

# ROLE OF THE BARRIER IN MAGNETIC TUNNEL JUNCTIONS

J.M. De Teresa, A. Barthélémy, J.P. Contour, A. Fert, deteresa@lcr.thomson-csf.com

Unité Mixte de Physique, CNRS/Thomson, domaine de Corbeville, 91404 Orsay (France)

## Abstract

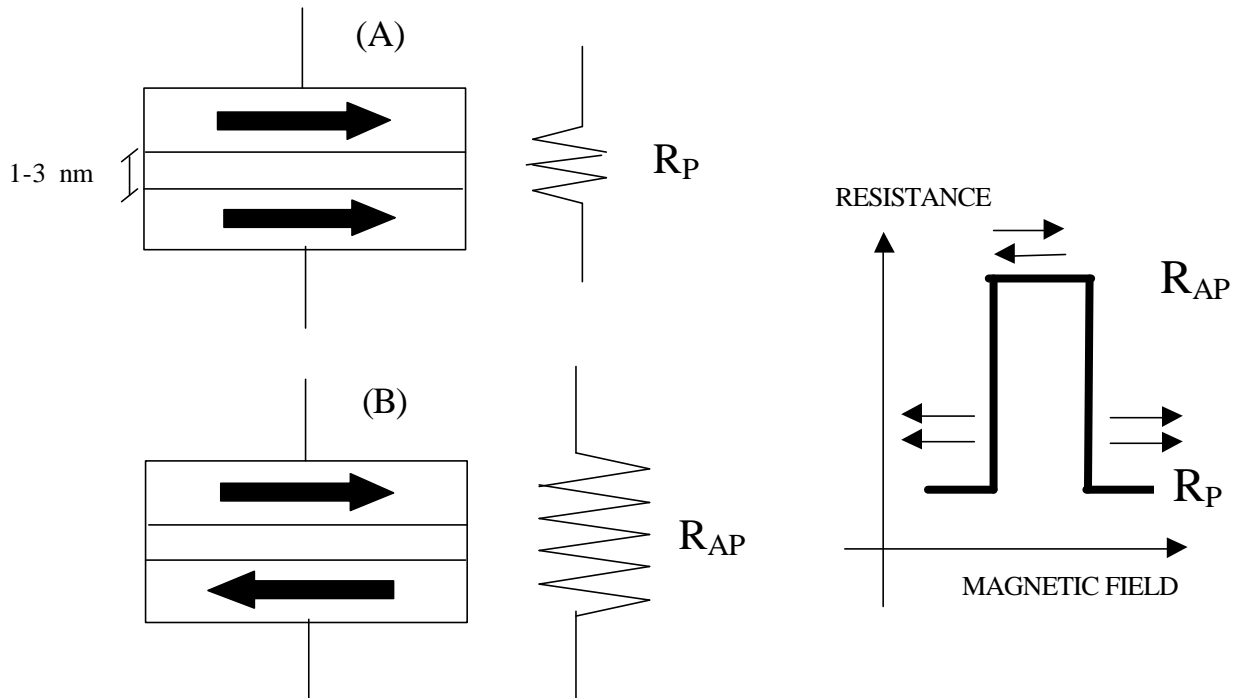
We present experimental evidence of the active role played by the barrier in magnetic tunnel junctions. We have prepared tunnel junctions of the type  $\text{Co}/\text{I}/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  with four different insulating barriers:  $\text{I} = \text{Al}_2\text{O}_3$ ,  $\text{SrTiO}_3$ ,  $\text{Ce}_{1-x}\text{La}_x\text{O}_2$ , and double barrier  $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ . Depending on the used barrier, the tunnel magnetoresistance can be normal (for  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3/\text{SrTiO}_3$ ) or inverse (for  $\text{SrTiO}_3$  and  $\text{Ce}_{1-x}\text{La}_x\text{O}_2$ ).

## 1 INTRODUCTION

One of the consequences of *Quantum Mechanics* is the possibility of tunnelling through a *classical* forbidden region. In the 60's and 70's, the advance in material technology allowed an optimum benefit of this concept when artificial tunnel junctions of the type Metal/Insulator/Metal, Metal/Insulator/Superconductor,

etc. were grown. In these types of sandwiches with typical size some nanometres, the electrons can tunnel from the first electrode to the second one through the insulating layer providing a tunnelling current. In **magnetic tunnel junctions** [1], say, *sandwiches of the type F/I/F*, where *F* stands for a ferromagnetic electrode and *I* for the insulating barrier, Jullière measured for the first time in 1975 a large change of resistance by applying a magnetic field. He put forward that the tunnelling current should depend on the relative orientation of the magnetizations of the two ferromagnetic electrodes. By applying a magnetic field, one can modify the angle between the magnetizations, which can give rise to a large magnetoresistance. The magnetoresistance ratio is normally defined as

$$\text{TMR}(\%) = 100 * (\mathbf{R}_{\text{AP}} - \mathbf{R}_{\text{P}}) / \mathbf{R}_{\text{AP}} \quad (1)$$



**Figure 1.** Schematic representation of a magnetic tunnel junction: two metallic ferromagnetic electrodes separated by an insulator. The **parallel** (A) and **antiparallel** (B) magnetic configurations of the electrodes have different resistance. The switching between both states by application of a magnetic field brings about a magnetoresistive effect which can be used in several technological applications.

where  $R_P$  and  $R_{AP}$  is the resistance of the tunnel junction in the parallel and antiparallel configurations respectively. After this pioneering work, this effect was not further developed due to the difficulty in preparing good insulating barriers and reproducible results. It is only since 1995, with the discovery of a large and reproducible TMR at room temperature by Moodera et al. [2] in  $Co/Al_2O_3/CoFe$  junctions that the subject has known a renewed interest due to the potential technological applications.

In fact, magnetoresistive systems are widely applied in the *magnetic recording industry* and as *magnetic field sensors*. In the magnetic recording industry, magnetoresistive materials are mainly used in read heads to read information stored magnetically (like in computers, video or audio tapes, etc.), in a market estimated to be on the order of \$ 1 billion per year [3]. First, thin films of ferromagnets showing *anisotropic magnetoresistance* (different resistance of the material depending on the angle formed by the magnetisation and the current) were used and, from 1997, IBM makes use of *magnetic multilayers* showing *giant magnetoresistance* (GMR), which has led to much larger storage densities ( $\sim 20$  Gbit/inch<sup>2</sup>). These multilayers consist of sandwiches of ferromagnetic layers (Fe, Co,...) separated by metallic non magnetic layers (Cr, Cu,...). Between the parallel and antiparallel magnetic configurations, magnetoresistance ratios as large as 50% can be obtained [4]. The physical origin of the GMR is the spin-dependent scattering of the carriers at the interfaces and bulk of the sandwiches [5]. A large effort is presently devoted to study the viability of non-volatile memories (the stored information remains even when the power is off) based on magnetoresistive materials. Recently, Honeywell Corporation announced the demonstration of MRAM (magnetic random access memories) based on GMR materials. This is a \$100 billion annual market [3]. A device has also been proposed to detect magnetic fields as small as  $10^{-12}$  tesla [6], which would be of great interest for medical applications as well as for aeronautical and space industries. *Magnetic tunnel junctions* appear as excellent candidates to be used as magnetoresistive materials in all these applications. They show some advantages when compared to GMR systems as their higher resistance imply lower power consumption and they can be further reduced in size. Large TMR ratios at room temperature ( $\sim 20$ -30%) were recently reported in tunnel junctions composed of transition metal ferromagnets (Fe, Co, Ni) as electrodes and alumina ( $Al_2O_3$ ) barriers [2]. Their growth and patterning is rather well controlled and they could constitute the core of the first-generation magnetic-tunnel-junctions-based devices.

Both, the GMR and the TMR, exist thanks to the spin of the electron, which is an intrinsic microscopic

magnet carried by each electron. That is the reason why the general topic studying these new effects is called **Spin Electronics**. In regard to *the physical origin of the TMR*, one can figure out that in the tunneling process the electrons keep their spin direction and the probability of tunnelling from the first electrode for one electron with a certain spin direction depends on the number of states with the same spin direction available in the second electrode (as occurs in Fermi's gold rule). Thus, it is not equivalent for the tunnelling electrons the parallel and antiparallel configurations because they correspond to different densities of states of the electrodes and, consequently, to different resistances. In the simplest model to explain the TMR [1], its value only depends on the spin polarisation of the ferromagnetic electrodes 1 and 2,

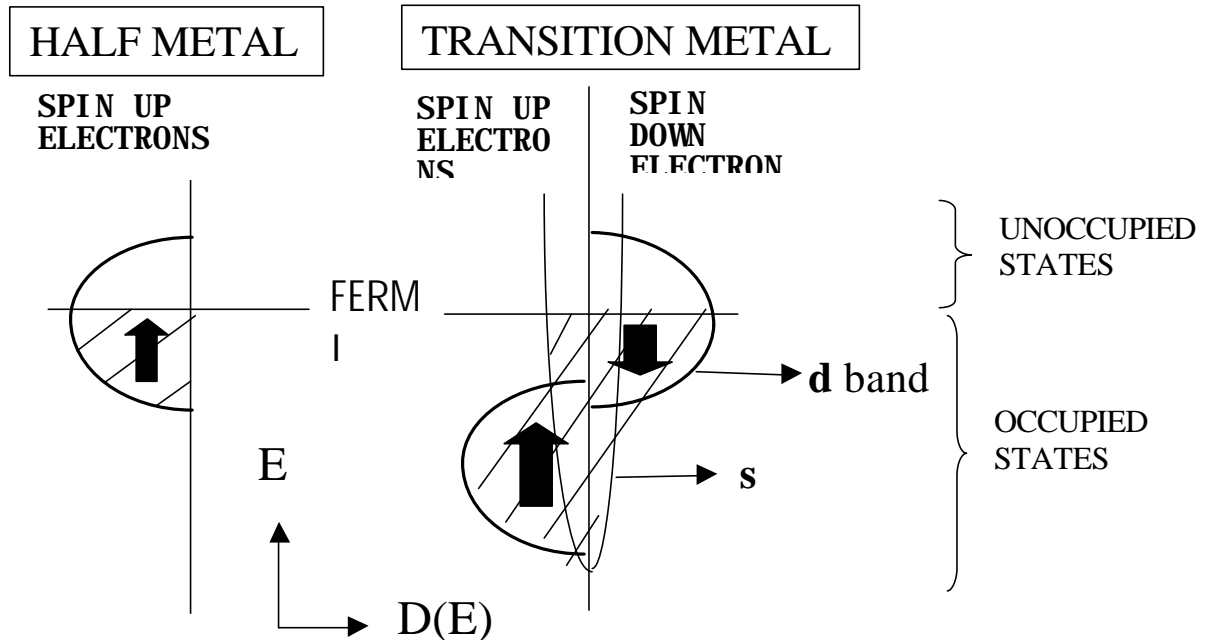
$$TMR(\%)=2P_1P_2/1+P_1P_2 \quad (2).$$

The **spin polarisation** is a subtle concept related to the difference between the number of *spin-up* and *-down* electrons participating in a certain electronic process. In tunnel experiments like those reported in this article, the electrons participating in the process are those in the vicinity of the Fermi level, say, the most energetic electrons of the material. Consequently, the spin polarisation relevant in eq. (2) is the spin polarisation at the Fermi level, which can be defined as

$$P=[N_{EF}(-)-N_{EF}(+)]/[N_{EF}(-)+N_{EF}(+)] \quad (3),$$

say, the difference between the number of spin-up and spin-down electrons at the Fermi level normalised to one. In this definition spin-up electrons means electrons with spin parallel to the magnetisation and spin-down electrons, antiparallel to the magnetisation. Therefore, a positive spin polarisation means that there are more electrons at the Fermi level with spin parallel to the magnetisation and a negative spin polarisation means the contrary. In transition metals (TM) like Fe, Co, Ni, etc., and due to an exchange interaction that lowers the energy of the electrons, the spin-up and spin-down **d** subbands are shifted in energy leading to the presence of more electrons in one of the spin directions. In transition metals there are **s** and **d** bands present at the Fermi level as illustrated in Figure 2. Whereas the **d** band is strongly polarised, the **s** band is less polarised (this polarisation arises from hybridisation with the **d** band). Thus, when performing experiments that probe the spin polarisation at the Fermi level, one essentially expects to find that of the **d** band.

One can deduce the individual polarisation of one electrode by substituting the second electrode by a superconductor. Those experiments were carried out by Tedrow and Meservey in the seventies on  $TM/Al_2O_3$ /Superconductor junctions [7]. In their



**Figure 2.** Schematic representation of the electronic band filling in a half metal and in a transition metal.  $D(E)$  is the density of states available for a certain energy,  $E$ . In the case of the half metal, like  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , there is only one spin direction available at the Fermi level. In the case of a transition metal, like Co, we have spin-up and spin-down electrons belonging to  $s$  and  $d$  bands present at the Fermi level. In this case, the spin polarisation can be positive or negative depending whether there are more spin-up or spin-down electrons at the Fermi level. In this example the spin polarisation for the transition metal is negative.

experiments, the spin splitting of the superconducting gap by application of a magnetic field allows the determination of the absolute value and sign of the spin polarisation of the tunnelling electrons. Surprisingly, they found for all these compounds a *positive* spin polarisation even though a *negative* one was expected for Co and Ni as deduced from their **3d** band structure. Additionally, when magnetic junctions of the type  $\text{TM}_1/\text{Al}_2\text{O}_3/\text{TM}_2$  were measured, a higher resistance was always found in the antiparallel magnetic configuration [2] (called *normal TMR* hereafter), which was consistent (see equations 1 & 2 above) with the uniform positive spin polarisation found by Tedrow and Meservey. Some ideas have been put forward but a satisfactory explanation has never been given. For instance, it has been proposed that only  $s$ -type electrons, with a positive spin polarisation, can tunnel [8, 9]. One can notice that, due to the difficulty of preparation, most of the tunnelling experiments of transition metals reported in literature have been performed with  $\text{Al}_2\text{O}_3$  barriers and, incidentally, it has generally been assumed the existence of a *unique spin polarisation of a ferromagnetic electrode independently of the barrier*.

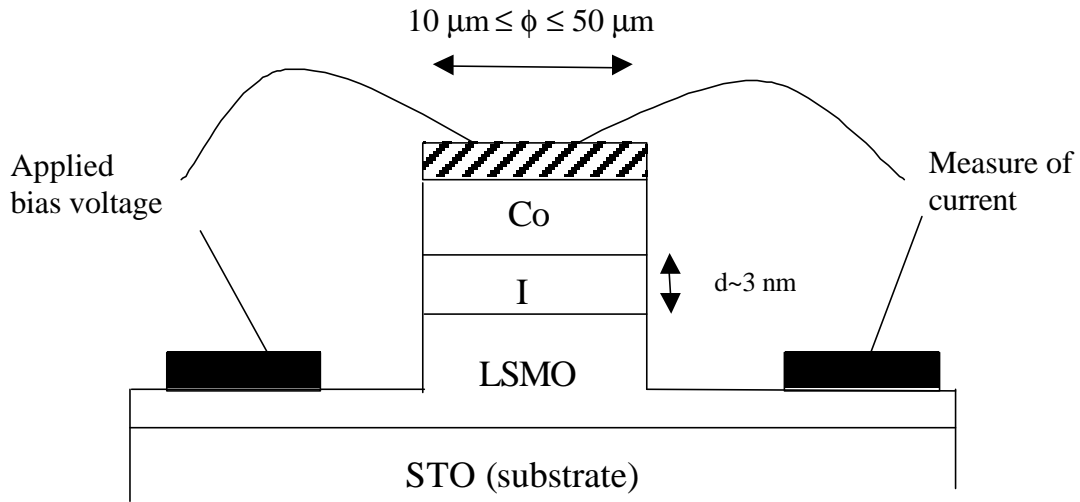
In order to explain Tedrow and Meservey's results and study the role played by the barrier in the tunnelling process, we have prepared magnetic tunnel

junctions of the type  $\text{Co}/\text{I}/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO), say, always with the same magnetic electrodes but with three different types of barriers:  $\text{I} = \text{Al}_2\text{O}_3$  (ALO),  $\text{SrTiO}_3$  (STO),  $\text{Ce}_{1-x}\text{La}_x\text{O}_2$  (CLO), and double barrier ALO/STO.

In our experiments we use LSMO because at low temperature it is known to be half-metallic, say, it exhibits only one spin direction at the Fermi level ( $P \sim +1$ ) [10]. In the same spirit of Tedrow and Meservey's experiments in which the superconductor is used to analyse the spin polarisation of the other electrode, the role of LSMO in our junctions is to be a spin analyser of the spin polarisation of Co when faced to four different barriers, which can be deduced from combination of eq. (1) and (2).

## 2 EXPERIMENTS

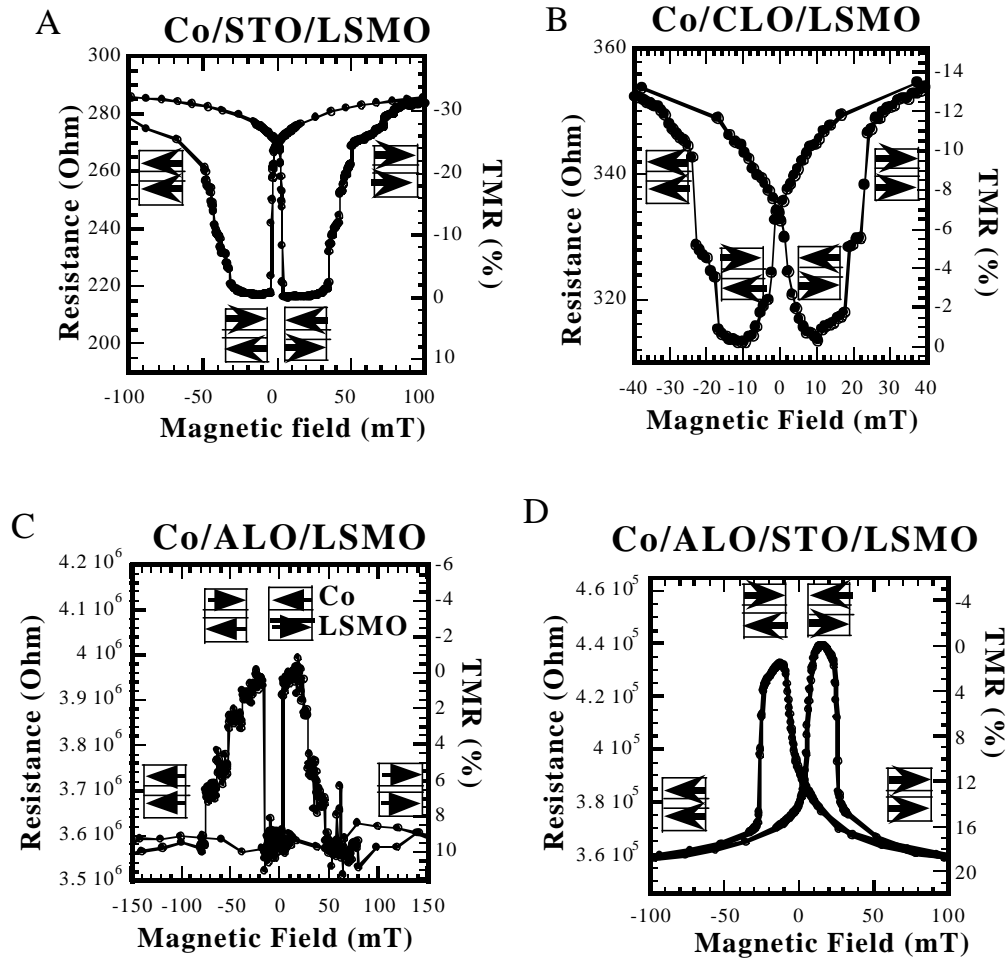
The studied magnetic tunnel junctions were made in the following way. First, 35 nm of LSMO was epitaxially grown by laser ablation on single-crystal STO substrates (size  $10 \times 10 \text{ mm}^2$ ). Barriers of size 2.5-3 nm were subsequently grown on the LSMO layer. STO and CLO barriers were deposited by laser ablation and present an epitaxial growth. The ALO barrier and 30 nm of Co were grown by sputtering. ALO is amorphous and Co polycrystalline. All the heterostructures were capped with 5 nm of gold.



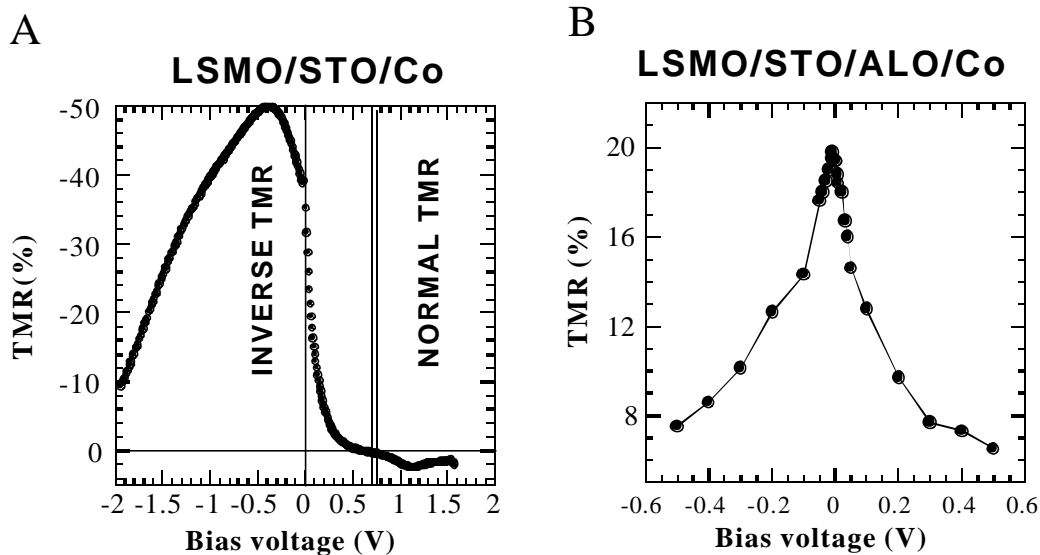
**Figure 3.** Schematic representation of the measurement of resistance in our magnetic tunnel junctions once the heterostructures have been patterned with a lithography process. Gold contacts on the electrodes (LSMO and Co) allow the current injection through the junctions.

After a lithography process (described in detail in reference [11]), junctions of diameter 10, 20 and 50  $\mu\text{m}$  and gold contacts on the top and bottom electrodes are defined as shown schematically in figure 3. By measuring with the four-point technique the resistance of the junctions has been determined. At magnetic fields of the order of 0.1 T, the magnetisations of both electrodes are aligned (parallel magnetic configuration). The change of resistance with magnetic field for junctions with four different barriers at an applied bias voltage of -10 mV is shown in figure 4. Whereas for the junction with ALO barrier we obtain the *normal TMR* which has always been found with ALO barriers (higher resistance in the antiparallel than in the parallel magnetic configuration), in the junctions with STO and CLO barriers the resistance is higher in the parallel than in the antiparallel magnetic configuration. We have coined this new effect "**inverse tunnel magnetoresistance**" [12]. According to equations (1) and (2), the inverse TMR can only be explained if the sign of the spin polarisation is different for both electrodes. As LSMO is polarised positively [10], this means a negative spin polarisation for Co in those tunnel junctions. Consequently, *the spin polarisation of Co is different depending on the insulating barrier*: positive with ALO barriers and negative with STO and CLO barriers. Inserting a STO layer between ALO and LSMO does not change the behaviour compared to an ALO barrier (Fig.1D), which suggests that the positive sign of the Co polarisation is associated with the Co/ALO interface rather than with the propagation through the barrier [13].

The positive polarisation of transition metals when the barrier is ALO has been explained either assuming that only *s*-type electrons, with a positive spin polarisation, can tunnel [8, 9] or, more recently with *ab initio* calculations, due to the selection of the *s*-character electrons by bonding effects at the Co/ALO interface [14]. The band structure of Co roughly resembles that one schematically represented in figure 2. Thus, at the Fermi level the *d* band of Co is strongly negatively polarised. We propose that the negative spin polarisation we observe for Co/STO and Co/CLO interfaces is associated with a preferential tunnelling of *d* electrons for those interfaces. This hypothesis is supported by the bias dependence of the TMR (see figure 5). Application of a certain bias voltage  $V$  shifts the Fermi levels of LSMO and Co in the quantity  $eV$ . By applying positive and negative bias voltages we probe the spin polarisation of Co below and above the Fermi level respectively, reflecting its density of states around the Fermi level. In the case of ALO and ALO/STO barriers (figure 5B) the TMR decreases with increasing positive and negative bias and no special features are observed. This matches with the smooth *s* band of Co around the Fermi level. However, with a Co/STO interface (figure 5A) we observe a strong bias dependence of the TMR, which exhibits a maximum in the TMR at around  $-0.3$  V and the normal TMR is recuperated at positive bias voltages higher than 0.8 V. This reflects the main features of the *d* band of Co below and above the Fermi level supporting the tunnelling of *d* electrons [12].



**Figure 4.** TMR curves recorded at 40 K with a bias voltage of -10 mV for (A) Co/STO/LSMO, (B) Co/CLO/LSMO, (C) Co/ALO/LSMO, (D) Co/ALO/STO/LSMO junctions. At this low voltage we probe the spin polarisation around the Fermi level.



**Figure 5.** Bias dependence of the TMR ratio in (A) Co/STO/LSMO and (B) Co/ALO/STO/LSMO tunnel junctions. The behaviour observed in (A) matches with tunnelling of *d* electrons and in (B) with that of *s* electrons.

The experiments reported in this article (more in detail in references [12] and [13]) as well as those ones recently reported by Sharma et al. [15] on the negative spin polarisation of  $\text{Fe}_{0.8}\text{Ni}_{0.2}/\text{Ta}_2\text{O}_5$  interfaces demonstrate the important role of the electronic structure of the metal/oxide interface in determining the spin polarisation of the tunneling electrons. Even though a general theory predicting the sign of the spin polarisation of transition metal/oxide interfaces does not exist, the *ab initio* calculations by D. Nguyen-Mahn et al. [14] seem to indicate that ***the type of bonding between the metal and the oxide at the interface*** is the crucial parameter controlling the preferential transfer of **s** or **d** electrons and thus the spin polarisation. We note that a negative polarisation exists with barriers of oxides of **d** elements (STO, CLO,  $\text{Ta}_2\text{O}_5$ ) and a positive one when there are only **s** and **p** states (ALO, AlN).

### 3 CONCLUSIONS AND PERSPECTIVES

In this article we have illustrated the important role played by the barrier in the spin polarisation of the tunnelling electrons in magnetic tunnel junctions. The troubling Meservey and Tedrow's experiments of the 70's [7] are now naturally explained as a consequence of the dependence of the sign of the spin polarisation of the transition metals with the type of insulating barrier. This is a forward step in the understanding of the process of spin-polarised tunnelling, which is relevant in artificial magnetic tunnel junctions and, more generally, in the solid (for instance tunnelling through grain boundaries in magnetic polycrystalline materials).

From a technological point of view, an active role of the barrier in the tunnelling process implies another free parameter available in order to enhance and tailor the tunnel magnetoresistance in magnetic tunnel junctions. Although for some of the junctions presented here we obtain magnetoresistance values of 5% at room temperature (the highest up to now with an oxide electrode), this ratio is not currently competitive with magnetic tunnel junctions composed of transition metal electrodes and alumina barriers. This is due to the low magnetic ordering temperature of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (~350 K), which is too close to room temperature. However, we can foresee that the use of other oxides with a strong spin polarisation (close to 1) and much higher ordering temperatures as well as the suitable insulating barrier can boost the magnetoresistance values at room temperature and lead to a second generation of magnetic tunnel junctions. In this sense, materials like  $\text{Sr}_2\text{FeMoO}_6$  are very promising [16] but this is another story.

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