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We have used the electromigration technique to fabricate a C_{60} single-molecule transistor (SMT). We present a full experimental study as a function of temperature, down to 35 mK, and as a function of magnetic field up to 8 T in a SMT with odd number of electrons, where the usual spin-1/2 Kondo effect occurs, with good agreement with theory. In the case of even number of electrons, a low temperature magneto-transport study is provided, which demonstrates a Zeeman splitting of the zero-bias anomaly at energies well below the Kondo scale.

A single-molecule transistor is the smallest three terminal electronic devices, consisting of two electrodes (source and drain) and a gate, as shown on Fig. 1a. Due to nanometric confinement of the wave-function of the electrons in a SMT, Coulomb blockade phenomena are expected [1–6]. Depending on the voltage bias V_b and the gate voltage V_g, the transistor can be tuned to allow current flowing or not through the single-molecule, resulting in Coulomb diamond diagrams (Figs. 1b,c,d). The number of observed Coulomb diamonds in an experiment strongly depends on the molecule-to-gate coupling as well as on the charging energy of the SMT. However, the molecular level spacing ϵ and the charging energy U extracted from the SMT measurements are perturbated compared to those of a molecule in solution, leading to a decrease of the addition energy $\epsilon + U$. As a result, this latter quantity strongly depends on the coupling to the reservoirs [5], as well as on its redox state. For example, $\epsilon + U$ is expected to be of the order of 7.5 eV when we consider the HOMO-LUMO gap of C_{60}, but can be much lower [7] if we consider intra fivefold-degenerate HOMO or threefold-degenerate LUMO transitions ($E(C_{60}^{2-}) - E(C_{60}^{-}) = \epsilon + U = 90$ meV).

Focusing on an odd number of electrons in a SMT, when a spin-1/2 magnetic impurity in the quantum dot (QD) is strongly coupled antiferromagnetically to the electrons in the reservoirs, the electronic states of the QD hybridize with the electronic states of the reservoirs. As a result, even if the energy of the QD state is far below the Fermi level of

the reservoirs, hybridization creates an effective density of states on the site of the dot, which is pinned to the Fermi level of the reservoirs, leading to a zero-bias conductance anomaly where a Coulomb gap would have naively been expected. This is known as the Kondo effect in QD devices [8,9], and this signature has been widely observed in semiconducting devices [10,11], carbon nanotubes [12] or single-molecule QDs [4,13]. Universality is a fundamental property of the Kondo effect and a single energy scale, associated with the Kondo temperature T_K, fully describes the physical properties at low energy. When the typical energy of a perturbation, such as temperature, bias voltage, or magnetic field, is higher than T_K, the coherence of the system is suppressed and the Kondo effect disappears.

We report here on a full experimental study of the spin-1/2 Kondo effect in a single C_{60} molecule embedded in a nanoconstriction fabricated by means of electromigration. The spin-1/2 Kondo effect in a C_{60} molecular junction was observed for the first time by Yu and Natelson [13] (see also [14] in the case of ferromagnetic electrodes), and more recently by Parks *et al.* [15] using mechanically controllable break junctions. However, to our knowledge, no electromigration procedure has been carried out in a dilution refrigerator with a high degree of filtering. Improvements of the original procedure [16] have already been reported recently [17–21]. The creation of nanogaps with this technique requires minimizing the series resistance [22,23], which is generally incompatible with dilution refrigerator

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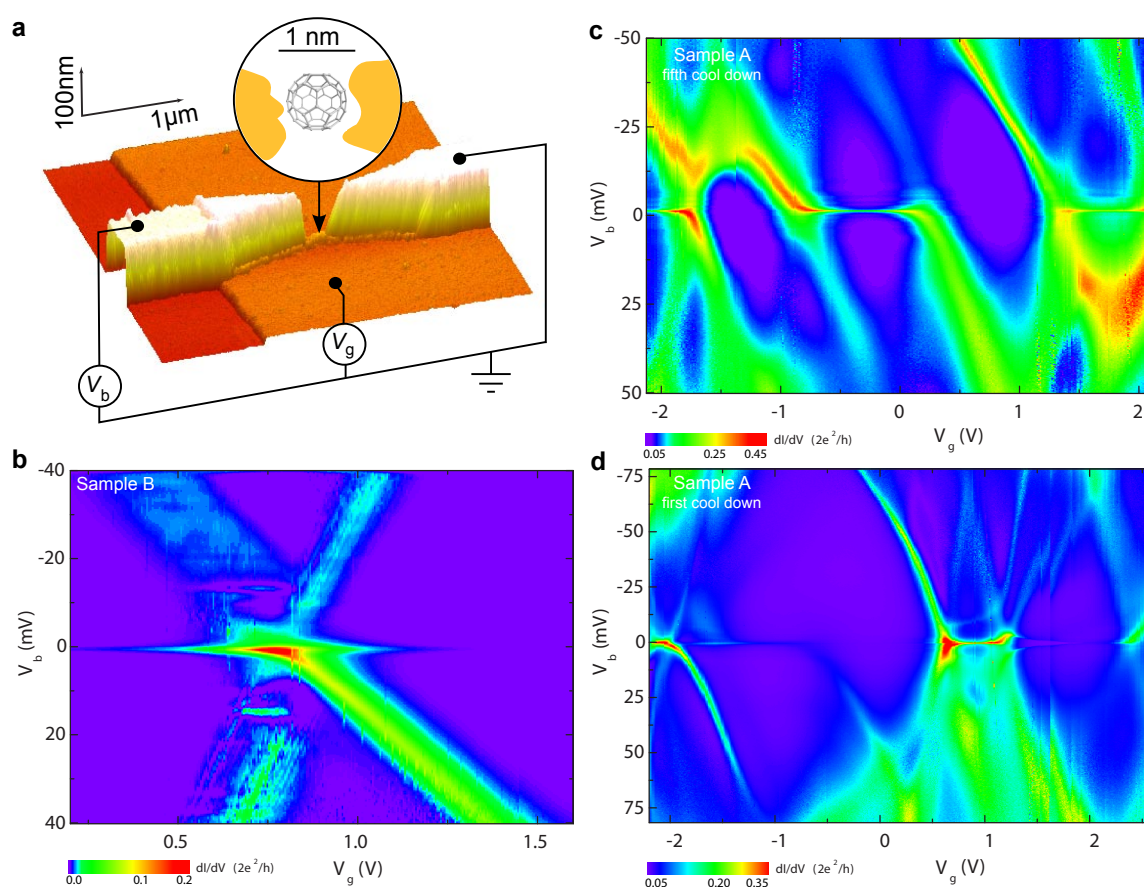
Figure 1 a) Single-molecule transistor: AFM image of the device showing the gold nano-wire over an Al/Al_2O_3 gate. b) Color-scale map of the differential conductance as a function of bias voltage V_b and gate voltage V_g at 35 mK and zero magnetic field for sample B. c) Color-scale map of the differential conductance after 5 thermal cycles to room temperature for sample A (same conditions). d) Color-scale map of the differential conductance for sample A (same conditions).

wiring and filtering. To overcome this problem, we developed a specific measurement setup described in the supplementary information of reference [24]. Another disadvantage encountered during the electromigration process, when the molecule under investigation is deposited before the realization of the nano-gap, is local heating of the nano-wire up to approximately 450 K [19,25]. We have then chosen to realize our SMT using C_{60} molecules, because fullerenes can easily undergo such annealing.

Preparation of the SMT was realized by blow drying a dilute solution of a C_{60} molecules in toluene onto a gold nano-wire realized on an Al/Al_2O_3 back gate (see Fig. 1a for a schematic view of the setup). Before blow drying the solution, the electrodes were cleaned with acetone, ethanol, isopropanol and an oxygen plasma. The connected sample is inserted into a copper shielded box, enclosed in a high frequency low-temperature filter, which is anchored to the mixing chamber of the dilution refrigerator. The nano-wire coated with molecules is then broken by electromigration [16], via a voltage ramp at 4 K. However, it is dif-

ficult to guarantee that transport in the fabricated SMT is through a single C_{60}, because even if the electromigration procedure is well controlled, there is always a possibility to fabricate a few atoms gold aggregate transistor [26]. In our opinion, an "interesting" device to investigate must show at least one order of magnitude change in the current characteristics as a function of the gate voltage for a 1 mV voltage bias, and a charging energy greater than 20 meV. Within these criteria, we tested 38 bare junctions with pure toluene and 51 with a dilute C_{60} solution in toluene. While 3 of the bare junctions showed one order of magnitude changes in the current as a function of the gate voltage after electromigration, only 2 had a charging energy higher than 20 meV, and only 1 of those 2 exhibited a zero bias anomaly. In this case no clear Coulomb diagram was distinguishable. For junctions prepared with C_{60}, we observed 7 junctions out of 51 with one order of magnitude changes in the current as a function of gate voltage, and 6 of those 7 had a charging energy higher than 20 meV and exhibited pronounced
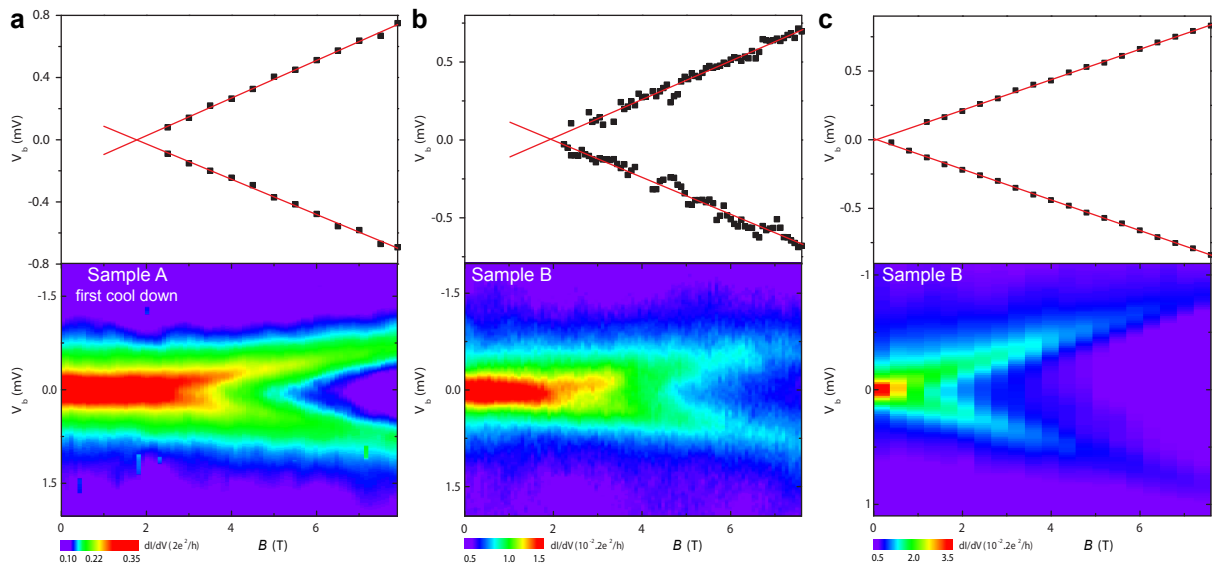
Figure 2 Magnetic field dependence of the zero bias anomalies. a) Sample A at $V_g = 1.2$ V. b) Sample B on the right side ($V_g = 1.1$ V) of the charge degeneracy point. c) Sample B on the left side ($V_g = 0.45$ V) of the charge degeneracy point.

zero bias anomalies. In the following, we will focus on two particularly representative samples labeled A and B.

Figures. 1b, c, d show the typical features of a SMT: conducting and non-conducting regions are typical fingerprints of Coulomb blockade and zero-bias anomalies are usually assigned to the spin-1/2 Kondo effect [1–6, 10, 11, 13]. We note that for sample A an even-odd electronic occupation number effect is present as shown in Fig. 1c. We emphasize that the observation of several charge states in this experiment was helped by the realization of a local gate [4] very close to the QD, and a large decrease of the charging energy due to a strong coupling to the reservoirs, as vindicated by the clear Kondo ridge measurements.

First, we discuss the characteristics of sample A presented in Figs. 1c,d. We note that this device was cooled down to 35 mK, and warmed up slowly (3 hours) to room temperature several times, without breaking the vacuum, so that the color-scale map of Fig. 1c presents the measurement after the fifth cool down. These data exhibit a clear even-odd effect, and broad Kondo ridges are readily identified. The comparison with Fig. 1d demonstrates that the coupling of the QD to the reservoirs can sometimes be tuned towards larger values under several warm up procedures.

We now turn to the measurement of sample A presented in Fig. 1d for the first cool down, for which a full experimental study in the case of even number of electrons is presented in reference [24]. The charging energy U can be extracted from the slope of the Coulomb diamond dV_b/dV_g, using $U = (1/2)e(dV_b/dV_g)\Delta V_g$, where ΔV_g is the voltage spacing between successive charge states. For sample A, we find $U \approx 40$ meV. While the even-odd

alternation is not totally clear, a sharp high-conductance ridge in the zero-bias differential conductance, is clearly observed in the vicinity of $V_g = 1.1$ V. Since the coherence of the system is suppressed and the Kondo effect disappears for a perturbation of energy larger than T_K, we present in Fig. 2a a differential conductance measurement as a function of magnetic field up to 8 T. A method to study the Kondo behavior and extract the typical energy scale $k_B T_K$, where k_B denotes the Boltzmann's constant, is to use the magnetic field dependence of the conductance [27]. The Zeeman effect competes with the Kondo resonance so that a non-equilibrium Kondo peak appears roughly at $V_b = g\mu_B B$, where g is the Landé factor, and μ_B denotes the Bohr magnetron, as shown in Fig. 2a. This spin-1/2 splitting is predicted to appear for $g\mu_B B_c = 0.5 k_B T_K$ [29], and the slope of the splitting is a direct measurement of the g-factor of the quantum device. In Fig. 2a we linearly interpolate the position of these peaks and find $B_c = 1.78 \pm 0.05$ T, which yields $T_K = 4.78 \pm 0.1$ K, and $g = 1.98 \pm 0.09$. Another method to estimate the Kondo temperature is to measure the half width at half maximum (HWHM) of the peak for $T \ll T_K$. At $T = 260$ mK (inset of Fig. 3), we find $V_b^{HWHM} = 380 \pm 5$ µV, corresponding to $T_K = 4.42 \pm 0.05$ K. A complementary method to estimate the Kondo temperature is to measure the evolution of the zero-bias conductance as a function of temperature, as presented in Fig. 3. The precise shape of this curve is universal (up to the value of energy scale T_K), and can be calculated by the Numerical Renormalization Group (NRG) theory [29]. Following [30] we fit the data using the empirical formula:

$$G(T) = G_0 \left(T^2/T_{K,1/2}^2 \left(2^{1/s} - 1 \right) + 1 \right)^{-s} + G_c$$

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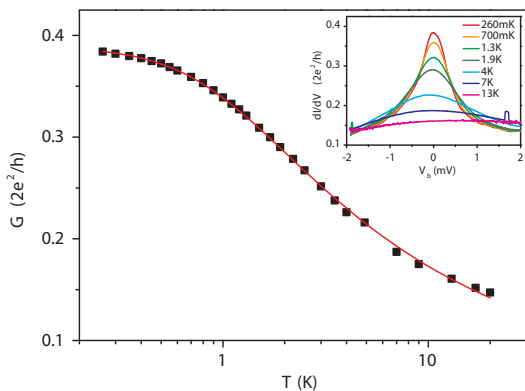
Figure 3 Temperature dependence of the differential conductance for sample A at $V_b = 0$ mV extracted from the inset, with a fit to the empirical formula [30]. Inset: Evolution of $\partial I/\partial V$ versus V_b for several temperatures from 260 mK to 20 K.

where G_0 is the conductance at $T = 0$, G_c a fixed background conductance, and $s = 0.22$. We find $T_K = 4.46 \pm 0.08$ K, which is in excellent agreement with the values determined previously, thus demonstrating a well defined Kondo energy scale.

Now, we turn to sample B, for which a color-scale map of the differential conductance as a function of V_b and V_g is presented in Fig. 1b. By tuning V_g from -2 V to 2 V, only one charge degeneracy point was observed. The charging energy of this SMT is then much higher ($U > 450$ meV) than for sample A, and may indicate that we are not addressing the same redox state of the C_{60} SMT, or that the coupling to the electrodes is lower than for sample A. However, zero-bias anomalies are measured on both sides of the degeneracy point. We present the evolution of these zerobias anomalies as a function of magnetic field on the right side (Fig. 2b) and the left side (Fig. 2c) of the degeneracy point. On the right side, from $B_c = 1.93 \pm 0.05$ T, we obtain $T_K = 5.4 \pm 0.1$ K, while from $V_b^{\text{HWHM}} = 310 \pm 5$ μV, we extract $T_K = 3.6 \pm 0.1$ K. The value of T_K obtained with the two different methods are comparable. Moreover, by linearly interpolating the position of this peaks, we find $g = 2.09 \pm 0.05$.

However, if we now focus on the left side of the degeneracy point, we measure $B_c = 70 \pm 5$ mT, and obtain $T_K = 180 \pm 13$ mK, while $g = 1.92 \pm 0.02$. However, from $V_b^{\text{HWHM}} = 125 \pm 5$ μV, we extract $T_K = 1.45 \pm 0.1$ K, which is one order of magnitude higher than the value obtained with B_c. If we assume a spin-1/2 Kondo effect on the right Coulomb diamond then the occupation number of the left diamond must be even. Therefore this large discrepancy in the two different methods of determining the Kondo temperature on the left Coulomb diamond, leads us to the hypothesis of a spin-1 Kondo effect. While a complete Kondo screening of the two-electron states is in principle possible [28], the one order of magnitude of differ-

ence in the determination of the Kondo temperature indicates that we may measure an underscreened spin-1 Kondo effect [24]. Unfortunately, we did not perform a temperature dependent measurement of this differential conductance peak, thus we cannot fully characterize this underscreened spin-1 Kondo effect.

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