Inverse Tunnel Magnetoresistance in $Co/SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$: New Ideas on Spin-Polarized Tunneling

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(Received 9 December 1998)

We report tunnel magnetoresistance (TMR) measurements on $Co/SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$ junctions. The half-metallic $La_{0.7}Sr_{0.3}MnO_3$ electrode is used as a spin analyzer. The large (-50%) inverse TMR indicates a negative spin polarization of Co, in agreement with the density of states (DOS) of the d band in Co. The bias dependence of the TMR, with a maximum inverse TMR at -0.4 V and a crossover to normal TMR above $+0.8$ V, reflects the structure of this DOS. Our results demonstrate that the choice of the insulating barrier can strongly influence and even reverse the spin polarization of tunneling electrons. [S0031-9007(99)09225-X]

PACS numbers: 73.40.Gk, 73.40.Rw, 75.70.Pa

Magnetic tunnel junctions, i.e., structures composed of two ferromagnetic layers (F_1 and F_2) separated by a thin insulator barrier (I), have recently attracted attention for their large tunnel magnetoresistance (TMR) which appears when an applied magnetic field changes the angle between the magnetizations of the two ferromagnetic electrodes [1]. Most of the experiments have been carried out with Ni, Co, Fe, and their alloys as magnetic electrodes and an Al_2O_3 barrier [1,2]; a few results have also been reported with NiO, MgO, and HfO_2 barriers [3,4]. In the Jullière model [5], the TMR ratio is given by

$$\frac{\Delta R}{R} = \frac{R_{AP} - R_P}{R_{AP}} = \frac{2P_1P_2}{1 + P_1P_2}, \qquad (1)$$

where R_{AP} and R_P are the resistances in the antiparallel (AP) and parallel (P) states, respectively, and P_1 and P_2 are the electron spin polarizations of the two electrodes.

All the measurements with transition metal electrodes and an Al_2O_3 barrier reported until now have shown a positive TMR, that is, $R_{AP} > R_P$, which we call "normal" TMR. This implies that the sign of the spin polarization coefficient P is the same for all the transition metals and alloys used as electrode. P can also be determined by measurements on $F/Al_2O_3/S$ junctions where the spin splitting of the gap of the superconductor (S) is used to analyze the spin polarization of the electrons tunneling from or into the ferromagnetic electrode F. Extensive data have been obtained in this way with $F/Al_2O_3/Al$ junctions by Meservey and Tedrow [6] and positive P have been found in all cases. These coefficients are often introduced into Eq. (1) to predict the TMR of $F_1/Al_2O_3/F_2$ junctions and this generally leads to an approximate agreement with the experimental data. However, the positive sign found for the polarization coefficient P is surprising, especially for metals such as Co or Ni in which a negative polarization could be expected due to the smaller density of states (DOS) at the Fermi level for the majority spin direction (the majority d band is below the Fermi level for Co or Ni). The current interpretation of this positive polarization is that the tunneling of s-character electrons is favored [7,8]. For alumina barriers and Co electrodes, this can be justified by first principle calculations [9] which explain the positive polarization by the "strong bonding between the minority spin d-orbitals of Co and the sp orbitals of Al at the interface" and by the resulting reduction of the minority sp-DOS on Al. In other words, the spin polarization of the evanescent wave in the barrier depends on the character of the bondings at the F/I interface. In contrast with results for Al_2O_3, we will see that, in experiments we report here, the polarization of electrons tunneling from or into cobalt across a $SrTiO_3$ (STO) barrier is definitely negative (note that a negative polarization for a transition metal has also been found in scanning tunneling microscopy experiments with a Ni tip [10], consistently with calculations for F/vacuum interfaces [11]).

Ferromagnetic oxides have also been used as an electrode, particularly mixed valence oxides of the type $La_{1-x}Sr_xMnO_3$ (LSMO). In the ferromagnetic phase of these manganites, the conduction is due to the transfer of majority spin e_g electrons between Mn sites and the minority spin band is empty. This means half-metallic (HM) character (that is, metallic character for one spin direction and insulating character for the other) or, in other words, 100% spin polarization of the carriers. Direct evidence of this HM behavior has been provided by Park *et al.* [12] by spin resolved photoemission measurements on $La_{0.7}Sr_{0.3}MnO_3$ compounds. A perfect half-metallic behavior would lead to a 100% value for the TMR in $HM/I/HM$ tunnel junctions. On the experimental side, measurements on junctions with HM electrodes [13–16] have been performed and, in LSMO/STO/LSMO junctions, have shown a very large TMR effect corresponding to an effective polarization of 80% for LSMO [13,14].

As the spin polarization of the carriers in LSMO is known to be positive and close to 100%, we use the

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LSMO electrode as an analyzer of the spin polarization of Co in LSMO/STO/Co junctions (in the same spirit of what has been done with a superconducting electrode [6]). Our clear observation of a large negative TMR indicates that the spin polarization of the electron tunneling from or into Co is negative, as the polarization of the *d* band. We will also show that the bias dependence of the TMR reflects the structure of the DOS of the Co *d* band.

The tunnel junctions studied are composed of 35 nm of LSMO for the bottom electrode, 2.5 nm of $SrTiO_3$ (STO) for the barrier, and 30 nm of Co for the top electrode. The sample is protected by 5 nm of Au. The LSMO and STO thin films were grown using pulsed laser deposition under an oxygen pressure of 350 mTorr at about a temperature of 700 °C. The Co layers and the Au capping layers were deposited by molecular-beam epitaxy (sample 2) or by sputtering (sample 1). The trilayers are etched using a conventional UV lithography in order to define a mesa structure (with a diameter of 10 or 20 μm) for tunneling measurements (with a dc technique) [17]. The magnetization was measured with a SQUID magnetometer.

The $I(V)$ curves clearly show a non-Ohmic behavior and the expected asymmetry corresponding to the asymmetry of the structure. The fit with theoretical expressions [18] indicates a mean barrier height of about 1.2 eV. We also note that the in-plane resistance of the LSMO bottom electrode is only 0.02% of the tunnel resistance, and we can therefore rule out any additional geometrical effect [19].

Figure 1 shows the magnetoresistance (at a voltage of -0.4 V) and magnetization curves recorded on the same sample. The two-step reversal in the magnetization curve [Fig. 2(b)] indicates a good decoupling of the two magnetic layers, so that an AP alignment is obtained between the two coercive fields. The interesting effect is *the inverse TMR* shown in Fig. 1(a). When, in a decreasing field, the magnetization of the LSMO layer switches at about -3 mT, the resistance of the junction decreases rapidly, by a factor of 1.7 for this sample. It remains nearly constant until -40 mT and then, with the progressive reversal of the Co layer, returns to its saturation value. The magnetic fields corresponding to the different transitions in the $R(H)$ curves are larger than those observed for the magnetization curve, which is not surprising when one considers that tunneling is sensitive to the magnetization of the interface which can switch at higher field than the bulk. The same behavior is observed for the 10 and 20 μm diameter junctions of sample 2. In that case, the TMR is around 30%, a lower value certainly due to the lower quality of the LSMO/STO interface.

As the spin polarization of the LSMO is *positive*, the *inverse TMR* observed in LSMO/STO/Co junctions is the signature of a *negative polarization for Co* in this type of junction. The inverse TMR recently observed in Fe_3O_4/STO/LSMO junctions [16] is also probably due to a combination of positive and negative polarizations

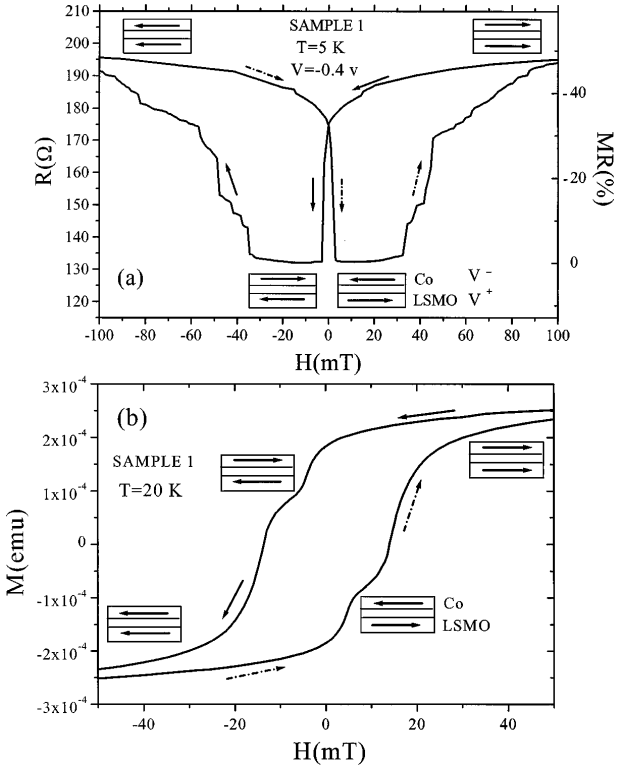

FIG. 1. (a) Resistance versus applied magnetic field for a 10 μm Co/STO/LSMO junction at 5 K (sample 1). The applied bias is -0.4 V. The resistance is minimum in the AP configuration, which we call an inverse TMR. (b) Magnetization versus field curve measured on the same sample at 20 K.

in the two electrodes. But, in this latter case, the negative polarization of Fe_3O_4 is quite expected due to the conduction mechanism by hopping between minority spin states in the Fe_3O_4 oxide and is not related to the important problems currently raised by the tunneling from ferromagnetic transition metals, i.e., the respective role of *s* and *d* electrons [7,9], the influence of the insulator on the polarization [9], and the correlation between the bias dependence and the *s*- or *d*-band DOS. Whereas the *positive polarization of Co* in junctions with Al_2O_3 is ascribed to the *s electrons* [7,9], the *negative* one we observe agrees with the *conventional picture of the Co d band with a higher DOS at E_F for the minority spin direction* (a negative polarization also confirmed by calculation of the DOS at the surface of the Co [11]). According to preliminary calculations [20], this is due to the predominance of *d*-*d* bonding between Co and Ti or Sr at the interface. We now describe how the bias dependence of the TMR reflects the structure of the *d*-band DOS and confirms the interpretation.

As shown in Fig. 2, when a negative voltage is applied between the LSMO and the Co electrodes, one observes an increase in the magnetoresistance. The TMR reaches its maximum value for an applied voltage around -0.4 V

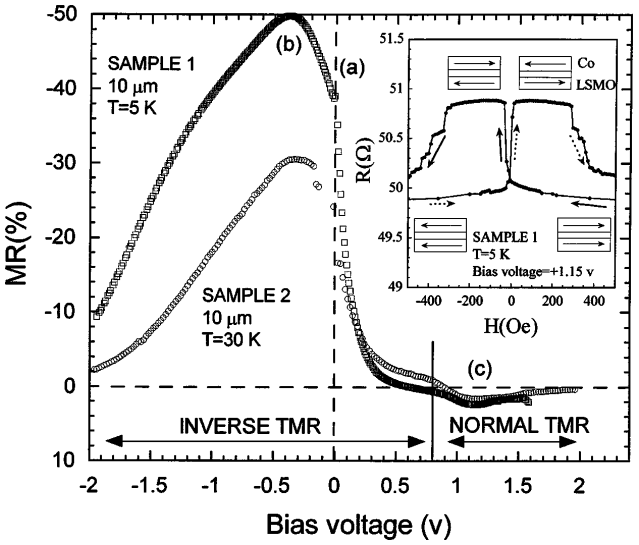

FIG. 2. TMR ratio as a function of the applied dc bias for 10 μm Co/STO/LSMO junctions of samples 1 and 2. The inverse TMR is maximum at about -0.4 V and reaches -50% and -30% for samples 1 and 2, respectively. At positive bias the TMR decreases rapidly and a normal TMR of, respectively, 1.5% and 1% is measured at $+1.15$ V for samples 1 and 2. The inset is the normal TMR measured at 5 K on sample 1 for a positive bias of 1.15 V.

(-50% for sample 1 and -30% for sample 2) and then decreases slowly. The maximum value is obtained at the same voltage for the two samples and for all the junctions demonstrating the intrinsic character of the phenomenon. For a positive applied voltage, the TMR decreases rapidly and changes its sign at $+0.8$ V. A *normal TMR* of 1.5% is obtained for an applied voltage around 1.2 V, as shown by the inset of Fig. 2.

To see the correlation between the bias dependence of the TMR and the structure of the DOS of the d band of Co, we have represented in Fig. 3 the relative positions of the DOS for Co (majority and minority d bands) and for LSMO (majority spin e_g band) at several biases. The DOS for Co comes from calculations performed by Wang [8] for a fcc(001) Co/vacuum interface. The DOS of LSMO is taken from a direct observation by spin-resolved photoemission spectroscopy [21].

(a) $V \approx 0$ [Fig. 3(a), point (*a*) in Fig. 2]: Since, in Co, the d-character DOS at E_F is higher for the minority spin direction, the most probable transitions (represented by the arrow) are those between the minority (spin $\downarrow$) d band of Co and the majority (spin $\uparrow$) band of LSMO occurring in the AP configuration. This explains the inverse TMR observed at low bias.

(b) $V = -0.4$ V [Fig. 3(b), point (*b*) in Fig. 2]: The inverse TMR is maximum because, in the AP configuration, the electrons can tunnel from the Fermi level of LSMO to the peak in the spin $\downarrow$ DOS at about 0.4 eV above E_F in the d band of Co (see arrow). At a higher energy, the spin $\downarrow$ DOS of Co decreases progressively, which is consistent with the progressive decrease of the TMR between -0.4 and -2 V.

(c) Positive bias and $V = +1.15$ V [Fig. 3(c), point (*c*) in Fig. 2]: For positive bias, the Fermi level of LSMO goes down into the energy range of the spin $\uparrow$ d band of Co, which opens the possibility of tunneling from the spin $\uparrow$ d band of Co to the spin $\uparrow$ d band of LSMO in the P configuration. Consequently, the inverse TMR drops rapidly. At $+1.15$ V, the Fermi level of LSMO is at about the energy of the peak in the spin $\uparrow$ d band of Co, the tunneling from the spin $\uparrow$ DOS of Co to LSMO (arrows) in the P configuration exceeds that from spin $\downarrow$ DOS of Co to LSMO in the AP configuration, and the TMR is normal.

It thus turns out that the maximum of inverse TMR at -0.4 V, the crossover to normal TMR above about $+0.8$ V, and other features of the bias dependence reflect the structure of the DOS of the d band of Co, in contrast with the absence of structure in the bias dependence observed for conventional junctions with an Al_2O_3 barrier.

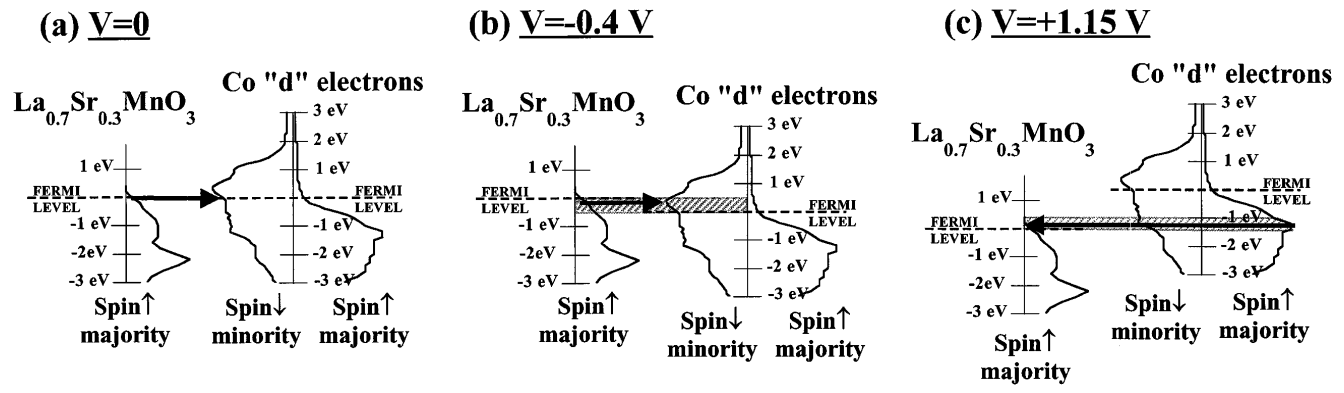

FIG. 3. Relative positions of the d DOS in Co and LSMO for (a) a bias around zero, (b) a negative bias of -0.4 V, and (c) a positive bias of $+1.15$ V. The DOS of Co interface is taken from Ref. [11] and that of LSMO from Ref. [21]. In each case, arrows indicate the route of higher tunneling rate which occurs between majority states of LSMO and minority states of Co in the AP configuration [(a),(b)] or between majority states of LSMO and majority states of Co in the P configuration (c).

Quantitatively, if we assume a polarization factor of 0.8 for LSMO at low temperature [14], a fit of the TMR at 5 K and -0.4 V with Eq. (1) leads to an effective polarization coefficient $P_{\mathrm{Co}} = -0.25$.

As the temperature increases, the TMR decreases rather rapidly, as this has always been observed for junctions with LSMO [13,14]. However, on our junctions, the TMR does not vanish and is still 5% at RT for sample 1. This type of junction, with its TMR keeping up at relatively large negative bias, can even be of interest for applications, at least with HM oxides exhibiting a higher Curie temperature [22]. At room temperature, the bias dependence of the TMR exhibits the same structure related to the DOS of the *d* band in Co but is less pronounced than at 5 K.

In conclusion, we sum up the results of this work.

(i) The large (-50%) inverse TMR of Co/STO/LSMO tunnel junctions and the definite correlation between its bias dependence and the DOS of the *d* band of Co clearly demonstrate that the major contribution to the tunneling current comes from *the negatively polarized d electrons of Co.* This is in contrast with the tunneling of *s*-character electrons proposed to explain the positive polarization in junctions with an Al_2O_3 barrier, and can be related to the electronic structure of the Co/STO interfaces (with also a possible additional influence of the LSMO second electrode).

(ii) Our finding that the *choice of the barrier can influence and even reverse the spin polarization* of the tunneling current is of general interest, since this adds additional parameters to enhance the TMR of ferromagnetic junctions. In particular, we can emphasize that it is easy to shape the DOS of a *d* band by alloying, as illustrated, for example, by the calculation of Ref. [23].

(iii) Ferromagnetic transition metal/I/LSMO junctions, or more generally junctions combining half-metals and transition metals, appear of definite interest to *probe the effective polarization* of electron tunneling from ferromagnetic transition metals and the bias dependence of this polarization. The method is complementary of measurements on (F/I/superconductor) junctions [6] or Andreev Reflection (AR) experiments [24]. In contrast to measurements on tunnel junction, conventional AR experiments do not determine the sign of the polarization and also cannot reflect the influence of an insulating barrier.

We thank J. Nassar and J. M. George for their help for the experimental work and acknowledge fruitful discussions with J. Barnas, P. M. Levy, F. Petroff, and M. Viret. The work was partly supported by the European Community and the NEDO of Japan.

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