The effect of Coulomb interaction at ferromagnetic–paramagnetic metallic perovskite junctions

The effect of Coulomb interaction at ferromagnetic–paramagnetic metallic perovskite junctions

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Abstract
We study the effect of Coulomb interactions in transition metal oxide junctions. In this paper we analyze charge transfer at the interface of a three layer ferromagnetic–paramagnetic–ferromagnetic metallic oxide system. We choose a charge model considering a few atomic planes within each layer and obtain results for the magnetic coupling between the ferromagnetic layers. For large numbers of planes in the paramagnetic spacer we find that the coupling oscillates with the same period as in Ruderman–Kittel–Kasuya–Yoshida (RKKY) theory but the amplitude is sensitive to the Coulomb energy. At small spacer thickness however, large differences may appear as a function of the number of electrons per atom in the ferromagnetic and paramagnetic materials, the dielectric constant at each component, and the charge defects at the interface plane, emphasizing the effects of charge transfer.

1. Introduction

Magnetic multilayer films have attracted the attention of the physics community since the discovery of 'giant magnetoresistance' (GMR) in metallic superlattices by Baibich *et al* [1] and they have been the subject of intensive basic and applied research. The fundamental physics giving rise to GMR has been clarified, the role of RKKY interactions being prominent. Application to read heads of magnetic memories is already a reality. The oscillations in the magnetic coupling have been beautifully derived by analogy to the de Haas–Van Alphen effect by Edwards *et al* [2] and were used to calculate realistically the magnetic coupling between Co layers in CoCuCo trilayers [3]. A comprehensive discussion of the problem of interlayer coupling is given in [4]. Studies of metal to insulating oxide interfaces based on density functional theory (DFT) are reported in [5].

On the other side, the discovery of 'colossal magnetoresistance' by von Helmholt *et al* [6] in $La_{1-x}Sr_xMnO_3$ type compounds, has also polarized research on these materials, their phase diagrams as a function of composition and temperature have been determined, but even though there has been considerable progress, the basic physics of the bulk materials is not yet quite completely understood [7].

Furthermore, several magnetic oxide heterostructures based on colossal magnetoresistance materials have been the subject of important research, including magnetic coupling mediated by a metallic spacer [8, 9]. We study here the effect of the charge transfer (CT) at the interface on the magnetic coupling. RKKY, being a perturbation theory, cannot be applied to these materials where the coupling energy between moments and conduction electrons is larger than the bandwidth. The theories mentioned before are appropriate for metallic magnets in which screening is strong and Coulomb interactions play a minor role in the charge transfer at the interface. In this paper we focus on a trilayer formed by ferromagnetic–paramagnetic–ferromagnetic ionic compounds and alloys where the Coulomb interaction dominates the charge transfer at the interface. We calculate self-consistently the charge profile in terms of a minimum set of parameters and study the effect of these parameters on the magnetic coupling between ferromagnetic layers. To this end, we build a Hamiltonian that contains the essential features of a fully polarized ferromagnet (FF) and a paramagnetic metallic (PM) spacer and parametrize the interfaces in the simplest possible way.

2. Model

We study a model for electrons moving in a three layer structure (FF–PM–FF) formed by two N-cell units (N-c.u.) of
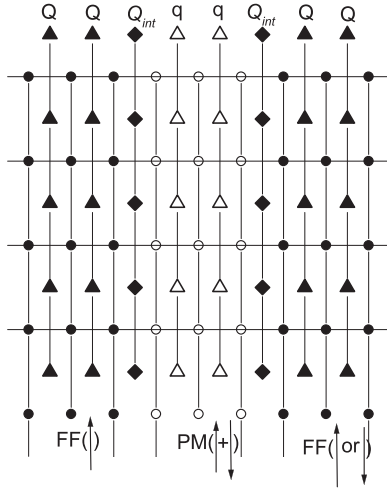
Figure 1. Schematic figure of the model used in this study. Solid and open circles show the positions of electron lattice sites for FF and PM materials, respectively. Solid and open triangles show the positions of positive lattice sites for FF and PM, respectively. Solid diamonds show the positions of positive charge Q_{int} in both planes adjacent to the PM region.

half-metallic ferromagnetic perovskites, such as for example $La_{1-x}Sr_xMnO_3$ $(0.2 \leqslant x \leqslant 0.5)$ separated by M-c.u. of non-magnetic metal, such as $LaNiO_3$. The Mn and Ni sites form a simple cubic structure and we take the interfaces perpendicular to a cubic axis. La (Sr) at the center of the cubes form another interpenetrating cubic lattice with opposite charge, so that La(Sr) planes are in between the Mn planes. We will consider this alternating planar structure as shown schematically in figure 1. To describe the charge transfer between the different layers we follow the pioneering papers of Gorkov and Kresin [10] and Okamoto and Millis [11]. More recently, the same procedure has been used by Brey [12] to study manganite-insulator oxide interfaces. Since charge transfer at the interfaces is determined by the competition between kinetic energy and Coulomb energy, we define a Hamiltonian for the kinetic energy of manganites H_N, and for the spacer H_M and a Coulomb Hamiltonian H_{Coul} that accounts for the Coulomb interactions between electrons and the positively charged background, and between themselves. Because of the large intrasite Coulomb interaction and exchange energies, double occupation of the e_g orbitals is inhibited. To include this fact in the model Hamiltonian we use a single spinless orbital in the Hamiltonian following previous models for manganites [13]. In manganites each Mn ion has three localized 3d electrons in the t_{2g} orbitals which, due to Hund's rule, produce a local spin $S = 3/2$, while the additional e_g electrons are itinerant and have their spin parallel to the local spin, again due to Hund's rule. When both manganite layers are strongly ferromagnetic, the conduction electrons can be completely spin polarized parallel to the magnetization in each manganite region, the situation we are considering here. The itinerant electrons in the right and left FF regions can be modeled by a tight-binding Hamiltonian:

$$H_N = \sum_{i,j} \epsilon_i c_{i,j}^\dagger c_{i,j} - t \sum_{\langle i,j,\delta,\delta' \rangle} c_{i,j}^\dagger c_{i+\delta,j+\delta'}, \qquad (1)$$

where i identifies the planes and runs between 1 and N in the left FF layer and between $N + M + 1$ and $2N + M$ in the right one, δ runs over nearest neighbor (nn) layers, j covers each plane in the layer, and δ' runs over nn in the plane j.

For the spacer, with $LaNiO_3$, a metallic paramagnet [14], in mind, we take again a similar single orbital Hamiltonian H_M with the only difference that now it includes the spin of the electrons, and i will run from $N + 1$ to $N + M$; all other indices keeping the same meaning. For simplicity we take a single value for the hopping parameter t between all nearest-neighbor orbitals. We then consider either ferro-(F) or antiferromagnetic (AF) alignments between the left and right FF layers to calculate the difference of energy between the two configurations. This energy difference arises from the fact that in the ferromagnetic alignments electrons with spin up can move freely within the three layers and those with spin down are confined to the spacer, while in the case of AF alignments, electrons with spin up move between the first and second layer and those with spin down between the second and third.

The electrons move in a background of positive charges centered at the interpenetrating lattice, which will be defined later. The average number of electrons per site n is fixed such that the whole system is neutral. Electrons hopping between all nn orbitals feel a potential arising from the extra positive charges and the electron–electron repulsion. The diagonal energies ϵ_i in equation (1) will result here from a self-consistent calculation involving the Coulomb energy due to the charges at the positive and negative interpenetrating lattices. This is the main contribution of this paper to the study of magnetic coupling between layers. The Coulomb interaction, which is the most relevant ingredient in the model, takes the following form:

$$H_{Coul} = -\sum_{i,l} \frac{e^2 n_i q_l}{\epsilon |R_i - R_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2 n_i n_j}{\epsilon |R_i - R_j|}$$
$$+ \frac{1}{2} \sum_{m \neq l} \frac{q_m q_l e^2}{\epsilon |R_m - R_l|}, \qquad (2)$$

where i, j refer to the electron lattice while l, m refer to the positive lattice, both indexes run over the whole system. The first term represents the attraction between electrons and positive charges while the second and third correspond to the repulsion between charges of the same sign. ϵ is the dielectric constant which can be quite high. The electronic charge at each FF site or PM site i is $-en_i$. n_i will be calculated self-consistently by mean field theory. To simplify the notation we use a single parameter $U = \frac{e^2}{\epsilon * a}$ where a is the lattice parameter. The factor eq_l represents the average charge per unit cell in the positive lattice. To represent the three layer structure we take three different values for q_l: $q_l = Q$ in the FF layers, $q_l = q$ for the spacer, and to model possible distortions of charge or structure at the plane between FF and PM we use as a first approach $q_l = Q_{int}$. Here, Q_{int} is a single interface parameter which allows us to introduce different charge in both positive planes adjacent to the PM. Note that since positive planes are intercalated between electron planes, the number of positive planes is $2N + M - 1$. In figure 1 we show schematically the charge structure in a $N = 3$, $M = 3$ FF–PM–FF example.

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To consider the example of the manganites and nickelate FF–PM–FF structure as mentioned above, we would define the positive charges in the following way. The e_g-orbitals are empty for Mn^{4+} and occupied with one electron in Mn^{3+}. In this way the neutral $Sr^{2+}Mn^{4+}O_3^{2-}$ background has ionic character with no conduction electrons and we will describe the charges in our system as the additional charges with respect to this background. La has a nominal valence $3+$ therefore each La produces an excess charge $+1$ together with one conduction electron. So in $La_{1-x}Sr_xMnO_3$ the number of conduction electrons per unit cell is $1 - x$ and $Q = 1 - x$. We take the same reference background of positive charges also in $LaNiO_3$, so that now in the spacer one would have one itinerant electron per nickel site and $q = 1$.

3. Results

Since the model contains several parameters, to fix ideas we present the results choosing values of the parameters appropriate to describe the charge effects in the three layer systems investigated in [8]. Accordingly, we chose $N = 12$, $Q = 2/3$, and $q = 1$ in most of our results. We adjust the Fermi energy so that the total number of electrons equals the positive charge ($(2N+M)n = 2(N-1)Q+(M-1)q+2Q_{int}$). We take t as the unit of energy.

We begin by looking at the effect of the charge of the interface plane Q_{int} on the electron charge distribution. We find that the charge distribution is almost insensitive to the magnetic alignment of the FF layers. However, an important charge transfer occurs in the planes very near to the interface FF/PM. In figure 2 we show n_i as a function of i for $M = 14$, $U/t = 1$, $Q = 0.66$, and three different values of Q_{int}. Not surprisingly the average electron charge of the nearest planes follows the excess or deficit of charge of the interface plane. However, the charge of the first separator plane exceeds its mean value ($\sim q$) by 10% at average $Q_{int} = 0.83$ and can go up or down according to Q_{int}. By contrast, the charge at the first FF layer is lower than Q while one would expect that the charge would accumulate on both sides of the interface. This seemingly surprising result is a consequence of the fact that each site at the separator can be doubly occupied while the FF sites can be only singly occupied. Since many of the FF are manganites and they are extremely sensitive to the average charge, this fact could affect strongly the magnetic properties of the interface. Here we assume that all atomic planes at the FF are fully polarized. The effects of charge inhomogeneity in the FF planes will be reported in a different publication.

In this paper we focus on the CT effects on the separator (planes $i = 13$–26). To study the magnetization in these planes we define first $S_{zi} = (n_{i\uparrow} - n_{i\downarrow})$ the magnetic polarization at each PM plane. We show the effect of Q_{int} on the magnetization inside the PM displaying S_{zi} as a function of i for the antiferromagnetic arrangements (figure 3(a)) of the FF layers. We observe that the amplitude of the oscillations of S_{zi} at the interface increases with Q_{int} while the opposite occurs far from the interface, a change of sign of S_{zi} occurs for different values of Q_{int} as one can observe in figure 3(a). For F or AF alignments we calculate the ground state energies
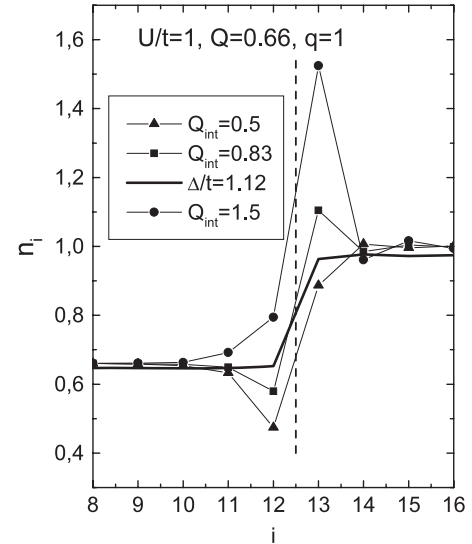

Figure 2. The mean value of the number of particles per site n_i at the ith plane as a function of i for $N = 12$, $M = 14$, $U/t = 1$, $Q = 0.66$, $q = 1$, and three different values of Q_{int} in the AF alignments. The vertical dashed line ($i = 12.5$) is a guide to the eye to show the interface plane between FF and PM materials. The broad line corresponds to a step potential $\Delta/t = 1.12$.

E_{GF} and E_{GAF} respectively for each value of M. The resulting exchange coupling $E_x = E_{GF} - E_{GAF}$ as a function of M is shown in figure 3(b). The period of oscillations of S_{zi} and E_x can be identified with the extremal spanning vectors of the Fermi surface of the spacer (k_{zF}). This is shown in figures 4(a) and (b), where one can observe that changing q, and consequently the Fermi energy, changes the period of oscillations accordingly. In figure 4(b) the continuous line corresponds to the first term in the stationary phase approximation (SPA) [3]. The SPA first term has the form $E_x = \frac{C}{(M+1)^2} \sin[2k_{zF}(M + 1) + \varphi]$, where C and φ are parameters that we choose to fit the numerical results in figures 4(b) and (c). Note that far from the interface the SPA reproduces quite well the numerical results (see the inset). In figure 4(c) we plot $(E_{GF} - E_{GAF})/t$ as a function of M for $q = 0.5$ and $Q_{int} = 1.5$, and compare with the SPA approximation. We adjust C and φ so as to fit the first point of the numerical result ($M = 1$). It can be seen that the latter attenuate rapidly with M much faster than the SPA result. This strong attenuation has been found in $La_{0.66}Ba_{0.34}MnO_3$–$LaNiO_3$–$La_{0.66}Ba_{0.34}MnO_3$ trilayers by Nikolaev *et al* in [8] and attributed to damping caused by strong electron scattering in the non-magnetic layer.

4. Discussion and conclusion

We have presented a simple four parameter model to describe the coupling between two magnetic half-metallic perovskites (such as, for example, $La_{1-x}Sr_xMnO_3$) separated by a metallic one ($LaNiO_3$). The coupling is strongly affected by the charge transfer at the interface due to the different effect of the Coulomb interaction in the two materials. Recent two orbital calculations by Ohsawa *et al* [15] using a potential difference
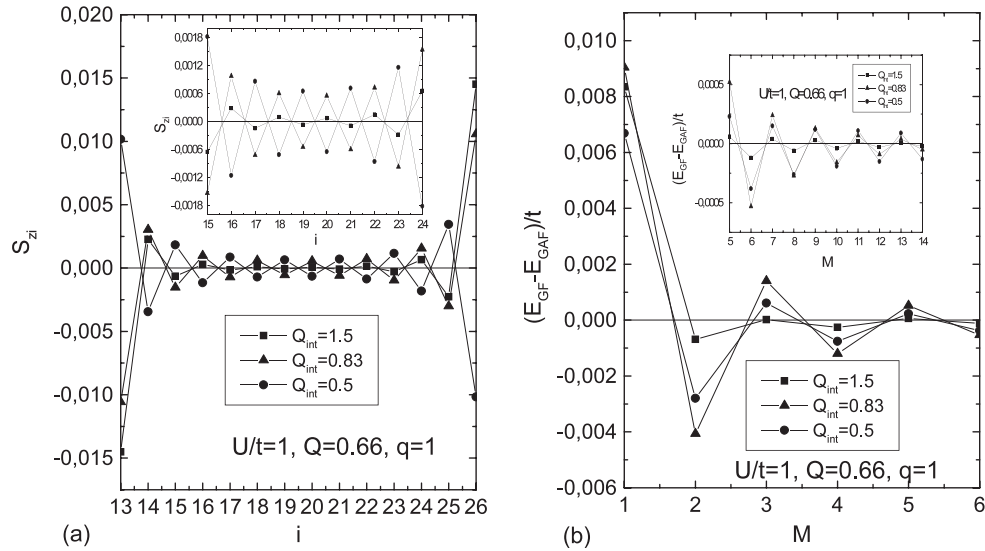
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Figure 3. (a) $S_{zi} = (n_{i\uparrow} - n_{i\downarrow})$ as a function of i for $N = 12$, $M = 14$, $U/t = 1$, $Q = 0.66$, $q = 1$, and three different values of Q_{int} in the AF alignments. Inset: S_{zi} for the same parameters and i from 15 to 24. (b) The energy difference $(E_{GF} - E_{GAF})/t$ as a function of the spacer planes number (M) for $N = 12$, $U/t = 1$, $Q = 0.66$, $q = 1$, and Q_{int} as in figure 2(a) in the AF alignments. Inset: $(E_{GF} - E_{GAF})/t$ for the same parameters and M from 5 to 14.

Table 1. Charges and magnetic moments (MM) obtained from the *ab initio* calculations and using Bader's definition of atomic basins [20].

	$LaMnO_3$		$CaMnO_3$	
	Charge	MM	Charge	MM
La/Ca	2.08	0.00	1.66	0.00
Mn	1.66	3.53	1.81	2.92
O1	−1.25	0.11	−1.15	0.00
O2	−1.24	0.00	—	—

to distinguish between manganite and spacer do not show these effects. For example in figure 2 the broad line indicates the charge values at each atomic plane obtained using simply a potential difference adjusted to reproduce the values of Q and q (potential difference $\Delta/t = 1.12$). We can see that the result is a monotonous increase at the left interface from 0.66 to 1 and the opposite at the right interface.

Of the four parameters, only U/t is not determined by the material's characteristics: Q controls the number of e_g electrons in the manganites, Q_{int} is the charge at the interface and is a parameter that represents the possible differences between bulk and interface, q ($q = 1$ in this calculation) controls the number of electrons in the separator. The single free parameter U is hard to estimate: it contributes to the Coulomb interaction as the sum of point charge interactions in the lattice. This would be a good approximation if the charge distribution were punctual or if there were no overlap between charges. This is far from reality, an *ab initio* calculation of the effective charges filling the atomic basin according to Bader's theory gives significantly smaller values than the ideal ionic value. Hybridization with the nearest oxygen ions affects strongly the space charge distribution in non-overlapping volumes. This reduces significantly the values of U. The *ab initio* calculations were performed using

the full-potential linearized/augmented plane wave plus local orbital (L/APW + lo) method, as implemented in the WIEN2K code [16–18]. The exchange–correlation effects were treated within the GGA (generalized gradient approximation) using the Perdew–Burke–Ernzerhof form [19]. For the calculation of charges, we used Bader's definition of atomic basins [20] calculated with the electronic densities obtained from the *ab initio* calculations. The atomic basins were calculated with the total electronic density and then used to integrate the number of up and down electrons assigned to each atom.

In table 1 we show the results for two cases: $LaMnO_3$ in the A-type antiferromagnetic phase, and $CaMnO_3$ in a cubic G-type antiferromagnetic phase. While in $CaMnO_3$ all oxygen atoms are equivalent (O1 in table 1), in $LaMnO_3$ there are two inequivalent oxygen atoms: the atoms within each ferromagnetic plane (O1) and the atoms located between two opposite ferromagnetic planes (O2).

The results presented in table 1 indicate that the charge transferred by substitution of La by Ca is transferred not only to Mn as one purely ionic picture would indicate but it is transferred evenly to Mn and O. This is a consequence of the strong covalent bond between the transition metal and oxygen. This result agrees with the conclusions obtained by Raebiger *et al* reported in *Nature* [21] and extends their results to perovskites. Another factor that reduces U is screening. We have also modified the calculation, including a term $e^{-\lambda|R_i - R_j|}$ in the interaction, and used different values of λ which is also difficult to estimate in the ionic perovskites. We do not include here a study of the relaxation of the interface plane which could enhance the charge effects at the interface. We have also estimated the corrections due to different hopping magnitudes for the spacer and found that these corrections do not produce qualitative changes in the results.

A quantitative calculation describing these types of interfaces is still far from being obtained. It should include
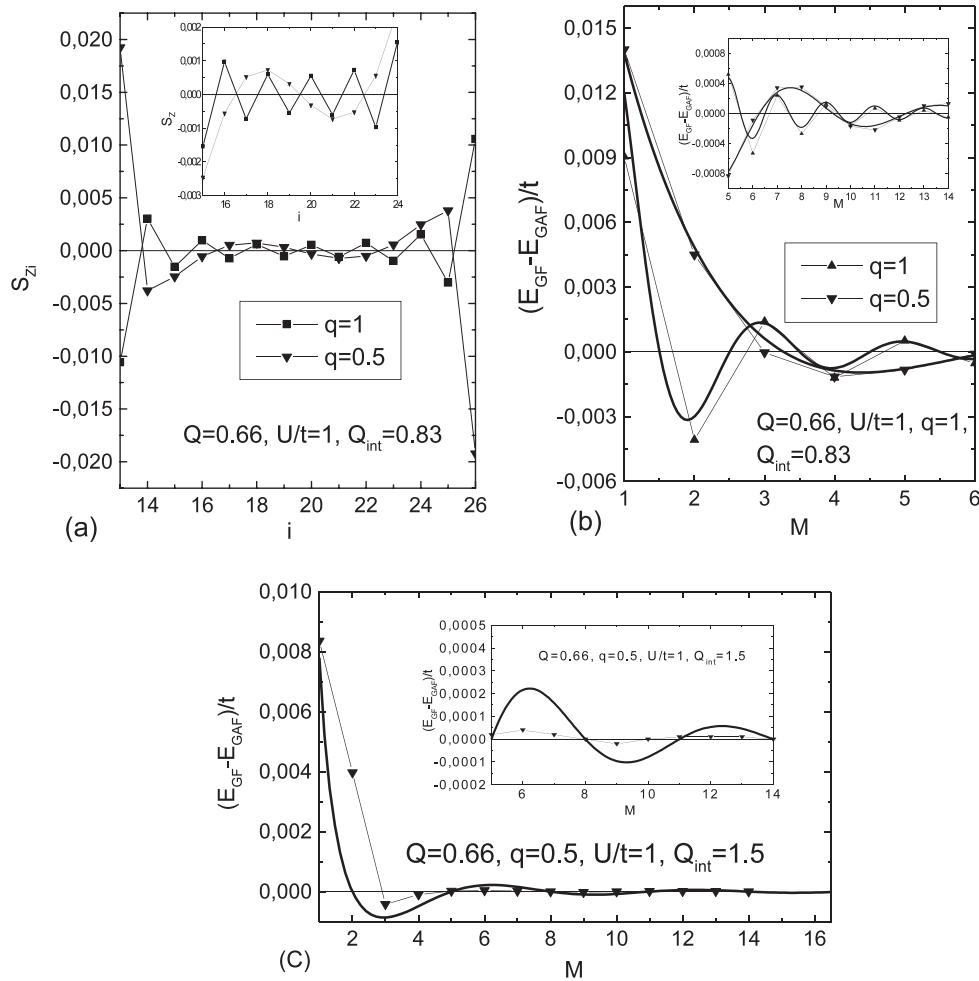
Figure 4. (a) $S_{zi} = (n_{i\uparrow} - n_{i\downarrow})$ as a function of i for $N = 12$, $M = 14$, $U/t = 1$, $Q = 0.66$, $Q_{int} = 0.83$, and two different values of q in the AF alignments. Inset: S_{zi} for the same parameters and i from 15 to 24. (b) The energy difference $(E_{GF} - E_{GAF})/t$ as a function of M for $N = 12$, $U/t = 1$, $Q = 0.66$, $Q_{int} = 0.83$, and two different values of q. Inset: $(E_{GF} - E_{GAF})$ for the same parameters and M from 5 to 14. The solid lines correspond to the first term in the stationary phase approximation (SPA). (c) The energy difference $(E_{GF} - E_{GAF})/t$ as a function of M for $N = 12$, $U/t = 1$, $Q = 0.66$, $Q_{int} = 1.5$, and $q = 0.5$. Inset: $(E_{GF} - E_{GAF})$ for the same parameters and M from 5 to 14. The solid lines correspond to the first term in the stationary phase approximation (SPA).

at least a two orbital description of the electronic structure as well as the effects of strain and defects at the interface. We believe that our study of the effect of Coulomb interactions contributes to the understanding of some qualitative aspects of their properties.

In conclusion, we have shown that the charge transfer at the interface between a half-metallic and a metallic oxide is quite anomalous due to the ionic nature of the materials under study. These anomalies transfer to the different properties of the layered structures, such as for example conductance through the layers, magnetization in the spacer, and magnetic coupling between the ferromagnetic layers. We have analyzed here the magnetic exchange in a trilayer formed by two half metals spaced by a metal.

Acknowledgment

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