Spin-Polarized Inelastic Tunneling through Insulating Barriers

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Spin-conserving hopping transport through chains of localized states has been evidenced by taking benefit of the high degree of spin-polarization of CoFeB-MgO-CoFeB magnetic tunnel junctions. In particular, our data show that relatively thick MgO barriers doped with boron favor the activation of spin-conserving inelastic channels through a chain of three localized states and leading to reduced magnetoresistance effects. We propose an extension of the Glazman-Matveev theory to the case of ferromagnetic reservoirs to account for spin-polarized inelastic tunneling through nonmagnetic localized states embedded in an insulating barrier.

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Magnetic tunnel junctions (MTJs) based on MgO as an insulating barrier sandwiched between two ferromagnetic reservoirs are key elements for the next generation of data storage devices owing to their giant tunneling magnetoresistance (TMR) effect [1–3]. From a fundamental point of view, epitaxial MgO represents a model system to address spin-dependent symmetry filtering effects occurring during the tunneling transfer of carriers [4,5]. In this context, the high degree of spin-polarization of MgO-based MTJs allows to revisit other fundamental questions such as the existence of spin-conserving inelastic tunneling processes and related TMR effects [6–10]. Until now, this mechanism was neglected as conventional ferromagnetic reservoirs are far from fully spin polarized. The essence of this Letter is to demonstrate that (i) spin-conserving inelastic processes through chains of localized states exist and that (ii) they give rise to reduced magnetoresistance effects. To demonstrate this, we have fabricated by sputtering series of boron (B) doped CoFeB-MgO-CoFeB MTJs with different barrier thicknesses. In-depth x-ray photoemission spectroscopy (XPS) was used to analyze the diffusion of boron in MgO as well as its chemical state. Through the analysis of the thermal behavior of both conductance and TMR, we evidence spin-conserving hopping processes through localized states (LS), e.g., played by B sites.

We first proceed to a generalization of the Glazman-Matveev theory for inelastic tunneling transport [11,12] to the case of spin-polarized reservoirs giving a more general description of spin-dependent inelastic tunneling through insulating barriers. A reasonable approach consists in partitioning the total conductivity $\mathcal{G}$ into different varieties ($\mathcal{N}$) of conducting chains containing N localized states assuming spin-conserving hopping processes. This gives $\mathcal{G}^{\sigma\sigma'} = \sum_{\mathcal{N}} \mathcal{G}^{\sigma\sigma'}_{\mathcal{N}} = \frac{e}{\hbar}(f_L - f_R)\sum_{\mathcal{N}} \zeta_{\mathcal{N}} \mathbf{\Gamma}^{\sigma\sigma'}_{\mathcal{N}}$, where f is the Fermi distribution and ζ_N represent the number of accessible chains containing N different sites (σ, $\sigma' = \pm 1$ are spin indices for respective L and R reservoirs) and where $\mathbf{\Gamma}^{\sigma\sigma'}_{\mathcal{N}}$ is the effective coupling strength.

In a series resistor picture, the latter quantity can be expressed as $[\Gamma^{\sigma\sigma'}_{\mathcal{N}}]^{-1} = [\Gamma^{\sigma}_{L} \exp\{-2\kappa z_1\}]^{-1} + \sum_{i<N}[\gamma \times \exp\{-2\kappa(z_{i+1} - z_i)\}]^{-1} + [\Gamma^{\sigma'}_{R} \exp\{-2\kappa(d - z_N)\}]^{-1}$, where z_i are the consecutive LS positions (see Fig. 1). This includes the spin-polarized elastic coupling with the contacts at both ends (Γ^{σ}_{L}, $\Gamma^{\sigma'}_{R}$) and the successive hopping processes in the barrier through the LS positions z_i by the characteristic inelastic interaction with phonons γ ($\propto k_B T$). For a given variety $\mathcal{N}$, the optimal path is the one that minimizes the total resistance giving *in fine*:

$$\mathbf{\Gamma}^{\sigma\sigma'}_{\mathcal{N}} = \frac{1}{N+1}[\Gamma^{\sigma}_{L}\Gamma^{\sigma'}_{R}\gamma^{N-1}]^{1/N+1} \exp\left\{-\frac{2\kappa d}{N+1}\right\}, \quad (1)$$

where κ^{-1} is the characteristic localization length and d is the total barrier thickness. Correspondingly, the configuration number $\zeta_{\mathcal{N}}$ scales like $\zeta_{\mathcal{N}} \propto [g^{\mathrm{LS}} k_B T]^N \kappa^{-2N+1} d^{N-1}$ per unit area where g^{LS} is the density of states of LS. To extend this model to spin-polarized systems, $P_{L(R)}$ are defined as $P_{L(R)} = \frac{\Gamma^{\uparrow}_{L(R)} - \Gamma^{\downarrow}_{L(R)}}{\Gamma^{\uparrow}_{L(R)} + \Gamma^{\downarrow}_{L(R)}}$. To simplify, we assume an

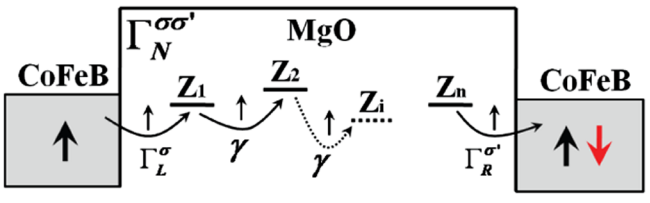

FIG. 1 (color online). Sketch showing the principle of spin-polarized inelastic transport processes involving the effective coupling strength $\mathbf{\Gamma}^{\sigma\sigma'}_{\mathcal{N}}$. γ represents the characteristic inelastic interaction with phonons.

identical spin polarization $P = \sqrt{P_L P_R}$ for both contacts. The resulting spin-selective conductivity $\mathcal{G}_{\mathcal{N}}$ in the parallel (PA) and antiparallel (AP) magnetic arrangement gives ${\mathcal{G}_{\mathcal{N}}}^{PA} \propto (k_B T)^{\nu_N} \times [(1+P)^{2\beta_N} + (1-P)^{2\beta_N}] \times \exp\{-\frac{2\kappa d}{N+1}\}$ and ${\mathcal{G}_{\mathcal{N}}}^{AP} \propto (k_B T)^{\nu_N} \times [2(1-P^2)^{\beta_N}] \times \exp\{-\frac{2\kappa d}{N+1}\}$ where $\nu_N = N - 2/(N+1)$ and $\beta_N = 1/(N+1)$ are two characteristic exponents. We recover a thermal power law T^{ν_N} identical to the one expected for unpolarized systems [12]. Although no thermal dependence is normally found for elastic tunneling processes ($\nu_N = 0$ for $N = 0$ and $N = 1$), the tunnel transmission is refined into $\mathcal{G}_{0(1)}(T) \propto \frac{CT}{\sinh(CT)}$ taking into account thermal electrons in the electrodes [13] where $C \propto 10^{-2} d/\sqrt{\phi}$, with the barrier width (d) in nm and the barrier height (Φ) in eV (hereafter we take 3.3 eV for Φ [14]).

The TMR assigned to a variety $\mathcal{N}$ follows:

$$\mathrm{TMR}(\mathcal{N}) = \frac{(1+P)^{2\beta_N} + (1-P)^{2\beta_N}}{2(1-P^2)^{\beta_N}} - 1. \qquad (2)$$

We recover the results of Bratkovsky [15] giving the same TMR(1) for resonant tunneling ($N = 1$) through an impurity band and established within a free electron model as well as the standard Jullière model [16] for direct tunneling in the limit $\beta_N = 1$. Our model extends the expression of TMR($\mathcal{N}$) to the case $N > 1$. The interesting result is that even with spin conserving channels, the TMR gradually decreases when N is incremented. When different varieties of N-LS conduction channels merge, the effective TMR $= \sum_{\mathcal{N}} \mathcal{W}_{\mathcal{N}}(T) \times \mathrm{TMR}(\mathcal{N})$ is the sum of each magnetoresistance weighted by their fractional contribution $\mathcal{W}_{\mathcal{N}} = \frac{{\mathcal{G}_{\mathcal{N}}}^{AP}}{\mathcal{G}^{AP}}$ to the conduction in the AP state [17] as extracted from their specific thermal fingerprint. In our fitting procedures, the spin-wave excitations within the ferromagnetic reservoirs leading to a natural loss of polarization are considered by taking $P = P_0 \times (1 - \alpha T^{3/2})$ (Bloch's law [8]), where α is a material dependent parameter related to the interfacial Curie temperature and P_0 is the full effective spin polarization at 0 K. In the following, a large polarization $P_0 = 0.87$ was considered for MgO. This choice extracted from our fit procedure will be discussed further.

MTJs were grown using a magnetron sputtering system. The layers in the stack are (in nm): Si_{02}/Ta (5)/Ru(15)/$Ir_{0.2}Mn_{0.8}$(8)/$Co_{0.7}Fe_{0.3}$(5)/Ru(0.8)/$Co_{0.4}Fe_{0.4}B_{0.2}$(5)/Mg(0.4)/MgO(t)/$Co_{0.4}Fe_{0.4}B_{0.2}$(5)/Ta (5)/Ru(10). The detailed growth conditions can be found elsewhere [18]. Three wafers with different MgO thicknesses were prepared (sample A: 2.5 nm, B: 3.0 nm and C: 4.0 nm). The wafers were then patterned following a standard optical lithography process to define micron-sized MTJs. In order to promote the crystallization of CoFeB electrodes [19], the junctions were then annealed at 450 °C during 30 min under a field of 200 Oe. This procedure is known to favor a consequent B diffusion throughout the structure and, in particular, in MgO [20,21]. A sample identical to A but without the top electrode (replaced by a 10 nm Ta capping layer) was prepared for the in-depth XPS analysis. After annealing, the sample was etched by Ar^+ ions with a rate of about 0.4–0.5 nm/min to remove the Ta layer and carry out the in-depth analysis. In Fig. 2, we show typical XPS B1s spectra acquired in the MgO layer. Al Kα (1486.6 eV) was used as the x-ray source. Two components in the B1s spectra can be distinguished. The one at low binding energies (BE) of about 188 eV is assigned to metallic B from the bottom CoFeB electrode. The other peak at 193 eV can be assigned to oxidized B in the MgO layer induced by B diffusion from the CoFeB electrode. The position is found at 1 eV higher than the peak of oxidized B in a CoFeB reference sample oxidized by oxygen plasma (marked with an arrow). We then conclude that in our samples, boron diffused in MgO has a higher oxidation state, close to B^{3+}, than that found in the CoFeB oxidized electrode which results in a nonmagnetic electronic state [22]. Moreover, this confirms the claims of Read *et al.* [21] that an intermediate oxide MgB_xO_y could form after the annealing procedure. In our case, the B:Mg ratio in the oxide barrier can be estimated to 0.23 ± 0.03 after annealing.

We now focus on transport properties. First, we note that the resistance-area (RA) products of junctions A, B, and C acquired at low temperature and low bias voltage in the parallel state of 0.1 MΩ μm^2 (A), 3 MΩ μm^2 (B, not shown), and 1.5 GΩ μm^2 (C), match quite fairly with data of Yuasa *et al.* [2], giving an evolution law of the form RA $\propto \exp(6.41d)$. We can thus extract a characteristic decay rate (imaginary wave vector) κ of 6.41 nm^{-1} considering solely resonant elastic tunneling ($N = 1$) at low T. Figure 3 displays the TMR curves of MTJs with thinner (sample A) and thicker (sample C) MgO barriers acquired under a bias of 1 mV at 3 K and room temperature (RT). For sample A, the TMR drops from 136% at 3 K to 79% at RT. The decrease of TMR is stronger for sample C from 108% down to 10.8% in the same temperature range. Sample B displays an intermediate behavior (123% at 3 K

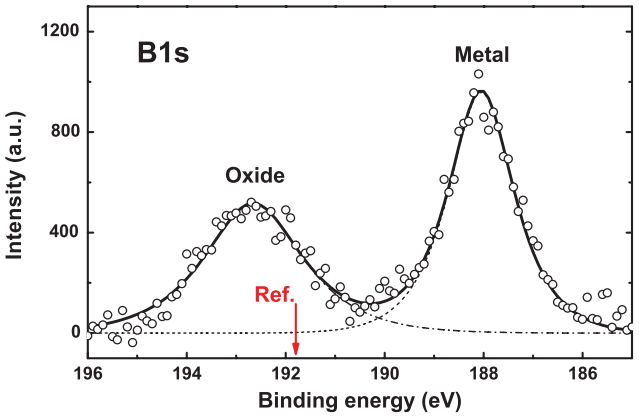

FIG. 2 (color online). Typical B1s spectrum obtained on the MgO layer. The position of boron oxide from a reference oxidized CoFeB sample is indicated by an arrow.

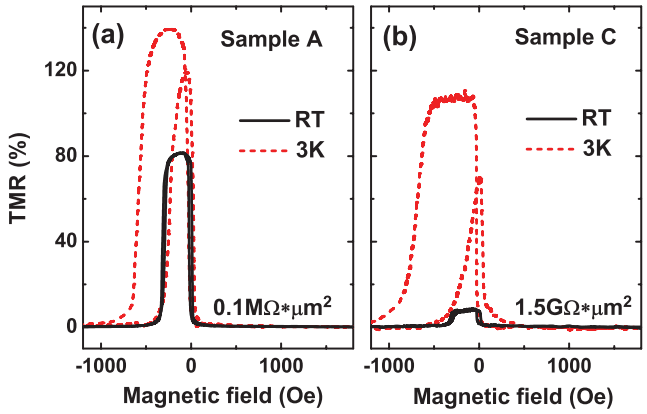

FIG. 3 (color online). TMR curves of (a) sample A (MgO 2.5 nm) and (b) sample C (MgO 4 nm) measured at RT (black solid line) and 3 K (red dotted line).

down to 40% at RT) and has not been shown for clarity reasons. This rapid drop of TMR with temperature can be ascribed to a crossover from elastic to inelastic processes through LS in MgO. As all samples acquire their specific thermal dependence of TMR after the annealing procedure, such LS reasonably arise from ionized boron species as supported by the large concentration of B found in MgO and as evidenced by recent electron energy loss spectroscopy (EELS) analysis [23].

The thermal dependence of TMR is analyzed within our generalized Glazman-Matveev model. In Figs. 4(a) and 4(b), we have plotted the AP conductance of samples A and C from which it is possible to extract the different N-LS conduction chains from their specific T^{ν_N} signature. For sample A, G^{AP} can be fitted with $A + BT^{1.33}$, which means that the conduction contains no more than 2-LS chains. However, for sample B (not shown) and C, G^{AP} needs to be fitted with a function of the form $A + BT^{1.33} + CT^{2.5}$ including the contribution of 3-LS chains. From the fit of G^{AP}, the respective 2-LS and 3-LS chains conductivities can be determined as well as their weighted contributions, $\mathcal{W}_{\mathcal{N}}$. These are reported on Fig. 4(c) and 4(d) for samples A and C. An increase of 2-LS and 3-LS contributions is clearly found when (i) the MgO barrier is made thicker and (ii) when the temperature rises. For sample C, the 3-LS chain dominates the tunneling conduction at RT. Finally, the TMR temperature dependence is fitted by the sum of TMR($\mathcal{N}$) weighted by their fractional contribution $\mathcal{W}_{\mathcal{N}}$ as shown in Fig. 5(a). The general trend is that thick barriers favor conduction channels through large N-LS chains giving a smaller TMR. The 3-LS tunneling channel is responsible for the large drop of TMR on temperature for sample C.

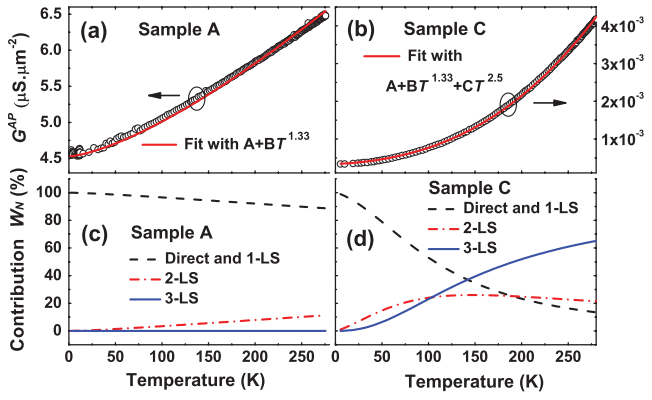

FIG. 4 (color online). Temperature dependence of the tunnel conductance in AP state for (a) sample A and (b) sample C. Relative contribution $\mathcal{W}_N$ of the different N-LS chains to the AP conductance for (c) sample A and (d) sample C.

A major point of our argument is the analysis of $\Delta G(T) = G^{PA}(T) - G^{AP}(T)$ [Fig. 5(b)]. As expected for standard tunnel junctions, for samples A and B (not shown), ΔG strongly decreases with temperature. This is expected from depolarization processes in the electrodes characterized by the aforementioned α parameter. Quite astonishingly, sample C shows an increase of ΔG by 22% from 3.6×10^{-4} $\mu S \cdot \mu m^{-2}$ at 3 K to 4.4×10^{-4} $\mu S \cdot \mu m^{-2}$ at $T_m \approx 220$ K before decreasing up to RT. This increase cannot be explained by unpolarized inelastic processes that cancel out in ΔG [8]. It clearly supports our assumption of thermally activated spin-dependent inelastic channels. A nonzero TMR($\mathcal{N}$) assigned to a thermally activated inelastic process is expected to lead to a significant increase of ΔG with T according to $\Delta G(T) \propto \mathrm{TMR}(\mathcal{N}) \times T^{\nu_N}$. If a single N-LS variety contributes, the specific temperature T_m for which ΔG is maximum

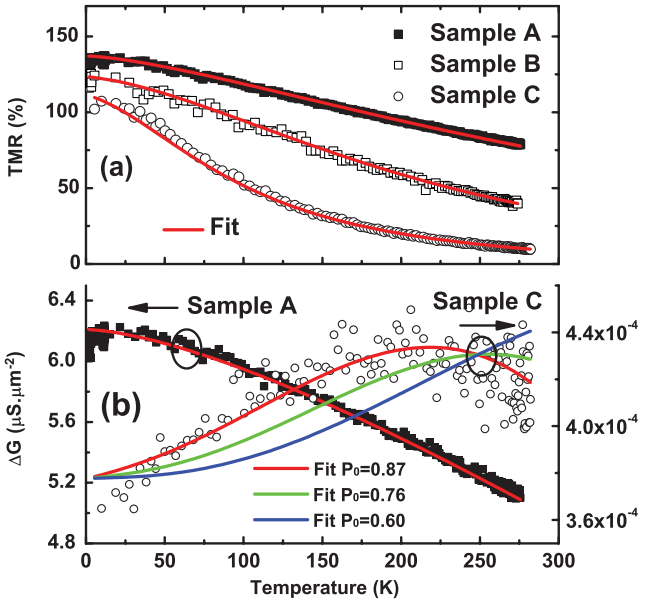

FIG. 5 (color online). (a) TMR vs T of samples A (black square), B (open square), and C (open dot). (b) ΔG vs T for sample A (black square) and C (open dot). In each case, the fits were realized with $P_0 = 0.87$, $C = 2 \times 10^{-3}$ (A), 2.5×10^{-3} (B), 3.5×10^{-3} (C) and $\alpha = 2 \times 10^{-5}$ (A), 3.3×10^{-5} (B), and 6.9×10^{-5} (C). For ΔG of sample C, we also show two additional fits with $P_0 = 0.76$ and 0.60 for comparison.

gives out the α parameter $\alpha = T_m^{-3/2}/(1 + 3\nu_N^{-1})$ [24]. A greater ν_N assigned to a larger number of LS pushes this maximum towards higher T_m. In the same way, a higher value of α moves the maximum to a lower T_m as it seems to be the case for a (Zn,Cr)Te magnetic electrode [25]. The latter single variety expression gives roughly $\alpha \approx 1.4 \times 10^{-4}$ for sample C. However, α is found $(6.9 \pm 0.1) \times 10^{-5}$ following our fitting procedure involving several varieties $\mathcal{N}$. We observe that the value of α appears to be thickness-dependent: $\alpha = 2.0 \pm 0.1 \times 10^{-5}$ [26] and $3.3 \pm 0.1 \times 10^{-5}$ for sample A and B, respectively. Generally, contamination at interfaces leads to a larger α that strongly reduces the polarization with temperature [8].

A critical point of the current work is the value of P_0 chosen throughout our fitting procedure. P_0 is generally deduced from the TMR value from the Jullière formula regardless of possible resonant inelastic processes. Figure 5(b) shows the fit of $\Delta G(T)$ for sample C obtained with different values of P_0. The best result is obtained for $P_0 = 0.87$ corresponding to purely elastic resonant tunneling ($N = 1$) and justifies our previous choice. Nonetheless, the spin-filtering effects acting on carriers tunneling through crystalline MgO [4,5] are clearly not addressed in our generalized Glazman-Matveev model. It is still possible to extend our model by considering two different decay rates, k_{Δ_1} and k_{Δ_5}, for majority and minority spin channels in the minimization procedure of $[\Gamma_{\mathcal{N}}^{\sigma\sigma'}]^{-1}$ at both ends accounting for respective Δ_1 and Δ_5 symmetries. Our conclusion is that, within such an extended model (not presented here), one can fit ΔG by lowering P_0 down to about 0.6 [27].

To conclude, the TMR temperature dependence of MTJs with MgO:B barrier has been investigated. The large drop of TMR with temperature as well as the increase of ΔG for the 4 nm MgO sample was shown to be correlated to the thermal activation of spin conserving inelastic tunneling channels predominant for thicker barriers. The extension of Glazman-Matveev theory adapted to spin-polarized reservoirs was successfully used to fit both conductance and TMR vs T. More widely, our model of spin-polarized inelastic conduction could be helpful to describe spin transport through organic junctions.

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