Charge order induced in an orbital density-wave state

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Motivated by the recent ARPES measurements (Evtushinsky et. al., PRL \textbf{105}, 147201 (2010)) and evidence for the density-wave state for the charge and orbital ordering (García et al., PRL \textbf{109}, 107202 (2012)) in La$_{0.5}$Sr$_{1.5}$MnO$_4$, the issue of charge and orbital ordering in a two orbital tight-binding model for layered manganite near half doping is revisited. We find that the charge order is induced by the orbital order in the transversal orbital density-wave state which, on the other hand, results from the strong Fermi-surface nesting with the nature of orbital order parameter determined by the anisotropy of the kinetic energy in the orbital space and the crystal-field splitting of $e_g$ levels. Three important features, the primary role of orbital density-wave for the composite charge and orbitally ordering, the behavior of orbital order parameter as a function of temperature, and the jump in the charge and orbital order parameters near zigzag spin ordering transition are found to be in agreement with the x-ray experiments.

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I. INTRODUCTION

Orbital degree of freedom plays a crucial role not only in the transport properties as revealed in several experiments near metal-insulator transition associated with the colossal magnetoresistance (CMR),\textsuperscript{1,2} but also in stabilizing a range of magnetically ordered phases in manganites. For instance, the role of orbital ordering was recognized in stabilizing CE-type spin arrangement very early.\textsuperscript{3} This state consists of ferromagnetically ordered zigzag chains with spins on the neighboring chains oriented in the opposite directions. In addition, the state also exhibits the charge and orbital ordering with wavevectors \((\pi, \pi, 0)\) and \((0.5\pi, 0.5\pi, 0)\), respectively, with more charge accumulated at the orbitally polarized sites.\textsuperscript{4–6} Several theoretical investigations have supported \(d_{3x^2-r^2}/d_{3y^2-r^2}\)-type orbital order, in which \(d_{3x^2-r^2}\) and \(d_{3y^2-r^2}\) orbitals are occupied at the bridge sites of the parts of the zigzag chain that run parallel to the \(x\) and \(y\) directions, respectively, so that the kinetic energy gain through the double exchange mechanism lowers the energy of the system with respect to any other possible orbital order.\textsuperscript{7–9} However, there is no consensus in various x-ray experiments yet regarding whether \(d_{3x^2-r^2}/d_{3y^2-r^2}\)\textsuperscript{10,11} or \(d_{x^2-z^2}/d_{y^2-z^2}\)\textsuperscript{12,13}-type orbital order exists.

Half-doped single-layer manganite \(\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4\), apart from showing a CE-type ordered state with a transition temperature \(T_{CE} \approx 110\) K, also exhibits a charge and orbitally ordered state (CO) above \(T_{CE}\) with transition temperature \(T_{CO} \approx 220\) K.\textsuperscript{5} The CO state has been observed in different single-layer manganites in the electron-doped region by several experiments such as x-ray experiments,\textsuperscript{16,14} optical spectroscopy,\textsuperscript{15} and high-resolution electron microscopy (HREM) has been described as a charge-density wave of \(d_{3x^2-y^2}\text{(}d_{3x^2-r^2}\text{)}\) electrons, where orbital ordering wavevector \(Q\) is related to the hole doping \(x\) through \(Q_x = Q_y = \pi(1 - x)\). In a recent experiment, incommensurate sinusoidal modulations were observed.\textsuperscript{17} The stabilization of a possible density-wave state is an indicative of a very important role of the structure of the Fermi surface not only for the CO state but also for the CE-type AFM state.

A density-wave state scenario\textsuperscript{18} for the CO state has been further substantiated by a recent angle-resolved photoemission spectroscopy (ARPES) on the half-doped \(\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4\).\textsuperscript{19} The Fermi surface comprises of a small circular electron pocket around the \(\Gamma\) point and a relatively large hole pocket around the \(M\) point. Major portions of the hole pockets are largely flat, and therefore susceptible to the Fermi surface instability. The nesting vector
(0.5\pi, 0.5\pi) corresponds to the orbital ordering wavevector observed in the system.

In this paper, we revisit the issue of orbital ordering in La_{0.5}Sr_{1.5}MnO_4 for both the CO state without any spin order and with CE-type AFM order by considering a two orbital tight-binding model which includes the salient features of the experimental Fermi surface. We explore the orbital ordering within a self-consistent meanfield theory, where all range of interaction arising due to the coupling between electron and Jahn-Teller distortions can be accessed. The Jahn-Teller phononic approach has been considered to be similar to the Coulombic approach as the interorbital Coulomb interaction term has a local SU(2) symmetry in the limit of large Hund’s coupling. Therefore, the interorbital Coulomb interaction term only renormalizes the effective electron-electron interaction due to the coupling of electron to the Jahn-Teller phonons.

Several studies have assigned the origin of the charge order to different reasons. For instance in the case of CE state, it has been argued that the inter-orbital interaction can also lead to the charge ordering as the electrons in the near-complete orbitally polarized state at the bridge sites experience a negligible interorbital interaction due to the vanishingly small probability of electrons to be found in other orbital at the same site. While an electron at a corner site with a mixture of both \(d_{x^2-y^2}\) and \(d_{3z^2-r^2}\) feels strong interorbital interaction, thereby is pushed to the neighboring bridge sites. Other studies have emphasized on the role of long-range Coulomb interaction in stabilizing the charge order, though the difficulty with it is two fold. First, it requires a fine tuning of the interaction parameter to describe the composite appearance of charge and orbital order at \(T_{CO}\). Secondly, the form of interaction necessary to explain the charge ordering away from half doping in the density-wave state with charge ordering wavevector \(2Q\) will be unrealistic. In the following, we will see that the charge order can be induced by the orbital density-wave which itself results from a very strong Fermi surface nesting.

II. MODEL HAMILTONIAN

We consider a two orbital Hamiltonian for the single-layer manganites in the basis of \(d_{x^2-y^2}\) and \(d_{3z^2-r^2}\) orbitals

\[
\mathcal{H} = - \sum_{i\gamma\gamma'\sigma a} t_{\gamma\gamma'}^{a} d_{i\gamma\sigma}^\dagger d_{i+\mathbf{a}\gamma'\sigma} + \varepsilon_z \sum_{i} T_i^z + \sum_{il} g_{il} T_i^l + \sum_{il} K_{il} q_{il}^2/2 - J_{\mathbf{H}} \sum_{i} \mathbf{S}_i \cdot \mathbf{s}_i. \tag{1}
\]
The kinetic term within the tight-binding description includes $d^\dagger_{i\sigma} (d^\dagger_{i2\sigma})$ as the electron creation operator at site $i$ with spin $\sigma$ in the orbital $d_{x^2-y^2}$ ($d_{3z^2-r^2}$). $t_{\gamma\gamma'}^a$ are the hopping elements between $\gamma$ and $\gamma'$ orbitals along $a$ connecting the nearest-neighbor sites, which are given by $t_{x11}^x = -\sqrt{3}t_{x12}^x = 3t/4$ for $a = x$ and $t_{x11}^y = \sqrt{3}t_{y12}^y = \sqrt{3}t_{y21}^y = 3t_{y22}^y = 3t/4$ for $a = y$, respectively. $t$ is set to be the unit of energy in the following. Second term accounts for the crystalline-electric field (CEF) responsible for the splitting of $e_g$ levels in the tetragonal symmetry, where $T_{zz}^i = \sum_\sigma \psi^\dagger_{i\sigma} \hat{\tau}^z \psi_{i\sigma}$ with $\psi^\dagger_{i\sigma} = (d^\dagger_{i1\sigma}, d^\dagger_{i2\sigma})$ and $\hat{\tau}^z$ is the $z$-component of the Pauli matrices. According to the convention adopted here, a positive $\varepsilon_z$ which favors the occupancy of $d_{3z^2-r^2}$ orbital over $d_{x^2-y^2}$ orbital. Third term describes the coupling between the electron and Jahn-Teller distortions, where $q_{i1}$ and $q_{i2}$ correspond to transverse ($x^2 - y^2$)- and longitudinal ($3z^2 - r^2$)-type Jahn-Teller distortions, respectively, and $T_{xx}^i = \sum_\sigma \psi^\dagger_{i1\sigma} \hat{\tau}^x \psi_{i\sigma}$ with $\hat{\tau}^x$ as the $x$-component of the Pauli matrices. Fourth term accounts for the potential energy of these distortions with $K_l$ as the spring constant. Fifth term represents the Hund’s coupling ($J_H$) between the spin $s_i = \sum_{\gamma\gamma'} d^\dagger_{i\gamma\sigma} \sigma \sigma d_{i\gamma'\sigma}$ of $e_g$ electrons and the localized $t_{2g}$ spin $S_i$.

## III. ELECTRONIC STATE AND ORBITAL ORDERING INSTABILITY

Since the electron-phonon coupling term of the Hamiltonian has a rotation symmetry in the orbital space while the kinetic part does not have this symmetry, therefore a crucial role is played by the anisotropy in the orbital space in stabilizing the orbital order. To consider this aspect more, we write the kinetic and CEF terms in an orthogonal basis of orbitals rotated by an angle $\theta$ from the original basis of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$.

$$\hat{H}(\mathbf{k}, \theta) = \hat{U}(\theta)(\hat{K} + \varepsilon_z \hat{\tau}_z)\hat{U}^\dagger(\theta),$$

where kinetic part after the Fourier transformation is given as

$$\hat{K} = \begin{pmatrix}
\frac{-\sqrt{3}}{2}(\cos k_x + \cos k_y) & \frac{\sqrt{3}}{2}(\cos k_x + \cos k_y) \\
\frac{\sqrt{3}}{2}(\cos k_x + \cos k_y) & -\frac{1}{2}(\cos k_x + \cos k_y)
\end{pmatrix},$$

and the unitary matrix corresponding to the rotation $\theta$ in the orbital space has been defined as

$$\hat{U}(\theta) = \begin{pmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{pmatrix}.$$
FIG. 1. Orbital density distributions on the Fermi surface plotted for $\theta = \pi/4$ for different hole dopings (a) $x = 0$, (b) $x = 0.3$, and (c) $x = 0.6$, where $\varepsilon_z = 0$.

Then, the elements of matrix $\hat{H}(k, \theta)$ are

$$
H_{11}(k, \theta) = -\frac{1}{2} \left( (2 + \cos 2\theta)(c_x + c_y) - 2\varepsilon_z \cos 2\theta - \sqrt{3} \sin 2\theta (c_x - c_y) \right)
$$

$$
H_{12}(k, \theta) = \frac{1}{2} \left( \sin 2\theta (c_x + c_y - 2\varepsilon_z \cos 2\theta) + \sqrt{3} \cos 2\theta (c_x - c_y) \right)
$$

$$
H_{22}(k, \theta) = -\frac{1}{2} \left( (2 - \cos 2\theta)(c_x + c_y) + 2\varepsilon_z \cos 2\theta + \sqrt{3} \sin 2\theta (c_x - c_y) \right),
$$

(5)

where $c_x = \cos k_x$, $c_y = \cos k_y$. Orbital densities $w_\theta$ and $w_{\theta + \pi}$ corresponding to the orthogonal orbitals $d_\theta$ and $d_{\theta + \pi}$ are given by

$$
w_{\theta (\theta + \pi)} = \frac{1}{2} \left( 1 \mp \frac{H_{11}(k, \theta) - H_{22}(k, \theta)}{\sqrt{(H_{11}(k, \theta) - H_{22}(k, \theta))^2 + 4(H_{12}(k, \theta))^2}} \right)
$$

$$
= \frac{1}{2} \left( 1 \mp \frac{-\cos 2\theta (c_x + c_y - 2\varepsilon_z) + \sqrt{3} \sin 2\theta (c_x - c_y)}{2(c_x^2 - c_x c_y + c_y^2 - \varepsilon_z (c_x + c_y) + \varepsilon_z^2)} \right).
$$

(6)

Fig. 1 shows the orbital densities on the Fermi surface for several values of hole doping for $\theta = \pi/4$ which corresponds to the orbital basis of $d_-$ and $d_+$ given by $d_\pm = \frac{1}{\sqrt{2}}(d_{3x^2-r^2} \mp d_{x^2-y^2})$. There exists a very good nesting for all hole dopings with strongest being at $x = 0$, and nesting vector components $Q_x = Q_y = \pi(1 - x)$. A common feature of the Fermi surfaces for these dopings is the near-complete orbital polarization of the hole pockets in the flat region susceptible to the Fermi surface nesting, which can lead to the longitudinal orbital instability in the rotated basis, for example to the $d_-/d_+$-type ordering instability in this case. However, such orbital polarization near the flat region persists even if the basis is rotated away from $\theta = \pi/4$, for example a new basis of $d_{y^2-z^2}$ and $d_{3x^2-r^2}$ orbitals with $\theta = \pi/6$. Therefore, to find out the unique $\theta^*$ corresponding to the orbital ordering instability, which is due to the anisotropy in the kinetic part of the Hamiltonian (Eq. (1)),
we consider $\theta$ dependent orbital susceptibility which is defined as follows:

$$
\chi^{ij}(q, \theta, i\Omega_n) = \int_0^\beta d\zeta e^{i\Omega_n \zeta} \langle T_\zeta [T_i^j(\theta, \zeta) T_{-q}^{ij}(\theta, 0)] \rangle. \tag{7}
$$

Here, $\langle ... \rangle$ denotes thermal average, $T_\zeta$ imaginary time ordering, and $\Omega_n$ are the Bosonic Matsubara frequencies. $T^i_q(\theta)$ is obtained as the Fourier transformation of rotated orbital operator $T^i_\theta$. After a unitary transformation, the static orbital susceptibility $\hat{\chi}(q, \theta)$ can be expressed in the basis of 11, 22, 12, and 21 as a 4×4 matrix with 1 and 2 being orbital indices. The matrix elements of $\hat{\chi}(q, \theta)$ are given by

$$
\chi_{\mu\nu,\alpha\beta}(q, \theta) = -T \sum_{k,n} G_{\alpha\mu}(k + q, \theta, i\omega_n) G_{\nu\beta}(k, \theta, i\omega_n), \tag{8}
$$

where $G_{\alpha\mu}(k, i\omega_n)$ is the bare Green’s function for the electrons propagating from $\alpha$- to $\mu$-orbital with momentum $k$. Here, $\mathbf{1}$ is a 2×2 unit matrix. $\omega_n = \pi T (2n + 1)$ is the Fermionic Matsubara frequency with $n$ as an integer, and $T$ is the temperature. The bare susceptibility can be is given as follows

$$
\chi_{\mu\nu,\alpha\beta}(q, \theta) = -\frac{1}{N} \sum_k \sum_{i,j} a^{\mu*}_{jk+q}(\theta) a^\nu_{ik}(\theta) a^{\beta*}_{ik}(\theta) a^\alpha_{jk+q}(\theta) \frac{n(E_i(k)) - n(E_j(k + q))}{E_i(k) - E_j(k + q)}, \tag{9}
$$

where $a^{\nu\mu}_{ip}$ are the unitary coefficients of the $i$-band to $\nu$-orbital obtained from Eq. (8), and $n(\xi)$ is the Fermi distribution function. Electronic dispersion is given by the eigenvalues of

FIG. 2. Longitudinal orbital susceptibility as a function of $\theta$ for different values of nesting vectors $Q = (\pi, \pi), (0.7\pi, 0.7\pi),$ and $(0.4\pi, 0.4\pi)$ corresponding to the hole dopings $x = 0, 0.3,$ and $0.6,$ respectively for (a) $\epsilon_z = 0$ and (b) $\epsilon_z = 0.3.$ In addition, $\theta$ dependence has been also shown in the case of $Q = (0.5\pi, 0.5\pi)$ corresponding to the half doping in (b).
\( \hat{H}(\mathbf{k}, \theta) \)

\[
E_{\pm}(\mathbf{k}) = \varepsilon_+(\mathbf{k}) \pm \sqrt{\varepsilon_-^2(\mathbf{k}) + \varepsilon_{12}^2(\mathbf{k}) - \mu},
\]

where

\[
\begin{align*}
\varepsilon_+(\mathbf{k}) &= -(\cos k_x + \cos k_y) \\
\varepsilon_-(\mathbf{k}) &= -\frac{1}{2}(\cos k_x + \cos k_y) + \varepsilon_z \\
\varepsilon_{12}(\mathbf{k}) &= \frac{\sqrt{3}}{2} (\cos k_x - \cos k_y),
\end{align*}
\]

Fig. 2 shows the longitudinal orbital susceptibility for the representative values of the hole dopings \( x = 0, 0.3 \) and 0.6. Interestingly, susceptibility exhibits a maximum value for \( \theta = \pi/4 \) for all hole dopings in the case of \( \varepsilon_z = 0 \), implying an important role for the \( d_-/d_+ \)-type orbital correlations in the entire hole doping regime. However for \( \varepsilon_z = 0.3 \), it displays maximum value for \( \theta = \pi/4 \) near half doping and for \( \theta = \pi/6 \) near zero doping corresponding to the orbital correlation of type \( d_{x^2-y^2}/d_{3y^2-r^2} \) as the orbital distributions are sensitive to the tetragonal crystal-field splitting of the \( e_g \) levels. Here and hereafter, the consideration of \( \varepsilon_z = 0.3 \) is motivated by the good agreement with the ARPES experiments on the Fermi surface of \( \text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4 \) for which \( d_-/d_+ \)-type orbital correlations is crucial as discussed below.

**IV. CHARGE AND ORBITALLY ORDERED STATE AT HALF DOPING**

Half-doped \( \text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4 \) exhibits a charge and orbitally ordered state in the temperature range \( T_{CE} < T < T_{CO} \), with the charge and orbital ordering wavevectors \( \mathbf{Q}_c = (\pi, \pi) \) and \( \mathbf{Q}_o = (0.5\pi, 0.5\pi) \), respectively. To explore the nature of the CO state with the local moment’s direction thermally disordered, we consider large Hund’s coupling limit where the double occupancy of the \( e_g \) orbitals is not allowed energetically and the \( e_g \) spins are enslaved to the \( t_{2g} \) spins. Therefore, we drop the spin index in this Section. Then, the Fermi surface corresponding to the electron density persite \( 1 - x \approx 0.52 \) and the crystalline-electric field \( \varepsilon_z = 0.3 \) obtained using Eq. (10) is shown in Fig. 3, which is in good agreement with the experimental ARPES result. The Fermi surface, consists of a small circular electron pocket around the \( \Gamma \) point and a large hole pocket around the \( M \) point with portions being almost flat near the zone boundary at \( X \). Among two nesting possibilities with vectors \( (0.5\pi, 0) \)
FIG. 3. Fermi surface plotted in the basis of $d_-$ and $d_+$ for chemical potential $\mu = -1.25$, and $\varepsilon_z = 0.3$, where $d_\mp = \frac{1}{\sqrt{2}}(d_{3z^2-r^2} \mp d_{x^2-y^2})$. Various features including a small hole pockets around the $\Gamma$ point is in good agreement with the experiments. The Fermi surface is predominantly composed of $d_-$ and $d_+$ orbitals around $X$ and $X'$, respectively.

FIG. 4. (a) $J_x$ vs $J_z$ phase diagram, where dashed line represents $J_x = J_z$. (b) orbital and charge order parameters as a function of interaction along $J_x = J_z$.

and $(0.5\pi, 0.5\pi)$, the latter one corresponds to the stronger orbital ordering instability, and therefore will lead to the orbital ordering with wavevector $(0.5\pi, 0.5\pi)$. To describe the orbital density-wave state resulting from the Fermi-surface nesting with ordering wavevector $(0.5\pi, 0.5\pi)$ in the half-doped La$_{0.5}$Sr$_{1.5}$MnO$_4$, we consider following Hamiltonian given by a $8 \times 8$ matrix in a four-sublattice basis after carrying out a meanfield decoupling for the electron-phonon coupling term.
Hamiltonian parameters are determined self consistently by carrying out the numerical diagonalization of the Hamiltonian \( H_{CO}(\mathbf{k}) \) with

\[
H_{CO}(\mathbf{k}) = \sum_{\mathbf{k},\mu} \Psi_{\mathbf{k}}^\dagger \begin{pmatrix}
\Delta_{cr} & \hat{K} & 0 & \hat{K}^\dagger \\
\hat{K}^\dagger & -\Delta_o + \hat{\Delta}_{cr} & \hat{K} & 0 \\
0 & \hat{K}^\dagger & \hat{\Delta}_{cr} & \hat{K} \\
\hat{K} & 0 & \hat{K}^\dagger & \Delta_o + \hat{\Delta}_{cr}
\end{pmatrix} \Psi_{\mathbf{k}},
\]

where \( \Psi_{\mathbf{k}} = (d^i_{A\mathbf{k}1}, d^i_{A\mathbf{k}2} \ldots d^i_{D\mathbf{k}1} ; d^i_{D\mathbf{k}2}) \) is the electron field operator. Orbital exchange and crystalline-electronic fields are given by 2×2 matrices

\[
\hat{\Delta}_o = J_x m_{ox} \hat{\tau}^x + J_z m_{oz} \hat{\tau}^z
\]

\[
\hat{\Delta}_{cr} = \varepsilon_z \hat{\tau}^z,
\]

where \( J_x = g^2/K_x \), \( J_z = g^2/K_z \). The Bloch phase factor is

\[
\hat{K} = -\frac{1}{4} \begin{pmatrix}
3(e^{ik_x} + e^{ik_y}) & -\sqrt{3}(e^{ik_x} - e^{ik_y}) \\
-\sqrt{3}(e^{ik_x} - e^{ik_y}) & (e^{ik_x} + e^{ik_y})
\end{pmatrix}
\]

The band filling \( (n = 1 - x) \), orbital order \( (m_{ox} \text{ and } m_{oz}) \) and charge order \( (m_c) \) parameters are determined self consistently by carrying out the numerical diagonalization of the Hamiltonian \( \hat{H}_{CO} \) with

\[
n = \frac{1}{4N} \sum_{\mathbf{k}s\gamma} (\phi_{s\mathbf{k} \gamma}^i \phi_{s\mathbf{k} \gamma}^{i*}) n(\xi_{\mathbf{k}}^i)
\]

\[
m_{ox} = \frac{1}{2N} \sum_{\mathbf{k}i} (\phi_{B\mathbf{k}1}^i \phi_{B\mathbf{k}2}^{i*} + \phi_{B\mathbf{k}2}^i \phi_{B\mathbf{k}1}^{i*} - \phi_{D\mathbf{k}1}^i \phi_{D\mathbf{k}2}^{i*} - \phi_{D\mathbf{k}2}^i \phi_{D\mathbf{k}1}^{i*}) n(\xi_{\mathbf{k}}^i)
\]

\[
m_{oz} = \frac{1}{2N} \sum_{\mathbf{k}i} (\phi_{B\mathbf{k}1}^i \phi_{B\mathbf{k}2}^{i*} - \phi_{B\mathbf{k}2}^i \phi_{B\mathbf{k}1}^{i*} - \phi_{D\mathbf{k}1}^i \phi_{D\mathbf{k}2}^{i*} + \phi_{D\mathbf{k}2}^i \phi_{D\mathbf{k}1}^{i*}) n(\xi_{\mathbf{k}}^i)
\]

\[
m_c = \frac{1}{2N} \sum_{\mathbf{k}i} (\phi_{B\mathbf{k}1}^i \phi_{B\mathbf{k}2}^{i*} + \phi_{B\mathbf{k}2}^i \phi_{B\mathbf{k}1}^{i*} - \phi_{C\mathbf{k}1}^i \phi_{C\mathbf{k}2}^{i*} - \phi_{C\mathbf{k}2}^i \phi_{C\mathbf{k}1}^{i*}) n(\xi_{\mathbf{k}}^i)
\]

\[
+ \phi_{D\mathbf{k}1}^i \phi_{D\mathbf{k}2}^{i*} + \phi_{D\mathbf{k}2}^i \phi_{D\mathbf{k}1}^{i*} - \phi_{A\mathbf{k}1}^i \phi_{A\mathbf{k}2}^{i*} - \phi_{A\mathbf{k}2}^i \phi_{A\mathbf{k}1}^{i*}) n(\xi_{\mathbf{k}}^i),
\]

where \( \phi_{s\mathbf{k} \gamma}^i \) is the amplitude of an electron in the \( \gamma \) orbital of sublattice \( s \), and \( \mathbf{k} \) belongs to the reduced Brillouin zone. \( n(\xi_{\mathbf{k}}^i) \) is the Fermi distribution function with \( \xi_{\mathbf{k}}^i = E_{\mathbf{k}}^i - \mu \), where \( E_{\mathbf{k}}^i \) is the \( i \)th eigenvalue of the Hamiltonian given by Eq. (2) and \( \mu \) is the chemical potential.

The phase diagram of \( J_x \) vs \( J_z \) is shown in Fig. 4(a), which consists of three regions, ferro orbitally ordered (FO) with net positive \( \langle \mathcal{T}_i^z \rangle \) orbital moment due to the anisotropy in the orbital space, CO\((d_-/d_+)\) with \( m_{oz} = 0 \), and CO\((d_{x^2-y^2}/d_{3z^2-r^2})\) with \( m_{ox} = 0 \). The CO\((d_-/d_+)\) state, which is stabilized for \( J_x \geq 1.2 \) in the region \( J_x \geq J_z \) and also in a
FIG. 5. (a) Charge and orbital order parameter as a function of temperature for $J_x = J_z = 1.8$ with solid circles as experimental data.$^{10}$ (b) Heat capacity as a function of temperature.

part of region $J_x < J_z$, while CO($d_{x^2-y^2}/d_{3z^2-r^2}$) state is stabilized for $J_z \geq 1.9$ in rest of the region. Each CO state has an induced charge order due to the orbital ordering, with the charge accumulation at orbitally polarized sites. This feature is in agreement with the x-ray experiment where orbital correlation length was found to be larger than the charge correlation length suggesting a crucial role of orbital order.$^{23}$ Further, the straight line $J_x = J_z$ becomes phase boundary line separating the two CO phases in strong coupling limit, which is due to the fact that the electron-phonon coupling term of Hamiltonian possesses the rotational symmetry in orbital space for $J_x = J_z$. If we assume that the relation $J_x = J_z$, which is valid exactly only in the cubic symmetry where $e_g$ levels are degenerate, is still a good approximation in the tetragonal symmetry where two fold degeneracy is no longer present, then the $d_{-}/d_{+}$ orbital order is stabilized robustly except in the strong coupling limit (Fig. 4(b)).

Fig. 5(a) shows the orbital and the induced charge order parameter as a function of temperature in good agreement with the resonant x-ray experiment data.$^{10}$ However, our calculation shows the nature of transition to be of the second order as can be seen from the behavior of the heat capacity near $T_{CO}$ as shown in Fig. 5(b) unless it involves a change in lattice parameter which cannot be accounted for in this calculation. The heat capacity is obtained as

$$C = -T \frac{d^2 F}{dT^2}, \quad (15)$$
FIG. 6. Orbital, charge, and spin arrangement in the CE-type state, with top view of $d_-$ and $d_+$ orbitals. Ferromagnetic chains of opposite spin orientations have been shown in different colors.

where the free energy $F$ is given by

$$F = -\sum_{k,i} T \ln (1 + e^{-\beta \varepsilon_k}) - \frac{1}{2} \sum_{l,s} J_l \langle T^l_s \rangle \langle T^l_s \rangle + \mu N \tag{16}$$

in terms of Boltzman constant with $\beta = 1/T$, while the contributions from the spin degree of freedom has not been incorporated. $k$ belongs to the reduced Brillouin zone, $s$ is the sublattice index, and $N$ is the total number of electrons in a unit cell. This density-wave state scenario can be further extended to the hole doped region $0.5 \leq x \leq 0.7$ with the relation between orbital ordering ($Q_o$) and charge ordering wavevector ($Q_c$) as $Q_c = 2Q_o$ in consistent with x-ray experiments on several single-layer manganites, where orbital ordering wavevector was observed to depend linearly on the hole doping $Q_{ox} = Q_{oy} = \pi(1 - x)$.

V. CE-TYPE AFM STATE

Local moments, which are directionally disordered due to the thermal fluctuations in the CO state prior to the transition to low temperature CE-type state, try to attain a configuration on lowering of the temperature that will increase the kinetic energy gain through the 'double Exchange' mechanism,\textsuperscript{26} which may change the orbital order parameter of the CO state. Therefore, to find the exact nature of this change in the orbital order stabilized in
the CE state as shown in Fig. 4, we consider a meanfield Hamiltonian for an electron with spin \( \sigma \) given by 16\times16 matrix in a 4+4 sublattice basis

\[
\hat{H}_{CE}(k) = \sum_{k,\mu} \Psi_k \begin{pmatrix} \hat{H}^{11}(k) & \hat{H}^{12}(k) \\ \hat{H}^{12\dagger}(k) & \hat{H}^{22}(k) \end{pmatrix} \Psi_k,
\]

(17)

where \( \Psi_k = (d_{A1}^\dagger, d_{A2}^\dagger, \ldots, d_{D1}^\dagger, d_{D2}^\dagger, d_{A'1}^\dagger, \ldots, d_{D'1}^\dagger, d_{D'2}^\dagger) \) is the electron field operator with primed \( d \) electron operators acting on the basis with spin oriented in the opposite direction. Here, \( A, C, \) and \( A', C' \) correspond to the corner sites on the two 4 sublattice basis, while \( B, D, \) and \( B', D' \) correspond to the bridge sites on the 4+4 sublattice basis. Further,

\[
\hat{H}^{11(22)}(k) = \begin{pmatrix} \Delta_{cr} & \hat{K}_x & 0 & \hat{K}_y^\dagger \\ \hat{K}_x^\dagger & -\Delta_o + \Delta_{cr} & \hat{K}_x & 0 \\ 0 & \hat{K}_x^\dagger & \Delta_{cr} & \hat{K}_y \\ \hat{K}_y & 0 & \hat{K}_y^\dagger & \Delta_o + \Delta_{cr} \end{pmatrix} \mp \sigma J_H S \mathbf{i},
\]

(18)

and

\[
\hat{H}^{12}(k) = \begin{pmatrix} \hat{K}_y & 0 & \hat{K}_y^\dagger \\ \hat{K}_y^\dagger & 0 & \hat{K}_y \\ 0 & \hat{K}_y^\dagger & \hat{K}_y \\ \hat{K}_x & 0 & \hat{K}_x^\dagger \end{pmatrix}.
\]

(19)

\( \hat{K}_x \) and \( \hat{K}_y \) are Bloch phase factors in the \( x- \) and \( y- \)directions given by Eq. 13, and here \( \mathbf{i} \) is a 8\times8 identity matrix. The band filling, orbital and charge order parameters are determined self consistently as in the CO state by numerically diagonalizing the Hamiltonian \( \hat{H}_{CE} \).

Fig. 7(a) shows the phase diagram of \( J_x \) vs \( J_z \) with \( J_H = 8t \) in the CE-type spin arrangement, which consists of two types of charge and orbitally ordered state, CO\((d_-/d_+)\) stabilized for \( J_x \geq J_z \) and also in a part of the region \( J_x < J_z \), another CO state with the character of orbital ordering depending on the strength of \( J_z \) stabilized in the rest of the region. The latter CO state transforms to the CO\((d_{x^2-y^2}/d_{3z^2-r^2})\) in the limit of large \( J_z \) as shown in Fig. 7(b). Here, the phase boundary line is pushed further inside the region \( J_z > J_x \) as compared to the CO state without CE-type spin arrangement. In other words, CE state supports in breaking the four-fold rotational symmetry in the orbital space due to the zig-zag spin arrangement with the help of double-exchange mechanism, and stabilizes the \( d_-/d_+ \) orbital order further.
FIG. 7. In the CE-type spin arrangement with $J_H = 8t$, (a) $J_x$ vs $J_z$ phase diagram, (b) nature of orbital order parameter in the CO state as a function of $J_z$ for fixed $J_x = 1.8$, (c) orbital order ($m_{ox}$ and $m_{oz}$) and charge order ($m_c$) parameters as a function of interaction $J_x$, where $J_x = J_z$.

The stabilization of CO($d_-/d_+$) for $J_x \approx J_z$ even in the CE-type spin arrangement is not surprising if we look at the hopping matrix in the new basis consisting of $d_+$ and $d_-$ orbitals

$$\hat{H}(\mathbf{k}, \pi/4) = -\frac{1}{2} \begin{pmatrix} ac_x + bc_y & c_x + c_y \\ c_x + c_y & bc_x + ac_y \end{pmatrix},$$

where $c_x = \cos k_x$, $c_y = \cos k_y$, $a = 2 - \sqrt{3}$, $b = 2 + \sqrt{3}$, $\varepsilon_z = 0$. In the new basis, the ratios of hopping parameters in the $x$- and $y$-directions for the $d_-$ and $d_+$ orbitals are $t_{--y}/t_{--x} = t_{++x}/t_{++y} \approx 0.07$. Therefore, the intraorbital hopping is quasi-one dimensional for each orbital, that is, the dominant hopping occurs in the $x$- and $y$-directions for the $d_-$ and $d_+$ orbitals, respectively. At the same time, interorbital hopping is isotropic with respect to the magnitude and phase.

With CO ($d_-/d_+$) order, kinetic energy gain can be maximized through the double-exchange mechanism if the electrons move along the zigzag chains as shown in Fig. 6, which is consistent with the quasi-one dimensional intraorbital hopping discussed above. In other
words, the electrons hop through $d_-$ and $d_+$ orbitals along $x$- and $y$- directions at bridge sites like $B$ and $D$, respectively, while the corner sites like $A$ and $C$ will have equal mixture of $d_-$ and $d_+$ orbitals as interorbital hopping is isotropic and equal for both the orbitals. Fig. 7(c) highlights this interesting aspect through the dependence of orbital order parameter on the interaction in the CE-type spin arrangement, where a near-complete orbital polarization with non-zero $m_{ox}$ exists even in limit of vanishing interaction strength at sites like $B$ and $D$. Moreover, we note a significant jump in the magnitude of both charge ($\approx 100\%$) and orbital order ($\approx 40\%$) parameters for the same value of $J_x = J_z = 1.8$ in the case of CE state as compared to the CO state without any spin order. A jump in the orbital order parameter has been also noticed in the x-ray experiments.$^{13}$ In this spin arrangement, the electrons avoid hopping in the direction perpendicular to the chain due to less kinetic energy gain as the hopping parameter is very small in this direction, which in the presence of a small antiferromagnetic coupling between the $t_{2g}$ spin, will force the neighboring zigzag chains to have spins pointing in the opposite directions. However, this fine balance in cooperation between orbital density-wave and a spin ordering commensurate with lattice due to the large $t_{2g}$ local moments, which exists only near half doping, may be destroyed on moving away from this special doping.

**VI. CONCLUSIONS**

In conclusion, we have investigated the charge and orbital order in a two orbital tight-binding model for half-doped layered La$_{0.5}$Sr$_{1.5}$MnO$_4$ with realistic electronic state as observed in the ARPES measurement. The role of orbital density-wave as suggested in the recent x-ray experiments, which results from the strong nesting of Fermi surface due to almost flat regions near $k_x \approx \pm 0.25\pi$ and $k_y \approx \pm 0.25\pi$, is found to be crucial for the stabilization of the composite charge and orbital order. On the other hand, the nature of orbital order depends on the orbital anisotropy as well as on the CEF of $e_g$ levels in the kinetic part of the Hamiltonian, and leads to the transverse orbital order ($d_-/d_+$-type) at half doping. The behavior of orbital ordering parameter as a function of temperature, which is in agreement with the x-ray experiments, close to a second-order phase transition. Moreover, the orbital and charge order parameters show a jump for the transition from CO state to the CE-type AFM state in accordance with the experiments.
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