Multiple double-exchange mechanism by Mn$^{2+}$-doping in manganite compounds

P. Orgiani$^{1,2}$, A. Galdi$^{1,3}$, C. Aruta$^4$, V. Cataudella$^5$, G. De Filippis$^4$, C. A. Perroni$^4$, V. Mariglino Ramaglia$^4$, R. Ciancio$^5$, N. B. Brookes$^6$, M. Moretti Sala$^7$, G. Ghiringhelli$^7$, and L. Maritato$^{1,2}$

$^1$CNR-SPIN, I-84084 Fisciano (SA), Italy.
$^2$Department of Mathematics and Informatics, University of Salerno, I-84084 Fisciano (SA), Italy.
$^3$Department of Physics, University of Salerno, I-84084 Fisciano (SA), Italy.
$^4$CNR-SPIN and Department of Physics, University of Napoli, I-80126 Napoli, Italy.
$^5$CNR-IOM, TASC Laboratory, I-34149 Trieste, Italy.
$^6$European Synchrotron Radiation Facility, F-38043 Grenoble, France.
$^7$CNR-SPIN and Department of Physics, Politecnico di Milano, I-20133 Milano, Italy.

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Double-exchange mechanisms in RE$_{1-x}$AE$_x$Mn$_2$O$_3$ manganites (where RE is a trivalent rare-earth ion and AE is a divalent alkali-earth ion) relies on the strong exchange interaction between two Mn$^{3+}$ and Mn$^{4+}$ ions through interstitial oxygen 2p states. Nevertheless, the role of RE and AE ions has been understood “silent” with respect to the DE conducting mechanisms. Here we show that a new path for DE mechanism is indeed possible by partially replacing the RE-AE elements by Mn$^{2+}$-ions, in La-deficient La$_x$MnO$_{3-\delta}$ thin films. X-ray absorption spectroscopy demonstrated the relevant presence of Mn$^{2+}$ ions, which is unambiguously proved to be substituted at La-site by Resonant Inelastic X-ray Scattering. Mn$^{2+}$ is proved to be directly correlated to the enhanced magneto-transport properties because of an additional hopping mechanism through interstitial Mn$^{2+}$-ions. Such a scenario has been theoretically confirmed by calculations within the effective single band model. The use of Mn$^{2+}$ both as a doping element and an ions electronically involved in the conduction mechanism reveals a new phenomena in transport properties of manganites. More important, such a strategy might be also pursued in other strongly correlated materials.

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I. INTRODUCTION

Since its discovery, colossal magneto-resistance (CMR) effect has undoubtedly been among the most studied phenomena in solid state physics. CMR phenomenon has been explained within the framework of double exchange (DE) mechanism, based on a strong exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ ions through interstitial oxygen 2p states. The metallicity in these systems, as its strong dependence from an external magnetic field, comes from the mixed valence of Mn ions, which can transfer both charge and spin between their Mn$^{3+}$ and Mn$^{4+}$ states. Due to Hund’s rule, this transfer occurs only if the core spin of Mn$^{3+}$ is aligned with that of Mn$^{4+}$, thus explaining the colossal effects on the resistance values by the application of a spin-aligning external magnetic field. CMR effect has been intensively investigated in RE$_{1-x}$AE$_x$Mn$_2$O$_3$ (where RE is a trivalent rare-earth ion and AE is a divalent alkali-earth ion) manganites. The mandatory Mn$^{3+}$/Mn$^{4+}$ mixed population is generally controlled by the chemical substitution of the trivalent RE$^{3+}$-ion with a divalent AE$^{2+}$-ion. Indeed, to satisfy the overall charge neutrality within the manganite unit cell, when RE$^{3+}$-ions are substituted by AE$^{2+}$, some of the Mn atoms are forced into a 4+ state.

Here we show that a partial substitution of Mn$^{3+}$-ions at the La-site is indeed possible in La-deficient La$_x$MnO$_{3-\delta}$ manganite thin films. By combining polarization dependent x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray spectroscopy (RIXS), the relevant Mn$^{2+}$ content is demonstrated, and it is unambiguously assigned its crystallographic site (namely, the La-site). Similarly to AE$^{2+}$-doped manganites, the La$^{3+}$/Mn$^{2+}$ substitution induces the required Mn$^{3+}$/Mn$^{4+}$ mixed population. However, differently from the AE$^{2+}$-doping, the Mn$^{2+}$-ions at La-site are electronically involved in the transport mechanisms, having their electronic bands crossing the Fermi energy. Such an energetic configuration favors the hopping of electrical charge through that site (usually silent), in addition to the traditional Mn$^{3+}$/Mn$^{4+}$ hopping path, thus contributing to the ferromagnetic and metallic state. Such a Multiple-DE phenomenon has never been reported and it opens new perspectives in both fundamental studies on transport mechanism in strongly correlated manganites as in possible application by using these new class of materials.

II. THIN FILM GROWTH AND STRUCTURAL PROPERTIES

LMO thin films, with different values of the La/Mn ratio, were fabricated by Molecular-Beam Epitaxy (MBE) on SrTiO$_3$ (STO) substrates. Oxygen content was systematically varied by postannealing all the LMO samples, by varying the duration and the temperature of the process (thus providing LMO films at different stages of oxygenation, i.e. oxygen content). X-ray diffraction (XRD) analyses show that all the investigated LMO samples are in-plane matched with STO substrates. However, the out-of-plane lattice parameter monotonically depends on the La/Mn stoichiometric ratio. For each annealing batch (i.e., oxygen content), such a systematic trend in c-lattice parameter has always been observed.
Within the LMO samples with different La/Mn stoichiometric ratio, which appears to be the major factor in c-lattice variation within each set of samples. XRD spectra for optimized LMO series (i.e., highest metallicity) are reported in Fig.1.

All the spectra only shows the [001] peaks, indicating the preferential orientation of the film along the [001] substrate crystallographic direction, and no secondary phase is detected. The out-of-plane lattice parameters vary from 3.859 (measured in the sample with La/Mn = 0.66) to 3.878 Å (sample with La/Mn = 1.07). Considering that Mn ionic radius (which varies from 0.53 to 0.89Å, depending on its electronic configuration) is sizably smaller than those measured for the La-ions (ranging from 1.17 to 1.5Å), the monotonic decrease of the out-of-plane lattice parameter values is compatible with the gradual substitution of Mn atoms at the La-site, which was confirmed possible by neutron diffraction investigations of bulk samples. It is worthwhile to remark that, in polycrystalline LMO bulk-samples, it was shown a La-vacancies limiting value of 0.125 (i.e., La_{0.875}MnO_3), while further excess of Mn in the structure favors the formation of spurious phases, mainly Mn_3O_4. Such a scenario is sustained by XRD investigation of those samples, showing no variation in the LMO XRD peaks positions (i.e., saturation in structural and/or chemical composition of La-deficient LMO) and, more important, the appearing of Mn_3O_4 diffraction peaks. On the contrary, heavily La-deficient LMO thin films were proved to be structurally stable when grown on suitable substrates. In such a specific form, XRD investigation shows a monotonic and continuous change in structural lattice parameters, and no sign of diffraction peaks associative to any spurious phase, mainly Mn_3O_4. It is clear that the substrate plays a crucial role in stabilizing the LMO structure, which otherwise would be no longer stable for large La-deficiency.

III. TRANSPORT PROPERTIES

Transport properties were also investigated as a function of the La/Mn stoichiometry. Temperature dependence of the resistance for a series of four LMO films, with different values of the La/Mn ratio is reported in Fig.2 (data refer to the same LMO samples which XRD structural characterization is reported in Fig.1).

As the La-deficiency increases, more and more Mn ions are expected to be pushed into a 4+ state. According to the general phase diagram of manganites, $T_{MI}$ is expected to be maximum for a 33% doping level of Mn$^{4+}$ and subsequently to drop to zero for higher Mn$^{4+}$ concentration. In La$_{2/3}$MnO$_3$ where the Mn partial substitution at La-site does not occur, such an optimal doping occurs for a 10% deficiency of La. A further decrease of the La-content should force more a more Mn ions into a 4+ state, finally reaching a full Mn$^{4+}$ population for a La/Mn ratio of 0.66. Mn$^{4+}$-doping phase diagram is confirmed only for a small La-deficiency, in which a monotonic increase of the $T_{MI}$ is indeed observed. However, the highest metallicity ($\Delta\rho/\Delta T > 0$ at any temperature) is measured in La$_{0.66}$MnO$_{3-\delta}$, which is otherwise expected to be insulating and antiferromagnetic. Similarly, a monotonic increase of the Curie temperature ($T_C$) has been measured within the LMO series, reaching the highest value of 350K for the La$_{0.66}$MnO$_{3-\delta}$.
sample. It is evident that the metallic and ferromagnetic state in heavily La-deficient manganite films can not be explained by the self-doping mechanism.

We also investigated the possibility that the observed phenomena could be due to a different oxygen diffusion into the various samples. Such a diffusion can be affected by many extrinsic factors such as chemical composition, strain, oxygen content, film thickness, and so on. In order to rule out possible effects related to the only oxygen content, we systematically investigated the structural and the transport properties of our samples, by changing the time and the temperature of a post-annealing process, therefore probing different oxygen content in the LMO films. In the inset of Fig.2, the metal-insulator transition temperature $T_{MI}$ for different post-annealing process (keeping fixed the duration at 54 hours and by only changing the temperature $T_a$) is reported. The temperature and the duration of the annealing process directly affected the oxygen content in LMO films, and, as a matter of fact, the $T_{MI}$ is also the resistivity values. As the annealing temperature increases, the metallicity of the LMO samples also increases, thus confirming the incorporation of more and more oxygen within the structure. In this respect, by increasing the annealing temperature (i.e. oxygen content) we are exploring the manganite $T_{MI}$ vs doping phase diagram, which foresees both an under-doped and an over-doped regime. Nevertheless, if we look for instance at the La/Mn=0.88 series, $T_{MI}$ shows a maximum for an annealing temperature of 1000°C and subsequently a reduction of that value for an annealing temperature of 1030°C. Therefore, it should be concluded that the La$_{0.88}$MnO$_{3-\delta}$ sample annealed at 1000°C is the optimally doped samples, showing the optimal $\text{Mn}^{3+}/\text{Mn}^{4+}$ mixed population. However the highest $T_{MI}$ among the La$_{0.66}$MnO$_{3-\delta}$ samples is well above to such a value (in the inset of Fig.2, we have indicated a value of $T_{MI}$ for this samples as high as 430K; such a value corresponds to the destroying of any possible polaronic insulating state by the thermal energy), while it should have been equal to that measured in La/Mn=0.88 series, even if obtained with a different annealing process (i.e. oxygen content). From these data it is clear that the physical phenomena at play in heavily La-deficient LMO samples is not the one at play in conventional manganites. Finally, it is well-known that chemical and structural inhomogeneities (such as spurious phases, oxygen stoichiometry, grain size, and others) can play an important role in transport properties of manganite thin films. In this respect, as for general inhomogeneities, strong structural and chemical disorder, spurious insulating phase, impurities cooperate to worsen the transport properties of manganite thin films (for instance, because of low-resistance percolation paths, $T_{MI}$ usually decreases and the resistivity increases). However, this is clearly not what we observed, thus strongly supporting the hypothesis that a novel mechanism is at play in heavily La-deficient thin films.

IV. X-RAY ABSORPTION SPECTROSCOPY MEASUREMENTS

To probe the electronic structure close to the Fermi level, which is dominated by the Mn 3d and O 2p states, X-ray absorption spectroscopy (XAS) at the Mn L$_{2,3}$ and O K edges were performed at the ID08 beamline of ESRF in Grenoble. The anisotropy effects related to the different doping levels were investigated by varying the polarization of the grazing incidence synchrotron radiation from horizontal (H-polarization) to vertical (V-polarization) which correspond roughly to investigate the out-of-plane and the in-plane directions, respectively. All Mn-L spectra reported in Fig.3 show two broad multiplet structures, L$_3$ and L$_2$, separated by spin-orbit splitting.

Figure 3: (Color online) Room temperature XAS (panel a, in V-polarization and panel b in H-polarization), and LD at Mn L$_{3,2}$ edge of LMO films with different La/Mn ratio. Data refer to LMO film with La/Mn ratio 0.66 (black), 0.88 (red), 0.98 (green) and 1.07 (blue), respectively. XAS spectra for a MnO single-crystal are also reported (cyan). All the spectra in V- and H-polarization are shifted vertically for clarity.

The effect of doping can be seen more clearly in the L$_3$ region where the spectra are similar to $\text{Mn}^{3+}/\text{Mn}^{4+}$ manganites when La/Mn $\geq$1, while the increasing of $\text{Mn}^{2+}$ content in LMO films with La/Mn<1 gives rise to typical pronounced features. The Linear Dichroism (LD) obtained from the difference between the two XAS (V-H) is also particularly interesting when the La/Mn<1. Indeed, the spectra are similar to the theoretical calculations for the single 3d$^4$ configuration ($\text{Mn}^{3+}$) in case of a tetragonal distortion of the octahedra, with an elongation of the out-of-plane Mn-Mn distances. Unlike $\text{Mn}^{3+}$, it may be noted that $\text{Mn}^{4+}$ (3d$^3$) and $\text{Mn}^{2+}$ (3d$^5$) do not tend to distort their own octahedral environment by Jahn-Teller effect. Therefore, no-contribution is expected to the orbital component of LD from $\text{Mn}^{4+}$ and $\text{Mn}^{2+}$. The enhancement of LD intensity can be a consequence of the elongation of the $\text{Mn}^{3+}$ octahedra to compensate the reduced O-Mn$^{2+}$-O distances, thus being an indirect demonstration of the increased $\text{Mn}^{2+}$ content.
It is worthful to remark that in LaMnO$_3$ single-crystals Mn$^{2+}$-Mn$^{3+}$ coexistence was already observed, pointing to an intrinsic mixed valence state in insulating manganite, rather than Mn$^{2+}$-signal generated by spurious MnO surface layers. However, such Mn$^{2+}$-Mn$^{3+}$ coexistence is expected to decrease by increasing the metallicity of the system. In our investigation, some films do not show any Mn$^{2+}$-features (ruling out the possibility of a MnO surface layer due to post-annealing process and/or surface reconstruction) and these last are observed in the most metallic samples, while they are absent in the insulating ones. Finally, XAS spectra at the Mn L-edge undoubtedly proves the strict correlation between the La-deficiency and the presence of Mn$^{2+}$ in heavily La-deficient LMO samples.

V. RESONANT INELASTIC X-RAY SPECTROSCOPY MEASUREMENTS

In order to fully comprehend the role of the Mn$^{2+}$ in the transport mechanisms at play in La-deficient LMO films, it is mandatory to unambiguously determine its structural configuration. Manganites are mostly arranged in a perovskite structure, having the general formula ABO$_3$, which can be seen as a stacking sequence of AO- and BO$_2$-planes. Mn atoms are usually placed at the B-site, while the RE$^{3+}$/AE$^{2+}$ atoms lie within the AO-planes. In this respect, it is crucial to assign to the Mn$^{2+}$-ions either the perovskite A-site or the B-site. In order to do that, we exploited the almost unique capability of L-edge RIXS to measure the set of the local dd excitations to assign the crystallographic site of divalent Mn$^{2+}$-ions and, possibly, to derive some indications on its direct or indirect involvement in the DE ferromagnetism in LMO films. The two possible cation sites have different coordination and ion-oxide distances: site A (panel a in the inset in Fig.4) is cubo-octahedral (12 O$^{2-}$ neighbors), with A-O distance $\approx$ 2.7 A, site B (panel b in the inset in Fig.4) is octahedral (6 O$^{2-}$ neighbors), with B-O distance $\approx$ 1.9 A. In a simple point charge crystal field model one thus expects a much smaller splitting of $e_g$ to $t_{2g}$ states at A than B sites. Moreover the crystal field parameter $10Dq = E(e_g) - E(t_{2g})$ should be negative at A and positive at B. As a reference we use MnO, which has the NaCl structure: Mn$^{2+}$ ion is at octahedral site with Mn-O distance $\approx$ 2.2 A, i.e., intermediate between sites A and B in LMO. Naming $d$ the cation-ligand distance, and recalling that point charge crystal field predicts $10Dq \propto$$d^{-5}$, we expect $10Dq$ to be smaller (greater) at site A (B) than in MnO. We have measured the dd excitation spectra of Mn$^{2+}$ in LMO and MnO using RIXS excited at the Mn $L_3$ absorption edge. In particular we have chosen the photon energy 640.0 eV, which is peculiar of Mn$^{2+}$ sites (see XAS spectra of Fig.3). The RIXS spectra are shown in Fig.4.

In heavily La-deficient LMO metallic films, where XAS demonstrates a strong presence of Mn$^{2+}$, the dd excitations are very different from those of MnO. To estimate quantitatively $10Dq$ we have calculated the RIXS spectra within a single ion crystal field model and tuned $10Dq$ and the rescaling of the inter-atomic Slater integrals so to fit the main experimental features. The result is shown in the top panel of Fig.4. For MnO we essentially confirm the results of Ghiringhelli et al. $10Dq = 1.0$ eV, Slater integrals rescaled to 70% of their Hartree-Fock value. For Mn$^{2+}$-doped LMO films, we find a much smaller crystal field: $10Dq = -0.1$ eV, Slater integrals rescaled to 64%. This indicates univocally that Mn$^{2+}$ sits at site A and that the Mn-O bond has a non negligible covalent character (indicated by the strong renormalization of Slater integrals). As further support to our interpretation of the RIXS spectra, we show an example of insulating LMO films, excited at the same energy as for the other cases: the spectrum is incompatible with dd excitations of Mn$^{2+}$ and is rather typical of Mn$^{3+}$ in manganites.

VI. THEORETICAL MODEL

With the Mn$^{2+}$-ions indeed at the A-site, one would expect that they could play the role of the divalent AE$^{2+}$-
ion in manganites by hole-doping the MnO$_2$ planes. In this respect, the substitution of La$^{3+}$ ions with an atom having a smaller ionic radius (namely 0.89 and 1.17Å for Mn$^{2+}$ and La$^{3+}$, respectively) should decrease the tolerance factor, thus pushing the system into a more a more insulating state. In this respect, a novel approach based on electron-hole Bose liquid has been recently proposed to describe metallic states in manganites which are supposed to be in an insulating and antiferromagnetic state. However, even though such phases are indeed metallic, they are described in terms of “poor metallic phase” with respect to the strong metallic and ferromagnetic state, which ultimately can not described the enhanced metallicity that we observed in our samples.

The observed enhanced metallicity can be understood by assuming that the Mn$^{2+}$ ions at A-sites contribute to the electron hopping via a new DE mechanism. The need for an alternative conducting mechanism stems from the fact that a smaller tolerance factor depresses the usual DE mechanism, but favor a new hopping path involving Mn$^{2+}$ ions. Beside the hopping mechanism in the traditional DE-framework (panel a of Fig.5), two extra possible paths for the added hole were considered: namely, a hopping mechanism between two Mn-ions directly through an intervening Mn$^{2+}$-ion (panel b of Fig.5) and a Multiple-DE hopping path through the Oxygen-Mn-Oxygen ions (panel c of Fig.5).

The effective hopping $t$ of Mn$^{3+}$-Mn$^{2+}$-Mn$^{4+}$ hopping mechanism can be estimated following Hasegawa-Anderson scheme, with the O$^{2−}$ replaced by Mn$^{2+}$ via $t = t_1^2/(E_1 − E_2)$, where $t_1$ is the resonance integral for the bond with the intermediate ion, $E_1$ and $E_2$ are the energy levels of the two atomic orbitals participating to the bond. In order to validate our proposal we estimate the overall hopping of an $e_g$ electron through Mn$^{2+}$ ions in an undistorted cubic lattice. We adopt the values of ionic radii and the energy levels that are reported in the literature. Using as reference value the effective hopping Mn$^{3+}$-Mn$^{4+}$, through the $t_2$ oxygen level along $x$ direction, $t_x$, we obtain an effective hopping parameter of the order of $10^{-4}$ for both 3$x^2$-$r^2$ and $x^2$-$y^2$. This analysis shows that a direct DE-hopping through Mn$^{2+}$ is very unlikely. On the contrary, the effective DE hopping of the added hole through the following path $Mn^{3+}−O^{2−}−Mn^{2+}−O^{2−}−Mn^{3+}$ is relevant. It can be estimated extending the approach used above. By using a renormalization procedure that allows to decimate the three intermediate sites we get:

$$t_5 = \frac{t_1^2}{(E_1 − E_2)(E_1^2 − E_1(E_2 + E_3) - 2t_2^2 + E_2E_3)}.$$  

Such a value has been obtained by assuming that all the ions are structurally arranged in an undistorted perovskite. In fact, manganites, and in particular LaMnO$_3$, generally show a distorted orthorhombic/rhombohedral perovskite unit cell, characterized by O-ions slightly displaced out of the joining lines among the Mn-ions (see Fig.5). In this respect, because of the buckling angle between the Mn-plane and the Mn-O bonds in distorted perovskites, the superimposition of Mn$_{I}$-O$_{X}$-Mn$_{II}$ orbitals is actually reduced, thus subsequently reducing the $t_x$ value. Moreover, the smaller size of Mn$^{2+}$-ionic radius (compared to La$^{3+}$’s ones) should increase the cubic distortion of the perovskite cells, thus further reducing the $t_x$ value. On the contrary, because of the tilting of the oxygen octahedra, the distance between some oxygen ions and the central Mn$^{2+}$-ion should be shortened with respect to the undistorted structure (in which the A-O distance is $\sqrt{2}/2$ times unit cell lattice parameter). As a consequence, the superimposition between O$^{2−}$-Mn$^{2+}$ orbitals actually increases, thus increasing the $t_5$-value. Eventually, in real distorted perovskite, a substantial increment of the $t_5/t_x$-ratio is expected, thus pointing out towards a significative role of the proposed new Multiple-DE conducting path.

![Figure 5](https://via.placeholder.com/150)

Figure 5: (Color online) Possible hopping mechanisms in conventional and Mn$^{3+}$-substituted manganites. In panel a, the traditional DE-mechanism (blue arrows). In panel b and c, two possible additional hopping paths in Mn$^{3+}$-doped manganites are reported: a direct hopping (panel b) between two Mn-ions (Mn$_{I}$ and Mn$_{II}$, respectively) through intervening Mn$^{2+}$-ion (namely, Mn$_{I}Mn_{II}$) and a Multiple-DE hopping path (panel c) through the Oxygen-Mn-Oxygen ions (O$_{II}$Mn$_{I}$O$_{III}$ and O$_{III}$Mn$_{II}$, respectively).
VII. CONCLUSIONS

In conclusions, a new phenomenon for charge-hopping mechanism in manganites (named Multiple double-exchange, or Multiple-DE) has been observed. We have shown that, in La$_2$MnO$_{3-δ}$ manganite thin films, as La content decrease, a partial substitution of Mn-ions at the La-site is indeed possible. Polarization dependent XAS characterization has demonstrated the relevant Mn$^{2+}$ content in heavily La-deficient LMO samples. RIXS investigation has allowed us to unambiguously assign the crystallographic site (namely, the perovskite A-site) of the divalent Mn$^{2+}$. This last is experimentally and theoretically proved to be more efficient with respect to traditional DE-mechanism. Such a further increase of the Curie temperatures in manganites could possible allow the use of manganite-based devices at room temperatures, which nowadays is limited because of the depression of magnetic alignment at that specific temperatures. The very idea of using multiple-valence atoms both as a dopant and as an active element electronically involved in the conduction mechanism (namely, the Mn$^{2+}$ in manganites) opens new scenarios in the study of physical properties of CMR-materials. More important, such a strategy might be also pursed in other strongly correlated electrons materials.

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