RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 56, NUMBER 10 1 SEPTEMBER 1997-II

Spin-dependent tunneling with Coulomb blockade

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(Received 3 April 1997)

We have fabricated Co/Al_2O_3/Co tunnel junctions in which the Al_2O_3 layer includes a unique layer of small and disconnected cobalt clusters, with a typical mean diameter ranging from 2.0 to 4.0 nm. We observe spin-dependent tunneling properties with, below about 50 K, typical Coulomb-blockade effects induced by intermediate electron tunneling into cobalt clusters. The tunnel magnetoresistance ratio is approximately the same in the Coulomb-blockade regime (low-temperature range with very high tunnel resistance) and in the room-temperature regime without Coulomb blockade. It also depends weakly on the applied voltage. [S0163-1829(97)51434-2]

Electron tunneling between ferromagnetic electrodes through an insulating layer depends on the relative orientation of the magnetizations in the electrodes: this is the so called spin-dependent tunneling. When the relative orientation of the magnetizations can be changed by applying a magnetic field, it gives rise to tunnel magnetoresistance (TMR). Although this effect was discovered by Julliere[1] in 1975, it is only very recently that large and reproducible TMR ratios could be found.[2,3] Typically, in the work of Moodera *et al.*[2] on Co/Al_2O_3/CoFe junctions, TMR ratios of 18% at room temperature (RT) have been found, and the interest of TMR for applications has been recently emphasized.[4,5]

Electron tunneling into a small particle (dot or cluster) gives rise to another interesting effect, namely the Coulomb blockade.[6,7] Tunneling of an electron into a small cluster increases the energy of the system by a charging (Coulomb) term, $E_c = e^2/2C$, where C is the capacitance of the cluster. This charging energy introduces a gap for electron tunneling and gives rise to the Coulomb blockade effect.[6,8] Roughly speaking, if the applied voltage V and the thermal energy k_BT are much smaller than E_c, only electrons at E_c above the Fermi level can tunnel thus increasing the tunnel resistance by a factor of the order of $\exp(E_c/2k_BT)$. When eV or k_BT exceeds E_c, the bare tunnel resistance is approximately restored.

Coexistence of spin-dependent tunneling and Coulomb blockade has first been seen for nickel clusters in SiO_2 (Ref. 8) and, more recently, investigated by Fujimori *et al.*[9] for several types of granular systems. When the cluster concentration is just below the percolation threshold, the conduction is dominated by tunneling between metallic clusters, with a tunnel resistance enhanced by the Coulomb blockade at low temperatures and also dependent on the relative orientation of the magnetization in the two clusters (it decreases when an applied field aligns the magnetic moments of the clusters). However, in granular materials, the conduction involves a large number of clusters, with generally a broad distribution of size and inter-cluster distance. This leads to relatively complex Coulomb blockade effects[8–10] that cannot be analyzed as quantitatively as in the simpler structures usually fabricated for Coulomb-blockade studies.[6] The objective of the present work is to study the interplay between spin-dependent tunneling and Coulomb blockade in a simpler structure, derived from classical planar tunnel junctions. Our samples are composed of two ferromagnetic electrodes (cobalt films) separated by a thin Al_2O_3 insulating layer in which one layer of cobalt clusters is embedded, as shown in Fig. 1(a). We note t and t' the thicknesses of the Al_2O_3 layers separating the clusters from, respectively, the bottom and the top electrodes. We have studied junctions with values of t and t' in the range 0.5–3.0 nm. We can also control the cluster size in the range 1.0–4.0 nm, as it will be discussed below. The present paper focuses on the Coulomb-blockade behavior and its interplay with spin-dependent tunneling. However, we will see that this type of junction can also be of interest for applications as the TMR effects that we observe remain at a relatively high voltage (the bias dependence is small up to 1 V) and also can be obtained at a fairly small magnetic field.

The junctions are sputtered onto Si substrates (or Si covered by a SiO_2 layer) from Co and Al_2O_3 targets and masks are used to obtain a cross pattern geometry. As shown in Fig. 1(a), a layer of cobalt clusters is embedded in the Al_2O_3 layer separating two Co films. The Co clusters are obtained by depositing an ultrathin layer of Co. The large difference between the surface energies of Co and Al_2O_3 leads to a tridimensional growth of Co and to the formation of clusters. Clustered layer obtained by depositing 0.7 nm of Co (nominal thickness) can be seen on electron microscopy images of Figs. 1(b) and 1(c). The clusters are approximately spherical, with diameters ranging between 3.0 and 4.0 nm, and compose a well-defined layer. In this layer, the clusters are disconnected and, as can be particularly seen in Fig. 1(b), are uniformely distributed (a sort of self-organized distribution). Our smallest clusters (around 2.0 nm) have been obtained by depositing 0.2 nm of Co. When 1.5 nm of Co is deposited, the clusters begin to be partly connected and, above 2 nm, the Co layers are continuous. We have also prepared samples without ferromagnetic electrodes to single out the magnetic behavior of the Co clusters in magnetization measurements. We find a typical superparamagnetic behavior with a bifurcation between the field-cooled and zero-field-cooled magnetizations at a blocking temperature T_b ranging from a few K

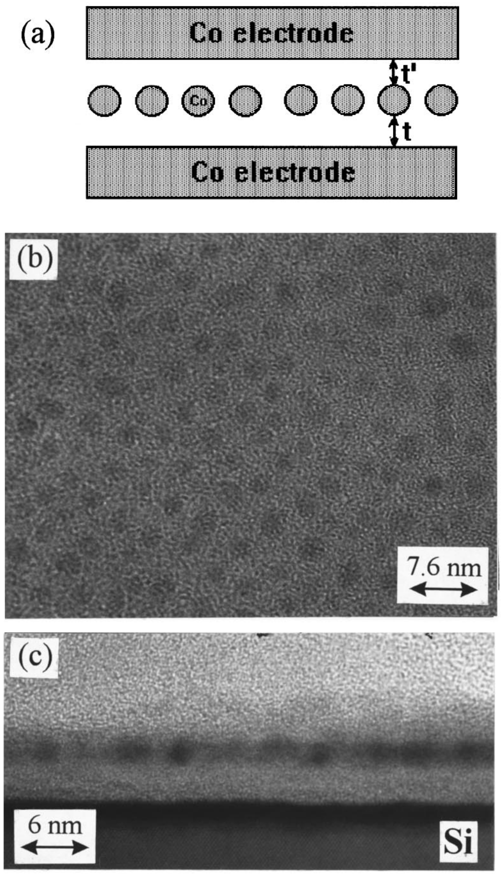

FIG. 1. (a) Schematic of the fabricated junctions (cross section). (b) Transmission electron microscopy (TEM) plane view of a cobalt cluster layer sandwiched between two Al_2O_3 layers deposited on a carbon-coated microscopy grid (the diameter of the clusters range from 3 to 4 nm). (c) TEM cross-section image of the same structure deposited on Si.

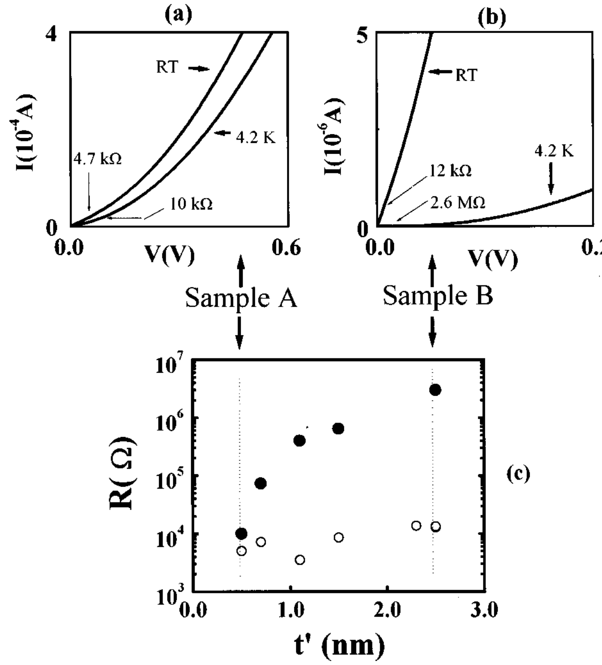

FIG. 2. $I(V)$ curves and resistance in the low-voltage limit for samples with clusters of 3.5 nm mean diameter separated from the bottom electrode by a 2.7-nm-thick Al_2O_3 layer (i.e., $t = 2.7$ nm). (a) $I(V)$ curves at RT and 4.2 K for sample A with $t' = 0.5$ nm (clusters poorly isolated from the top electrode and bare tunnel effect without Coulomb blockade). (b) $I(V)$ curves at RT and 4.2 K for sample B with $t' = 2.5$ nm (well isolated clusters and Coulomb blockade). (c) Resistance in the low-voltage limit at RT (open circles) and 4.2 K (black dots) as a function of the distance t' between the cluster layer and the top electrode.

for the smallest clusters (1.5 obtained by depositing only 0.2 nm of Co) to RT for the largest ones (1.5 nm of Co deposited). Below T_b, the coercive field of the Co clusters can be as large as 1000 Oe. The Co films deposited as electrodes exhibit a soft magnetic behavior with a coercive field of 20 Oe at RT and around 100 Oe at 4.2 K. Details of structural and magnetic characterization will be published elsewhere.

We have studied the tunneling properties between 4.2 K and RT with a dc technique (we report values at constant voltage). The MR measurements have been performed in the field of a superconducting coil (up to 8 T).

We first present tunneling results for a series of samples in which the thickness of the bottom Al_2O_3 layer is constant ($t = 2.7$ nm), while the top Al_2O_3 layer varies from $t' = 0.5$ nm to $t' = 2.5$ nm. The diameter of the clusters is between 3.0 and 4.0 nm. We want to show that, as t' varies from 0.5 nm (clusters almost touching the top electrode and therefore poorly isolated) to 2.5 nm (clusters well isolated from both electrodes), one observes a crossover from conventional tunneling to tunneling with Coulomb blockade.

Figure 2(a) displays the $I(V)$ curves at 4.2 K and RT for sample A, with $t' = 0.5$ nm. The nonlinear variation of I with V is characteristic of electron tunneling. As expected for a barrier height in the eV range, the $I(V)$ curves do not depend significantly on temperature, the initial tunnel resistance (inverse of the initial slope) increasing only from 4.7 kΩ at RT to 10 kΩ at 4.2 K. In order to fit the classical Simmon's expressions[12] to our experimental $I(V)$ curves, we have supposed that, in first approximation, the predominant contribution to the tunnel resistance comes from the thicker junction (that with $t = 2.7$ nm). We have also estimated an effective junction area at 4.5×10^{-2} mm^2 from the proportion of the total area covered by clusters; see Fig. 1(b). Reasonably good fits at both RT and 4.2 K are obtained with $\Delta = 1.4$ eV for the barrier height and $s = 1.7$ nm for the effective thickness (s is somewhat smaller than the nominal thickness of Al_2O_3, $t = 2.7$ nm, as usually found in fits with theoretical expressions and ascribed to thickness fluctuations induced by roughness). We conclude that the results for sample A with poorly isolated clusters are consistent with simple tunneling without significant Coulomb-blockade effects.

Figure 2(b) displays $I(V)$ curves at 4.2 K and RT for sample B with $t' = 2.5$ nm. The $I(V)$ curve at RT is similar to that of sample A in Fig. 2(a), with also an initial tunnel resistance in the kΩ range (13 kΩ). The main difference between A and B is at 4.2 K: the $I(V)$ curve of B departs from the $I = 0$ line of the figure only above 0.05 V. More quantitatively, the low-voltage resistance of B increases dramatically at low temperatures and reaches 3 MΩ at 4.2 K. This huge increase of the tunnel resistance of B at low temperatures cannot be accounted for in any way with Simmon's equations and reasonable values of the parameters (in the

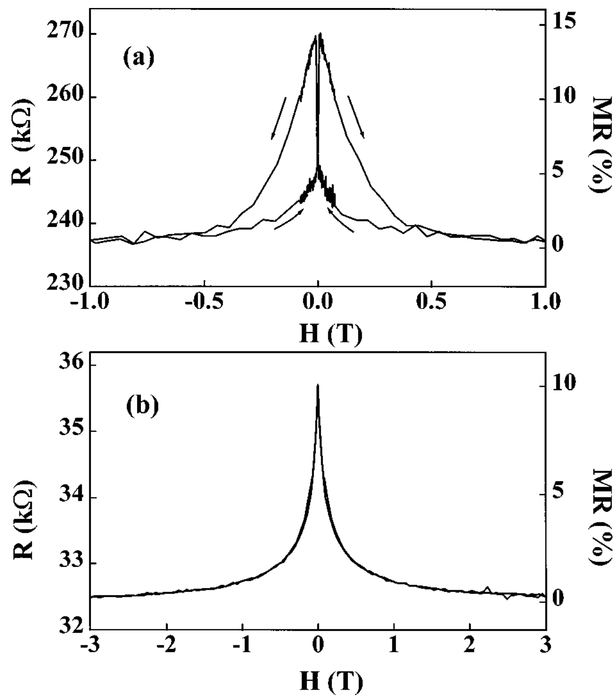

FIG. 3. Resistance ($R=V/I$ at constant V) versus magnetic field for a junction with cobalt clusters of mean diameter 3.5 nm separated from the electrodes by Al_2O_3 thicknesses $t=2.7$ nm and $t'=1.5$ nm. (a) at 4.2 K and 25 mV; (b) at 120 K and 50 mV.

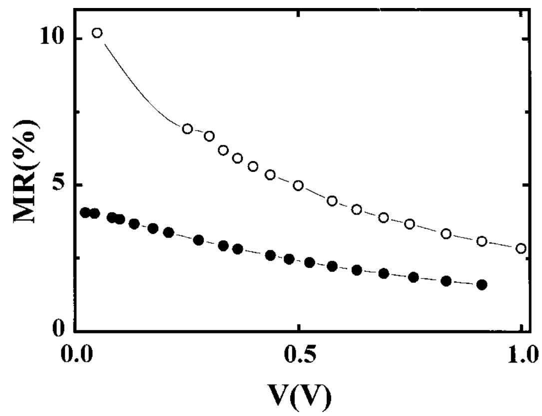

FIG. 4. Magnetoresistance ratio as a function of applied voltage at 4.2 K (open circles) and RT (black dots) for a sample with clusters of 2.5 nm mean diameter, $t=2.7$ nm and $t'=1.4$ nm.

range of those used to account for the results of A) and must be ascribed to Coulomb blockade. To estimate the Coulomb-blockade energy $E_c=e^2/2C$, we have considered the simplest case of an isolated spherical cluster (this is strictly valid when the distance between the clusters and the electrodes and other clusters is larger than the cluster diameter) and introduced $C=2\pi\epsilon_0\epsilon_r d$. With $d\approx 3.5$ nm for the junction of Fig. 2 and $\epsilon_r=8$ for Al_2O_3,[13] we obtain 0.05 V for $e/2C$. This is the right order of magnitude to account for the voltage range with a strong blockade in Fig. 2(b). This characteristic energy is also consistent with our finding that the enhancement of the tunnel resistance is not limited to the helium temperature and that some resistance increase begins just below RT.

In Fig. 2(c) we show the progressive onset of Coulomb blockade as the distance t' between the Co clusters and the top electrode increases from its value in A ($t'=0.5$ nm) to its value in B ($t'=2.5$ nm). The enhancement factor of the resistance between RT and 4.2 K increases as the clusters are more and more isolated from the top electrode and goes from 2 for sample A to 230 for sample B. An enhancement factor in the range of 200–300 seems to be almost a saturation value for the samples of the series of Fig. 2(c).

In Fig. 3(a) we present a magnetoresistance curve at 4.2 K and 25 mV, that is, in the Coulomb-blockade regime and also below the blocking temperature of the clusters. At $H=+1$ T, the electrodes and cluster magnetizations are saturated in the positive direction and the resistance is minimum. When H decreases, there is a partial and progressive disalignment of the magnetic moments of the clusters from the positive direction, that is from the magnetization of the electrodes and, consequently, there is some increase of the resistance (from our measurements we know that the magnetization of the clusters decreases from saturation to a remanent magnetization of about 50%). Then, at a small negative field (coercive field of the electrodes), the magnetization of the electrodes is reversed and becomes antiparallel to the positive remanent magnetization of the clusters, which gives rise to an abrupt increase of the tunnel resistance, with a peak at about 90 Oe. Then the magnetic moments of the clusters are progressively reversed and aligned in the negative direction of the magnetization in the electrodes, and the resistance decreases again to its initial value. For the measurement at 4.2 K in Fig. 3, the MR ratio is 14% and 2/3 of the total effect is associated with the abrupt reversal of the electrode magnetization with respect to the remanent magnetization of the clusters.

In Fig. 3(b) we show the MR curve at 120 K, in the superparamagnetic regime ($T_b\sim 30$ K). In this regime, the remanent magnetization of the clusters is zero, so that the reversal of the electrode magnetization cannot induce any change in the mean relative orientation of the electrode and clusters magnetizations. The MR is only due to the progressive alignment of the cluster moments along the direction of the electrode magnetization, when the field increases from 0 to 3 T. The sample of Fig. 3, with its T_b below RT and a fairly large field at RT to produce MR effects, is not appropriate for applications. Abrupt resistance changes as those observed at low temperatures [Fig. 3(a)] can only be found at RT in samples with larger clusters for which the superparamagnetic regime is repelled above RT. This is discussed in another publication.[11]

A characteristic feature of our results is that the resistance R is considerably enhanced by Coulomb blockade at low temperatures (enhancement by more than 10^2 between RT and 4.2 K) whereas the relative MR ratio $\Delta R/R$ changes moderately (see Fig. 4). This is roughly consistent with the simplest model predicting a spin-independent enhancement factor of $\exp(E_c/2k_BT)$ in first approximation. However, it has been recently suggested that Coulomb blockade, by changing the energy range of the tunneling electrons, can lead to some enhancement of the MR ratio.[14] From our measurements it is difficult to clear up this point. As shown in Fig. 4, the MR ratio increases by a factor of 2.5 from RT to 4.2 K, which is of the same order of magnitude found in conventional ferromagnetic junctions without Coulomb-blockade effects. At this stage, it is impossible to conclude that the Coulomb blockade contributes to the temperature dependence of the MR.

Finally, we discuss the dependence of the MR ratio on the applied voltage; see Fig. 4. The decrease of $\Delta R/R$ with V is much less pronounced than generally observed in ferromagnetic junctions.[2–5] Typically, in the classical work of Moodera *et al.*[2] on CoFe/Al_2O_3/Co junctions, the MR ratio at RT decreases by almost a factor of 20 between low voltage and 0.7 V, while in our samples the MR decreases only by a factor of 2 over the same voltage range. The structure of our junction, with two junctions in series, cannot explain this difference since the major part of the voltage is applied across the thicker junction. A possible explanation is that the rapid decrease of the MR with the bias voltage in classical junctions is related to some fine structure in the spin polarized density of states; in our samples, this fine structure might be blurred either by size effects on the electronic structure of the clusters or by the broadening of the electrons energy range due to Coulomb blockade.

In summary, we have fabricated tunnel junctions in which a layer of cobalt clusters is embedded in the Al_2O_3 layer separating two cobalt electrodes. We have established the existence of tunneling with Coulomb-blockade effects that can be controlled by varying the distance between clusters and electrodes. The tunneling is spin dependent and gives rise to magnetoresistance. Similar MR ratios are observed inside and outside the Coulomb-blockade regime, making a definitive conclusion about the influence of Coulomb blockade on magnetoresistance impossible at the present time. Measuring a single cluster and introduction of a gate capacitively coupled to the cluster should be the next step required to characterize the influence of the magnetic arrangement on Coulomb blockade and to go a little further on the way towards a magnetically controlled single electron device.

This work was supported in part by the Esprit Program of the European Community [Project (NM^2) 20-027] and the NEDO of Japan (International Joint Research, project «Spin dependent quantum effects»). L.F.S. was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq, Brazil.

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