Modelling of strain effects in manganite films

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Thickness dependence and strain effects in films of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ perovskites are analyzed in the colossal magnetoresistance regime. The calculations are based on a generalization of a variational approach previously proposed for the study of manganite bulk. It is found that a reduction in the thickness of the film causes a decrease of critical temperature and magnetization, and an increase of resistivity at low temperatures. The strain is introduced through the modifications of in-plane and out-of-plane electron hopping amplitudes due to substrate-induced distortions of the film unit cell. The strain effects on the transition temperature and transport properties are in good agreement with experimental data only if the dependence of the hopping matrix elements on the $\text{Mn} – \text{O} – \text{Mn}$ bond angle is properly taken into account. Finally variations of the electron-phonon coupling linked to the presence of strain turn out important in influencing the balance of coexisting phases in the film.
The perovskite oxides $La_{1-x}A_xMnO_3$ ($A$ stands for a divalent alkali element such as Sr or Ca) have been studied intensively since the discovery of "colossal" magnetoresistance (CMR) in thin films.¹ These dramatic changes in electron and magnetic properties are found at temperatures around the combined ferromagnetic-paramagnetic and metallic-insulating (MI) transitions. The ferromagnetic phase was usually explained by introducing the double exchange mechanism,² in which hopping of an outer shell electron from a $Mn^{3+}$ to a $Mn^{4+}$ site is favored by a parallel alignment of the core spins. In addition to the double-exchange term that promotes hopping of the carriers, a strong interaction between electrons and lattice distortions has been proposed to play a non negligible role in these compounds³,⁴ and confirmed by many experimental measurements.⁵–⁷ Actually for the $Mn^{3+}$ site, with three electrons in the energetically lower spin triplet state $t_{2g}$ and the mobile electron in the higher doublet $e_g$, a Jahn-Teller distortion of the oxygen octahedron can lead to splitting of the doublet and the trapping of the charge carriers in a polaronic state. A second important connection between crystal structure and MI transition lies in the dependence of the $Mn – Mn$ electron transfer on the $Mn – O – Mn$ bond angle $\theta$, that is on the orientation of the oxygen octahedra with respect to the main crystal axes. This implies a strong effect of either external pressure or mean $A$-site ionic radius on the ferromagnetic critical temperature $T_C$.⁸,⁹ Finally, due to the complex interplay of electron, orbital, spin and lattice degrees of freedom, strong tendencies toward phase separation are present in these materials.¹⁰

In recent papers,¹¹–¹³ some of us have shown on the basis of a variational approach that the interplay of the electron-phonon ($el-\text{ph}$) interaction and the double- and super-exchange magnetic effects can be important to explain the experimentally observed tendency of manganite bulk to form inhomogeneous magnetic structures near the phase boundaries. Employing this scheme, spectral and optical properties in absence and in presence of magnetic field have been derived in the regime of CMR finding good agreement with experimental data.

The situation for manganite films is more complicated. Maximum $MR$ values in films are usually larger and at lower temperatures than in equivalent bulk materials.¹⁴,¹⁵ This
enhanced change of the resistivity of the films has immediately suggested device applications based on the sensitivity to magnetic fields. An essential issue for manganite films is to understand the role of the strain due to lattice mismatch between the substrate and the film. Indeed it has been found that properties such as magnetoresistance, magnitude of the temperature $T_C$, resistivity, magnetization, transport and magnetic anisotropies, and spin and orbital order structure are sensitive to the epitaxial strain. These properties are different from the changes induced by hydrostatic or chemical pressure, since in-plane strain generally leads to an out-of-plane strain of different sign. Moreover the effects induced by the substrate are able to influence the tendency toward phase separation, induce inhomogeneities in films, and cause new electronic behavior not found in bulk materials of the same composition. Actually, the strain affects so many quantities that it could be used to control the properties of interest by depositing films on various substrates, changing the deposition conditions and the post-annealing procedure, and varying the thickness.

In this paper we extend the variational approach of the bulk in order to deal with manganite films. The size of the film is taken into account considering the system made of a finite number of planes and imposing open boundary conditions along the out-of-plane direction of growth. The thickness dependence has been studied finding similar results in the weak $el-ph$ coupling regime appropriate for large bandwidth systems such as $La_{1-x}Sr_xMnO_3$ (LSMO) films and in the intermediate regime suitable for $La_{1-x}Ca_xMnO_3$ (LCMO) films: reduction of the critical temperature, decrease of the magnetization and increase of the resistivity especially at low temperatures. For thin films characterized by a thickness larger than the possible dead layer, the calculated results are in good agreement with experimental behaviors.

The strain in the film is simulated through modifications of in-plane and out-of-plane hoppings, that are related to lattice parameters measured in these systems. It is found that the compressive strain leads to an enhancement of the critical temperature, while tensile strain weakens the ferromagnetic phase. When the dependence on the bond angle $\theta$ is properly taken into account, it is shown that also for compressive strain a reduction of the
transition temperature can occur. The strain introduces also anisotropies in the transport properties showing the consistency of the theory with experimental data. Finally substrate-induced variations of the $el - ph$ coupling are considered pointing out that, together with finite size and strain effects, they can strongly influence the subtle balance of coexisting phases favoring insulating phases when the thickness of the film decreases.

In section I experimental and theoretical issues about strain in manganite films are discussed; in section II the variational approach and the transport properties of the bulk are generalized to deal with manganite films; in section III the thickness dependence is analyzed; in section IV the strain effects on the phase diagram and transport properties are calculated; in section V changes of the $el - ph$ coupling induced by the substrate are considered.

I. EXPERIMENTAL AND THEORETICAL BACKGROUND

In this section we discuss experimental and theoretical issues about strain in manganite films.

In most cases tensile strain suppresses ferromagnetism and, consequently, critical temperature $T_C$. On the contrary, compressive strain should reduce the resistivity and shifts $T_C$ toward higher temperatures with respect to the transition temperature of the bulk. The observed strain effect is usually interpreted within the double-exchange model, since the hopping matrix element $t$ can be altered by epitaxial strain through the change of the $Mn - O$ bond length $d$ and the bond angle $\theta$. However, recent studies show that compressive strain does not always lead to enhancement of $T_C$ and some anomalous results have been also reported for tensile strain.\cite{35,36}

In order to explain unusual results in manganite films, an extra mechanism mediated by the orbital state has been proposed.\cite{36} Furthermore the theoretical work concerning manganite films has distinguished between uniform bulk strain and biaxial strain effects on the Curie point.\cite{37} The biaxial strain increases the Jahn-Teller splitting and favors electron localization in $e_g$ levels, causing $T_C$ to decrease. The agreement with experimental data is in sign and
order of magnitude pointing out that a Jahn-Teller coupling is a crucial variable.\textsuperscript{37–39} However, this model does not account for the observed decrease of $T_C$ upon thickness reduction mainly in films of LCMO on $SrTiO_3$ (STO) and $LaAlO_3$ (LAO).\textsuperscript{22,32}

When the properties of epitaxial films are studied as a function of thickness, different and complex features are usually observed. First, a reduction of the Curie point $T_C$ and the MI transition temperature $T_P$ of LSMO and LCMO films has been reported when thickness decreases. This occurs both for films with a gradually relaxed structure\textsuperscript{20,22,40} and for fully strained films\textsuperscript{32} showing that the strain cannot be the only factor responsible for the reduction of $T_C$ in very thin films. Second, when thickness is reduced, the resistivity increases and the magnetic moment often decreases. This has been usually interpreted as due to the presence of a dead layer located at interfaces.\textsuperscript{20,32,41,42} The thickness of these dead layers is of the order of a few nm depending on the substrate. The decrease of the Curie temperature and the increase of resistivity are gradual suggesting that regions with higher resistivity could be present at distances from the interface larger than size of the dead layer. Third, changes in the phase coexistence linked to the thickness dependence can lead to charge trapping in thin films.\textsuperscript{32} Thus the thickness dependence and the strain effect are far from being fully understood and challenging.

**II. VARIATIONAL APPROACH AND TRANSPORT PROPERTIES**

The adopted model takes into account the double-exchange mechanism, the coupling of the $e_g$ electrons to lattice distortions and the super-exchange interaction between neighboring localized $t_{2g}$ electrons.\textsuperscript{11–13} Within the single orbital approximation (reasonable in the doping regime where CMR occurs), the Hamiltonian reads

$$H = \sum_{i,\delta} \left( \frac{\delta_{S_i}^{i+\delta} + 1/2}{2S+1} \right) t_\delta c_i^\dagger c_{i+\delta} + \omega_0 \sum_i a_i^\dagger a_i + g \omega_0 \sum_i c_i^\dagger c_i \left( a_i + a_i^\dagger \right) + \epsilon \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j - \mu \sum_i c_i^\dagger c_i. \quad (1)$$
The quantities in eq.(1) have been discussed in previous papers. In films the electron transfer element is assumed to be depending on the direction of hopping and open boundary conditions are imposed along the \( z \) axis assumed as the out-of-plane axis of growth. As in the bulk, the dimensionless parameter \( \lambda = \frac{g^2 \omega_0}{6t} \) is introduced to measure the strength of the \( el - ph \) interaction in the adiabatic regime.

Two canonical transformations are performed in order to treat the \( el - ph \) interaction variationally. Then the Bogoliubov inequality is employed in order to derive the variational free energy of the system using a test Hamiltonian characterized by free electron, phonon and spin degrees of freedom. The electron free energy per site reads

\[
 f_{\text{test}}^{el} = \frac{(-T)}{(N_x N_y N_z)} \sum_k \log \left[ 1 + e^{-\beta \xi_k} \right] + \mu \rho, \tag{2}
\]

where \( T \) is the temperature, \( \beta \) the inverse of \( T \), \( N_i \) the number of sites along the \( i \) axis, and \( \rho \) the electron density. In eq.(2) we have \( \xi_k = \bar{\varepsilon}_k - \mu \), where \( \bar{\varepsilon}_k = \varepsilon_k + \eta \) is the renormalized electronic band. The band dispersion \( \varepsilon_k \) is

\[
 \varepsilon_k = \varepsilon_{k_x, k_y} + \varepsilon_{k_z} = -2t_{eff}^x \cos(k_x) + \cos(k_y) - 2t_{eff}^z \cos(k_z), \tag{3}
\]

where the effective transfer integrals \( t_{eff}^x \) and \( t_{eff}^z \) take into account the polaronic and double-exchange effects, and the quantity \( \eta \) measures the electronic band shift due to the \( el - ph \) interaction. Due to the finite size along the \( z \) axis, the values of \( k_z \) are given by

\[
 k_z = \frac{m \pi}{(N_z + 1)}, \tag{4}
\]

with \( m = 1, \ldots, N_z \). The thermodynamic limit is performed along \( x \) and \( y \) directions, using a constant electronic density of states \( g_{2D}(\varepsilon) = 1/(8t_{eff}^x) \), that represents a simple approximate expression for the exact density of states used for a 2D lattice.

Within the variational approach, in a way analogous to the bulk case, the linear response to an external electromagnetic field of frequency \( \omega \) and, consequently, the transport properties in the limit \( \omega \to 0 \) can be calculated. The focus is on the real part of the conductivity tensor \( \Re \sigma_{\alpha, \gamma}(\omega) \) given by
\[ \Re \sigma_{\alpha,\gamma}(\omega) = -\frac{3 \Pi_{\alpha,\gamma}^{\text{ret}}(\omega)}{\omega}, \]

(5)

where the \( \Pi_{\alpha,\gamma}^{\text{ret}} \) is the retarded current-current correlation function. It can be deduced making the analytic continuation of the correlation function defined in Matsubara frequencies as

\[ \Pi_{\alpha,\gamma}(i\omega_n) = -\frac{1}{(N_x N_y N_z)} \int_0^\beta d\tau e^{i\omega_n \tau} \langle T_\tau j_\alpha^\dagger(\tau) j_\gamma(0) \rangle, \]

(6)

where the current operator \( j_\alpha \) suitable for the film geometry is

\[ j_\alpha = ie \sum_{i,\delta} \delta t_\alpha \left( \frac{S_0^{i+\delta} + 1/2}{2S + 1} \right) c_{i+\delta}^\dagger c_i, \]

(7)

with \( e \) electron charge.

We perform the two canonical transformations and make the decoupling of the correlation function in electron, phonon and spin terms through the introduction of the test mean-field hamiltonian. In manganite films the electron correlation function is

\[ \langle T_\tau c_i^\dagger(\tau)c_{i+\delta}(\tau)c_{i'}^\dagger+\delta\gamma c_{i'} \rangle_t = -\sum_{k,k_1} \Phi_{R_i}(k) \Phi_{R_i+\delta\gamma}(k_1) \Phi_{R_i'}(k) G^{(0)}(k, -\tau) G^{(0)}(k_1, \tau), \]

(8)

where the function \( \Phi_{R_i}(k) \) is

\[ \Phi_{R_i}(k) = \left( \frac{e^{ik_x i_x}}{\sqrt{N_x}} \right) \left( \frac{e^{ik_y i_y}}{\sqrt{N_y}} \right) \phi_{iz}(k_z), \]

(9)

with \( \phi_{iz}(k_z) \) given by

\[ \phi_{iz}(k_z) = \frac{2 \sin(k_z i_z)}{\sqrt{(2N_z + 1) - \sin[(2N_z + 1)k_z]/\sin(k_z)}}, \]

(10)

and \( G^{(0)}(k, \tau) \) free electron Green’s function. To derive the optical properties, second order fluctuations on the mean-field approach are fundamental since they introduce scattering between charge carriers.\(^{12}\) The effect of the damping can enter the calculation substituting \( G^{(0)} \) for \( \tilde{G} \) that in Matsubara frequencies is expressed as

\[ \tilde{G}(k, i\omega_n) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{\tilde{A}(k, \omega)}{i\omega_n - \omega}, \]

(11)
where the spectral function $\tilde{A}$ is assumed to be

$$\tilde{A}(k, \omega) = \frac{\Gamma(k)}{[\Gamma(k)]^2/4 + (\omega - \xi_k)^2},$$

with $\Gamma(k)$ rate of the scattering with optical phonons and spin fluctuations evaluated on the energy shell.$^{12}$

The conductivity tensor $\Re\sigma_{\alpha,\gamma}(\omega)$ is deduced following the lines of our previous works.$^{13,43,44}$ In the film geometry this tensor is diagonal with $\Re\sigma_{xx}(\omega) = \Re\sigma_{yy}(\omega)$, thus, in the limit $\omega \to 0$, two different resistivities are obtained: in-plane resistivity $\rho_{xx}$ and out-of-plane resistivity $\rho_{zz}$.

**III. THICKNESS DEPENDENCE**

In this section we analyze the effects of the thickness on the phase diagram, the magnetization and the transport properties of the film. For the moment we do not introduce hopping anisotropies being $t = t^i$, with $i = x, y, z$.

First the role of the size is investigated in the regime of weak $el-ph$ coupling appropriate for $LSMO$ films. In Fig. 1 the phase diagram of the film is reported for the bulk (solid line), for a film made of 10 planes (dashed line) and 5 planes (dotted line). For these values of the parameters the system exhibits a continuous transition from a double-exchange ferromagnet to a metallic paramagnet. A decrease of size leads to a reduction of the ferromagnetic phase that seems to be a generic feature of magnetic films.$^{45}$ Actually the critical temperature shifts to lower temperatures than that of the bulk when the spin-spin correlation exceeds the film thickness.$^{46}$ In the inset of Fig.1 the variation of the Curie temperature as function of the number of the planes is reported. The critical temperature shows a large decrease as the number of planes is reduced. This effect is very pronounced when the number of planes is smaller than 10: in fact in this case there is a shift of the critical temperature larger than 10% of the corresponding temperature of the bulk.

We have investigated the thickness dependence also for a manganite film in the regime of intermediate $el-ph$ coupling and bandwidth suitable for $LCMO$ films. In this case near the
The $MI$ transition the system segregates in ferromagnetic and antiferromagnetic or paramagnetic domains of itinerant and localized carriers, respectively.\textsuperscript{11–13} In Fig. 2 the phase diagram for these systems is shown in correspondence with different sizes of the system. We find that the reduction of the ferromagnetism does not depend on the order of the transition. Although the transition lines are different from the phase diagram of the film in the weak-coupling regime, the decrease of the ferromagnetic phase is of the same order. This is confirmed also by the behavior of the critical temperature as a function of the number of planes, as reported in the inset of Fig. 2. Even if the transition temperatures are lower, the shape of the curve bears a strong similarity with the corresponding plot for systems in weak-coupling regime: in both cases the shift of Curie temperature $S(N) = 1 - T_C(N)/T_C(\infty)$ follows a power law $S(N) \sim N^{-r}$.\textsuperscript{45}

We note that, in manganite films grown without detectable lattice defects, the decrease of the critical temperature occurs for a thickness smaller than 20\,nm.\textsuperscript{20} Therefore for thin films characterized by thickness larger than the possible dead layer, the size effect can be relevant in the interpretation of experimental behaviors allowing to explain the gradual decrease of the critical temperature with decreasing film size. Actually, the tendency towards the localization in the thinnest films cannot be entirely ascribed to the presence of a dead layer.

Due to the thickness effect, the ground state presents a weaker order of spins, that can be easier destroyed with increasing temperature. Indeed, as the size of the film is reduced, the magnetization assumes smaller values at low temperatures.\textsuperscript{42} In a double-exchange model a weakening of the ferromagnetism is expected to reduce the mobility of the carriers. This is confirmed by the calculated in-plane resistivity $\rho_{\langle x\rangle}$ that, as reported in Fig. 3, at $T = 0.05\omega_0$, exhibits a significant increase as the number of planes decreases (the out-of-plane resistivity $\rho_{\langle z\rangle}$ shows a similar behavior). Like the critical temperature, large variations occur when the film is very thin suggesting that size effect can be important to explain the gradual increase of the resistivity as the thickness decreases. However, the behavior of resistivity with respect to the number of planes is different as the temperature increases. In fact, as shown in the inset of Fig. 4, at higher temperatures the resistivity of the
film is smaller for thinner films. This can be understood considering that the differences in the spin order due to size effects diminish with increasing temperature. So the bare behavior of the scattering rate with optical phonons emerges: this type of scattering decreases when the size of the system is reduced in agreement with what happens in quantum wells. At high temperatures, in addition to size effect, other effects such as the strain have to be considered in order to get a better agreement with experimental data.

IV. STRAIN EFFECTS

In this section we deal with strain effects on the properties of the film.

The strain in the film is introduced through the modifications of in-plane and out-of-plane hoppings, that are linked to lattice parameters measured in these systems. It can be assumed \( t^x = t^y \propto \cos(\phi_{in})/d_{in}^{3.5} \), where \( d_{in} \) is the in-plane bond length and \( \phi_{in} = (\pi - \theta_{in})/2 \), with \( \theta_{in} \) in-plane bond angle. In an analogous manner, we can have \( t^z \propto \cos(\phi_{out})/d_{out}^{3.5} \), where \( d_{out} \) is the out-of-plane bond length and \( \phi_{out} = (\pi - \theta_{out})/2 \), with \( \theta_{out} \) out-of-plane bond angle. If one neglects the angular dependence, the ratio of the hopping amplitudes of the film with respect to the bulk values are given by \( t^x/t_B = (a_B/a)^{3.5} \) and \( t^z/t_B = (c_B/c)^{3.5} \), where \( a_B = c_B \) is the lattice parameter of bulk, \( a \) and \( c \) are in-plane and out-of-plane lattice parameters of the film measured by X-ray diffraction experiments. These ratios simulate the strain of the film within the variational approach, so its effects on the phase diagram and the transport properties can be estimated.

The variations of the phase diagram are controlled mainly by the changes of in-plane hopping, so that compressive strain \( (c/a > 1) \) leads to an enhancement of the critical temperature, while tensile strain \( (c/a < 1) \) to a reduction. The increase of the compressive (tensile) strain is able to perturb the system also at low temperatures where the ferromagnetic alignment of the spins is reinforced (reduced). Deriving in-plane and out-of-plane hoppings from the lattice parameters of a compressively strained \( LSMO \) film, it is found that the strain introduces anisotropies in the transport properties of the films in the weak coupling
Indeed, as shown in Fig. 4, the in-plane resistivity $\rho_{x,x}$ decreases in temperature with increasing compressive strain, while the out-of-plane resistivity $\rho_{z,z}$ increases. This is explained by the fact that, increasing the strain, the in-plane hopping is enhanced, while the out-of-plane hopping is reduced. In any case, at low temperatures, due to the enhancement of the ferromagnetic order induced by the compressive strain, both the resistivities decrease with increasing strain.

Next we have investigated the effects of compressive and tensile strain on the phase diagram of a manganite film in the intermediate coupling regime. The in-plane and out-of-plane hopping amplitudes have been deduced considering the lattice parameters of LCMO films grown on different substrates.\textsuperscript{18} The film on LAO corresponds to the ratio $c/a = 1.009$, that on MgO to $c/a = 1.002$, finally that grown on STO to $c/a = 0.981$. As shown in Fig. 5, in the first case, the compressive strain (dotted line with diamonds) leads to an enhancement of the critical temperature with respect to the bulk value (solid line with circles) unlike experimental results.\textsuperscript{18} In the second case, even if field strain is near the unity (dash-dotted line with down triangles), the critical temperature shifts at lower temperatures in agreement with experimental data. Actually in this case both the lattice parameters exceed the bulk value, determining a reduction of the in-plane hopping. In the third case, for tensile strain (dashed line with squares), the shift of the Curie temperature in comparison with the bulk value is consistent with experimental measurements.\textsuperscript{18}

We stress that the results discussed above have been obtained neglecting the dependence of hopping amplitudes on the $Mn - O - Mn$ bond angle $\theta$. However, in bulks of $La_{1-x}A_xMnO_3$ perovskites, it has been shown that changes in A site ionic size affect only $\theta$, while the bond length $d$ seems to be unchanged ($d^* = 0.196nm$) suggesting as a maximum lattice parameter $2d^* = 0.392nm$.\textsuperscript{9} Recent measurements in LCMO thin films on LAO and STO substrates\textsuperscript{51} have showed that $d_{in}$ is fixed to a value that does not depend on the type of strain, while the in-plane bond angle is changed. The angle $\theta_{in}$ becomes larger (smaller) under tensile (compressive) strain, showing consistency with the elongation (contraction) of $a$. Similar results have been observed also in LSMO films on LAO.\textsuperscript{50} Hence, it is reasonable
to assume that values of the lattice parameter larger than those of the bulk imply stretching of \(d\) (\(\theta\) near \(\pi\)) and smaller lattice parameters induce a contraction of \(\theta\) (\(d\) near \(d^*\)). Thus, for \(L \text{CMO}\) films grown on \(L\text{AO}\) the angular dependence is not negligible.\(^{52}\) Actually, deriving \(\theta_{in}\) from experimental data\(^{51}\) (\(\theta_{in} \simeq 152.5^\circ\)) and considering only the changes of in-plane parameters (that are the most important), we can deduce the variation of the in-plane hopping from the knowledge of the \(Mn-O-Mn\) angle of the bulk\(^{53}\) (\(\theta \simeq 160^\circ\)). As reported in Fig. 5 (dash-dotted line with up triangles), even if the strain is compressive, the critical temperature is reduced compared with bulk value in agreement with experimental data.\(^{18}\)

**V. VARIATIONS OF THE \(EL-PH\) COUPLING**

In this section we focus our attention on the variations of the \(el-ph\) coupling linked to the presence of strain that can be included in order to improve the description of manganite films.

Both uniform bulk strain and biaxial strain can affect the \(el-ph\) coupling strength of the carriers in manganite films.\(^{37}\) While the biaxial distortions tend to increase the localization of the carriers, the bulk strain can lead to an increase or a decrease of \(el-ph\) coupling depending on the sign of the strain. Actually, a uniform compression tends to increase the electron hopping amplitudes reducing the importance of the \(el-ph\) coupling. So, unlike tensile strain, for compressive strain two opposite behaviors influence the variations of the \(el-ph\) coupling. In any case, for very thin films, the tendency towards localization can be simulated in our scheme by an enhancement of the \(el-ph\) coupling.

For \(L\text{SMO}\) films grown on \(S\text{TO}\) the size and strain dependence of the transition temperature is strongly influenced by the strain-induced \(el-ph\) coupling.\(^{38}\) Actually we have verified that a small reduction (increase) in \(el-ph\) coupling can induce a large enhancement (decrease) of the critical temperature in the \(C\text{MR}\) regime.

For fully strained \(L\text{CMO}\) films grown on different substrates the delicate balance of segregating phases is strongly influenced by finite size and strain effects. Deducing sizes and
strain fields of the LCMO films grown on STO,\textsuperscript{32} in Fig. 6 we show the corresponding phase diagrams calculated supposing a likely distribution of the quantity $R_g$, that represents the ratio between the $el-ph$ coupling $g$ of the film and that of the thickest film. The concomitant effects induce a strong lowering of the transition temperature and at low $T$ an increase in the weight of antiferromagnetic insulating phases. In fact, for a film characterized by a thickness of 6 planes and a ratio $R_g = 1.05$, an antiferromagnetic insulating phase of localized charges is stabilized at low temperatures in agreement with experiment.\textsuperscript{32} Therefore, the insulating dead layer could originate as natural consequence of reduced size of the film, strain effect and increased $el-ph$ coupling. In Fig. 7 the magnetization (upper panel) and the in-plane resistivity (lower panel) are reported as function of the temperature for three different values of the strain and $el-ph$ coupling. As result of the competition between ferromagnetic metallic and antiferromagnetic or paramagnetic insulating phases,\textsuperscript{30,12,13,43} the magnetization is strongly reduced, while the resistivity is largely enhanced showing consistency with experiments\textsuperscript{32}. Finally we stress that the nearly constant behavior of the resistivity at intermediate temperatures is characteristic of the antiferromagnetic phase of localized carriers. Only at higher temperatures, in the paramagnetic phase, the resistivity strongly diminishes with increasing temperature.

**VI. SUMMARY AND CONCLUSIONS**

In this paper we have analyzed the thickness dependence and strain effects in films of $La_{1-x}A_xMnO_3$ perovskites within the CMR regime.

A variational approach previously proposed for manganite bulk has been generalized in order to consider the film geometry. A reduction in the thickness of the film causes a decrease of the transition temperature and the magnetization, and increase of the resistivity especially at low temperatures. If the film is very thin but has thickness larger than the possible dead layer, the calculated results show good agreement with experimental behaviors. The strain is associated with the changes of in-plane and out-of-plane electron hopping amplitudes
induced by the substrate. The variations of the phase diagram with respect to the bulk are controlled mainly by the changes of in-plane hopping, so that the compressive strain leads to an enhancement of the critical temperature, while tensile strain weakens the ferromagnetic phase. If the dependence of the hopping matrix elements on the $Mn-O-Mn$ bond angle is properly considered, the strain effects on the transition temperature and transport properties are consistent with experimental data. Finally it is shown that substrate-induced variations of the $el-ph$ coupling, together with finite size and strain effects, can strongly influence the subtle balance of coexisting phases favoring insulating phases when the thickness of the film decreases.

Although the results presented in this paper are quite satisfactory, we wish to mention other mechanisms that could influence the thermodynamic and transport properties, at least qualitatively. First a strain-induced modification of $e_g$ electron orbital stability can affect the phase diagram of the system.$^{36,54-57}$ Changes in oxygen content resulting in cationic vacancies due to the annealing may shift the critical temperature at values much higher than any bulk values in the series compounds.$^{17,23}$ The loss of magnetic moment and the increase of resistivity could be caused by the domain-type disorder.$^{15,58}$ Even if in manganite films spatial inhomogeneities can be intrinsic,$^{31}$ the disorder induced by the substrate could be responsible also for phase separation.$^{10,32}$

As stressed in the previous section, the tendencies toward phase separation can be important to explain the presence of the insulating dead layer in manganite films. The variational approach used in this paper can be further generalized to consider insulating planes separated through an interface from metallic planes. Strain effects and thickness dependence could strongly perturb the size of insulating and metallic planes giving rise to the dead layer. Work in this direction is in progress.
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FIGURE CAPTIONS

F1 Phase diagrams corresponding to \( t = 2.5\omega_0 \), \( \lambda = 0.48 \) and \( \epsilon = 0.05\omega_0 \) for different numbers of film’s planes. \( PM \) means Paramagnetic Metallic, \( FM \) Ferromagnetic Metal. In the inset the corresponding variation of the critical temperature \( T_C \) as a function of the number of the film’s planes at \( x = 0.3 \). The temperatures are expressed in units of \( \omega_0 \).

F2 Phase diagrams corresponding to \( t = 1.8\omega_0 \), \( \lambda = 0.65 \) and \( \epsilon = 0.01\omega_0 \) for different numbers of film’s planes. \( PI \) stands for Paramagnetic Insulating. In the inset the resulting variation of the critical temperature \( T_C \) as a function of the number of the film’s planes at \( x = 0.3 \). The temperatures are expressed in units of \( \omega_0 \).

F3 The resistivity \( \rho_{x,x} \) as a function of the number of planes for \( T = 0.05\omega_0 \) at \( x = 0.3 \) and \( t = 2.5\omega_0 \). In the inset the variation in temperature (in units of \( \omega_0 \)) of the resistivity \( \rho_{x,x} \) for different numbers of planes (the arrows indicate the transition temperatures). The resistivity is in units of \( \frac{m\omega_0}{e^2c} \), where \( c \) is the hole concentration and \( m = \frac{1}{2t} \).

F4 (a) The resistivity \( \rho_{x,x} \) as a function of the temperature (in units of \( \omega_0 \)) for different values of strain at \( t = 2.5\omega_0 \) and \( x = 0.3 \).

(b) The resistivity \( \rho_{x,z} \) as a function of the temperature (in units of \( \omega_0 \)) for different values of strain at \( t = 2.5\omega_0 \) and \( x = 0.3 \).

The resistivities are expressed in units of \( \frac{m\omega_0}{e^2c} \), where \( c \) is the hole concentration and \( m = \frac{1}{2t} \) and the arrows indicate the transition temperatures.
F5 Phase diagrams corresponding to \( t = 1.8\omega_0 \), \( \lambda = 0.65 \) and \( \epsilon = 0.01\omega_0 \) for different values of strain. \( PI \) means Paramagnetic Insulating. The temperatures are expressed in units of \( \omega_0 \).

F6 Phase diagrams corresponding to \( t = 1.8\omega_0 \), \( \lambda = 0.68 \) and \( \epsilon = 0.02\omega_0 \) for different values of size, strain and \( el-ph \) coupling. \( PI \) means Paramagnetic Insulating. The temperatures are expressed in units of \( \omega_0 \).

F7 Magnetization (in units of the saturation magnetization) and resistivity (in units of \( \frac{m_{\text{sat}}}{e^2c} \), with \( c \) hole concentration and \( m = \frac{1}{2}t \)) as a function of the temperature (in units of \( \omega_0 \)) at \( t = 1.8\omega_0 \) and \( x = 0.3 \) for different values of size, strain and \( el-ph \) coupling.

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$T = 0.05$

$t = 2.5$

$x = 0.3$

$N$ planes

$\rho_{x,x}$

$\rho$
$t = 1.8$

Symbols:
- $c/a = 0.979 \ Rg = 1$
- $c/a = 0.977 \ Rg = 1.005$
- $c/a = 0.976 \ Rg = 1.02$
- $c/a = 0.9769 \ Rg = 1.03$ - 30 planes
- $c/a = 0.9767 \ Rg = 1.03$ - 15 planes
$M_{c/a=0.979 \ R_g=1}$

$M_{c/a=0.976 \ R_g=1.02}$

$M_{c/a=0.9769 \ R_g=1.03}$

$t=1.8$

$x=0.3$