Spin-Polarized Tunneling Spectroscopy in Tunnel Junctions with Half-Metallic Electrodes

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We have studied the magnetoresistance (TMR) of tunnel junctions with electrodes of $La_{2/3}Sr_{1/3}MnO_3$ and we show how the variation of the conductance and TMR with the bias voltage can be exploited to obtain precise information on the spin and energy dependence of the density of states. Our analysis leads to a quantitative description of the band structure of $La_{2/3}Sr_{1/3}MnO_3$ including the energy gap δ between the Fermi level and the bottom of the t_{2g} minority-spin band, in good agreement with data from spin-polarized inverse photoemission experiments. This shows the potential of magnetic tunnel junctions with half-metallic electrodes for spin-resolved spectroscopic studies.

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A magnetic tunnel junction (MTJ) is composed of two conducting ferromagnetic electrodes separated by a thin insulating barrier. Its resistance depends on the relative orientation of the magnetizations of the electrodes, a property which is called TMR (tunneling magnetoresistance). The TMR ratio is defined as

$$\mathrm{TMR} = \frac{R_{\mathrm{AP}} - R_{\mathrm{P}}}{R_{\mathrm{P}}}, \tag{1}$$

where R_{P} and R_{AP} are the junction resistances in the parallel (P) and antiparallel (AP) configuration, respectively. MTJs are extensively investigated given the interest of the TMR in spintronic devices such as MRAM (magnetic random access memory) or magnetic sensors [1], but they also raise interesting fundamental problems. In this Letter, we present an example on exploiting TMR to obtain a precise information on the spin and energy dependence of the density of states (DOS) of a ferromagnetic conductor. This shows the potential of MTJs for spin-resolved spectroscopic studies.

Electron tunneling at different dc bias voltages (V_{dc}) probes different energy ranges of the DOS. This was first used to extract information on the electronic structure of a superconducting electrode by Giaever in 1960 [2]: the presence of a quasiparticle gap in the DOS of the superconductor is reflected in the voltage dependence of the current tunneling into the superconductor, thus allowing a quantitative determination of this gap. More recently, Xiang *et al.* [3] have also performed a numerical analysis of TMR vs V_{dc} curves in transition metal-based MTJs to estimate the spin-dependent DOS of a Co collecting electrode. However, as we will see below, DOS investigations above the Fermi level E_F through bias-dependent TMR studies are better suited to narrow band metallic oxides with rich DOS features.

Also, conceptually, to extract information on the DOS above the Fermi level of a ferromagnetic collecting electrode from the bias dependence of the TMR, it is highly desirable to use a fully spin-polarized emitting electrode, i.e., a half-metal [4]. Supposing, for example, a half-metal (HM) electrode that emits only electrons with majority spin, tunneling will probe separately the majority-spin DOS of the collecting electrode in the P configuration (mainly at an energy eV_{dc} above E_F) and the minority one in the AP configuration.

MTJs in the present work integrate electrodes of the mixed-valence manganite $La_{2/3}Sr_{1/3}MnO_3$(001) (LSMO) which, associated with the insulating oxide $SrTiO_3$(001) (STO), has unambiguously demonstrated its HM character in tunneling experiments with a TMR ratio of 1800% (at $V_{\mathrm{dc}} = 1$ mV) [5] and a spin polarization (SP) of 95%. Working with epitaxial LSMO/STO/LSMO samples grown in the same pulsed laser deposition (PLD) system and the same conditions as in Ref. [5] guarantees a quasi-fully spin-polarized tunneling from the emitting electrode. Moreover, the electronic structure of the LSMO collecting electrode displays sizeable features within the energy range accessible to TMR experiments at different bias voltages. In particular, we will see that the gap δ separating the Fermi level from the bottom of the minority-spin t_{2g} conduction band of LSMO is in the range of a few tenths of eV, i.e., easily accessible through studies of biased MTJs. The LSMO/STO/LSMO MTJs are thus ideally suited for spin-resolved spectroscopic investigations. As quantitatively predicted by Bratkovsky [6], a very large TMR is expected at low bias, and the TMR(V_{dc}) dependence should present a sharp decrease when V_{dc} becomes equal to δ/e due to the opening of new conducting channels in the antiparallel configuration. From the bias dependence of the TMR we will extract the gap δ between the Fermi level (E_F) and the bottom of the minority-spin t_{2g} band, which we find to span 340 ± 20 meV. To confirm our observation, we have performed spin-polarized inverse photoemission (SPIPE) on a LSMO/STO interface to explore the DOS of LSMO above E_F in an alternative spin-resolved technique. Quite good agreement is found between the two values of δ.

The heterostructures in this study were grown by PLD on STO(001) substrates and are fully epitaxial [7]. A detailed structural and spectroscopic characterization of the STO/LSMO(001) interface by high-resolution transmission electron microscopy and electron energy loss spectroscopy (EELS) has already been published [8]. Junctions as small as a few microns square were defined by standard optical lithography [5]. Since the polarization at the interface is the relevant spin polarization in tunneling measurements [9], SPIPE experiments [10] were carried out on an epitaxial LSMO film capped by a thin (0.8 nm) layer of STO. The small probe depth of this technique (~ 10 Å) allows one to probe the unoccupied part of the manganite DOS at the interface with STO. Furthermore, the STO overlayer acts as a capping layer for LSMO, so that problems arising from surface contamination in SPIPE experiments are reduced with respect to the case of the LSMO free surface [11].

We present in Fig. 1 the bias dependence of TMR for a $2 \times 6\ \mu\text{m}^2$ LSMO/STO/LSMO magnetic tunnel junction measured at $T = 4$ K. Three different regimes can be distinguished. At low bias, the TMR amplitude drops rapidly with bias before leveling off at about ± 120 mV. For clarity, the data have been normalized to the 350% value found at $V_{\text{dc}} = -10$ mV. In an intermediate bias range, $120\ \text{mV} \leq |V_{\text{dc}}| \leq 340$ mV, the TMR decreases only very slowly. Finally, in the high bias regime for $|V_{\text{dc}}| \geq 0.34$ V, the TMR decreases rapidly again. The small asymmetry between negative and positive bias, especially noticeable in this high bias regime, probably reflects a slight difference in the chemical structure of the upper and lower LSMO/STO interfaces in our junctions as observed by EELS [12].

The drop in TMR observed at low bias at $T = 4$ K is associated with a zero-bias conductance anomaly [13–15] that also occurs for $|V_{\text{dc}}| \leq 120$ mV, as illustrated in Fig. 2. Both the conductance anomaly and the drop of TMR at low bias are what is expected [14] from spin wave excitations induced by the tunneling electrons at the LSMO/STO interface. As expected for spin wave excitations, the zero-bias anomaly progressively disappears as temperature increases; see Fig. 2. A more detailed report on this zero-bias anomaly will be reported elsewhere. We thus conclude that this low bias regime, involving a change of TMR with bias predominantly due to spin wave excitations, does not describe DOS effects in our case. On the other hand, these variations clearly saturate at a bias of about 120 mV, independently of the temperature as can be seen, for example, in the inset of Fig. 2, which shows the derivative of the conductance as a function of the bias at several temperatures.

As shown in Fig. 1, the TMR decreases slowly as a function of bias in the intermediate regime, $120\ \text{mV} \leq |V_{\text{dc}}| \leq 340$ mV. The inset of Fig. 1 confirms the fairly constant evolution of the spin asymmetry Δ_{spin} [defined as $\Delta_{\text{spin}} = (I_{\text{P}} - I_{\text{AP}})/(I_{\text{P}} + I_{\text{AP}}) = \text{P}^2$] in this bias range. This intermediate regime of slow variation is followed by a much more rapid decrease of the TMR beyond an inflection point at $|V_{\text{dc}}| = 0.34$ V. Looking separately at the conductances in the P and AP states in Fig. 3(a), we see that the conductance in the P state, $(dI/dV)_{\text{P}}$, which reflects the tunneling between the majority-spin states of the two electrodes, increases smoothly within the bias range $120\ \text{mV} \leq |V_{\text{dc}}| \leq 500$ mV. In contrast, the conductance in the AP configuration, $(dI/dV)_{\text{AP}}$, which reflects the tunneling from majority-spin states in the emitting electrode to the minority-spin band in the collecting one, shows an upturn around $|V_{\text{dc}}| = 0.34$ V. This change of behavior appears even more clearly in the derivative of the conductance in the AP state [see Fig. 3(b)]. This value of $|V_{\text{dc}}| = 340$ mV has been corroborated for both interfaces of several MTJs to within an error of 40 meV.

The inflection point at 340 mV in the TMR(V_{dc}) curve, together with the slope change in the variation of d^2I/dV^2 with V_{dc} in the AP state, indicates a strong increase of the DOS of the minority-spin subband at about this energy.

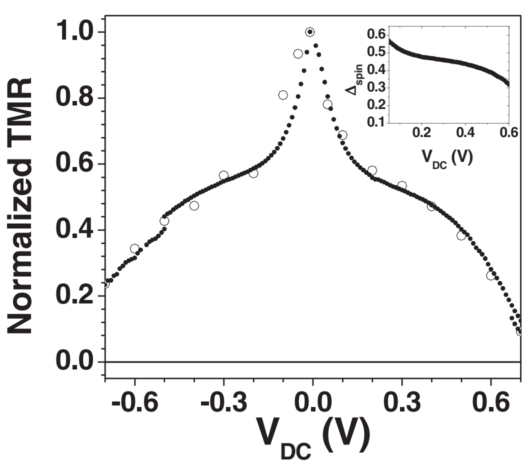

FIG. 1. Bias dependence of TMR (normalized to the value found at $V_{\text{dc}} = -10$ mV) at $T = 4$ K for a LSMO/STO/LSMO junction from R(H) (open circles) and P/AP $I(V_{\text{dc}})$ data (solid circles). Inset: spin asymmetry $\Delta_{\text{spin}} = (I_P - I_{\text{AP}})/(I_{\text{P}} + I_{\text{AP}}) = \text{P}^2$.

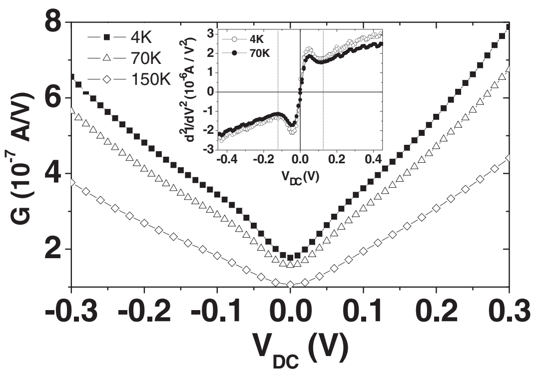

FIG. 2. Temperature evolution of the parallel conductance from 4 K (solid squares) to higher temperatures (open symbols). Inset: bias dependence of the parallel conductance derivative at 4 and 70 K.

Such features are consistent with the band structure of LSMO proposed in Fig. 3(c) with the bottom of a minority t_{2g} subband located at $\delta = (340 \pm 20)$ meV above the Fermi level. Increasing the bias voltage above 340 mV in the AP configuration opens a tunneling channel between the majority-spin band of the emitting electrode and the minority-spin band of the collecting one, which gives rise to the upturn of the AP conductance and to the renewed TMR drop.

Beyond a DOS-only picture, we have to consider that the symmetry matching of the wave functions is also an important factor of the tunneling probability [16,17]. In the P configuration of our junctions, according to the calculation of the complex band structure of STO by Bellini [18], the majority-spin e_g states of the LSMO electrodes are predominantly connected by a slowly decaying MIGS (metal induced gap state) of symmetry Δ_1. On the contrary, for the tunneling between the majority-spin e_g and the minority-spin t_{2g} band in the AP configuration at large bias, such a connection by a slowly decaying MIGS does not exist. Symmetry breaking by disorder (interface roughness, disordered distribution of La and Sr, which are not taken into account in the calculation) can, however, introduce some coupling but less efficiently than with the Δ_1 MIGS of the parallel configuration. This possibly explains that, in spite of the similar amplitude of the DOS in the majority-spin e_g and minority-spin t_{2g} bands [19], the conductance G_{AP} of the AP configuration above 0.34 eV does not rapidly reach G_{P} and remains markedly smaller (60% of G_{P} at 0.5 eV). The relatively gradual increase of G_{AP} above 0.34 eV can also be due to some broadening of the t_{2g} band edge by interface disorder.

Discarding the zero-bias anomaly, the variation of the TMR and the conductance with V_{dc} can actually be compared to the DOS-based predictions of Bratkovsky [6] for HM/I/HM MTJs. As in our interpretation, Bratkovsky predicts an increase of the conductance in the AP state associated with a drop of the TMR above the threshold bias corresponding to the minority gap ($\delta = 0.3$ eV in Ref. [6] and 0.34 eV in our case). Furthermore, above this threshold value, a variation of the conductance in the AP state as $G_{\text{AP}} = (V_{\text{dc}} - \delta)^{5/2}$, corresponding to a variation of the derivative of the conductance as $dG_{\text{AP}}/dV = (V_{\text{dc}} - \delta)^{3/2}$ is expected. As shown in the inset of Fig. 3(a), which presents the experimental variation of the derivative of the conductance in the antiparallel state as a function of $(V - \delta)^{3/2}$ with $\delta = 0.34$ eV, good agreement is found between the theoretical prediction and our experimental results.

We have performed SPIPE experiments on a LSMO layer covered by two unit cells of STO to confirm the experimental value of δ and to see if the band structure is probed in a similar way by spin-dependent tunneling and SPIPE. The SPIPE spectra taken at 100 K in an energy range close to E_F for a LSMO/STO bilayer are presented in Fig. 4. Two distinct line shapes for the majority- (solid dots) and minority-spin channels (open dots) can be clearly distinguished. A sizable signal is visible at E_F in the majority-spin channel [20] but appears only at higher energy for the minority spin. This clearly indicates that the sample is metallic for majority electrons and insulating for minority electrons. Because of both the very low counting rate at E_F and the rescaling procedure to 100% polarization of the incident electron beam [10], the data present a significant scattering. This prevents a precise determination of the spin polarization at E_F, which nevertheless can be estimated to be ~90%. The t_{2g} band responsible for the delayed onset of the minority signal in the SPIPE spectrum thus defines a gap δ between E_F and the low-energy edge of the minority-spin subband. The extent of this minority gap can be estimated from the energy difference between the minority- and majority-channel onsets, as its absolute position on the energy scale is affected by experimental broadening. We obtain a value of 380 ± 50 meV for δ, as

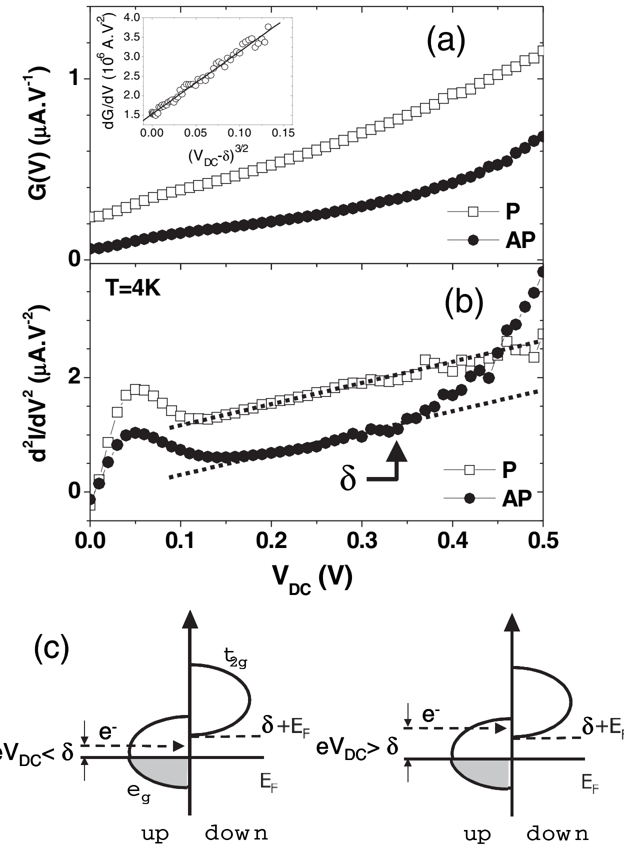

FIG. 3. (a) Bias dependence of the parallel and antiparallel conductances $G_{\text{P}} = (dI/dV)_{\text{P}}$ and $G_{\text{AP}} = (dI/dV)_{\text{AP}}$ at $T = 4$ K. (b) Bias dependence of the conductance derivatives showing the onset of tunneling into the minority-spin t_{2g} subband for the antiparallel conductance at 350 mV. Dotted lines are guides to the eye. The conductance derivative in the AP configuration is plotted vs $(V_{\text{dc}} - \delta)^{3/2}$ in the inset of (a); symbols are experimental data and the line is a linear fit. (c) Schematic representation of tunneling towards a half-metallic collecting electrode for eV_{dc} smaller (left panel) and larger (right panel) than δ.

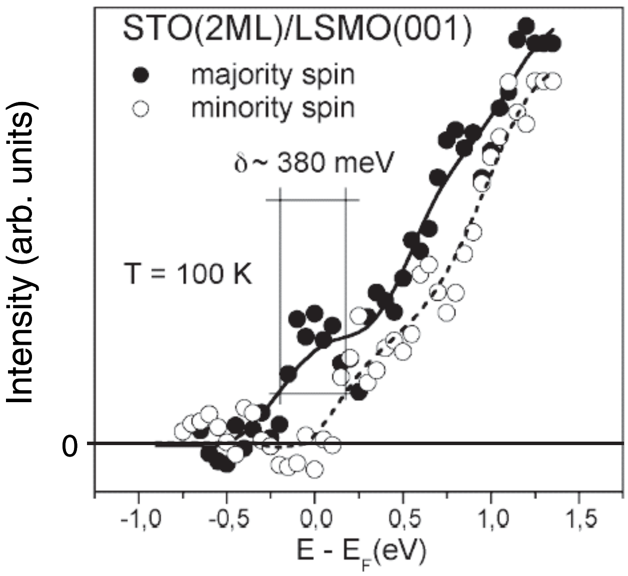

FIG. 4. Spin-resolved spectra taken at 100 K for a STO/LSMO interface. A smoothing of experimental data at 100 K is plotted for the two spin channels.

shown in Fig. 4, where the result of smoothing the experimental data, coherently with our energy resolution, is also plotted. This value is close to what is obtained for a free LSMO surface [11] and in good agreement with what we find from spin-dependent tunneling.

The values of δ derived from theoretical calculations for bulk LSMO range from 0 [21] to 1.6 eV [19], a broad range including our experimental value. We note, however, that the value of δ at the interface with STO can be different from that calculated for bulk LSMO, due to bandwidth contraction and possible Anderson localization effects [22]. The importance of this type of effect could be addressed by systematic studies of different types of interfaces ($LSMO/TiO_2$, $LSMO/LaAlO_3$).

In conclusion, the interpretation of the bias dependence of the conductance and TMR of LSMO/STO/LSMO MTJs provides us with a quantitative spin-resolved information on the band structure at the LSMO/STO interface and, especially, on the gap between the Fermi energy of LSMO and the bottom of the t_{2g} minority-spin band. We have also found that this band structure is quite consistent with spin-polarized inverse photoemission measurements. The agreement between these two types of experiments strengthens the interpretation of the TMR on the basis of the Bratkovsky model of tunneling between two half-metals. It also turns out that a half-metallic emitting electrode confers to a MTJ the potential for spin-resolved spectroscopy capabilities which can be of high interest to probe the electronic structure of some new ferromagnetic materials, such as dilute magnetic semiconductors.

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