Spin-polarized tunneling spectroscopy in tunnel junctions with half-metallic electrodes

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(Dated: March 23, 2022)

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 a 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$_3$ and allows the determination of the gap $\delta$ 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.

PACS numbers: 75.47.Lx, 85.75.-d, 79.60.Jv

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

$$TMR = \frac{R_{AP} - R_P}{R_P}$$  \hspace{1cm} (1)

where $R_P$ and $R_{AP}$ are the junction resistances in the parallel (P) and antiparallel (AP) configuration respectively. The MTJs are extensively investigated for 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 of exploitation of the 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 bias voltages ($V_{DC}$) probes different energy ranges of the DOS and this was first used to extract information on the electronic structure of a superconducting electrode by Giaever in 1960 : the presence of a quasi-particle 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. \cite{2} 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, the relatively narrow energy range ($E_F \pm 0.4$ eV) probed by TMR is not well suited to investigate the DOS of a wide band transition metal. We will see that the technique is more appropriate for narrow band metallic oxides.

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 \cite{3}. Supposing, for example, a half-metal (HM) electrode emitting only electrons of its majority spin direction, the 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.

The MTJs of the present work have both electrodes of the mixed-valence manganite La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) which, associated with the insulating oxide SrTiO$_3$ (STO), has unambiguously demonstrated its HM character in tunneling experiments with a TMR ratio of 1800% (at $V_{DC} = 1$ mV) \cite{4} and a spin polarization (SP) of 95%. Working with LSMO/STO/LSMO samples grown in the same pulsed laser deposition (PLD) system and the same conditions as in Ref. \cite{4} 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 $\delta$ 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 and well accessible in TMR. The LSMO/STO/LSMO MTJs are thus ideally suited for spin-resolved spectroscopic investigations. As quantitatively predicted by Bratkovsky \cite{5}, 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 $\delta/e$ due to the opening of new conducting channels in the antiparallel configuration. From the bias dependence of the TMR we will extract the gap $\delta$ between the Fermi level ($E_F$) and

\[\delta\]
the bottom of the minority spin $t_{2g}$ band, which we find to amount at $340\pm 20$ 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. A quite good agreement is found between the two values of $\delta$. 

The heterostructures of this study have been grown by pulsed laser deposition (PLD) and are fully epitaxial. A detailed structural and spectroscopic characterization of the STO/LSMO(001) interface by High Resolution Transmission Electron Microscopy and Electron Energy Loss Spectroscopy has already been published. Junctions as small as a few microns square were defined by standard optical lithography. Since the polarization at the interface is the relevant spin polarization in tunneling measurements, SPIPE experiments 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 ($\sim 10$ Å) allows 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.

In Fig. 1 we present the bias dependence of the parallel conductance from 4K (closed squares) to higher temperatures (open symbols). Insert: bias dependence of the parallel conductance at 4K and 70K. The drop in TMR observed at low bias at T=4K is associated with a zero-bias conductance anomaly which is occurring also for $|V_{DC}| \leq 120$ mV, as illustrated in Fig. 2. Both the conductance anomaly and the drop of TMR at low bias are what is expected 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 published elsewhere.

Here we conclude that the low bias regime, with a change of TMR with bias predominantly due to spin wave excitations, is not appropriate to study DOS effects. On the other hand, these variations clearly saturate at a bias of about 120mV independently of the temperature as can be seen, for example, in the insert of Fig. 2 which shows the derivative of the conductance as a function of the bias at several temperatures.

As shown in figure the TMR decreases slowly as a function of the bias in the intermediate regime, 120 mV $\leq |V_{DC}| \leq 340$ mV. The insert of figure 1 confirms the fairly constant evolution of the spin asymmetry $\Delta_{spin}$ (defined as $\Delta_{spin} = (I_P - I_AP)/(I_P + I_AP) = P^2$) in this bias range. This intermediate regime of slow variation is followed by a much more rapid decrease of the TMR after an inflection point at $|V_{DC}| = 0.34$ V. Looking separately
at the conductances in the parallel (P) and antiparallel (AP) states on Fig. 2, we see that the conductance in the P state, \( (dI/dV)_P \), which reflects the tunneling between the majority spin states of the two electrodes, increases smoothly within the bias range 120 mV \( \leq |V_{DC}| \leq 500 \) mV. In contrast, the conductance in the AP configuration, \( (dI/dV)_{AP} \), 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 \( |V_{DC}|=0.34 \) V. This change of behavior is even clearer on the derivative of the conductance in the AP state (reported on fig 3c)). This value of \( |V_{DC}|=340 \) mV, has been corroborated for both interfaces of several MTJs to within an error of 40 meV.

The inflection point at 340mV 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 sub-band at about this energy. Such features are consistent with the band structure of LSMO proposed in fig 3c with the bottom of a minority \( t_{2g} \) sub-band 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 to the minority spin band of the collecting one, which gives rise to the upturn of the conductance of the AP state and to the drop of the TMR.

Beyond a picture in terms of the only DOS, we have to consider that the symmetry matching of the wave functions is also an important factor of the tunneling probability \[ \text{and} \text{ in the P configuration of our junctions, according to the calculation of the complex band structure of STO by Bellini \[17\], the majority spin \( \epsilon_g \) states of the LSMO electrodes are predominantly connected by a slowly decaying MIGS (Metal Induced Gap State) of symmetry \( \Delta_1 \). On the contrary, for the tunneling between the majority spin \( \epsilon_g \) 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 the 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 \( \Delta_1 \) MIGS of the parallel configuration. This possibly explains that, in spite of the similar amplitude of the DOS in the majority spin \( \epsilon_g \) and minority spin \( t_{2g} \) bands \[19\], the conductance \( G_{AP} \) of the AP configuration above 0.34 eV does not catch rapidly \( G_P \) 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 \( G_{AP}=(V_{DC}-\delta)^{3/2} \), corresponding to a variation of the derivative of the conductance as \( dG_{AP}/dV=(V_{DC}-\delta)^{3/2} \) is expected. As shown in the insert of Fig 3b, 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, a good agreement is found between the theoretical prediction and our experimental results.

We have performed spin polarized inverse photoemission (SPIPE) experiments onto a LSMO layer covered by two unit cells of STO by using \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) and \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) 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 \( G_{AP}=(V_{DC}-\delta)^{3/2} \), corresponding to a variation of the derivative of the conductance as \( dG_{AP}/dV=(V_{DC}-\delta)^{3/2} \) is expected. As shown in the insert of Fig 3b, 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, a good agreement is found between the theoretical prediction and our experimental results.

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![FIG. 3: (a) Bias dependence of the parallel and antiparallel conductances \( G_P=(dI/dV)_P \) and \( G_{AP}=(dI/dV)_{AP} \) at \( T=4K \). (b) Bias dependence of the conductance derivatives showing the onset of tunneling into the minority-spin \( t_{2g} \) sub-band for the antiparallel conductance at 350mV. Dotted lines are guides to the eye. The conductance derivative in the AP configuration is plotted vs \( (V_{DC}-\delta)^{3/2} \) 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 \( \delta \).]
a similar way by spin-dependent tunneling and SPIPE. The SPIPE spectra taken at 100K 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- (full dots) and minority-spin channels (empty dots) can be clearly distinguished. A sizable signal is visible at \(E_F\) in the majority-spin channel \[21\], but appears only at an higher energy for the minority-spin. This clearly indicates that the sample is metallic for majority electrons and insulating for minority electrons. Due to both the very low counting rate at \(E_F\) and the rescaling procedure to 100% polarization of the incident electron beam \[11\], 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 \(\sim 90\%\). The \(t_{2g}\) band responsible for the delayed onset of the minority signal in the SPIPE spectrum thus defines a gap \(\delta\) between \(E_F\) and the low-energy edge of the minority-spin sub-band. 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 \(380\pm50\) meV for \(\delta\), as 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 \(\delta\) derived from theoretical calculations for bulk LSMO range from 0 \[22\] to 1.6 eV \[13\], a broad range including our experimental value. We however note that the value of \(\delta\) at the interface with STO can be different from that calculated for bulk LSMO, due to band-width 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 for tunneling between two half-metals. It also turns out that a half-metallic emitting electrode confers to MTJ a potential for spin-resolved spectroscopy capability which can be of high interest to probe the electronic structure of some new ferromagnetic materials, diluted magnetic semiconductors for example.

We would like to thank Mike Coey, Wulf Wulfhekel, Daniel Lacour, Patrick LeClair, Walter Temmerman, Grzegorz Banach and Pierre Seneor for stimulating discussions. This work was financed in part by the AMORE European contract (G5RD-CT-2000-00138) and the "Computational Magnetoelectronics" Research and Training Network.

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