The complicated interplay between charge, spin, orbital, and lattice degrees of freedom is believed to induce the unexpected magnetic and transport phenomena observed in Mn-oxides, such as the ‘colossal’ magnetoresistance (MR) effect [1]. The subtle properties of manganites are especially complex at 50% hole density where experiments have established that an insulating charge-ordered (CO) state exists in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ [2], Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ [3], La$_2$Sr$_2$Mn$_2$O$_7$ [4], and several others. The state has alternating d$_{3z^2}$-$t_2^2$, d$_{3x^2}$-$t_2^2$ orbital and CE-type antiferromagnetic (AF) order [3]. Its melting by a magnetic field leads to a huge negative MR [5], CE-type antiferromagnetic (AF) order [5]. Its melting by a magnetic field leads to a huge negative MR [5].

In spite of its importance, the origin of the x=0.5 CO-state is still unclear. The observation of charge populating only the even (or odd) Mn-ion sublattice in the xy plane naively suggests that the nearest-neighbor (NN) Coulomb repulsion V$_{NN}$ is important for its stabilization. However, the z-axis stacking of charge [1] and existence of bistripes at x>0.5 [10], both penalized by a strong NN-repulsion, show that V$_{NN}$ is smaller than expected and other ingredients are needed to understand the CO-state [5]. In addition, at x=0.5 experiments exhibited two other phases in competition: (i) A d$_{3z^2}$-$t^2$ orbital-ordered (OO) state with charge-disordered (CD) state with A-type AF state and two-dimensional (2D) metallicity (in, e.g., Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ [3]), (ii) A metallic spin ferromagnetic (FM) CD and orbital-ordered (OD) state (in, e.g., La$_{0.5}$Sr$_{0.5}$MnO$_3$). For a dominant V$_{NN}$, stable CD states at x=0.5 are difficult to understand. It may occur that electrons coupled only through on-site Coulomb interactions produce this exotic behavior, as suggested by Hartree-Fock calculations [12]. However, in this context unbiased many-body calculations are difficult and computational studies have technical complications such as the sign-problem. In addition, the ‘colossal’ oxygen isotope shift of the CO transition in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (NSMO) [13] cannot be explained using purely Coulombic approaches, which predict no isotope effect.

Searching for an alternative mechanism to stabilize the charge-stacked CO-state of manganites, in this paper the first comprehensive computational analysis of the half-doped two-orbital model with both non-cooperative and cooperative Jahn-Teller (JT) phonons in the large electron-phonon coupling (λ) regime is presented. Our main result is that a CE-type CO orbital-ordered ground state can be stabilized in this framework with charge properly stacked along the z-axis. Many other features found in the simulations are also in excellent correspondence with experimental observations.

The two-orbital Hamiltonian is given by

$$H = - \sum_{\langle i,j \rangle \sigma} t_{ij}^\alpha c_{i\alpha}^\dagger c_{j\sigma} - J_{H} \sum_i S_i \cdot S_i + J_{AF} \sum_{\langle i,j \rangle} S_i \cdot S_j + \lambda \sum_{\langle i,j \rangle \sigma} c_{i\sigma}^\dagger (Q_{21} \sigma_1 + Q_{31} \sigma_3)_{ab} c_{j\sigma} + \frac{1}{2} \sum_i (Q_{2i}^2 + Q_{3i}^2) \quad (1)$$

where $c_{i\alpha}$ ($c_{i\sigma}$) is the destruction operator for an $e_{g}$-electron with spin $\sigma$ in the d$_{3z^2}$-$t^2$ (d$_{3x^2}$-$t^2$) orbital at site $i$, $v$ is the vector connecting NN sites, and $t_{ij}^\alpha$ is given by $t_{ij}^x = -\sqrt{3} t_{ij}^y = -\sqrt{3} t_{ij}^z = 3t_{ij}^z = t$ (energy unit) for $v=x$, $t_{ij}^z = \sqrt{3} t_{ij}^y = \sqrt{3} t_{ij}^z = 3t_{ij}^z = t$ for $v=y$, and $t_{ij}^z = 4t/3$, $t_{ij}^z = t_{ij}^y = t_{ij}^z = 10$ for $v=z$. The Hund coupling $J_{H} (>0)$ links the $e_{g}$-electron spin $S_i = \sum_{\alpha \beta} c_{i\alpha}^\dagger c_{i\beta} \sigma_{\alpha} \sigma_{\beta}$ and the localized $t_{2g}$-spin $S_i$ assumed classical ($S_i^2 = 1$). The $e_{g}$-electron density $n_i$ varies with a chemical potential $\mu$ (the hole density is $x=1$-$\langle n_i \rangle$). $J_{AF}$ is the AF coupling between NN $t_{2g}$-spins. The fourth term couples e$_g$-electrons to JT-mode distortions, $Q_{2i}$ and $Q_{3i}$, assumed classical $S_i^2 = 1$. $\sigma_1$ and $\sigma_3$ are Pauli matrices. When the $\{Q\}$ are independent, “non-cooperative” phonons are used [3].

In real materials, however, adjacent MnO$_6$ octahedra share an oxygen. In this “cooperative” case, the proper variables are the oxygen displacements u$_q^i$ from equilibrium along the Mn-Mn bond in the $v$-direction, and extra terms are added to Eq. (1) for the breathing-mode phonon [12]. Standard Monte Carlo (MC) simulations for the classical spins and phonons are here used [13].

Figure 1(a) already illustrates one of the main results of the present study. Shown are the MC real-space charge correlations at x=0.5 for representative couplings in 2D at low temperature(T). For intermediate $J_{AF}$ ($0.1 \lesssim J_{AF} \lesssim 0.2$), the charge correlations were found to

Ferromagnetic, A-type, and Charge-Ordered CE-type States in Doped Manganites using Jahn-Teller Phonons

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be robust at all distances and they are positive (negative) on the even (odd) sites, compatible with the CO-pattern observed in x=0.5 experiments. Our results show that this behavior is essentially independent of $\lambda$ for intermediate $J_{AF}$, although the CO-pattern is more easily observed for large $\lambda$. For small $J_{AF}$ ($\lesssim 0.1$), on the other hand, the CO-state appears only for large $\lambda$. The observed CO-state originates from the tendency of the JT-distorted Mn$^{3+}$-ions to maximize their relative distances to exploit the kinetic energy of the mobile carriers. Figure 1(b) contains the Fourier transform of the $t_{2g}$ spin correlations $S(q)$ in the CO-regime. For intermediate $J_{AF}$, peaks at $q = (\pi, 0)$ and $(\pi/2, \pi/2)$ are observed in excellent agreement with the result of a perfect CE-spin arrangement. Note that size effects appear small in these calculations, and throughout the paper. For small $J_{AF}$, only one peak is detected at $q = (0,0)$, indicating the FM phase. Under the CE-type spin environment, it can be shown that the CO-state is stable even for small $\lambda$, since the system is effectively one-dimensional (1D) due to charge confinement along the zigzag FM-chain [16]. In this sense, $J_{AF}$ plays a role more important than $\lambda$ for the CE-state stabilization. This is in contrast to the FM state where a finite and large $\lambda$ is needed to stabilize the CO-state due to its higher dimensionality.

![Figure 1](image)

**Figure 1.** (a) Charge correlation $C(m)=\langle m_{i}m_{i+m}\rangle-\langle m_{i}\rangle^{2}$ with $m_{i}=\sum_{\alpha}n_{i\alpha}c_{i\alpha}^{\dagger}c_{i\alpha}$ for $H_{J}=\infty$, $T=1/100$, and $x=0.5$, using a $4 \times 4$ cluster with non-cooperative phonons and periodic boundary conditions. The squares (circles) [triangles] were obtained at $J_{AF}=0.1$, $\lambda=2.0$ (0.05, 2.0) [0.05, 1.6]. (b) Spin structure-factor $S(q)=\sum_{i,m}e^{iqm}\langle S_{i\alpha}S_{i+m\alpha}\rangle$ for the $t_{2g}$-spins at the same parameters of the squares in (a). The squares (circles) here denote the $4 \times 4$ MC (ideal CE-type state) results. Triangles are MC results on an $8 \times 8$ cluster. (c) $\theta_{A}$ and $\theta_{B}$ (see text) vs. $J_{AF}$ for $\lambda=1.6$ and 2.0. (d) Charge, spin and orbital arrangement compatible with our MC results.

Regarding the orbital arrangement, let us consider sites with substantial charge ($A$ and $B$ in Fig. 1(d)) [17]. The occupied orbital at each site is given by $|2\rangle_{i}=-\sin(\theta_{i}/2)|1\rangle+\cos(\theta_{i}/2)|2\rangle$ with $\theta_{i}=\tan^{-1}\left(|Q_{2i}|/|Q_{1i}|\right)$. In Fig. 1(c), $\theta_{A}$ and $\theta_{B}$ vs. $J_{AF}$ are plotted for $\lambda=1.6$ and 2.0. For small $J_{AF}$, $\theta_{A}=\pi(d_{x^2-y^2})$, since the orbitals prefer to have large overlaps both in the $x$- and $y$-directions. On the other hand, for intermediate $J_{AF}$, $\theta_{A}=2\pi/3(d_{x^2-y^2})$ and $\theta_{B}=4\pi/3(d_{x^2-y^2})$. To understand this result, note that the orbital is polarized along the hopping direction to improve the kinetic energy. Due to this effect, the zigzag hopping path in the CE-type CO-state induces the alternating $d_{x^2-y^2}$/$d_{y^2-x^2}$ orbitals. The above results in charge, spin, and orbital correlations for intermediate $J_{AF}$ are schematically shown in Fig. 1(d), which is the CE-type CO-state observed in experiments.

![Figure 2](image)

**Figure 2.** (a) MC energy per site $E/N$ vs. $J_{AF}$ at $x=0.5$, $\lambda=1.5$, $T=1/100$, and $H_{J}=\infty$ with non-cooperative phonons. The FM state is charge-disordered and orbital(uniform)-ordered. “AF(2)” is explained in Ref. [8]. “AF” is AF in both directions. The straight lines correspond to the finite $J_{AF}$ correction to $J_{AF}=0$ MC results, when a perfect spin configuration is assumed. (b) Drude weight $D_{W}$ vs. $J_{AF}$ at $T=1/100$, $x=0.5$, using a $4 \times 4$ cluster. The results with cooperative (non-cooperative) JT-phonons were obtained at $\lambda=1.5$ (1.2). (c) Phase diagram of the 2D two-orbital model with non-cooperative phonons at low-T. The phase boundaries were obtained as in (a) using $4 \times 4$ and $8 \times 8$ clusters. All transitions are of first-order. In the FM-phases, the OO-state is uniform in the $d_{x^2-y^2}$ orbitals, while in the CE-phase the pattern Fig. 1(d) was observed.

Figure 2(a) shows a typical MC energy vs. $J_{AF}$ for $\lambda=1.5$. At small $J_{AF}$, a FM-state is stabilized since even at large $\lambda$ the optimal background for electrons has all spins aligned. However, its energy is penalized by the AF exchange and at realistic values of $J_{AF}$ an equal AF-FM mixture such as the CO CE-state minimizes the energy. The discontinuity in $d(E/N)/dJ_{AF}$ signals a first-order transition, as in experiments. With increasing $J_{AF}$, the CE-state is destabilized by a novel state labeled “AF(2)” [8]. The metallic vs. insulating character of the various phases can be analyzed with the Drude weight $D_{W}$ [8]. Results at $\lambda=1.2$ (Fig. 2(b)) show that the FM-state is metallic ($D_{W} \neq 0$) and the CE-state is insulating ($D_{W}=0$). The jump in $D_{W}$ again signals a first-order transition. Based on results similar to those in Figs. 2(a) and (b), the phase diagram in 2D and low-T was constructed (Fig. 2(c)). It presents a rich structure includ-
ing FM and CE-phases. In particular, it contains a CD FM-state with uniform orbital order, which after consideration of three dimensional (3D) clusters will become a fully A-type state with charge and orbital characteristics as observed experimentally [2]. Then, all the currently known states at $z=0.5$ exist in our phase diagram, and they are in close competition. It is conceivable that small temperature, doping, or lattice spacing changes may alter their balance, as found experimentally. It is also possible that the other novel phases in Fig. 2(c), especially the CO and OO FM-state, may appear in future experiments.

Here the cooperative effect on the above results is briefly discussed. When the oxygen positions $\{\mathbf{Q}\}$, not $\{\mathbf{Q}\}$, are used as variables in the MC simulations, the charge, spin, and orbital correlations are found to be similar to the non-cooperative results. In particular, a clear evidence of a CO CE-type state was observed in a wide range of the phase diagram and to stabilize this state $J_{AF}$ was found to play an essential role as in the non-cooperative case. For $J_{AF}=0$, a CO-state is still obtained at large $\lambda$, but it is spin FM. In addition, note that the $\lambda$-type phase of Fig. 2(c) has $Q_3$ modes with an uniform mean-value at every site. This amount to a static deformation of the oxygen octahedra, shortening the c-direction (or elongating the a- and b-directions), similarly as in experiments [20]. If appropriate lattice constants are not used for cooperative phonons, the $\lambda$-type phase may not be stabilized. For this reason studying both non-cooperative and cooperative phonons is important.

It is instructive to calculate the $T$-dependence of the various order parameters to compare with experiments. In Fig. 3(a), $S(\mathbf{q})$ at $\mathbf{q}=(0,0)$ (FM) and $(\pi,0)$ (CE) and charge structure factor $N(\pi,\pi)$ vs. $T$. The spin structure factor $N(\pi,\pi)$ vs. $T$. For a $4 \times 4$ cluster with $\lambda=1.2$ and $J_{AF}=0.15$. The high-$T$ background, corresponding to on-site correlations only, is subtracted. (b) Same as (a) but at $\lambda=1.9$ and $J_{AF}=0.10$. (c) DOS vs. $\omega$ for $4 \times 4$ and $8 \times 8$ clusters for $J_{AF}=0.15$ and $\lambda=1.2$. (d) Schematic phase diagram in the $(J_{AF},T)$ plane for the small $\lambda$ (left) and large $\lambda$ (right) regions. PM means paramagnetic phase.

Let us understand intuitively the several transitions between phases. In the small $\lambda$ region, the FM transition temperature $T_{C}$ scales with $t$ due to the double exchange mechanism, while $T_{N}$ is determined by $J_{AF}$ irrespective of $\lambda$. In the FM phase, a CO-state never occurs in this region. However, if a sharp transition to the CE-type AF state occurs at $T=T_{N}$, the CO-state is also generated, since the CE-type state is a 1D band-insulator [14] and it can be shown using a standard mean-field approximation that $k_{B}T_{CO}\approx e_{F}^{-1/\lambda}$, where $e_{F}$ is the Fermi energy much larger than $J_{AF}$. Thus, $T_{CO} \sim T_{N}$ holds for small $\lambda$. Note that the ratio $\Delta_{CO}/k_{B}T_{CO}$ is large because $\Delta_{CO} \sim t$ in the band-insulating region. When $\lambda$ is increased, $\Delta_{CO}$ and $T_{CO}$ smoothly increase, keeping the relation $\Delta_{CO} \sim k_{B}T_{CO}$. Eventually, at large $\lambda$ $T_{CO}$ overcomes $T_{N}$ in this regime, $T_{C}$ is determined by the superexchange mechanism as $T_{C} \sim t^{-1/\lambda^{2}}$. The above estimations are summarized in Fig. 3(d). In the small $\lambda$ region, the metallic-like FM phase appears irrespective of $J_{AF}$ at high $T$, but at low $T$, the CE-type AF state occurs for intermediate value of $J_{AF}$ and the CO-state is concomitant only to the CE-phase. In the large $\lambda$ regime, the CO-state occurs in the whole region for $T<T_{CO}$, higher than $T_{C}$ and $T_{N}$. At low $T$, the system becomes FM-insulator or CE-type insulator depending on $J_{AF}$. All these results are supported by the MC simulations. Note that previously it was widely believed that modifications in the tolerance factor $t_{p}$ by chemical substitution lead to bandwidth changes sufficiently strong to drastically affect the properties of manganite compounds. However, our results established that the $t_{p}$-induced changes in $J_{AF}$ are equally important, and they should be carefully considered when studying Mn-oxides.

A difficult to understand feature of the manganite CO state is the $z$-axis charge stacking. To address the prediction of JT-phonon studies, in Fig. 4(a) the MC energy of a bilayer cluster vs. $J_{AF}$ with non-cooperative phonons is shown. At small $J_{AF}$ the FM-state dominates,
as in 2D (Fig. 2(c)). The CE-state in its \textquotedblleft Wigner Crystal\textquotedblright{} (WC) and \textquotedblleft Charge Stacked\textquotedblright{} (CS) versions (with a N(q) peak at (π, π, π) and (π, π, 0), respectively) appear as excited states at J_{AF}=0. WC has lower energy since the electronic kinetic energy improves when the Mn^{3+}-ions spread apart. However, with increasing J_{AF} the situation rapidly changes since the CS charge arrangement (CE-planes, one over the other, with opposite spins) has all z-axis bonds properly antiferromagnetically aligned. On the other hand, in the WC arrangement, with one plane shifted from the other by a lattice spacing along x or y, half the z-axis bonds are AF and the other half FM, making its energy J_{AF}-independent. For this reason, at realistic J_{AF}, the CS-state dominates. Since similar results are obtained with cooperative phonons and cubic clusters (Fig. 4(b)), the effect appears robust and independent of fine details. The important interaction to stabilize the CS-state is the z-axis J_{AF} exchange.

![Graph](image)

**FIG. 4.** (a) Energy per site vs. J_{AF} at \(\lambda=1.5, J_{H}=\infty,\) and T=1/100 with both cooperative and non-cooperative phonons. Solid (open) circles are MC results using a 4×4×2 (8×8×2) bilayer. Squares at J_{AF}=0 are the MC results on the 4×4×2 cluster assuming the t_{2g}-spin background according to the convention in (b), in a standard notation. The straight lines were obtained as in Fig. 2(a). (b) Same as (a) but for a cube \(4.\) Note that with non-cooperative phonons the A-type phase is stable in bilayers and cubes in a narrow J_{AF}-window. (c) Mean-field energy per site vs. V_{NN} for a bilayer. Couplings are realistic (U' is the on-site inter-orbital repulsion). Since J_{H} is assumed infinite, the on-site intra-orbital repulsion is irrelevant. Solid and dashed curves denote the CE-type CS- and WC-structures, respectively.

What is the influence of the V_{NN} repulsion in our results? It will certainly penalize the CS structure, and the WC-state will eventually become the ground state as this repulsion grows. However, the CS-state has a better magnetic energy than the WC-state. Comparing the energy per site gained (-J_{AF}) and lost (V_{NN}/2) in the 3D CS structure, a critical coupling V_{NN} = 2J_{AF} ~ 0.15eV is estimated if J_{AF} ~ 0.15t and t ~ 0.5eV. A more sophisticated mean-field approximation [24] at realistic manganite couplings provides V_{NN} ~ 0.22eV (Fig. 4(c)). Although the V_{NN} bare value is ~ 3.6eV, it is reduced by the dielectric constant \(\epsilon \approx 20-45\) [25], leading to V_{NN} = 0.08-0.18eV for manganites. Thus, it is concluded that the manganite NN repulsion is weak enough to allow for the CS-state to be stable due to the effect of J_{AF}.

Summarizing, evidence was provided that the CE-type CO-state with \(\Delta_{CO}/k_{B}T_{CO}>1\) and charge stacked along the z-axis observed at x=0.5 in several manganites can be stabilized using JT phonons. The competing FM and A-type states also appear in the simulations. Our results have established that purely Coulombic approaches are not the only procedure to stabilize CO-states in manganites, but strongly coupled electron JT-phonon systems provide an alternative framework where controlled many-body calculations are possible.

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