Ferromagnetism and metal-like transport in antiferromagnetic insulator heterostructures.

P. Padhan, P. Murugavel and W. Prellier*

Laboratoire CRISMAT, CNRS UMR 6508, ENSICAEN,
6 Bd du Maréchal Juin, F-14050 Caen Cedex, FRANCE.

(March 23, 2022)

Abstract

Strained Pr$_{0.5}$Ca$_{0.5}$MnO$_3$/La$_{0.5}$Ca$_{0.5}$MnO$_3$/Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ trilayers were grown on (001)-SrTiO$_3$ substrates using the pulsed-laser deposition technique. The coupling at the interfaces of several trilayers has been investigated from magnetization and electronic transport experiments. An increase of La$_{0.5}$Ca$_{0.5}$MnO$_3$ layer thickness induces a magnetic ordering in the strain layers and at the interfaces leading to ferromagnetic behavior and enhanced coercivity, while resistivity shows metal-like behaviors. These effects are not observed in the parent compounds, which are antiferromagnetic insulators, opening a path, to induce artificially some novel properties.
Over the past few years, perovskite type manganites such as $R_xA_{1-x}MnO_3$ ($R$=rare earth elements and $A$=alkaline earth elements) have been extensively investigated because of their colossal magneto-resistance properties$^1$, a huge decrease in the resistance with applied magnetic field. This material has been explored in the form of thin films including multilayer structures, made by several combinations among ferromagnetic ($FM$), antiferromagnetic ($AFM$), paramagnetic ($PM$) in addition to insulator and/or metal, whose properties are different from their single layer structures. Their physical properties have been attributed to the structural and magnetic modifications at the interfaces of the two constituents of the multilayers$^{2-4}$. For example, canted spin arrangements of ferromagnetic layer in La$_{0.6}$Sr$_{0.4}$MnO$_3$/La$_{0.6}$Sr$_{0.4}$FeO$_3$ and La$_{0.6}$Sr$_{0.4}$MnO$_3$/SrTiO$_3$ superlattice$^2$, formation of interfacial ferromagnetism in CaMnO$_3$/CaRuO$_3$ superlattice$^3$ and disorder interfacial phase of structural and magnetic origin in La$_{0.7}$Ca$_{0.3}$MnO$_3$/LaNiO$_3$ superlattice$^4$ have been observed. These examples have confirmed the importance of magnetic interfaces which, in fact, has already been revealed in other metallic systems$^5$. However, spin ordering is also observed at interfaces of the superlattices consisting of antiferromagnetic layers of LaFeO$_3$ and LaCrO$_3$$^6$. The manganites show interesting properties like the charge/orbital ordering ($CO/OO$)$^7$ that occurs in some half-doped compounds. This $CO/OO$ behavior corresponds to an ordering of charges and orbitals in two different Mn sublattices (i.e., a long-range ordering of $Mn^{3+}$ and $Mn^{4+}$ ions) below the $CO/OO$ temperature, when the materials is cooled down to low temperature. This $CO/OO$ state is highly an insulating state, but can be destroyed (i.e., inducing a metallic behavior) by the application of a magnetic field$^8$. Similar two prototype compounds are Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ ($PCMO$) and La$_{0.5}$Ca$_{0.5}$MnO$_3$ ($LCMO$) exhibits insulator like behaviour with $CO/OO$ temperature $\sim 175K$ and $\sim 180K$, respectively (bulk $LCMO$ does not show $FM$ behavior$^9$). Here, we report the interface effect between $PCMO$ and $LCMO$, in detail, through transport and magnetic measurements of $PCMO/LCMO/PCMO$ trilayer structures grown on (001)-oriented SrTiO$_3$ substrates (STO).
Thin films and heterostructures of PCMO and LCMO were fabricated by the pulsed laser deposition (PLD) technique using a KrF laser (λ = 248 mm) on STO substrates. The samples were grown at 720 °C in an oxygen ambient of 300 mtorr. The deposition rates (typically ~ 0.38A/pulse) of PCMO and LCMO were calibrated for each laser pulse of energy density ~3J/cm². After the deposition the chamber was filled to 400torr of oxygen at a constant rate, and then the samples were slowly cooled down to room temperature at the rate of 20°C/min. Trilayer structures comprising of 50-(unit cell, u.c.) PCMO/n-(u.c.) LCMO/10 -(u.c.) PCMO, with n taking integer values from 1 to 18, were thusly made. To reduce the substrate-induced strain, we have deposited a thicker bottom layer than the top layer, while the top layer is made thinner to have the effect of interface in the transport measurements. The structural study was done by x-ray diffraction (XRD) using a Seifert XRD 3000P (Cu, Kα1, λ = 0.15406nm). Special arrangement for the large intensity of x-ray beam and large surface area of the sample was used during the θ - 2θ scan. The resistivity (ρ) was measured using a four-probe method with in-plane current. The measurements are done by putting silver contact pads, with a separation of 6 mm between the voltage electrodes of the sample with lateral dimension close to 3×10 mm². Magnetotransport and magnetization measurements were performed with magnetic field aligned along the [100] direction of the substrate. The samples were cooled to a desired temperature from room temperature in the absence of electric and magnetic field to perform transport measurements.

All sample shows (00l) fundamental Bragg’s reflections of the substrate and the constituents of the heterostructure indicate the epitaxial growth of the trilayers. The pseudocubic lattice parameter of STO (∼ 3.905A) is larger than the lattice parameter of PCMO (3.802A) and LCMO (3.83A) provides in-plane tensile strain for their epitaxial growth. The θ - 2θ scan close to the fundamental (001) diffraction peak of the substrate for the samples with n = 5 and 18 are shown in the Fig. 1. The out-of-plane lattice parameter of various samples with different LCMO thicknesses are shown in the inset of Fig. 1. It also includes the bulk lattice parameters of LCMO and PCMO. The c-axis lattice parameter of these sample increases monotonically with the increase in LCMO. The c-axis lattice pa-
rameter of the sample with \( n = 18 \) is lower than the lattice parameter of both \( LCMO \) and \( PCMO \), which suggests the presence of substrate-induced strain state in these samples. As a consequence, this modification in the structure of \( PCMO \) and \( LCMO \) with the interfaces in the heterostructures are expected to effect the magnetic as well as transport properties of the constituents.

Both materials, \( PCMO \) and \( LCMO \), are insulators with an \( AFM \) behavior in the range of our measurements\(^{10,11} \). Similar insulator-like temperature dependent resistivity \( \rho(T) \) is observed in the thin films of \( LCMO \) and \( PCMO \). In Fig.2, we show the zero-field cooled \( \rho(T) \) in presence of 0\( T \) and 7\( T \) in-plane magnetic field for three heterostructures. Though the constituents of the samples are insulator the resistivity of these samples was calculated using their actual dimensions. As we cool the sample with 5 u.c. thick \( LCMO \) layer, the zero-field resistivity remains insulator-like down to 100 \( K \). Below 100\( K \), the resistance of the sample is high and it is limited by the input impedance of PPMS (Physical Properties Measurement System). However, for the sample with 10 u.c. thick \( LCMO \), the resistivity below room temperature is insulator-like down to 10\( K \). As the \( LCMO \) layer thickness increases 18 u.c. and the sample is cooled from room temperature the resistivity shows thermally activated behavior down to 150\( K \), shows metal-like behavior in the temperature range of 150\( K \) to 30\( K \) and an upturn below 30\( K \). In presence of 7\( T \) magnetic field, the \( \rho(T) \) of the superlattice with 5 u.c. \( LCMO \) is similar to that of the zero-field \( \rho(T) \) of the sample with 18 u.c. thick \( LCMO \). Qualitatively similar in-field \( \rho(T) \) with the broader metal-like window and higher metal-insulator transition temperature is observed for higher LCMO layer thickness. The temperature dependent magnetoresistance (\( MR \)) of these heterostructures are shown in the inset of Fig.2. The \( MR \) of both samples is decreasing as the temperature increasing, similar to the bulk materials.

To understand this transport behavior of these heterostructures, we have measured their magnetic properties. The temperature dependent field cooled (0.01\( T \)) magnetization of three heterostructures are shown in the Fig.3a. The magnetization is shown after the diamagnetic correction of \( STO \). On heating from 10\( K \), the heterostructure with 3 u.c. thick \( LCMO \)
shows a sharp antiferromagnetic transition at 30\textdegree{}K and a ferromagnetic-to-paramagnetic transition at 250\textdegree{}K. As the LCMO layer thickness increases the antiferromagnetic behavior suppress and these samples show the same Curie temperature (T_C). At 10\textdegree{}K, the magnetization of a thin film of PCMO is 1.51×10^{-3}~\text{emu/gauss/cm}^3 which is same order of magnetization (9.033×10^{-3}~\text{emu/gauss/cm}^3) observed for the heterostructure with 18 u.c. thick LCMO.

The zero-field-cooled magnetic hysteresis loop measured at 10\textdegree{}K of the samples with LCMO layer thickness above 5 u.c. shows ferromagnetic behavior. The magnetic hysteresis loop of the sample with 18 u.c. thick LCMO layer is shown in the Fig. 3b. The magnetization of the sample increases gradually with the increase in magnetic field and does not show a clear saturation. We have extracted the M_S (saturation magnetization) taking into account of the weak diamagnetic response of the substrate by extrapolating the linear part of the hysteresis loop to \( \mu_0H = 0 \). The extracted value of M_S is 1.98 \( \mu_B/Mn \). This value of M_S is small compare the theoretical value of a ferromagnetic phase of \((Pr,La)_{0.5}Ca_{0.5}MnO_3\) composition (~3.5 \( \mu_B/Mn \)). Though this sample does not exhibits a clear saturation magnetization, but shows a significant coercive field (H_C) (~0.07tesla). However, the shape of the hysteresis loop does not change as we cool the sample in presence of magnetic field. The field-cooled and zero-field-cooled magnetic behavior of these sample does not indicate the presence of FM cluster as expected from the FM/AFM exchange bias system. The interesting point is the origin of the FM behavior, where both materials are AFM. Ferromagnetic ordering of spin at the interfaces of the superlattices consisting of two antiferromagnet LaCrO_3 and LaFeO_3 has already been realized\(^6\), with the ordering along the [111] direction. These samples show clear saturation in the magnetic hysteresis loop and the author have explained FM ordering due to the Goodenough-Kanamori rules. However, to the best of our knowledge, the metal-like transport in an heterostructure using insulators as the constituent has not been reported so far.

Several interesting behaviors have been observed in manganites by changing average A-site ionic radius. This doping process provides modification in the MnO_6 octahedra and
formation of FM metallic phase in the AFM insulating matrix\textsuperscript{12–14}. As seen in the inset of Fig.1, both PCMO as well as LCMO are in the strain state due to the lattice mismatch between them and with the substrate\textsuperscript{11,15}. We believe that this effective strain modify the structure as well as the spin configurations in the PCMO, LCMO and at their interface. However, the modification at the PCMO/LCMO interface is expected to be more due to the interfacial-induced strain and the presence of A-site ion La, Pr and Ca. This interfacial stress might induce a spin re-orientation, which will modify the Jahn-Teller distortion of the \( MnO_6 \) octahedra compare to the bulk materials and it may results in spin ordering and/or spin canting at the interfaces, though interfacial magnetic modification like spin ordering, spin frustration and spin canting has been observed in different FM/AFM systems\textsuperscript{2,3,6,16}. The lower value of \( T_N \) in the sample with 5 u.c. thick LCMO, the increase in normalized magnetization and the same value of \( T_C \) with the increase in LCMO layer thickness suggest the possibility of the presence of FM domain at the interfaces due to the weakening of CO/OO ordered state, which is expected as CE type ordering is most susceptible to disorder. Since these samples show remarkable \( H_C \), we believe that the presence of FM domains at the interfaces and the coupling at the FM domain boundary between the FM − AFM may responsible for the remarkable value of \( H_C \). The existence of FM/AFM interaction should be realized in the field-cooled hysteresis loop, but perhaps we could not able to observed this effect due to the small interfacial volume. However, this effect was realized once the number of interface is increasing\textsuperscript{17}.

The heterostructures with LCMO layer thickness larger than 10 u.c. show a clear metal-insulator transition in the \( \rho(T) \). Also the resistivity as well as the activation energy in the insulator-like region decreases with the increase in LCMO layer thickness. For example, the activation energy of the heterostructure with 5 u.c. thick LCMO is \( \sim 0.12eV \) which is lower than the thin film of PCMO (\( \sim 0.29eV \)) and LCMO (\( \sim 0.32eV \)) on STO. However, the activation energy of these sample in the paramagnetic state of the \( \rho(T) \) is same. The in-field resistivity of these sample show thermally activated behavior below 30 K, which we attribute to the grain boundary-like tunneling\textsuperscript{18}. This also suggest the enhancement of FM phase at
the expense of $CO/OO$ phase in the $LCMO$ with the grain boundary modification$^8$. Since the resistance of the sample with $n = 5$ is insulator-like in the entire temperature range, we believe that the electronic and magnetic transport in these samples are due to spin polarized tunneling and percolative conduction as described in the conduction process of bulk $PCMO$ and $LCMO$$^8,^{11,19}$. Though there may be some other mechanisms responsible for the metal-like conduction in the $\rho(T)$, we attribute it mainly to the presence of $FM$ domains near or at the interfaces and the substrate-induced lattice distortion. The presence of $FM$ domains may partially open double exchange conducting percolative path, which induced the metal-like transport in these samples.

In conclusion, we fabricated epitaxial $Pr_{0.5}Ca_{0.5}MnO_3/La_{0.5}Ca_{0.5}MnO_3/Pr_{0.5}Ca_{0.5}MnO_3$ trilayers, where the parent compounds are $AFM$ insulator. We observed ferromagnetic and metal-like behavior with the increase in the $La_{0.5}Ca_{0.5}MnO_3$ layer thickness. We proposed that the distribution of magnetic order and magnetic moments near the interface are mainly responsible for the ferromagnetic behavior. The presence of interfacial spin ordering may opens the double exchange percolative conducting path to facilitate metal-like behavior in these heterostructures.

We greatly acknowledge financial support of Centre Franco-Indien pour la Promotion de la Recherche Avancee/Indo-French Centre for the Promotion of Advance Research (CEFIPRA/IFCPAR) under Project N°2808-1 and the Ministère de la Jeunesse et de l’Education Nationale (2003/87). We thank Dr. H.W. Eng for discussions.
REFERENCES

1 R. Von Helmolt, J. Wecker, R. Holzapfel, L. Schultz and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).

2 M. Izumi, Y. Murakami, Y. Konishi, T. Manako, M. Kawasaki, and Y. Tokura, Phys. Rev. B 60, 1211 (1999), M. Izumi, Y. Ogimoto, Y. Okimoto, T. Manako, P. Ahmet, K. Nakajima, T. Chikyow, M. Kawasaki and Y. Tokura, *idib* 64, 064429 (2001).

3 K.S. Takahashi, M. Kawasaki, Y. Tokura, Appl. Phys. Lett. 79, 1324 (2001).

4 P. Padhan and R.C. Budhani, Phys. Rev. B 67, 024414 (2003).

5 J. Shen, Z. Gai, J. Kirschner, Surf. Sci. Rep. 52, 163 (2004), I.K. Schuller, S. Kim, C. Leighton, J. Mag. Mag. Mater 200, 571 (1999).

6 K. Ueada, H. Tabata, T. Kawai, Science 280, 1064 (1998).

7 Z. Jirak, S. Krupicka, Z. Simsa, M. Doulka, and S. Vratislma, J. Magn. Magn. Mater. 53, 153 (1985).

8 P. Levy, F. Parisi, G. Polla, D. Vega, G. Leyva, H. Lanza, R.S. Freitas, L. Ghivelder, Phys. Rev. B 62, 6437 (2000).

9 C.N.R. Rao, A. Arulraj, A.K. Cheetham and B. Raveau, J. Phys.: Cond. Matter 12, R83 (2000).

10 W. Prellier, A.M. Haghiri-Gosnet, B. Mercey, Ph. Lecoeur, M. Hervieu, Ch. Simon, and B. Raveau, Appl. Phys. Lett. 77, 1023 (2000).

11 P. Padhan, W. Prellier and B. Mercey, Phys. Rev. B 70, 184419 (2004).

12 for a review see: A. Moreo, S. Yunoki, E. Dagotto, Science 283, 2034 (1999).

13 M. Fäth, S. Freisem, A.A. Menovsky, Y. Tomioka, J. Aarts, J.A. Mydosh, Science 285, 1540 (1999), L. Zhang, C. Israel, A. Biswas, R.L. Greene, A. de Lozanne, *idib* 285, 805
14 J. C. Loudon, N. D. Mathur, and P. A. Midgley, Nature 420, 797 (2002).

15 W. Prellier, M. Rajeswari, T. Venkatesan and R.L. Greene, Appl. Phys. Lett. 75, 1446 (1999).

16 K. Ueda, H. Tabata and T. Kawai, Phys. Rev. B 60, R12561 (1999).

17 P. Padhan and W. Prellier, Phys. Rev. B 71, 174419 (2005).

18 V. Moshnyaga, B. Damaschke, O. Shapoval, A. Belenchuk, J. Faupel, O.I. Lebedev, J. Verbeeck, G. Van Tendeloo, M. Mücksch, V. Tsurkan, R. Tidecks and K. Samwer, Nature Mat. 2 247 (2003).

19 F. Parisi, P. Levy, L. Ghivelder, G. Polla, and D. Vega, Phys. Rev. B 63, 144419 (2001).
Figures Captions:

Figure 1: Typical room temperature $\Theta - 2\Theta$ x-ray diffraction pattern around the (001) Bragg’s peak of (50 u.c.) $PCMO/(n$ u.c.) $LCMO/(10$ u.c.) $PCMO$ trilayer with (a) $n = 5$ and (b) $n = 18$ grown on (001)-oriented STO. The inset shows the out-of-plane lattice parameter of various trilayer structures with different $LCMO$ layer thicknesses. The bulk lattice parameters of $PCMO$ and $LCMO$ are also indicated.

Figure 2: Zero-field-cooled $\rho(T)$ in the presence of 0 tesla (open symbols) and 7 tesla (full symbols) magnetic field for different trilayers. The inset depicts the $MR$ ($MR = \frac{\rho(0) - \rho(7T)}{\rho(7T)}$) for the heterostructures with $n = 5$ and 18. Note that under magnetic field, all curves show an insulator-to-metal transition.

Figure 3(a): Field-cooled temperature dependent magnetization of different heterostructures at 10K at 0.01 tesla magnetic field. (b) Zero-field-cooled magnetic field dependent magnetization at 10K of the heterostructure with 18 u.c. thick $LCMO$. 

10