Structural transitions and transport-half-metallic ferromagnetism in LaMnO$_3$ at elevated pressure

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By means of hybrid density functional theory we investigate the evolution of the structural, electronic and magnetic properties of the colossal magnetoresistance (CMR) parent compound LaMnO$_3$ under pressure. We predict a transition from a low pressure antiferromagnetic (AFM) insulator to a high pressure ferromagnetic (FM) transport half-metal (tHM) characterized by a large spin polarization ($\approx 80$-$90\%$). The FM-tHM transition is associated with a progressive quenching of the cooperative Jahn-Teller (JT) distortions which transform the $Pnma$ orthorhombic phase into a perfect cubic one (through a mixed phase in which JT-distorted and regular MnO$_6$ octahedra coexist), and with a high-spin ($S=2$, $m_{\text{Mn}}=3.7\mu_B$) to low-spin ($S=1$, $m_{\text{Mn}}=1.7\mu_B$) magnetic moment collapse. These results interpret the progression of the experimentally observed non-Mott metalization process and open up the possibility of realizing CMR behaviors in a stoichiometric manganite.

I. INTRODUCTION

Half-metallic ferromagnets (HMFs) are magnetic compounds that are simultaneously metallic and insulator, depending on the spin channel. Their ability to provide fully spin-polarized currents make them ideal candidates for spintronic applications. A prominent class of HMFs is represented by strongly correlated CMR manganites ($\text{La}_{1-x}\text{A}_x\text{MnO}_3$, $\text{A}=\text{Ca, Sr, or Ba}$): hole-doping LaMnO$_3$ through the substitution of La with $\text{A}=\text{Ca, Sr, or Ba}$ creates itinerant holes that progressively lead to an antiferromagnetic (AFM)-insulator to ferromagnetic (FM) half-metal transition and critically determine the coexistence of half-metallic spin imbalance and the so called CMR effect, i.e. a dramatic change of the electrical resistance in the presence of a magnetic field. Soon after the pioneering observation of CMR effect by Jonker and van Santen, Zenesin proposed the double exchange (DEX) mechanism to explain the AFM-insulator ($x=0$) to FM-metal ($0.2 < x < 0.5$) transition, relying on the $O^2-$mediated transfer of an electron between inequivalent Mn$^{3+}$ and Mn$^{4+}$ sites. The DEX mechanism qualitatively explained the ferromagnetic interactions and the observed metallic behavior below the Curie temperature $T_C$, but it turned out to be inadequate to explain the observed high insulating-like resistivity above the transition temperature and, even more importantly, the observation of CMR in stoichiometric phases like $\text{Tl}_2\text{Mn}_2\text{O}_7$. Conversely, the more recent half-metallic ferromagnetic model, which is based on the spin-polarized calculation of the density of states (DOS) within the Density Functional Theory (DFT), provides several clues to the underlying processes involved in the CMR phenomena and since it does not rely on the mixed-valence (Mn$^{4+}$ and Mn$^{3+}$) picture it can explain the observation of CMR in stoichiometric phases.

Controlling and understanding CMR-HMFs phenomena in manganites within the DFT framework remains a great challenge because of two fundamental obstacles: (i) strong exchange-correlation effects and the concurrent orbital/lattice/spin correlations which are not well described by conventional DFT methods, and (ii) doping-induced structural disorder, which unavoidably limits the application of quantum mechanical schemes based on repeated unit cells. The drawbacks of DFT in dealing with insulating transition metal oxides can be corrected by employing more sophisticated methods such as hybrid functionals, which have been proven to provide substantially improved structural, electronic and magnetic properties thanks to the inclusion of a portion of exact ‘non-local’ exchange. Beyond-DFT approaches are particularly necessary to correctly predict structural distortions, magnetic energies and bandgap in LaMnO$_3$, which are wrongly described by DFT. As DFT is unable to describe the JT instabilities, and stabilize a metallic FM solution instead of the experimentally observed JT-distorted AFM insulating state. As for the structural disorder, the possibility to circumvent the problem by realizing CMR-HMF behaviors in stoichiometric samples would represent a substantial benefit not only for theory, but also for the experimental and technological research, thanks to the higher degree of control and manipulability of the relevant physical processes. However the task is hard, and up-to-date very few stoichiometric CMR compounds have been identified.

Boosted by the recent experimental observations of an insulator-to-metal transition (IMT) in dense LaMnO$_3$ at about 32 GPa, in this article we explore the structural and magnetoelectric response of LaMnO$_3$ upon compression up to 150 GPa.

We first recall the basic properties of LaMnO$_3$. At zero pressure and low temperature LaMnO$_3$ is a type-
A AFM insulator (alternating planes of similar spins along the c direction) characterized by staggered JT and GdFeO$_3$-type (GFO) distortions, manifested by long (l) and short (s) Mn-O in-plane distances and medium (m) Mn-O vertical ones (JT), and by the tilting of the the Mn$^{3+}$O$_6$ octahedra (see Fig. II(d)). These structural instabilities removes the $e_g$ orbital degeneracy and stabilize an orthorhombic high-spin ($t_{2g}$)$^3(e_g)^{\frac{1}{2}}$ orbitally ordered configuration. The application of hydrostatic pressure progressively quenches the cooperative JT distortions and leads to an IMT at $P_c$=32 GPa. The persistence of the structural distortions up to $P_c$ indicates that the IMT is not a Mott-Hubbard type. This conclusion was initially proposed by LDA+U and Dynamical mean field theory studies, and only very recently was confirmed by high pressure Raman measurements. Baldini and coworkers have also reported the coexistence of domains of distorted and regular octahedra in the pressure range 3-34 GPa, and connected the onset of metallicity with the increase of undistorted MnO$_6$ octahedra beyond a critical threshold. The concomitant presence of two distinct phases in this pressure range was confirmed by the X-ray absorption spectroscopy experiments of Ramos et al.

Our computational study, beside providing a detailed microscopic understanding of the IMT and of the associated competition between distorted and undistorted phases, predicts that the onset of metallicity is associated with a FM spin transition and that the FM-metal state develops towards a transport half-metal regime at elevated pressure ($\approx$ 100 GPa), where the current is nearly fully spin polarized. Our results are reported and discussed in Sec III. Before that we describe our computational setup, which is given in Sec II. Finally, in Sec IV we draw a summary.

II. METHODOLOGY AND COMPUTATIONAL ASPECTS

All calculations were performed using the the Vienna Ab initio Simulation Package (VASP) within the Heyd, Scuseria, and Ernzerhof (HSE) hybrid density functional scheme, in which the exchange-correlation functional is expressed as a suitable admixture of DFT and Hartee-Fock (HF):

\[ E^{HSE}_{X} = \alpha E^{HF}_{X} + (1-\alpha) E^{PBE}_{X} + E^{PBE}_{X} \]

where $\mu$=0.20Å$^{-1}$, controls the range separation between the short-range (sr) and long-range (lr) part of the Coulomb kernel, and $\alpha$ is the fraction of exact HF exchange incorporated. The parameter $\alpha$, which we set equal to 0.15, is chosen so as to provide accurate values for the band gap, structural distortions and magnetic energies, as discussed below.

We have used a computational unit cell containing four LaMnO$_3$ formula units (i.e. 20 atoms) to simulate both the $P_{nma}$ and simple-cubic phase within the ferromagnetic (FM) and type-A AFM orderings. Convergence tests on the energy cut-off has shown that at low and intermediate pressure range the energy difference $\Delta E$ between the FM and AFM phases (our most critical quantity) changes by less than 3 meV per formula unit (f.u.) when the energy cut-off is increased from 300 meV to 400 meV. We have therefore chosen the value 300 meV, and made use of a 4$\times$4$\times$4 Monkhorst-Pack k-point grid for both the exchange-correlation DFT kernel and the portion ($\alpha$=0.15) of exact HF exchange.

We have used the following structural optimization procedure. For each volume we have fully relaxed the cell shape (i.e., lattice parameters $a$, $b$, and $c$ as well as the corresponding angles between them) and all internal

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TABLE I. Structural parameters of LaMnO$_3$: low-temperature (4.2 K) experimental data versus fully optimized PBE and HSE results with different values of the exact-exchange mixing parameter $\alpha$.

| Volume ($\text{Å}^3$) | Exp$^a$ | HSE-35 | HSE-25 | HSE-15 | HSE-10 | PBE |
|-----------------|--------|--------|--------|--------|--------|------|
| $a$ (Å)        | 243.57 | 243.98 | 245.82 | 247.36 | 244.24 | 244.21 |
| $b$ (Å)        | 5.532  | 5.526  | 5.537  | 5.553  | 5.661  | 5.569  |
| $c$ (Å)        | 7.686  | 7.628  | 7.633  | 7.653  | 7.712  | 7.793  |
| Mn-O$_m$ (Å)   | 1.957  | 1.954  | 1.957  | 1.962  | 1.979  | 1.992  |
| Mn-O$_l$ (Å)   | 2.184  | 2.204  | 2.214  | 2.213  | 2.134  | 2.063  |
| Mn-O$_s$ (Å)   | 1.903  | 1.899  | 1.905  | 1.914  | 1.923  | 1.971  |
| Mn-O$_m$-Mn ($^\circ$) | 154.3 | 154.78 | 154.35 | 154.36 | 153.96 | 155.85 |
| Mn-O$_l$-Mn ($^\circ$) | 156.7 | 154.38 | 154.08 | 154.17 | 157.59 | 157.71 |
| $Q_2$          | 0.398  | 0.431  | 0.437  | 0.423  | 0.298  | 0.131  |
| $Q_3$          | -0.142 | -0.159 | -0.167 | -0.165 | -0.080 | -0.041 |

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\[ Q = 2(l - s) / \sqrt{2} \]

\[ Q = 2(m - l - s) / \sqrt{6} \]
The results, collected in Tab. I (optimized geometry) and Tab. II (bandgap, magnetic moment and magnetic energies), demonstrate that the best choice is \( \alpha = 0.15 \). For this value of the mixing parameter HSE delivers (see Tab. I and Tab. III) (i) an insulating bandgap, \( \Delta = 1.45 \), well within the measured data, (ii) a correct description of the critical cooperative Jahn-Teller (JT) parameters \( Q_2 \) and \( Q_3 \), and (iii) an AFM magnetic ground state in agreement with the experimental findings. Smaller mixing factors (0 and 0.10) lead to a significant underestimation of the JT parameters \( Q_2 \) and \( Q_3 \) (see Tab. III) and to a much too small bandgap (which is actually zero in PBE, see Tab. III), and to the stabilization of the FM spin arrangement (see Tab. III), in contrast to the experimental situation. This is in line with previous conventional DFT studies.\(^{18,33-35}\) We note that by using the experimental structure a small bandgap of about 0.2 eV is opened at PBE level, which is still too small as compared to the measured level. Conversely, an higher \( \alpha (0.25 \text{ and } 0.35) \) correctly favors the AFM ordering but overestimates the band gap (2.47 and 3.41 for \( \alpha = 0.25 \) and \( \alpha = 0.35 \), respectively). The value of the gap obtained for \( \alpha = 0.25 \) is very similar to the corresponding B3LYP value, 2.3 eV,\(^{36}\) and to the HSE value obtained using the experimental structure, 2.25 eV.\(^{37}\)

In terms of the band dispersions the effect of the mixing parameter is the progressively larger separation of the occupied and unoccupied \( e_g \) bands above and below \( E_F \) cross the Fermi level. The PBE bands along the ZTSR are shown as (red) dashed lines in panel HSE-10.

structural degrees of freedom (all atomic positions). This complete geometrical optimization allowed us to tread the structural path from the \( P_{nma} \) to the cubic phases. We have tested about 30 different volumes. The equation of states (Pressure-Volume curves) were calculated in two different ways: (i) by computing the pressure directly from the stress tensor (as automatically done by VASP) and (ii) by applying the Birch-Murnaghan equation.\(^{22}\) Both routes lead to the same result.

TABLE II. The band gap (\( \Delta, \text{ eV} \)), magnetic moment \( (m, \mu_B/\text{Mn}) \), and relative energy with respect to the FM ordering calculated by HSE for different values of the mixing parameter \( \alpha \).

| \( \Delta \)     | HSE-35 | HSE-25 | HSE-15 | HSE-10 | PBE     |
|-----------------|--------|--------|--------|--------|---------|
| 1.1, 1.7\(^b\) | 3.41   | 2.47   | 1.45   | 0.75   | 0.00    |
| 3.7\(^c\)       | 3.78   | 3.74   | 3.67   | 3.65   | 3.52    |
| A-AFM           | -7     | -8     | -24    | 3      | 171     |
| C-AFM           | 156    | 182    | 198    | 368    | 564     |
| G-AFM           | 161    | 192    | 208    | 428    | 899     |

\(^{a}\text{Ref.}\,31\) \(^{b}\text{Ref.}\,32\) \(^{c}\text{Ref.}\,30\)

A. Choice of the mixing factor \( \alpha \): ground state properties of \( \text{LaMnO}_3 \)

In order to determine the HSE mixing factor \( \alpha \), i.e. the fraction of non-local HF exchange included in the hybrid exchange-correlation functional, we have performed a set of calculations of the ground state structural, electronic and magnetic properties of \( \text{LaMnO}_3 \) for different values of \( \alpha \): 0 (corresponding to a purely PBE setup), 0.10 (HSE-10), 0.15 (HSE-15), 0.25 (HSE-25) and 0.35 (HSE-35).

III. RESULTS AND DISCUSSION

The progression of the structural properties of compressed \( \text{LaMnO}_3 \) computed by HSE as a function of \( v/V/V_0 \) is summarized in Fig. 2, whereas the corresponding development of the electronic and magnetic properties is shown in Figs. 3, 5 and 6. In the pressure range 0-35 GPa, for which experimental data are available, our results are in very good agreement with measurements in terms of: (i) the pressure-volume equation of states and bulk modulus \( B_0 \) (\( B_0^{\text{Expt}} = 108 \) GPa, \( B_0^{\text{HSE}} = 104 \) GPa, see Fig. 2(a)), (ii) the pressure-induced changes in the structural parameters (Fig. 2(b)), and (iii) the concurrent suppression of the JT modes \( Q_2 \) and \( Q_3 \) and the band gap at the same compression (\( \nu_2 = 0.82 \), slightly smaller than the experimental one, \( V/V_0 = 0.86 \), see Fig. 2(b) and Fig. 3(a)); the \( P = 0 \) HSE gap opened between occupied and empty \( e_g \) states, \( E_g = 1.45 \) eV (Fig. 3(c)), is well within the measured range, \( 1.1-1.7 \) eV.\(^{33,34}\) Similarly the HSE ground state values of \( Q_2 \) and \( Q_3 \) match exactly the experimental values.\(^{30}\)

The incremental compression of \( \text{LaMnO}_3 \) leads to a continuous structural transformation from the \( P=0 \) dis-
torted \textit{Pnma} phase to a perfect cubic structure via a gradual quenching of the JT modes, the rectification of the GFO tilting angles and the alignment of the a, b, and c lattice parameters towards the same value, \( \approx 5.1 \text{ Å} \) at \( V/V_0 = 0.76 \) as outlined in Fig. 2(b-d). The \( e_g \) bands around the Fermi energy \( (E_F) \) come progressively closer until the gap is closed (Fig. 2(c-f)). Concomitantly, the unoccupied \( t_{2g} \) bands are pushed down in energy and ultimately crosses the \( E_F \) at \( V/V_0 = 0.82 \), the onset of metallicity (see Fig. 3(f)). At this critical volume HSE predicts a jump in the relative stability between the AFM and FM ordering, with the latter becoming the most favorable one by about 90 meV/f.u., as illustrated in Fig. 3(b). At low/intermediate compressions \( (V/V_0 > V_2 = 0.82) \) the data displayed in Fig. 3(b) shows a strong competition between the AFM and FM phases. HSE predicts a crossover between the AFM and FM phases at \( V/V_0 = 0.95 \) (corresponding to a pressure of 11 GPa), below which the AFM and FM ordering become almost degenerate \( (\Delta E < 12 \text{ meV/f.u.}) \). Considering that in the FM phase the JT/GFO distortions are almost completely inhibited (see Fig. 3), this result strongly supports the latest Raman \cite{22} and X-ray absorption spectroscopy \cite{23} studies reporting the formation of a mixed state of domains of distorted and regular MnO\(_6\) octahedra in the range 13–34 GPa, which compare well with the corresponding theoretical pressure range, 11–50 GPa \( (V/V_0 < v_1) \). The coexistence of distorted and undistorted octahedra is clarified in Fig. 4 where we plot the comparison between the evolution of the JT distortions in the FM and AFM phases (panel (a)), and the energy-volume phase diagram (panel (b)). In the FM phase the \( Q_2 \) and \( Q_3 \) drop down to zero at about 11 GPa \( (V/V_0 = v_1 = 0.95) \), indicating that for pressure larger than 11 GPa the MnO\(_6\) octahedra are undistorted. Conversely, as already underlined, in the AFM phase the octahedra remain distorted until \( V/V_0 = v_2 = 0.82 \) (about 50 GPa). This different behaviour is interpreted graphically in the insets of Fig. 4(a) which represents the FM-undistorted (u) and AFM-distorted (d) octahedra. Summing up, at low/high pressures LaMnO\(_3\) is AFM-distorted/FM-undistorted, whereas in the volume range \( v_2 < V/V_0 < v_1 \) these phases coexists in a mixed domains of distorted and undistorted octahedra (see Fig. 4(b)).

The FM transition at \( V/V_0 = 0.82 \) comes right before an high spin (HS, \( S=2 \)) to low spin (LS, \( S=1 \)) moment collapse, which is correlated with the \( e_g \) and \( t_{2g} \) orbital occupations as shown in Fig. 4. Under compression the Mn\(^{3+}\) ion retains its P=0 \( (t_{2g})^{1} (e_g)^{1} \) orbital configuration down to \( V/V_0 = 0.80 \), with a magnetic moment of 3.7 \( \mu_B \); further compression yields a rapid reduction of the magnetic moment down to 1.7 \( \mu_B \); due the redistribution of electrons within the 3d shell which ultimately leads to
FIG. 3. (Color online) Evolution of the calculated electronic properties and magnetic ordering of LaMnO$_3$ upon pressure. (a) Band gap: IMT at $v_2=0.82$ (marked by the vertical full line; the dashed line refers to the corresponding experimental onset). Measured gaps are taken from Ref. 22. (b) Energy difference $\Delta E$ between the AFM and FM spin arrangements: AFM/FM crossover at $v_2=0.95$ (indicated by a vertical dashed line) and stabilization of the FM state at $v_2=0.82$. (c-l) Changes in the $e_g$ and $t_{2g}$ density of states around the Fermi level with pressure. The dashed (red) lines refer to the Oxygen $p$ states, whereas the thick (red) arrow indicates the transfer of one electron from the $e_g$ to the $t_{2g}$ sub-bands.

the low-spin configuration $(t_{2g})^{↑↑↓}(e_g)^0$. The HS-to-LS collapse starts to develop at about $V/V_0=0.8$ and is fully established at exactly the same volume at which the cubic phase emerges, $v_3=0.76$. This HS-orthorhombic to LS-cubic transition is also reflected in the DOS (Fig. 3 (g-i)), whose evolution from $V/V_0=0.79$ to $V/V_0=0.73$ clearly indicates the transfer of one electron from the $e_g$ to the $t_{2g}$ sub-bands and the subsequent realization of a nearly FM half-metallic state with a metallic minority $t_{2g}$ band and a quasi-insulating majority channel with a residual density of $e_g$ electrons at the bottom of the conduction band. In order to clarify further the HS-to-LS transition we display in Fig. 4 the partial and integrated density of states in a wide energy windows associated with the $e_g$ and $t_{2g}$ bands at $V/V_0=0.79$ and $V/V_0=0.73$, which show the transfer of one electron from the $e_g$ spin up channel at $V/V_0=0.79$ to the $t_{2g}$ spin-down channel at $V/V_0=0.73$, which yields to the $(t_{2g})^{↑↑↓}(e_g)^0$ transition.

Following the classical work of Nadgorny et al. 10 we have analyzed the spin polarization $P_n$ associated to this high pressure nearly HM-FM state in order to acquire information on the spin-dependent transport properties, using the formula suggested by Mazin. 15

$$P_n = \frac{N_\uparrow(E_F)v_\uparrow^n v_\uparrow^n - N_\downarrow(E_F)v_\downarrow^n v_\downarrow^n}{N_\uparrow(E_F)v_\uparrow^n v_\uparrow^n + N_\downarrow(E_F)v_\downarrow^n v_\downarrow^n}$$

(2)

where $N_\uparrow(E_F), N_\downarrow(E_F)$ and $v_\uparrow^n, v_\downarrow^n$ represent the majority and minority spin DOS and Fermi velocities, respectively, and the index $n$ refers to the different types of spin polarizations detected in spin-resolved photoemission measurements ($n=0$), and in ballistic ($n=1$) and diffusive ($n=2$) transport experiments. We have computed the Fermi velocities by interfacing the VASP with the BoltzTrap code 23 and obtained for $V/V_0=0.70$: $P_0 = 87\%$, $P_1 = 80.5\%$, and $P_2 = 71\%$, and for $V/V_0=0.65$: $P_0 = 92\%$, $P_1 = 87\%$ and $P_2 = 80\%$, values very similar to those reported for the doped CMR manganite La$_0.7$Sr$_0.3$MnO$_3$. 14 We can thus conclude, that the high pressure FM cubic phase of LaMnO$_3$ is a transport half-metal. For denser phases ($V/V_0<0.65$) the majority spin band gap (from the lower laying filled $t_{2g}$ and the unoccupied $e_g$ band) is progressively reduced to zero at $V/V_0<0.53$ ($P>300$ GPa, see Fig. 3(a)). Being the FM-thm regime the crucial common ingredient of all CMR manganites, its realization in the undoped (stoichiometric) phase of the CMR parent compound LaMnO$_3$ in a wide interval of compressions, could help in achieving new fundamental insights into the elusive phenomena of CMR.

IV. SUMMARY

Summarizing, we have traced the development of LaMnO$_3$ upon pressure and determined a sequence of
highly interconnected structural, electronic, and magnetic phase transitions: (i) At ambient conditions LaMnO$_3$ posses a distorted AFM insulating state. At $v_1=0.95$ a competition between (distorted) AFM and (undistorted) FM configuration begin to evolve. (ii) At the critical threshold $v_2=0.82$ LaMnO$_3$ undergoes a non-Mott IMT associated with a significant reduction of the JT/GFO instabilities. (iii) For $v_3=0.76$ all residual lattice distortions are suppressed and a perfect cubic phase emerges. (iv) At $v_4=0.70$ the strong crystal field splitting between $t_{2g}$ and $e_g$ drives a magnetic moment collapse from an HS to LS tHM-FM state, manifested by a significant disproportionation in the spin-dependent $N(E_F)$, $v_F$, and consequentially $P_n$. Our results, thus, predict...
that it is possible to establish a tHM-FM regime in a stoichiometric manganite at pressure accessible by high-pressure technology.

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