Proximity effect in a superconductor-metallofullerene-superconductor molecular junction

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We report low-temperature transport measurements through molecules of Gd metallocfullerenes between superconducting suspended electrodes. The presence and number of molecules in the 2-nm-wide gap between electrodes was determined by high resolution transmission electron microscopy. We find that a junction containing a single metallocfullerene dimer between superconducting electrodes displays signs of proximity-induced superconductivity. In contrast, no proximity effect develops in junctions containing a larger cluster of metallocfullerenes. These results can be understood by taking into account multiple Andreev reflections, and the spin states of the Gd atoms.

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The superconducting proximity effect, where superconducting correlations are induced in a nonsuperconducting (“normal,” N) metal in contact with a superconductor, has emerged as one of the most powerful tools to investigate the fundamental characteristics of a mesoscopic sample. One particularly useful configuration is the SNS junction, where “S” stands for superconducting electrodes and where “N” has in recent years spanned between mesoscopic metal wires,1 molecular wires such as carbon nanotubes,2–4 DNA molecules,5 or even a single atom in the case of breakjunctions.6 Concurrently, thanks to the fabrication of nanometer-sized gaps, it has been possible to investigate the transport properties of small molecules inserted in these gaps. However, so far only normal (gold, mostly) electrodes were used.7 Depending on the transmission of the electrode/molecule contact, transport proceeded via resonant tunneling through the discrete electronic levels of the molecule8 or through Kondo resonances.9 Proximity-induced superconductivity in S-molecule-S junctions (SMS) has not yet been explored and is expected to give rise to interesting phenomena, especially when spin degrees of freedom are involved. In particular we expect the formation of Andreev states to lead to nonlinearities in the IV characteristics and reveal phase coherent transport through the molecular levels when they are strongly coupled to the electrodes. In this paper we report the investigation of transport through dimers and small clusters of nanometer-size molecules (metallocfullerenes Gd@C82) in good contact with suspended superconducting electrodes. The suspended character of the device allows the observation by high-resolution transmission electron microscopy (HRTEM) of the very same molecules that have been measured.

Metallocfullerene molecules are particularly interesting because the metal atom in the fullerene (Gd here), by acting as a donor (Gd is ionized to state Gd3+), favors charge transfer through the molecule.10 Moreover, the Gd atoms possess an electronic spin S=7/2 which we find influences the proximity effect through the molecules.

A key experimental achievement is the design of the molecular junction, which starts with the fabrication and direct visualization of a nanometer-size gap between electrodes [Fig. 1(a)], and then enables the trapping, observation, and precise identification of molecules in the gap [Fig. 1(b)]. This visualization is crucial for proper interpretation of transport measurements, especially to determine the number of molecules within a cluster. In none of previous transport experiments on small molecules7–9 could the molecule be directly visualized.

We start with a suspended Si3N4 membrane with Au-Ta contacts, through which a micron- (or submicron-) wide slit has been etched by a focused ion beam (FIB).2 We then grow the 200–400-nm-wide, micron-long suspended W nanoelectrodes by local decomposition of a tungsten hexacarbonil vapor using a focused Ga ion beam with a diameter about 5 nm (accelerating voltage 30 kV). The growth of these nanowires (at a rate of 0.3 nm/s for the suspended part) is controlled via the display and can be stopped (by switching off the ion beam) within a second. It is thus possible to fabricate reproducibly two electrodes perpendicular to the slit with a gap less than 2 nm wide between them, as shown in Fig. 1(a). The use of a membrane with a slit as a substrate also enables the observation of the gap in a HRTEM. The tungsten nanowires grown with this technique are superconducting with a transition temperature Tc=5 K and a critical field Hc higher than 6 T at 0.5 K [Fig. 2(a)]. The Tc is that of amorphous tungsten,11 but Hc is higher because of a large concentration of impurities. Auger analysis has shown that FIB-deposited tungsten contains about 10% Ga, 10% C, and 5% O.12

The deposition of Gd@C82 molecules (with purity 99.9%) was carried out as follows. Nitrogen was injected through a capillary submerged in a Cs2 solution with a metallocfullerene concentration of 10 μg/ml (details about molecules in solution are given in Ref. 13). The popping of nitrogen bubbles causes microdrops of the solution with molecules to be sputtered at a large distance. The sample was placed about...
molecules and the electrodes, as in the experiment of Ref. 9. The surprisingly low values of junction resistances indicate good electron transmission between the electrodes. Below 1 K, the three samples behave quite differently (Figs. 1, 3, and 4).

Conductivity measurements of these molecular junctions were carried out in a dilution refrigerator at temperatures down to 60 mK, in a magnetic field up to 5 T with a nA current at 30 Hz superimposed to a dc current varying between −200 nA to 200 nA. The differential resistance is measured using a low noise voltage amplifier followed by lock-in detection. Samples Gd1, Gd2, and Gd3 have room temperature resistances, respectively, of 13, 3, and 1.5 kΩ and exhibit Ohmic behavior for current excitations between 1 nA and 1 μA. There is no sign of Coulomb blockade or resonant tunneling in these samples down to 1 K, certainly due to the good coupling to the W electrodes. Below 1 K, the three samples behave quite differently (Figs. 1, 3, and 4).

Sample Gd1 undergoes a transition to a low resistance state below 0.7 K and for magnetic fields smaller than 1 T [Fig. 1(c)]. This indicates a proximity effect in the sample. These values are well below the critical temperature and field of the contacts 5 K and 6 T. The possible origins of these reductions are discussed below. We note also that the transition is not complete (no zero resistance state and no supercurrent).

100 meV,10 so that the dimer is stable at room temperature. According to Ref. 10, the Gd atoms are placed asymmetrically with respect to the center of the dimer. Samples Gd2 and Gd3 contain a cluster of Gd@C82 molecules between the electrodes (about seven molecules for both samples; contamination during HRTEM observation prevented the exact determination of this number).

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The electronic transfer between fullerenes has indeed been measured with a small ac modulation of the current superimposed to the dc current at $I_p=65$ nA, which is very close to the value $I_p=65$ nA corresponding to the lowest current peak in $dV/dI$ [Fig. 3(b) and the inset of 3(c)]. Note, however, that we do not observe any Josephson supercurrent, which suggests that magnetic fluctuations acting as phase breaking events are not completely suppressed even at very low temperature. Moreover, $I_p(T)$ exhibits a nonmonotonic behavior, with a maximum at $T=150$ mK [Fig. 3(c)]. Such behavior cannot be explained by simple BCS theory, and may be related to the appearance of a noncompensated magnetic moment in the dimer induced by the ferromagnetic component of dipolar interactions (of the order of 0.1 K) competing with the antiferromagnetic exchange coupling of the Gd spins.

Beside the first peak associated with $I_p$, the differential resistance exhibits a complex structure with numerous hysteretic peaks not symmetric with respect to current reversal. This hysteresis is not present when the measurements are done with the sample voltage biased. In this case we observe...
that the current is a nonmonotonic function of voltage in the regions where hysteresis takes place in the current-biased data, as observed in Josephson junctions [see Fig. 3(c)]. In long molecular wires between S electrodes, peaks in the differential resistance can be attributed to the nucleation of phase slip centers, but there is no room for nucleation centers in short molecules. Rather, we attribute these peaks to multiple Andreev reflection (MAR) already observed in other SNS junctions when the bias is equal to $2\Delta/ne$, where $n$ is an integer. As shown in Fig. 3(a) where the differential resistance is plotted as a function of measured dc voltage, all these peaks shift linearly to lower bias with magnetic field. This linear variation is proportional to the field dependence of the gap deduced from the transition temperature of the plain tungsten wires depicted in Fig. 2. But, as mentioned previously, the field at which the proximity effect disappears is six times smaller than the critical field of the electrodes. This factor could be due, beside the magnetism of the dimer, to the local concentration of magnetic field lines in the gap between superconducting electrodes.

However, in addition to the peaks predicted by theory, we also find peaks which the simple MAR model does not explain [Fig. 3(a)]. In particular it seems as though the peaks at $2\Delta$ and $2\Delta/3$ are split. This behavior is indeed expected for quantum dots between S electrodes, which contain an energy level not exactly centered at the Fermi energy of the electrodes. The amplitude and shape of the peaks have been shown to depend on the transmission of the potential barrier between the superconducting and normal parts of SNS junctions.

The other samples, Gd2 and Gd3, have lower room temperature resistances, indicating a better transmission which should favor proximity effect. Surprisingly they do not undergo a transition to a low resistance state, in spite of the fact that a transition was clearly observed in the W electrodes (see Fig. 2). They exhibit a small resistance increase at low temperature (inset of Fig. 4) and a nearly bias-independent differential conductance (not shown). The HRTEM observation [not shown] reveals that Gd2 and Gd3 are composed of a cluster of seven or more fullerene molecules. We expect such a cluster with more than one dimer to have an uncom-