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

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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 \textit{et al} \cite{Baibich} 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 \textit{et al} \cite{Edwards} and were used to calculate realistically the magnetic coupling between Co layers in CoCuCo trilayers \cite{Kadowaki}. A comprehensive discussion of the problem of interlayer coupling is given in \cite{Rohr}. Studies of metal to insulating oxide interfaces based on density functional theory (DFT) are reported in \cite{Patterson}.

On the other side, the discovery of ‘colossal magnetoresistance’ by von Helmholtz \textit{et al} \cite{Helmholtz} in La\(_{1-x}\)Sr\(_x\)MnO\(_3\) 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 \cite{Sawatzky}.

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 \cite{Kadowaki, Kadowaki2}. 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
half-metallic ferromagnetic perovskites, such as for example \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) (0.2 \( \leq x \leq 0.5 \)) separated by \( M \)-c.u. of nonmagnetic 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 \( H_K \), and for the spacer \( H_M \) and a Coulomb Hamiltonian \( H_{\text{Coul}} \) 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 \( \frac{5}{2} \) 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:

\[
H = \sum_{i,j} \epsilon_{i,j} c_{i,j}^\dagger c_{i,j} - t \sum_{\langle i,j \rangle, \delta \delta'} c_{i,j}^\dagger c_{i+j+\delta,\delta'},
\]

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, \( \delta \) runs over nearest neighbor (nn) layers, \( j \) covers each plane in the layer, and \( \delta' \) 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 \( \epsilon_i \) 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:

\[
H_{\text{Coul}} = -\sum_{l,j} \frac{e^2 n_i q_l}{|R_l - R_j|} + \frac{1}{2} \sum_{m,j} \frac{e^2 n_i n_j}{|R_l - R_j|} + \frac{1}{2} \sum_{m,j} \frac{q_m q_{l}\epsilon^2}{|R_l - R_j|},
\]

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. \( \epsilon \) 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 \( e q_l \) 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 \( q_l = Q_{\text{int}} \). Here, \( Q_{\text{int}} \) 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.
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$_2^-$ 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$_x$MnO$_3$ 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 ($-q$) 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 effect may 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 $S_{ij} = (n_{i+} - n_{i-})$ the magnetic polarization at each PM plane. We show the effect of $Q_{int}$ on the magnetization inside the PM displaying $S_{ij}$ 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 $S_{ij}$ at the interface increases with $Q_{int}$ while the opposite occurs far from the interface, a change of sign of $S_{ij}$ 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 $E_{GF}$ and $E_{GAF}$ respectively for each value of $M$. The resulting exchange coupling $E_i = E_{GF} - E_{GAF}$ as a function of $M$ is shown in figure 3(b).

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$_x$MnO$_3$) 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 $U/t = 1.0$.
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 $\Delta q/t = 1.12$). We can see that the result is a monotonic 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, $Q_{\text{int}}$ 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 (LAPW + 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 $\exp(-i|R_i - R_j|/\lambda)$ in the interaction, and used different values of $\lambda$ 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

|         | LaMnO$_3$ | CaMnO$_3$ |
|---------|-----------|-----------|
| Charge  | MM        | Charge  | MM        |
| La/ Ca  | 2.08      | 1.66     | 0.00      |
| Mn      | 1.66      | 1.81     | 3.53      |
| O1      | -1.25     | -1.15    | 0.11      |
| O2      | -1.24     | —        | 0.00      |
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.

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References

[1] Baibich M N et al 1988 Phys. Rev. Lett. 61 2472
[2] Edwards D M, Mathon J, Muniz R B and Phan M S 1991 Phys. Rev. Lett. 67 493
Edwards D M, Mathon J, Muniz R B and Phan M S 1991 J. Magn. Magn. Mater. 93 85
[3] Mathon J et al 1997 Phys. Rev. B 56 11797
[4] Bruno P 1995 Phys. Rev. B 411 52
[5] Olevnik I I and Tsymbal E Y 2004 Interface Sci. 12 105
[6] von Helmholt R, Wecker J, Holzapfel B, Schulz L and Samwer K 1993 Phys. Rev. Lett. 71 2331
[7] Schlottmann P 2006 Phys. Rev. B 73 214428
[8] Nikolaev K R et al 2000 Phys. Rev. Lett. 85 3728
[9] Granada M et al 2007 Appl. Phys. Lett. 91 72110
[10] Gorkov L P and Krein V 2004 Phys. Rep. 400 149
[11] Okamoto S and Millis A J 2004 Phys. Rev. B 70 075101
[12] Brey L 2007 Phys. Rev. B 75 104423
[13] Allub R and Alascio B 1997 Phys. Rev. B 55 14113
Pavlenko N and Kopp T 2006 Phys. Rev. Lett. 97 187001
Okamoto S and Millis A J 2004 Phys. Rev. B 70 241104(R)
[14] Granada M et al 2006 Physica B 384 68
Medarde M L 1997 *J. Phys.: Condens. Matter* **9** 1678

[15] Ohsawa T, Kubota S, Itoh H and Inoue J 2005 *Phys. Rev. B* **71** 212407

[16] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *Wien2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*

Karlheinz Schwarz, T.U. Wien, ISBN 3-9501031-1-2

[17] Schwarz K, Blaha P and Madsen G K H 2002 *Comput. Phys. Commun.* **147** 71

[18] Schwarz K and Blaha P 2003 *Comput. Mater. Sci.* **28** 259

[19] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Lett.* **77** 3865

[20] Bader R F W 1995 *Atoms in Molecules* (Oxford: Oxford University Press)

[21] Raebiger H et al 2008 *Nature* **453** 763