Tunneling of electrons in conventional and half-metallic systems: Towards very large magnetoresistance

A. M. Bratkovsky
Hewlett-Packard Laboratories, 3500 Deer Creek Road, Building 26U, Palo Alto, California 94304-1392
(Received 28 February 1997)

The tunnel magnetoresistance (TMR) is analyzed for ferromagnet-insulator-ferromagnet junctions, including half-metallic systems. Direct tunneling in a corrected standard model 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, and spin-flip scattering from defect states will further reduce this value. A resonant tunneling diode structure would give a TMR of about 8%. The model applies qualitatively to half-metallics with 100% spin polarization, where the change in resistance in the absence of spin-flips may be arbitrarily large. Even in the case of imperfect magnetic configurations the resistance change can be a few 1000 percent. Examples of half-metallic systems are CrO_2/TiO_2 and CrO_2/RuO_2, and a brief account of their peculiar band structures is presented. [S0163-1829(97)04129-5]

Tunnel magnetoresistance (TMR) in ferromagnetic junctions, first observed more than a decade ago,[1,2] is of fundamental interest and potentially applicable to magnetic sensors and memory devices.[3] To find systems with acceptable performance, it is important to consider the generic properties affecting magnetoresistance and other characteristics. A model for spin tunneling has been formulated by Julliere[1] and further developed by Stearns[4] and Slonczewski.[5] This model is expected to work rather well for iron-, cobalt-, and nickel-based metals, according to theoretical analysis[4] and experiments.[6] However, it disregards important points 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 half-metallic systems which should in principle show the ultimate performance.

We shall describe electrons in ferromagnet-insulating–barrier-ferromagnet (FBF) systems by the Schrödinger equation[5] $(\mathcal{H}_0-\mathbf{h}\cdot\hat{\boldsymbol{\sigma}})\psi=E\psi$, where $\mathcal{H}_0=-(\hbar^2/2m_\alpha)\nabla^2+U_\alpha$ is the single-particle Hamiltonian with $U(\mathbf{r})$ the potential energy, $\mathbf{h}(\mathbf{r})$ the exchange energy ($=0$ inside the barrier), and $\hat{\boldsymbol{\sigma}}$ stands for the Pauli matrices; index $\alpha=1$, 2, and 3 marks the quantities for left terminal, barrier, and right terminal, respectively.

We start with the expression for direct tunnel current of spin σ,[7]

$$\frac{I_\sigma}{A}=\frac{e}{h}\int_{-\infty}^{\infty}dE[f(E)-f(E+eV)]\int\frac{d^2k_\parallel}{(2\pi)^2}T_\sigma(E,\vec{k}_\parallel). \tag{1}$$

Here A is the contact area, $f(x)$ is the Fermi-Dirac distribution function, $T_\sigma=\Sigma_{\sigma'}T_{\sigma\sigma'}$ is the transmission probability, which has a particularly simple form for a square barrier and *collinear* [parallel (P) or antiparallel (AP)] moments on electrodes:

$$T_{\sigma\sigma'}=\frac{16m_1m_3m_2^2k_1k_3\kappa^2}{(m_2^2k_1^2+m_1^2\kappa^2)(m_2^2k_3^2+m_3^2\kappa^2)}e^{-2\kappa w}, \tag{2}$$

where $k_1\equiv k_{1\sigma}$, $k_2\doteq\imath\kappa$, $k_3\equiv k_{3\sigma'}$ are the momenta normal to the barrier for the corresponding spin subbands, w is the barrier width, and we have used a limit of T at $\kappa w\gg 1$ (see Ref. 8). With the use of Eqs. (1),(2) and accounting for the misalignment of spin moments in ferromagnetic terminals (given by mutual angle θ), we obtain the following expression for the junction conductance, assuming $m_1=m_3$:

$$\frac{G}{A}=G_{FBF}[1+P_{FB}^2\cos(\theta)],$$

$$G_{FBF}=\frac{e^2}{\pi\hbar}\,\frac{\kappa_0}{\pi w}\left[\frac{\kappa_0(k_\uparrow+k_\downarrow)(\kappa_0^2+m_2^2k_\uparrow k_\downarrow)}{(\kappa_0^2+m_2^2k_\uparrow^2)(\kappa_0^2+m_2^2k_\downarrow^2)}\right]^2e^{-2\kappa_0 w}, \tag{3}$$

$$P_{FB}=\frac{k_\uparrow-k_\downarrow}{k_\uparrow+k_\downarrow}\,\frac{\kappa_0^2-m_2^2k_\uparrow k_\downarrow}{\kappa_0^2+m_2^2k_\uparrow k_\downarrow},$$

where P_{FB} is the effective polarization of the electrode $\kappa_0=[2m_2(U_0-E)/\hbar^2]^{1/2}$ and U_0 is the top of the barrier.[9] Equations (3) correct an expression derived earlier[5] for the effective mass of the carriers in the barrier. By taking a typical value of $G/A=4-5\ \Omega^{-1}\mathrm{cm}^{-2}$ (Ref. 6) $k_\uparrow=1.09\ \text{Å}^{-1}$, $k_\downarrow=0.42\ \text{Å}^{-1}$, $m_1\approx 1$ (for itinerant d electrons in Fe)[4] and a typical barrier height for Al_2O_3 (measured from the Fermi level μ) $\phi=U_0-\mu=3$ eV, and the thickness $w\approx 20$ Å, one arrives at the following estimate for the effective mass in the barrier: $m_2\approx 0.4$.[10] These values give $P_{\mathrm{Fe}}=0.28$, in fair correspondence with the experimental value of 0.4 (note that neglect of the mass correction would give a negative value of the effective polarization).[3,6] In practice barrier parameters should be extracted from independent experiments, such as internal photoemission, etc., but here we are concerned with the generic behavior, where the present formalism is sufficient for qualitative and even semiquantitative analysis.

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

$$\mathrm{MR}=(G^{\mathrm{P}}-G^{\mathrm{AP}})/G^{\mathrm{AP}}=2PP'/(1-PP'), \tag{4}$$

which differs by the minus sign in the denominator from the standard definition,[1,3] since the present definition (4) reflects a change in the resistance of the contact.

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 (DOS) for minority carriers up to their conduction band minimum $E_{\mathrm{CB}\downarrow}$. Then G^{AP} vanishes together with the transmission probability (2), since there is a zero DOS at $E=\mu$ for both spin directions.

Such a half-metallic behavior is rare, but some materials possess this amazing property, most interestingly the oxides CrO_2 and Fe_3O_4.[11] 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 of Eq. (1) for arbitrary biases and image forces,[7] and the results are shown in 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 $eV_c=E_{\mathrm{CB}\downarrow}-\mu=0.3$ 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 from Eq. (1) that above this threshold, $G^{\mathrm{AP}}\propto(V-V_c)^{5/2}$ at temperatures much smaller than eV_c. Thus, for $|V|<V_c$ in the AP geometry one has $\mathrm{MR}=\infty$. 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 the middle and the bottom panels in 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.

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 (see Ref. 12, and references therein). 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.[12] We shall estimate the spin conductance in this model. Impurity-assisted spin tunneling at zero temperature [the general case of nonzero temperature would require integration with the Fermi factors as in Eq. (1)] can be written in the form[12]

$$G_{\sigma}=\frac{2e^2}{\pi\hbar}\sum_i \frac{\Gamma_{l\sigma}\Gamma_{r\sigma}}{(E_i-\mu)^2+\Gamma^2}, \tag{5}$$

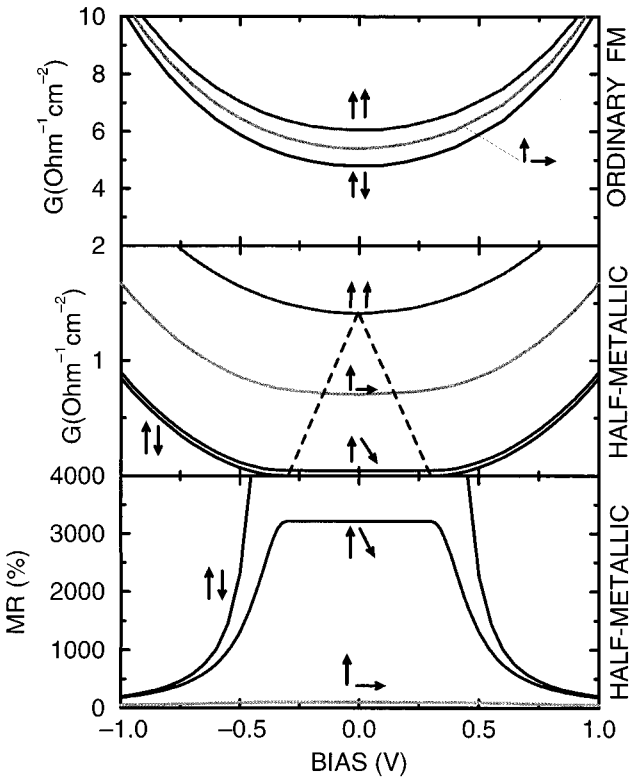

FIG. 1. Conductance and magnetoresistance of tunnel junctions versus bias. Top panel: conventional (Fe-based) tunnel junction (for parameters see text). Middle panel: half-metallic electrodes. Bottom panel: magnetoresistance for the half-metallic electrodes. Dashed line shows schematically a region where a gap in the minority spin states is controlling the transport. Even for imperfect antiparallel alignment ($\theta=160°$, marked $\uparrow\searrow$), the magnetoresistance for half-metallics (bottom panel) exceeds 3000% at biases below the threshold V_c. All calculations have been performed at 300 K with the use of Eq. (1) with inclusion of multiple image potential and exact transmission coefficients. Parameters are described in the text.

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. For the tunnel width we have $\Gamma_{(l,r)\sigma}=2\pi^2\kappa_0(\hbar^2/m_2)^2\Sigma_{\mathbf{k}_{(l,r)\sigma}}|\psi_{\mathbf{k}_{(l,r)\sigma}}(\mathbf{r}_i)|^2\delta(E_{\mathbf{k}_{(l,r)\sigma}}-E_i)$, where $\psi_{\mathbf{k}_{(l,r)\sigma}}(\mathbf{r}_i)$ is the value of the electrode wave function, exponentially decaying into the barrier, at an impurity site $\mathbf{r}_i$. We have for a rectangular barrier

$$\Gamma_{l\sigma}=\epsilon_i\frac{2m_2k_{\sigma}}{\kappa_0^2+m_2^2k_{\sigma}^2}\frac{e^{-\kappa_0(w+2z_i)}}{\kappa_0[(1/2)w+z_i]}, \tag{6}$$

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), $\epsilon_i=\hbar^2\kappa_0^2/(2m_2)$. 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. Replacing the sum by an integral in Eq. (5) and considering a general configuration of the magnetic moments on termi-

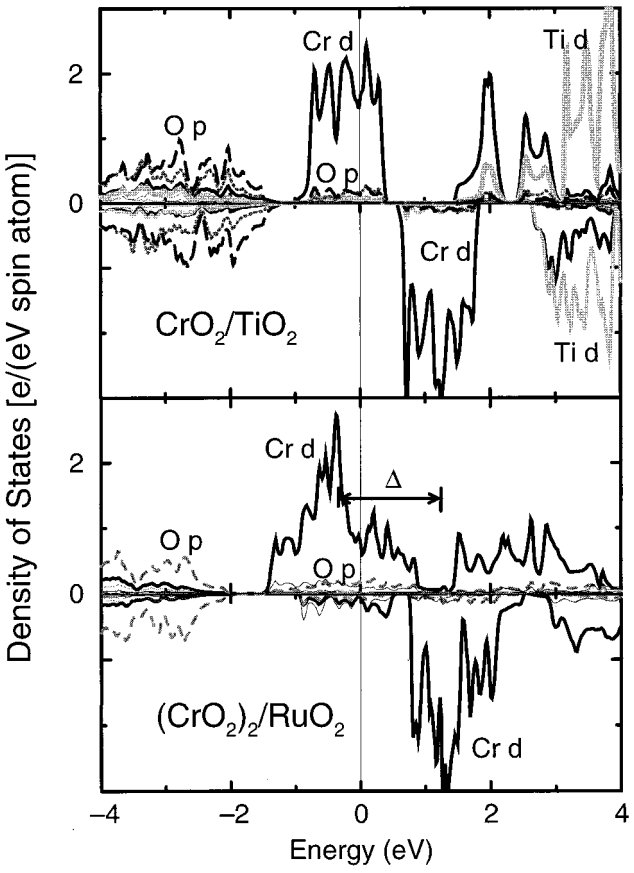

FIG. 2. Density of states of CrO_2/TiO_2 (top panel) and $(CrO_2)_2/RuO_2$ (bottom panel) half-metallic multilayers calculated with the use of the LMTO method. The partial contributions are indicated by letters. The zero of energy corresponds to the Fermi level. Δ indicates a spin splitting of the Cr d band near E_F (schematic). Note a strong hybridization of Cr d with O $2p$ states at E_F and below the hybridization gap. Growth direction is [001].

nals, we get the following formula for impurity-assisted conductance in leading order in $\exp(-\kappa w)$:

$$\frac{G_1}{A}=g_{FBF}[1+\Pi_{FB}^2\cos(\theta)], \tag{7}$$

where we have introduced the quantities

$$g_{FBF}=\frac{e^2}{\pi\hbar}N_1, \quad N_1=\pi^2\nu\Gamma_1/\kappa_0,$$

$$\Gamma_1=\epsilon_i\frac{e^{-\kappa_0 w}}{\kappa_0 w}\left(\sqrt{\frac{m_2\kappa_0 k_\uparrow}{\kappa_0^2+m_2^2k_\uparrow^2}}+\sqrt{\frac{m_2\kappa_0 k_\downarrow}{\kappa_0^2+m_2^2k_\downarrow^2}}\right)^2, \tag{8}$$

$$\Pi_{FB}=(r_\uparrow-r_\downarrow)/(r_\uparrow+r_\downarrow),$$

N_1 being the effective number of one-impurity channels per unit area and one may call Π_{FB} a ''polarization'' of the impurity channels, defined by $r_\sigma=[m_2\kappa_0 k_\sigma/(\kappa_0^2+m_2^2k_\sigma^2)]^{1/2}$.[9]

Comparing direct (3) and impurity-assisted contributions to conductance (7),(8), we see that the latter dominates when the impurity density of states $\nu\gtrsim(\kappa_0/\pi)^3\epsilon_i^{-1}\exp(-\kappa_0 w)$, and in our example a crossover takes place at $\nu\gtrsim 10^{-7}$ $\text{Å}^{-3}\,\text{eV}^{-1}$. When resonant transmission dominates, the magnetoresistance will be given by

$$\mathrm{MR}_1=2\Pi\Pi'/(1-\Pi\Pi'), \tag{9}$$

which is 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 case with a low concentration of defect levels.

With further increase of the defect density and/or the barrier width, the channels with two and more impurities will become more effective than one-impurity channels described before. The contribution of the many-impurity channels, generally, will result in the appearance of irregular intervals with negative differential conductance on the I-V curve.[12]

One may try to fabricate a resonant tunnel diode (RTD) structure to sharply increase the conductance of a system. We can imagine an RTD structure with an extra thin nonmagnetic 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 one-dimensional (1D) character of the transport in RTD in comparison with 3D impurity-assisted transport. However, the transmittance will have the same resonant form as in Eq. (5) and the widths (6) will contain an extra numerical factor $(4\pi)^{-1}$. The estimated magnetoresistance in the RTD geometry is, with the use of Eqs. (1),(5),

$$\mathrm{MR}_{\mathrm{RTD}}=[(r_\uparrow^2-r_\downarrow^2)/(2r_\uparrow r_\downarrow)]^2, \tag{10}$$

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. On the other hand, it may increase the current through the structure by many orders of magnitude, that may be useful in some potential applications.

It is very important that *in the case of half-metallics* $r_\downarrow=0$, $\Pi_{FB}=1$, 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 the best of both worlds: very large magnetoresistance with enhanced conductance (and hence a reduced noise) in tunnel MR junctions. One should be aware, however, that defect states (especially unpaired electrons) will increase the spin-flip rate, so the magnetoresistance could vanish with an increasing concentration of defects. In the case of conventional systems (e.g., FeNi electrodes) we have seen, however, that the 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.

I shall finish with a couple of examples of systems with half-metallic behavior, CrO_2/TiO_2 and CrO_2/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 multilayered 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 junctions in FBF geometry. The calculations show that CrO_2/TiO_2 is a perfect half-metallic, whereas $(CrO_2)_2/RuO_2$ is a weak half-metallic, since the density of states in the Cr layer is practically zero at E_F but there is some small DOS around E_F, and an exact gap opens up at about 0.58 eV above the Fermi level (Fig. 2). In comparison, there are only states in the majority spin band at the Fermi level in CrO_2/TiO_2. An immediate consequence of the fact that minority spin bands are fully occupied is an exact *integer* value of the magnetic moment in the unit cell ($=2\mu_B$/Cr in CrO_2/TiO_2), and this remarkable property is a simple check for possible new half-metallics.

The electronic structure of CrO_2/TiO_2 is truly stunning in that it has 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, a 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 starting at about 0.5 eV above the Fermi level. We note that states at the Fermi level are a mixture of Cr(d) and O($2p$) 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). It is worth noting that CrO_2 and RuO_2 are very similar in terms of a paramagnetic band structure but the difference in the number of conduction electrons and exchange splitting results in a usual metallic behavior of RuO_2 as compared to the half-metallic ferromagnet CrO_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, CrO_2/RuO_2 would have a normal metallic conduction, whereas in the AP one we expect it to have a semiconducting type of transport, with an interesting crossover between the two regimes. One interesting possibility is to form three-terminal devices with these systems, such as a spin-valve transistor,[13] and check the effect in a hot-electron region. CrO_2/TiO_2 seems to a 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.[14]

By using all-oxide half-metallic systems, as described herein, 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 such as in a resonant tunnel diode type of structure, reduces their magnetoresistance by several times but may dramatically increase the current through the structure.

I am grateful to my colleagues R. S. Williams, G. S. Lee, C. Morehouse, J. Brug, T. Anthony, and J. Nickel for interesting discussions.

[1] M. Julliere, Phys. Lett. **54A**, 225 (1975).
[2] S. Maekawa and U. Gäfvert, IEEE Trans. Magn. **18**, 707 (1982).
[3] For recent review of spin tunneling, see R. Meservey and P. M. Tedrow, Phys. Rep. **238**, 173 (1994).
[4] M. B. Stearns, J. Magn. Magn. Mater. **5**, 167 (1977).
[5] J. C. Slonczewski, Phys. Rev. B **39**, 6995 (1989).
[6] T. Miyazaki and N. Tezuka, J. Magn. Magn. Mater. **139**, L231 (1995); J. Appl. Phys. **79**, 6262 (1996); J. S. Moodera *et al.*, Phys. Rev. Lett. **74**, 3273 (1995); J. Appl. Phys. **79**, 4724 (1996).
[7] C. B. Duke, *Tunneling in Solids* (Academic, New York, 1969).
[8] W. A. Harrison, Phys. Rev. **123**, 85 (1961).
[9] 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 $k_\sigma \rightarrow k_\sigma / m_\sigma$.
[10] Even smaller $m_2 = 0.2$ has been used for Al-Al_2O_3-metal junctions by Q. Q. Shu and W. G. Ma, Appl. Phys. Lett. **61**, 2542 (1992).
[11] For a review of half-metallic ferromagnets, see, V. Y. Irkhin and M. I. Katsnelson, Sov. Phys. Usp. **164**, 705 (1994).
[12] A. I. Larkin and K. A. Matveev, Zh. Éksp. Teor. Fiz. **93**, 1030 (1987) [Sov. Phys. JETP **66**, 580 (1987)].
[13] D. J. Monsma *et al.*, Phys. Rev. Lett. **74**, 5260 (1995).
[14] C. T. Tanaka and J. S. Moodera, J. Appl. Phys. **79**, 6265 (1996).