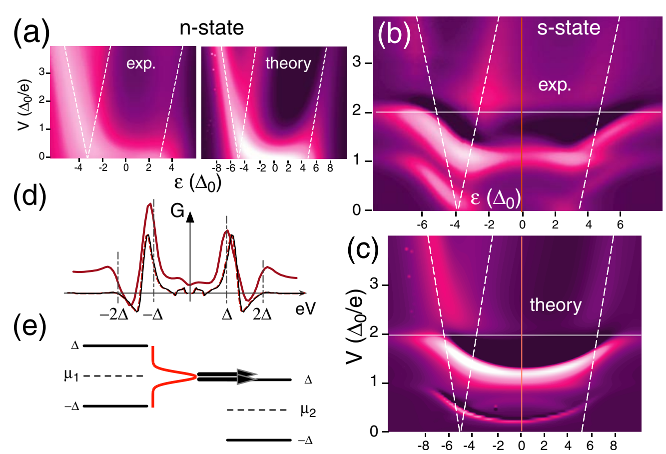

FIG. 4 (color online). Comparison of the dI/dV in the odd valley labeled 3 in Fig. 2(a) with a model calculation based a single-level Anderson model with interaction U, that is evaluated by a mean-field slave-boson ansatz. The n state is shown in (a), the s state in (b) and (c). ϵ denotes the level position. The experiment corresponds to $U = 7$–8 (in units of Δ_0), whereas the calculation was done for $U = 5$ and $U = 10$, where the latter is shown here. The upper solid (dashed) curve in (d) is a cross section in the s state at $\epsilon = 0$, taken from the experiment (theory). (e) illustrates how the enhancement of the Δ-feature comes along.

QD with superconducting contact. This effect originates from a Kondo resonance pinned to one contact only and defines a new regime. Whereas a high conductance channel from source to drain, driven by Kondo correlations persists in the superconducting state if $T_K \gg \Delta$, this channel is greatly suppressed in the opposite limit. In the intermediate regime $T_K \sim \Delta$, and, in particular, for asymmetric dot-electrode couplings, the (partial) Kondo-screening of the "impurity" spin may occur on one electrode only changing the relative weight of the MAR peaks. It would be interesting to explore the "robustness" of this feature in model calculation and to fabricate similar QDs with tunable electrode couplings.

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Note added.—Recently, we became aware of an independent study of the above phenomenon in a different material system, semiconducting nanowires, by T. Sand-Jespersen *et al.* [30].

*Christian.Schoenenberger@unibas.ch

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