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 La$_{1/2}$Ca$_{1/2}$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 La$_{1/2}$Ca$_{1/2}$MnO$_3$.—We begin by describing the results of our band calculations using the spin-density-functional theory for the prototypical half-doped compound La$_{1/2}$Ca$_{1/2}$MnO$_3$. It forms in the orthorhombic crystal structure (space group $P$2$_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 approximation (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 Mn(3$d$) 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 Mn$(e_g)$ orbitals $V_{dd} = -0.55$ 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 Mn$(e_g)$ orbitals]. For this model, we have an $8 \times 8$ 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

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

FIG. 1. Sketch of the charge-orbital order obtained from density-functional theory for La$_{1/2}$Ca$_{1/2}$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 planes are stacked one over the other, with identical Mn charges but reversed moments. The coordinates $z$ along the bond for A and normal to the plane for B.
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 $\mathbf{k}$ normal to the chain direction. In fact, the band dispersion along $\Gamma - X$ ($\mathbf{k}$ along the chain direction) is not much stronger than the dispersion along $\Gamma - Z$ ($\mathbf{k}$ on the basal plane and normal to the chain) or along $\Gamma - Y$ ($\mathbf{k}$ 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 $J_H \approx 2 - 3$ 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 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 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 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 $m_c/m_a = 3$ and $m_b/m_a = 8$, 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
calized the on-site and intersite Coulomb interactions, \( J_H \) that \( D_s \) and spin affect the motion of the itinerant electrons only via the one-dimensional (1D) zigzag chain and (ii) Hartree-Fock Hamiltonian by two methods: (i) exact diagonalization for the manganese sites in the CE structure: 

\[
H = \sum_{i\alpha\sigma} \varepsilon_{i\alpha} n_{i\alpha\sigma} - J_H \sum_{i} \hat{S}_i \cdot \hat{\sigma}_{i\alpha} + \sum_{(j)\alpha\beta\sigma\sigma'} t^{\beta}_{ij}(c^{\dagger}_{i\alpha\sigma} c_{j\beta\sigma} + \text{H.c.}) + U \sum_{i\alpha\beta\sigma} n_{i\alpha\sigma} n_{i\beta\sigma} + V \sum_{\langle ij \rangle} n_{i\alpha\sigma} n_{j\beta\sigma},
\]

where \( c^{\dagger}_{i\alpha\sigma} \) creates an \( \epsilon \) electron at site \( i \) with orbital \( \alpha \) and spin \( \sigma \), \( n \)'s are the number operators, \( U \) and \( V \) are the on-site and intersite Coulomb interactions, \( S \) is the localized \( t_{2g} \) classical spin, \( (ij) \) 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 \( \epsilon \) orbitals is included in the on-site energy \( \varepsilon_{i\alpha} \): \( \epsilon = \pm \Delta_{JT}/2 \) for the A2 and A1 orbitals, respectively, and zero for the B1 and B2 orbitals. Typical parameters are \( V_{dd\sigma} = -0.55 \text{ eV} \), \( \Delta_{JT} = 1 \text{ eV} \), \( J_H = 2 \text{ eV} \), \( U = 5 \text{ eV} \), and \( V \leq 0.05 \text{ eV} \) [18,19]. Of these, we expect \( \Delta_{JT} \), 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 \( \epsilon \) 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 \( \Delta_{JT} \). Of these, while the on-site \( U \) can produce a limited amount of charge order, \( \Delta_{JT} \approx 0.19 \) [9], \( V \) and \( \Delta_{JT} \) 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 \( \Delta_{n} \) with \( \Delta_{JT} \) is caused by the charge flow from the corner site to the bridge site. There being only half an \( \epsilon \) 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 \( \Delta_{JT} = 1 \text{ eV} \), 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
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 $\Delta n$ (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).

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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[15] We have also performed a full-potential LMTO calculation with a single-$\kappa$ basis set and up to $l = 4$ muffin-tin orbitals, with their tails expanded in spherical harmonics up to $l_{\text{max}} = 4$, and have found no substantial difference from the ASA band structure.
[17] If $n_{ij}$ is not diagonal, then the relevant orbitals for orbital order may be obtained by diagonalizing the $n$ matrix.
[19] The intersite $V$ is expected to be small, due to the large screening by oxygen present between two Mn atoms, and in view of our earlier constrained DFT results for Fe$_2$O$_4$, where $V \approx 0.05$–0.1 eV between two Fe atoms of comparable separation with no oxygen in between: Z. Zhang and S. Satpathy, Phys. Rev. B 44, 13319 (1991).