

Origin of Charge-Orbital Order in the Half-Doped Manganites

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The microscopic origin of the charge and orbital order in the half-doped manganites is examined from *ab initio* density-functional calculations and exact diagonalization studies. It is shown that the dominant mechanism responsible for the charge order is the Jahn-Teller coupling, with a lesser but significant contribution from the on-site Coulomb interaction. The band structure shows a sizable interchain coupling between the zigzag chains, leading to a considerable band dispersion normal to the chains, in sharp contrast with the zigzag chain physics.

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A fundamental issue in the physics of the manganites concerns the mechanism of the charge-orbital ordering and charge stripe formation. Perhaps the simplest of the charge-orbital orders occurs in the half-doped manganites such as $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ [1–3] and others [4] (Fig. 1). While this charge-orbital order (COO), the so-called “CE” order, has long been known since the seminal works of Goodenough [1] and of Wollan and Koehler [2], the mechanism of its origin is still being hotly debated [5–9]. Different authors have emphasized different mechanisms such as the on-site Coulomb interaction [9], the intersite Coulomb interaction [5], the Jahn-Teller (JT) coupling [6,10–12], anisotropic double exchange [13], etc. In this Letter, we study the microscopic origin of the COO in a systematic way starting from the spin-density-functional calculations and present a unifying picture of the relative importance of the various mechanisms.

Our main results can be summarized as follows: (i) The COO in the half-doped manganites is driven primarily by the strong JT coupling, with the on-site Coulomb interaction playing a significant but lesser role. (ii) Contrary to the popular belief (single chain physics), the electronic structure shows considerable interchain coupling among the zigzag chains, originating to a large extent from electron hopping to the upper Hund’s bands across the chains. (iii) The large dispersions in the valence and conduction bands indicate significant conductivity for doped carriers, both along and normal to the chains.

Spin-density-functional theory (DFT) results for $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$.—We begin by describing the results of our band calculations using the spin-density-functional theory for the prototypical half-doped compound $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$. It forms in the orthorhombic crystal structure (space group $P2_1/m$) [14] with 80 atoms in the magnetic unit cell. A noteworthy feature of the crystal structure is that the corner-site Mn atoms on the zigzag chains have negligible JT distortion (average Mn-O distance of 1.92 Å), while the distortion is sizable for the bridge-site Mn atoms (two long bonds of 2.06 Å along the chain and four short bonds of 1.92 Å).

The DFT calculations were performed with the linear muffin-tin orbitals method in the atomic spheres approxi-

mation (LMTO-ASA) [15] using the generalized-gradient approximation for the exchange-correlation energy [16]. An insulating band structure (Fig. 2) is obtained with a small gap, whose magnitude is well known to be underestimated in the DFT. As seen from Fig. 3, the important states in the gap region are the $\text{Mn}(3d)$ orbitals.

It is illustrative to compare the LMTO bands with the results of a single zigzag chain model [13], with nearest-neighbor hopping between the $\text{Mn}(e_g)$ orbitals $V_{dd\sigma} = -0.55$ eV, Hund’s-rule energy $J_H = \infty$, and A1 split below A2 by the JT energy $\Delta_{JT} = 1$ eV [A1 and A2 being the two bridge-site $\text{Mn}(e_g)$ orbitals]. For this model, we have an 8×8 Hamiltonian matrix for each spin in the four-site zigzag chain unit cell, resulting in the twofold degenerate eigenvalues: 0 and $\Delta_{JT}/2$, with the remaining four being

$$-(\Delta_{JT}/4) \pm (\Delta_{JT}^2/4 + 8t^2 \pm 4t^2 \cos k_x a)^{1/2}/2. \quad (1)$$

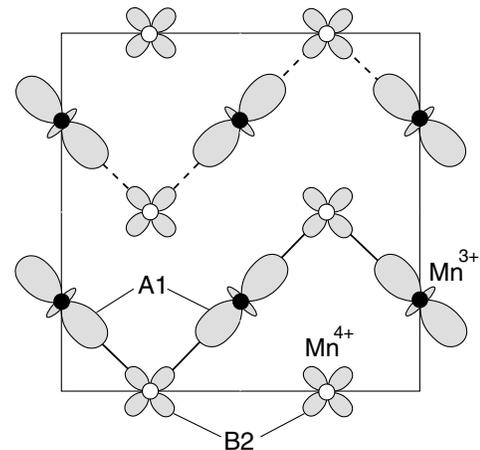


FIG. 1. Sketch of the charge-orbital order obtained from density-functional theory for $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$. Note that the corner-site atom, nominally Mn^{4+} , carries some e_g charge as well. Solid and dashed lines indicate ferromagnetic zigzag chains with opposite moments. The planes are stacked one over the other, with identical Mn charges but reversed moments. The e_g orbitals on the bridge-site (A) and the corner-site (B) Mn are denoted by A1, B1, A2, and B2, the first two being $z^2 - 1$ type and the other two, $x^2 - y^2$ type in the local coordinates (z along the bond for A and normal to the plane for B).

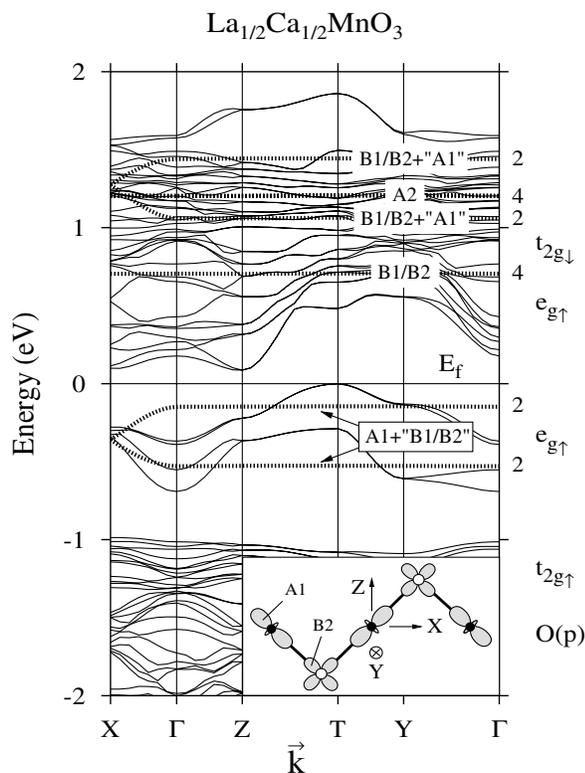


FIG. 2. DFT band structure for $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$. The top four valence bands are formed by the occupied $\text{Mn}(e_g)$ orbitals. Shown on the right-hand side are the orbital characters of the DFT bands and the degeneracies of the single chain bands, which are indicated by the dashed lines. (Degeneracies are doubled because there are two chains per unit cell.) Small admixtures are indicated by quotation marks, e.g., "A1." The inset shows directions of specific \vec{k} points.

These results are superimposed on the LMTO bands shown in Fig. 2. The bands just below the Fermi energy E_f are predominantly of A1 character with a small admixture from the B1/B2 orbitals, both in the zigzag chain model and in the LMTO results.

What is missing in the zigzag chain model is the significant band dispersion along k normal to the chain direction. In fact, the band dispersion along Γ -X (\vec{k} along the chain direction) is not much stronger than the dispersion along Γ -Z (\vec{k} on the basal plane and normal to the chain) or along Γ -Y (\vec{k} normal to both the basal plane and the chain). This can be explained in terms of the interchain hopping to the same-spin e_g orbitals on the nearest-neighbor zigzag chains, an effect forbidden in the Anderson-Hasegawa double-exchange picture with $J_H = \infty$, since the chains are arranged antiferromagnetically. However, the upper Hund's bands being separated by only about $J_H \approx 2-3$ eV from the lower, the hopping energy gain of $\approx t^2/J_H$ (second order perturbation theory) is appreciable. This gives rise to a significant dispersion normal to the chains. We were, in fact, able to fit the occupied $\text{Mn}(e_g)$ LMTO bands reasonably well by simply including the effect of the finite J_H on top of the tight-binding nearest-neighbor

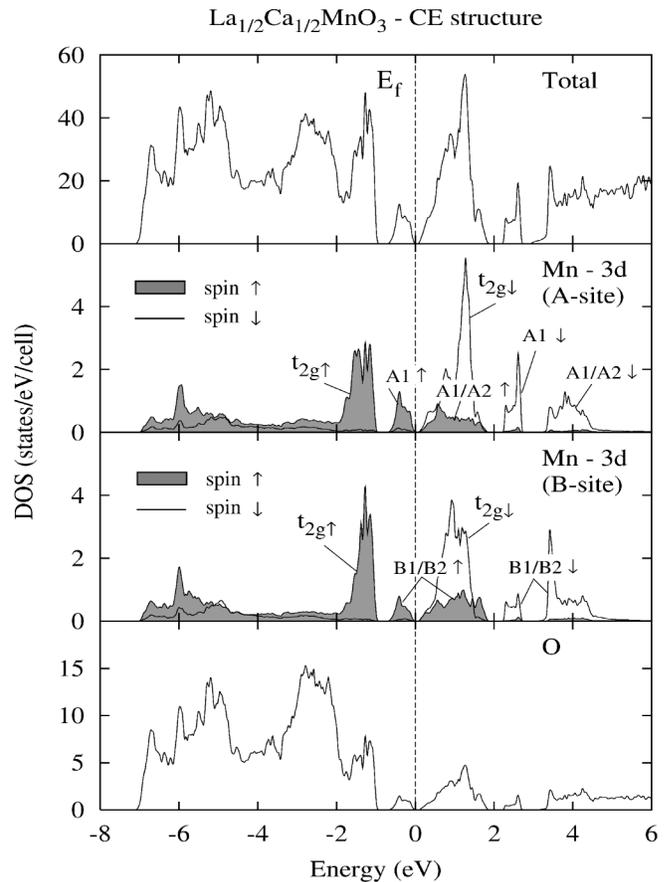


FIG. 3. Projected densities of states (DOS) for $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$. The corner-site (B) atoms, in addition to the A atoms, contribute significantly to the occupied $\text{Mn}(e_g)$ states, appearing just below E_f .

zigzag chain model. The essential physics that emerges is that the effective electron transfer is hindered in directions normal to the chain by double exchange, while along the chain, it is hindered by the mismatched JT splitting of the bridge-site vs the corner-site atom, which causes a misalignment of the $\text{Mn}(e_g)$ on-site energies.

The interchain coupling is strong enough that there is considerable band dispersion at both the valence top at T ($= Y + Z$) and the conduction bottom at Z . The calculated mass ratios for the valence top are $m_c/m_a \approx 3$ and $m_b/m_a \approx 8$, with directions defined such that zigzag chains lie on the a - c plane and "a" is along the chains. Thus for carriers induced by either chemical doping or temperature, the band theory predicts a significant conductivity normal to the chains as well. This is in contrast to the zigzag chain model where conduction normal to the chains is strictly forbidden.

We now turn to the charge-orbital ordering. The charge density contours (Fig. 4) corresponding to the four occupied e_g bands just below E_f , indicate a large A1 charge on the bridge-site Mn atom. However, a significant e_g charge also exists on the corner-site B atoms (nominally zero, being Mn^{4+}), a result also found from the zigzag chain model [9,13]. Finally, an oxygen atom on the zigzag chain

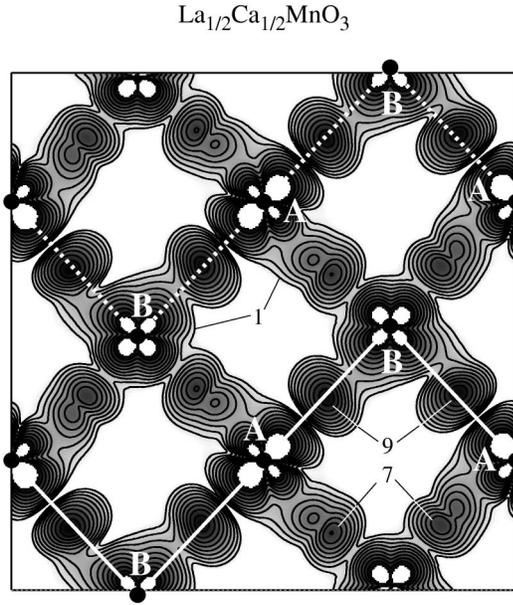


FIG. 4. Charge-density contours corresponding to the top four valence bands. Dashed and solid lines indicate ferromagnetic zigzag chains with opposite moments. The plane of the plot is the same as in Fig. 1. Contour values are $\rho_n = 1.35 \times 10^{-3} e^{0.53n} e^-/\text{\AA}^3$. The figure indicates an accumulation of e_g charge at the B sites, despite their traditional Mn^{4+} nomenclature. As indicated by the contour values, an oxygen atom located on the chain (between two Mn atoms) has a much larger hybridization charge as compared to one located between the chains, justifying the traditional zigzag chain picture.

has a much larger hybridization charge compared to the one positioned between the chains, justifying the zigzag chain picture. However, as already mentioned, there are important gross features of the band dispersion that the simple zigzag chain model fails to describe.

For a quantitative study of the COO, we define the order parameters: $\Delta n = [(n_{A1} + n_{A2}) - (n_{B1} + n_{B2})]/n$, $\eta_A = (n_{A1} - n_{A2})/n$, and $\eta_B = (n_{B2} - n_{B1})/n$, where n_i is the occupancy of the i th orbital including both spins and n is the total occupancy of the four e_g orbitals. The order parameters can be obtained from the occupation matrix, $n_{ij} = \sum_{\epsilon}^{\text{occ}} \langle i | \psi(\epsilon) \rangle \langle \psi(\epsilon) | j \rangle$, in the e_g subspace of the Mn atoms, with the basis orbitals i, j taken as A1/A2 or B1/B2 as appropriate. Summing over the four occupied e_g bands just below E_f , we find

$$n_A = \begin{pmatrix} 0.36 & 0 \\ 0 & 0.01 \end{pmatrix} \quad \text{and} \quad n_B = \begin{pmatrix} 0.10 & 0 \\ 0 & 0.12 \end{pmatrix}, \quad (2)$$

which yields $\Delta n = 0.25$, $\eta_A = 0.59$, and $\eta_B = 0.03$ [17]. The charge order is less robust than the nominal value of unity because of electron occupation of the corner-site (B) atom, which depletes the e_g charge from the bridge site. Electronic correlation missing in the DFT calculations is, however, expected to enhance the charge order.

Model Hamiltonian.—To include the correlation effects and to assess the importance of the various mechanisms for COO, we consider the following model Hamiltonian for the manganese sites in the CE structure:

$$\mathcal{H} = \sum_{i\alpha\sigma} \epsilon_{i\alpha} n_{i\alpha\sigma} - J_H \sum_{i\alpha} \hat{S}_i \cdot \vec{\sigma}_{i\alpha} + \sum_{\langle i,j \rangle \alpha\beta, \sigma} t_{ij}^{\alpha\beta} (c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + \text{H.c.}) + U \sum_{i\alpha\beta, \sigma\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} + V \sum_{\langle ij \rangle} n_i n_j, \quad (3)$$

where $c_{i\alpha\sigma}^\dagger$ creates an e_g electron at site i with orbital α and spin σ , n 's are the number operators, U and V are the on-site and intersite Coulomb interactions, \hat{S} is the localized t_{2g} classical spin, $\langle ij \rangle$ denotes nearest neighbors, and the prime over the summation indicates exclusion of the self-interaction terms. Note that with their spin orientations fixed as specified by the CE structure, the t_{2g} spins affect the motion of the itinerant electrons only via the Hund's rule coupling. The JT splitting of the e_g orbitals is included in the on-site energy $\epsilon_{i\alpha}$: $\epsilon = \pm \Delta_{JT}/2$ for the A2 and A1 orbitals, respectively, and zero for the B1 and B2 orbitals. Typical parameters are $V_{dd\sigma} = -0.55$ eV, $\Delta_{JT} = 1$ eV, $J_H = 2$ eV, $U = 5$ eV, and $V \leq 0.05$ eV [18,19]. Of these, we expect Δ_{JT} , determined to a large extent by the Mn-O distances, to show the maximum variability among the manganites, while the other parameters probably do not change much. We have studied the model Hamiltonian by two methods: (i) exact diagonalization for a one-dimensional (1D) zigzag chain and (ii) Hartree-Fock solution for the 3D lattice.

Exact diagonalization for a zigzag chain.—In the limit that $J_H = \infty$, the zigzag chains do not couple, and the Hamiltonian may be solved by exact diagonalization (ED) for a finite chain [9]. The ground state is expanded in terms of the many-particle configurations $|i\rangle$: $|G\rangle = \sum_i \alpha_i |i\rangle$,

and the resulting Hamiltonian matrix is diagonalized using the Lanczos method. We considered a 12-site chain with periodic boundary condition.

Figure 5 shows the ED results for a zigzag chain. The form of the e_g tight-binding hopping is such that [10,20] the band structure term by itself (case $U = V = \Delta_{JT} = 0$) produces a robust orbital order but no charge order. A charge order can be produced by any of the three parameters in the model, viz., U , V , or Δ_{JT} . Of these, while the on-site U can produce a limited amount of charge order, $\Delta n \leq 0.19$ [9], V and Δ_{JT} can, in principle, produce a maximal charge order of $\Delta n = 1$, in the limit of V or $\Delta_{JT} \rightarrow \infty$. The increase of Δn with Δ_{JT} is caused by the charge flow from the corner site to the bridge site. There being only half an e_g electron per Mn site, all charges reside on the lower JT-split orbital at the bridge site if $\Delta_{JT} \rightarrow \infty$, leading to a complete charge order.

For the typical value $\Delta_{JT} \approx 1$ eV, Fig. 5 shows that the JT term results in a charge order of $\Delta n = 0.32$, which is enhanced to 0.43 with the inclusion of U , which is further enhanced to 0.45 if we include V . Thus the JT coupling is the most important term for the COO.

Hartree-Fock results for the 3D lattice.—Since exact diagonalization is not feasible for the 3D lattice, we have

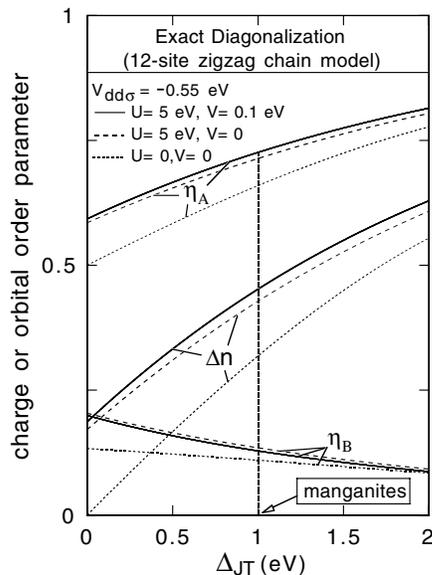


FIG. 5. The COO parameters from exact diagonalization for a single zigzag chain. Note that the kinetic energy term alone ($U = V = \Delta_{JT} = 0$) produces a large orbital order, but no charge order.

solved the Hamiltonian Eq. (3) using the self-consistent Hartree-Fock method, in order to assess the effect of dimensionality. In going from 1D to 3D, there are two competing effects: The increase in the bandwidth tends to reduce Δn (spreading out of the electron for kinetic energy gain), while the larger number of nearest neighbors in 3D enhances the effect of V , tending to strengthen the charge order. Of these two competing interactions, the effect of the band structure term turns out to be somewhat stronger, resulting in a slight weakening of the charge order in going from 1D to 3D (Fig. 6).

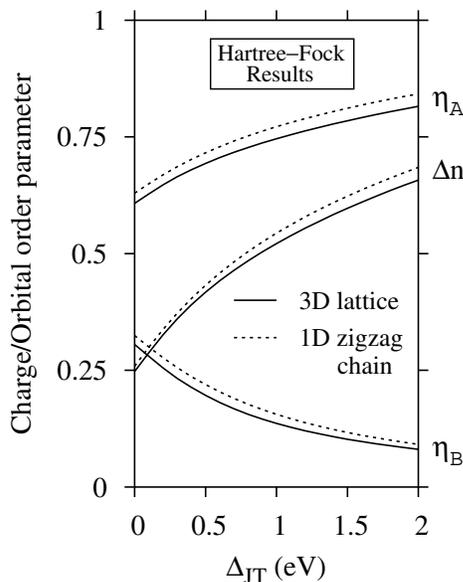


FIG. 6. Charge-orbital order parameters for the 3D lattice of coupled zigzag chains obtained in the Hartree-Fock approximation.

Finally, we note that while the original proposal of Goodenough envisioned a complete charge disproportionation between the Mn^{3+} and the Mn^{4+} atoms, we find it to be quite incomplete owing to the charge flow to the corner site Mn atoms. It would be gratifying to confirm this from direct experiments.

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