

THE POSSIBILITY OF A VERY LARGE MAGNETORESISTANCE IN HALF-METALLIC OXIDE SYSTEMS

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The tunnel magnetoresistance (TMR) is analyzed for ferromagnet-insulator-ferromagnet junctions, including novel half-metallic systems with 100% spin polarization. Direct tunneling is compared with impurity-assisted and resonant TMR. Direct tunneling in iron group systems leads to about a 20% change in resistance, as observed experimentally. Impurity-assisted tunneling decreases the TMR down to 4% with Fe-based electrodes. A resonant tunnel diode structure would give a TMR of about 8%. The model applies qualitatively to half-metallics, where the change in resistance in the absence of spin-flips may be arbitrarily large and even in the case of imperfect magnetic configurations the resistance change can be several thousand percent. The examples of half-metallic ferromagnetic systems are $\text{CrO}_2/\text{TiO}_2$ and $\text{CrO}_2/\text{RuO}_2$, and a discussion of their properties is presented.

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Tunneling of spin-polarized electrons is of fundamental interest and potentially applicable to magnetic sensors and memory devices.[1] In a search of systems with maximal performance it is important to consider the generic properties affecting magnetoresistance and other properties. A standard model for spin tunneling has been formulated by Julliere [2] and further developed by Stearns [3] and Slonczewski.[4] This model is expected to work rather well for iron, cobalt and nickel based metals, according to Refs.[3,5]. However, important points have not been taken into account, such as an impurity scattering and a reduced effective mass of carriers inside the barrier. Both issues have important implications for magnetoresistance and will be considered here, along with proposed novel half-metallic systems which should in principle show the ultimate performance.

We shall describe electrons in ferromagnet-insulating barrier-ferromagnet (f-b-f) systems by the Schrödinger equation [4] $(\mathcal{H}_0 - \hbar \cdot \hat{\sigma})\psi = E\psi$, where $\mathcal{H}_0 = -(\hbar^2/2m_\alpha)\nabla^2 + U_\alpha$ is the single-particle Hamiltonian with $U(r)$ the potential energy, $\hbar(r)$ the exchange energy ($\hbar(r) = 0$ inside the barrier), $\hat{\sigma}$ stands for the Pauli matrices; index $\alpha=1, 2$, and 3 marks the quantities for left terminal, barrier, and right terminal, respectively. Tunnel current in a standard formalism is given by some integral of a transmission coefficient $T = \sum_{\sigma\sigma'} T_{\sigma\sigma'}$, which has a particularly simple form for a square barrier and *collinear* [parallel (P) or antiparallel (AP)] moments on electrodes.[6] Here σ (σ') stands for the spin index of the initial (final) state.

Accounting for the misalignment of spin moments in ferromagnetic terminals (given by mutual angle θ), we obtain for the conductance of a square barrier a corrected Slonczewski's formula[4] in leading order in $\exp(-\kappa w)$, assuming for a moment equivalent electrodes,

$$G = G_{bf}(1 + P_b^2 \cos(\theta)), \quad (1)$$

$$G_{\text{fbt}} = \frac{e^2}{\pi \hbar} \frac{\kappa}{\pi w} \left[\frac{\kappa(k_{\uparrow} + k_{\downarrow})(\kappa^2 + m_2^2 k_{\uparrow} k_{\downarrow})}{(\kappa^2 + m_2^2 k_{\uparrow}^2)(\kappa^2 + m_2^2 k_{\downarrow}^2)} \right]^2 e^{-2\kappa w},$$

$$P_{\text{fb}} = \frac{k_{\uparrow} - k_{\downarrow}}{k_{\uparrow} + k_{\downarrow}} \frac{\kappa^2 - m_2^2 k_{\uparrow} k_{\downarrow}}{\kappa^2 + m_2^2 k_{\uparrow} k_{\downarrow}},$$

where G is the surface conductance per unit area, P_{fb} is the effective polarization of the electrode, $\kappa = [2m_2(U_0 - E)/\hbar^2]^{1/2}$, and U_0 is the top of the barrier¹⁾. By taking a typical value of $G = 4 - 5 \Omega^{-1} \text{cm}^{-2}$, Ref. [5], $k_{\uparrow} = 1.09 \text{\AA}^{-1}$, $k_{\downarrow} = 0.42 \text{\AA}^{-1}$, $m_1 \approx 1$ (for itinerant d electrons in Fe, Ref. [3]) and a typical barrier height for Al_2O_3 (measured from the Fermi level μ) $\phi = U_0 - \mu = 3 \text{eV}$, and the thickness $w \approx 20 \text{\AA}$, one arrives at the following estimate for the effective mass in the barrier: $m_2 \approx 0.4$ ²⁾. A reduced band mass for the oxide barrier is a natural consequence of the large width of the s - p bands in the insulator. These values give $P_{\text{Fe}} = 0.28$, in fair correspondence with the experimental value of 0.4 [1,5] ($P_{\text{Fe}} < 0$ if the mass correction is neglected). Present formalism and parameters are sufficient for present qualitative and even semi-quantitative analysis.

We define the magnetoresistance as the relative change in contact conductance with respect to the change of mutual orientation of spins from parallel (G^P for $\theta = 0$) to antiparallel (G^{AP} for $\theta = 180^\circ$) as

$$MR = (G^P - G^{AP})/G^{AP} = 2PP'/(1 - PP'), \quad (2)$$

which differs by the minus sign in the denominator from the standard definition [2,1].

The most striking feature of Eqs. (3),(4) is that MR tends to infinity for vanishing k_{\downarrow} , i.e. when the electrodes are made of a 100% spin-polarized material ($P = P' = 1$) because of a gap in the density of states for minority carriers up to their conduction band minimum $E_{CB\downarrow}$. Such a half-metallic behavior is rare, but some materials possess this amazing property, most interestingly the oxides CrO_2 and Fe_3O_4 [7]. These oxides are most interesting for future applications in combination with matching materials, as we shall illustrate below.

A more accurate analysis of the $I - V$ curve requires a numerical evaluation for arbitrary biases and inclusion of image forces[6] (Fig.1). The top panel in Fig.1 shows $I - V$ curves for an iron-based fbf junction with the above-mentioned parameters. The value of TMR is about 20% at low biases and steadily decreases with increased bias. In a half-metallic case ($k_{\downarrow} = 0$, Fig.1, middle panel, where a threshold $eV_c = E_{CB\downarrow} - \mu = 0.3 \text{eV}$ has been assumed) we obtain zero conductance G^{AP} in the AP configuration at biases lower than V_c . It is easy to see that above this threshold, $G^{AP} \propto (V - V_c)^{5/2}$ at temperatures much smaller than eV_c . Thus, for $|V| < V_c$ in the AP geometry one has $MR = \infty$. In practice there are several effects that reduce this MR to some finite value, notably an imperfect AP alignment of moments in the electrodes. However, from Fig.2 we see that even at 20° deviation from the AP configuration, the value of MR exceeds 3000% in the interval $|V| < V_c$, and this is indeed a very large value.

¹⁾For unlike electrodes G_{fbf} is to be replaced by $G_{fbf'}$ and $P_{fb}^2 \rightarrow P_{fb}P_{f'b}$ by substitutions $k_{\uparrow} \rightarrow k'_{\uparrow}$ and $k_{\downarrow} \rightarrow k'_{\downarrow}$. For the case of different masses $k_{\sigma} \rightarrow k_{\sigma}/m_{\sigma}$.

²⁾ Even smaller $m_2 = 0.2$ has been used by Q.Q. Shu and W.G. Ma for Al- Al_2O_3 -metal junctions [Appl. Phys. Lett. 61, 2542 (1992)].

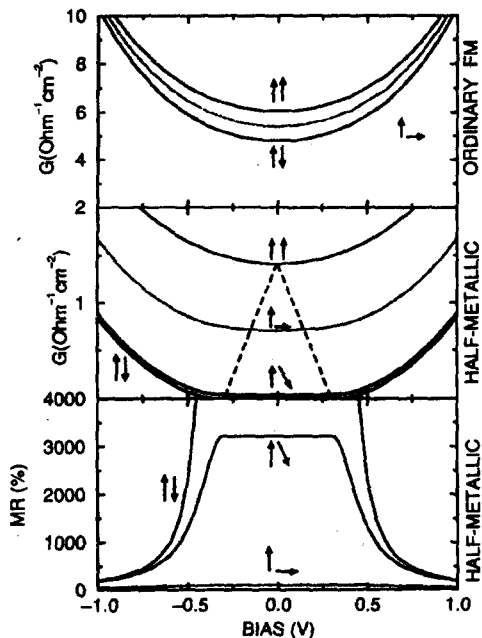


Fig.1. Conductance and magnetoresistance of tunnel junctions versus bias at 300K with multiple image potential and exact transmission coefficients. Top panel: conventional (Fe-based) tunnel junction (for parameters see text). Middle panel: half-metallic electrodes. Bottom panel: magnetoresistance for the half-metallic electrodes. Dashed line shows schematically a region where a gap in the minority spin states is controlling the transport. Imperfect antiparallel alignment ($\theta = 160^\circ$) is marked $\nearrow \searrow$.

An important aspect of spin-tunneling is the effect of tunneling through the defect states in the (amorphous) oxide barrier. Since the contacts under consideration are typically short, their $I-V$ curve and MR should be very sensitive to defect resonant states in the barrier with energies close to the chemical potential, forming "channels" with the nearly periodic positions of impurities[8]. Generally, channels with one impurity (most likely to dominate in thin barriers) would result in a monotonous behavior of the $I-V$ curve, whereas channels with two or more impurities would produce intervals with negative differential conductance, as shown by Larkin and Matveev [9]. We shall estimate the spin conductance in this model. Impurity-assisted spin tunneling at zero temperature (the general case would require integration with the Fermi factors) can be written in the form [9]

$$G_\sigma = \frac{2e^2}{\pi\hbar} \sum_i \frac{\Gamma_{l\sigma}\Gamma_{r\sigma}}{(E_i - \mu)^2 + \Gamma^2}, \quad (3)$$

where $\Gamma_\sigma = \Gamma_{l\sigma} + \Gamma_{r\sigma}$ is the total width of a resonance given by a sum of the partial widths Γ_l (Γ_r) corresponding to electron tunneling from the impurity state at the energy E_i to the left (right) terminal. We have for a rectangular barrier:

$$\Gamma_{l\sigma} = \epsilon_i \frac{2m_2 k_\sigma}{\kappa^2 + m_2^2 k_\sigma^2} \frac{e^{-\kappa(w+2z_i)}}{\kappa(\frac{1}{2}w + z_i)}, \quad (4)$$

where z_i is the coordinate of the impurity with respect to the center of the barrier (Γ_r is obtained from the previous expression by substituting $z_i \rightarrow -z_i$ and accounting for the final spin state), $\epsilon_i = \hbar^2 \kappa^2 / (2m_2)$. The conductance has a sharp maximum ($= e^2 / (2\pi\hbar)$) when $\mu = E_i$ and $\Gamma_l = \Gamma_r$, i.e. for the symmetric position of the impurity in the barrier. Following Larkin and Matveev, we assume that we have ν defect levels in a unit volume and unit energy interval in a barrier.

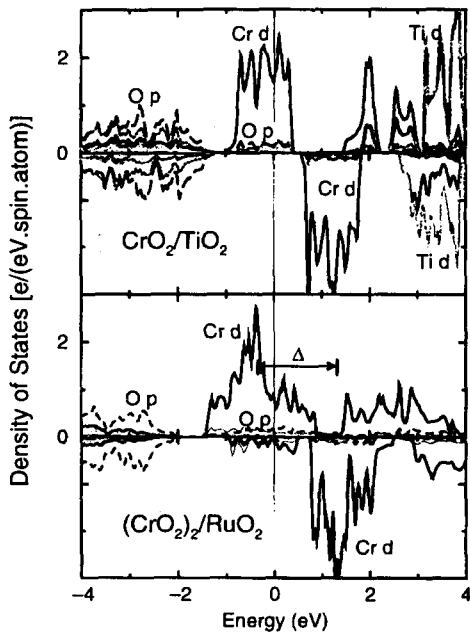


Fig. 2. Density of states of $\text{CrO}_2/\text{TiO}_2$ (top panel) and $(\text{CrO}_2)_2/\text{RuO}_2$ (bottom panel) half-metallic multilayers. Δ indicates a spin-splitting of the Cr d -band near E_F (schematic)

Averaging over impurities we obtain the following formula (which is similar to (2)) for impurity-assisted conductance in leading order in $\exp(-\kappa w)$:

$$MR_1 = 2\Pi_{fb} \Pi_{f'b}/(1 - \Pi_{fb} \Pi_{f'b}), \quad (5)$$

where $\Pi_{fb} = (r_{\uparrow} - r_{\downarrow})/(r_{\uparrow} + r_{\downarrow})$, $r_{\sigma} = [m_2 \kappa k_{\sigma}/(\kappa^2 + m_2^2 k_{\sigma}^2)]^{1/2}$. One may call Π_{fb} a "polarization" of the impurity channel. The impurity-assisted conductance per unit area is approximately $g_{fbf} = e^2/\pi \hbar N_1$, where $N_1 = \pi^2 \nu \Gamma_1/\kappa$ is the effective number of one-impurity channels per unit area, $\Gamma_1 = \epsilon_i (r_{\uparrow} + r_{\downarrow})^2 \exp(-\kappa w)/\kappa w$.

Comparing direct (3) and impurity-assisted contributions to conductance, we see that the latter dominates when the impurity density of states $\nu \sim (\kappa/\pi)^3 \epsilon_i^{-1} \exp(-\kappa w)$, and in our example a crossover takes place at $\nu \sim 10^{-7} \text{ \AA}^{-3} \cdot \text{eV}^{-1}$. When resonant transmission dominates, the magnetoresistance will be just 4% in the case of Fe. With standard ferromagnetic electrodes, the conductance is enhanced but the magnetoresistance is reduced in comparison with the clean limit. With further increase of the defect density and/or the barrier width, the channels with two- and more impurities will become more effective, as has been mentioned above [9].

It is interesting to consider a resonant tunnel diode (RTD) type of structure with e.g. an extra thin non-magnetic layer placed between two oxide barrier layers producing a resonant level at some energy E_r . The only difference from the previous discussion is an effectively 1D character of the transport in RTD in comparison with 3D impurity-assisted transport. However, all basic expressions remain practically the same, and the estimated magnetoresistance is:

$$MR_{RTD} = [(r_{\uparrow}^2 - r_{\downarrow}^2)/(2r_{\uparrow}r_{\downarrow})]^2, \quad (6)$$

which is 8% for Fe electrodes. We see that the presence of random impurity levels or a single resonant level reduces the value of the magnetoresistance as compared with direct tunneling.

It is very important that in the case of half-metallics $r_1 = 0$, $\Pi_{fb} = 1$ and even with an imperfect barrier magnetoresistance can, at least in principle, reach any value, limited by only spin-flip processes in the barrier/interface and/or misalignment of moments in the half-metallic ferromagnetic electrodes. This should combine a very large magnetoresistance with enhanced conductance in tunnel MR junctions. Comparing with conventional systems (e.g. FeNi electrodes), we see that resonant tunneling significantly reduces the tunnel MR by itself, so the possibility of improving the conductance and still having a very large magnetoresistance resides primarily with half-metallics.

We shall finish with a couple of examples of novel systems with half-metallic behavior, $\text{CrO}_2/\text{TiO}_2$ and $\text{CrO}_2/\text{RuO}_2$ (Fig.2). They are based on half-metallic CrO_2 and all species have the rutile structure type with almost perfect lattice matching, which should yield a good interface and should help in keeping the system at the desired stoichiometry. TiO_2 and RuO_2 are used as the barrier/spacer oxides. The half-metallic behavior of the corresponding multilayer systems is demonstrated by the band structures calculated within the linear muffin-tin orbitals method (LMTO) in a supercell geometry with [001] growth direction and periodic boundary conditions. The present conclusions should also apply to single fbf junctions. The calculations show that $\text{CrO}_2/\text{TiO}_2$ is a perfect half-metallic, whereas $(\text{CrO}_2)_2/\text{RuO}_2$ is a weak half-metallic, since there is some small minority DOS around E_F (Fig. 2). In comparison, there are only states in the majority spin band at the Fermi level in $\text{CrO}_2/\text{TiO}_2$ (hence an exact integer value of the magnetic moment in the unit cell ($=2\mu_B/\text{Cr}$ in $\text{CrO}_2/\text{TiO}_2$)).

The electronic structure of $\text{CrO}_2/\text{TiO}_2$ shows a half-metallic gap which is 2.6 eV wide and extends on both sides of the Fermi level, where there is a gap either in the minority or majority spin band. Thus, an huge magnetoresistance should in principle be seen not only for electrons at the Fermi level biased up to 0.5 eV, but also for hot electrons. We note that states at the Fermi level are a mixture of Cr(*d*) and O(2*p*) states, so that *p* - *d* interaction within the first coordination shell produces a strong hybridization gap, and the Stoner spin-splitting moves the Fermi level right into the gap for minority carriers (Fig.2).

Important difference between two spacer oxides is that TiO_2 is an insulator whereas RuO_2 is a good metallic conductor. Thus, the former system can be used in a tunnel junction, whereas the latter will form a metallic multilayer. In the latter case the physics of conduction is different from tunneling but the effect of vanishing phase volume for transmitted states still works when current is passed through such a system perpendicular to planes. For the P orientation of moments on electrodes, $\text{CrO}_2/\text{RuO}_2$ would have a normal metallic conduction, whereas in the AP one we expect it to have a semiconducting type of transport, with a crossover between the two regimes. One interesting possibility is to form a spin-valve transistor [10], and check the effect in a hot-electron region. $\text{CrO}_2/\text{TiO}_2$ seems to be a natural candidate to check the present predictions about half-metallic behavior and for a possible record tunnel magnetoresistance. An important advantage of these systems is an almost perfect lattice match at the oxide interfaces. The absence of such a match of the conventional Al_2O_3 barrier

with Heusler half-metallics (NiMnSb and PtMnSb) may have been among other reasons for their unimpressive performance [11].

By using all-oxide half-metallic systems, as the present examples show, one may bypass many materials issues. Then, the main concerns for achieving a very large value of magnetoresistance will be spin-flip centers, magnon-assisted events, and imperfect alignment of moments. As for conventional tunnel junctions, the present results show that presence of defect states in the barrier, or a resonant state like in a resonant tunnel diode type of structure, reduces their magnetoresistance by several times but may dramatically increase the current through the structure.

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