Mean-field model for the CE-phase of manganites

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Abstract. The CE phase of La$_{0.5}$Ca$_{0.5}$MnO$_3$ displays long-range magnetic, charge and orbital order of the $e_g$ states of the Mn ions. The magnetic order of the $t_{2g}$ spins of Mn is determined by the antiferromagnetic superexchange and the ferromagnetic double-exchange. The checkerboard charge and the orbital order is the consequence of the Jahn-Teller coupling of the $e_g$ orbitals to the lattice. Using a mean-field slave-boson approach for the $e_g$ electrons in two orbitals per site with excluded multiple occupancy and Hund’s rule coupling between the $e_g$ and $t_{2g}$ states, we obtain the tight-binding band structure of the CE phase. The unit cell of the CE phase consists of 16 sites. The 32 $e_g$ bands in the Brillouin zone are grouped into two sets of 16 bands separated by a charge order gap. The charge gap does not directly affect the properties of the compound. If long-range orbital order is included an additional gap opens at the Fermi level.

1. Introduction
The rich phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) is the consequence of the interplay of charge, spin, orbital and lattice degrees of freedom [1, 2]. The end-compounds of LCMO, LaMnO$_3$ and CaMnO$_3$ are antiferromagnetic (AF) insulators, while for intermediate $x$ the system is either a ferromagnetic (F) metal or a charge-ordered AF and may display phase separation [3, 4, 5]. Many of the phases of LCMO were identified in early papers [6, 7] and denoted with A, B, C, CE and G according to their magnetic and charge order. In the B phase all localized spins are F correlated, while in the G phase each up spin is surrounded by neighbors with down spins and vice versa. In the A phase the localized spins are F oriented in the $x$-$y$ planes and these planes are AF stacked along the $z$-direction. The C phase consists F chains along the $z$-direction, which are AF correlated to each other in the $x$-$y$-plane. The CE is considerably more complex involving sixteen sites per unit cell with magnetic, charge and orbital order. Early models for the CE phase involve F zig-zag chains [1] and Monte Carlo simulations on smaller system sizes [8, 9]. Mean-field approaches [10, 11] and ab initio band structure calculations [12] were carried out more recently. In this paper we extend our mean-field many-body calculation for the A, B, C and G phases to include the CE phase.

2. Quasi-cubic manganites and the CE phase
In LCMO the Mn ions form a simple cubic lattice with one oxygen ion located approximately on the center of each side and the La or Ca atoms at the body center of the cube. The O$^{2-}$ ions mediate the binding between the Mn ions, while the role of La$^{3+}$ and Ca$^{2+}$ is to provide conduction electrons [7]. In nearly cubic symmetry the five 3$d$ levels are split into a $t_{2g}$ triplet and an $e_g$ doublet. Within octahedral coordination the $t_{2g}$ states have lower energy than the $e_g$ orbitals. The Mn ions are in a mixed trivalent (3$d^4$) and tetravalent (3$d^3$) state, so that the
three $t_{2g}$ orbitals are all singly occupied with their spins coupled to form a total spin $3/2$. The $e_g$ orbitals, on the other hand, are empty for Mn$^{3+}$ and occupied by one 3$d$ electron in Mn$^{3+}$, which is F correlated with the $t_{2g}$ electrons via Hund’s rule coupling. The intermediate valence character of the Mn ions arises from the hopping of the $e_g$ electrons.

The CE phase has a checkerboard charge order in addition to the complex magnetic order in the $x$-$y$ plane shown in Fig. 1. All spins are reversed in the neighboring planes, but the $\vec{Q}$-vector for the charge order is $(\pi, \pi, 0)$. Note that up-spins form a zig-zag chain in the $(1, 1, 0)$ direction with a unit length of two lattice spacings. The dashed lines in Fig. 1 denote the unit cell.

**Figure 1.** Checkerboard pattern for the charge order in the CE phase of LCMO. The open (filled) circles correspond to a site with decreased (increased) charge. The arrows indicate the magnetic order in the plane. The spins in successive planes are alternately antiparallel and parallel to this plane with identical charge configuration. The dashed lines denote the unit cell which altogether contains 16 sites (two planes).

### 3. The model

In a previous publication [13] we studied a cubic lattice of mixed-valent Mn ions with the $t_{2g}$ spins (treated classically) oriented in the spin arrangements of the A, B, C and G phases of the manganites [6]. The Hamiltonian is the sum of $H_t$, which represents the hopping of the $e_g$ electrons between the Mn sites on a simple cubic lattice, and $H_{\text{mag}}$, which is the magnetic energy arising from the superexchange between the $t_{2g}$ spins [13],

$$H_t = -\mu \sum_{jM^*m} |jS^*M^*m\rangle\langle jS^*M^*m| - t \sum_{(jl)m_jm_l\sigma M_lM_j} \left(\langle SM_l, 1/2\sigma | S_{1/2}^1S_{1/2}^j\rangle \times \right)$$

$$\left(\langle SM_l, 1/2\sigma | S_{1/2}^jS^*_{1/2}\rangle \{ |jSM_l\rangle\langle jS^*M^*_l|M_{m_jm_l}(R_{jl}) |lS^*_lM^*_l\rangle \langle lSM_l| + H.c. \}, \right) \quad (1)$$

$$H_{\text{mag}} = -\alpha JS^2N \quad (2)$$

Here the bra and ket denote the states of the Mn$^{4+}$ configuration represented by a spin $S(=3/2)$ and $z$-projection $M$, and the states of the Mn$^{3+}$ configuration of spin $S^* = S + 1/2$ and spin projection $M^*$. The localized 3$d$ electrons are then all F correlated (first Hund’s rule) with the Clebsch-Gordan coefficients selecting the spin components. $j$ labels the sites on a simple cubic lattice, the index $m = x^2-y^2, z^2$ labels the $e_g$ orbitals and $\sigma$ is the spin component of the $e_g$ electron. The Mn$^{3+}$ states have in addition a label $m$ to indicate which of the $e_g$ states is occupied. The completeness condition for the states requires that at every site

$$\sum_{M^*m} |jS^*M^*m\rangle\langle jS^*M^*m| + \sum_M |jSM\rangle\langle jSM| = 1 \quad , \quad (3)$$

which excludes the multiple occupancy of the $e_g$ levels, i.e. they can only be empty or occupied by one electron. This corresponds to an implicit infinite on-site Coulomb repulsion.

The first term in Eq.(1) determines the chemical potential $\mu$ for the itinerant electrons, while the second term corresponds to the nearest neighbor intersite hopping. The sum is over all the nearest neighbor pairs $(jl)$ and $R_{jl}$ is the vector joining the sites $j$ and $l$. The hopping matrix $M_{m_jm_l}(R_{jl})$ depends on $R_{jl}$, i.e. $M_x = (2\hat{I} + \hat{\tau}_x + \sqrt{3}\hat{\tau}_z)/4, M_y = (2\hat{I} + \hat{\tau}_z - \sqrt{3}\hat{\tau}_x)/4$, and
$\hat{M}_z = (\hat{I} - \hat{\tau}_z)/2$. Here $\hat{I}$ and $\hat{\tau}_z$ are the identity and Pauli matrices for the orbital pseudospin of components $(x^2-y^2, z^2)$. These hopping matrices are determined by the overlap of the asymptotes of the $e_g$ wavefunctions.

The magnetic energy $H_m$ arises from the superexchange of the $t_{2g}$ spins mediated by the O atoms and depends on the spin configuration of each phase. In mean-field the Heisenberg superexchange reduces to Eq. (2) with $\alpha_A = -1$, $\alpha_B = -3$, $\alpha_C = +1$, $\alpha_{CE} = +1$ and $\alpha_G = +3$. Here $N$ is the number of Mn sites. The coupling strength $J$ can be estimated from the $T_N$ of the end-compounds and is of the order of 100 times smaller than the hopping amplitude $t$ [13].

The spin-projections $M_j = \pm S$ of the $t_{2g}$ moments at each site are determined by the magnetic phase. The spin-projection of the Mn$^{3+}$ ion is $M_j^I = \pm S + \sigma$ and hence the spin component $\sigma$ of the $e_g$-electron is a good quantum number. $\sigma$ is either parallel or antiparallel to $M_j$ yielding a Clebsch-Gordan coefficient equal to 1 or $1/\sqrt{2S+1}$, respectively. Hence, the hopping is much more favorable if $\sigma$ is parallel to the spins of the two sites, which gives rise to the ferromagnetic double-exchange [14, 15]. We introduce slave-boson creation and annihilation operators [16, 17], $b_j^{\pm S}$ and $b_j^{\pm S}$, which act as projectors onto the states of the Mn$^{3+}$ configuration at site $j$, and fermion operators for the Mn$^{3+}$ states at the site $j$, $d_{j\sigma m}$ and $d_{j\sigma m}$. The Hamiltonian $H_I$ is now rewritten in terms of these operators [13] and studied in the mean-field approximation by replacing the boson operators by their expectation values [18]. The staggered charge order requires two different boson expectation values, $b_1$ and $b_2$, one for each sublattice. The completeness condition (3) is incorporated via Lagrange multipliers $\lambda_j$. Again, two values of the Lagrange parameters are needed, $\lambda_1$ and $\lambda_2$, one for each sublattice. To drive the charge imbalance between sublattices an additional energy $H_W = Wn_1n_2$, also treated in mean-field, is included. Here $n_1$ and $n_2$ are the sublattice charges. The origin of this interaction is discussed below. The total energy is then minimized with respect to $b_1$, $b_2$, $\lambda_1$ and $\lambda_2$. This yields transcendental equations, which are solved self-consistently.

4. Band structure of the CE phase

The band structure for the $e_g$ electrons is obtained by Fourier transforming and diagonalizing the mean-field Hamiltonian. All five phases have different magnetic unit cells. While the unit cell of the B phase has only one Mn ion, the ones of the A, C and G phases have two and the CE phase sixteen Mn ions [6]. The Brillouin zones of the A, C, G and CE phases are then contained in the simple cubic one of the B phase. To facilitate a direct comparison between the phases we adopt the simple cubic Brillouin zone for all phases. There is then redundant information contained in the Brillouin zone for all but the B phase [13].

Due to the magnetic order, the $x$, $y$ and $z$ directions in the cubic Brillouin zone are in general not equivalent. We consider the band structure along the following directions: From $\Gamma$ to $X$ along $k = (k_x, 0, 0)$, then from $X$ to $M$ varying $k_y$ from 0 to $\pi$ along $(\pi, k_y, 0)$, from $M$ to $R$ along $(\pi, \pi, k_z)$, from $R$ to $\Gamma$ along $(k/\sqrt{3})(1, 1, 1)$, and from $\Gamma$ to $M$ along $(k/\sqrt{2})(1, 1, 0)$. Finally, $X$ to $R$ refers to the line $(\pi, k/\sqrt{2}, k/\sqrt{2})$.

The band structure of the $e_g$ electrons in the CE phase is shown in Fig. 2 for $W = 3.31t$ and $x = 0.5$, leading to a selfconsistent solution with $n_1 = 0.84483$ and $n_2 = 0.15517$. There are altogether 32 bands (two orbitals for 16 sites) for each spin direction. The 32 bands are split into two groups of 16 bands due to the charge order gap. Panel (a) shows the bands below the gap and panel (b) those above. Within each group of 16 bands they are further grouped into four sets of four bands. Since there is at most one $e_g$ electron per site, the bands in panel (b) are not occupied. The charge order gap then plays no role neither for the ground state nor the low-energy excitations. The Fermi level is indicated by the thin horizontal line in panel (a).

The interaction $H_W$ driving the charge order is mediated by the Jahn-Teller effect involving the $Q_1$-mode, rather than a Coulomb repulsion between nearest neighbor Mn sites. The $Q_1$-
Figure 2. Band structure for electrons in the $e_g$ orbitals of the CE phase at $x = 0.5$. The parameters are $W = 3.31t$, $n_1 = 0.84483$, $n_2 = 0.15517$, $\lambda_1 = 1.3998$ and $\lambda_2 = 0.25935$. (a) The 16 bands below the charge order gap and (b) the 16 bands above the gap. The Fermi level is shown as a thin horizontal line in panel (a).

mode modifies the volume of each MnO$_6$ octahedron without changing its symmetry. A complete description should as well include the Jahn-Teller distortions due to the $Q_2$ and $Q_3$ modes [19, 20], which locally change the symmetry of the octahedra without changing their volume and lift the degeneracy between the two $e_g$ orbitals. Long-range order of these modes gives rise to orbital order [21]. With sufficient strength, orbital order would open a gap at the Fermi level, separating the lowest 4 bands from the next 12 bands. The CE phase is then an insulator, which is a consequence of the orbital order and only indirectly of the charge order. Orbital order and orbital exchange are also necessary to stabilize the $\vec{Q}$-vector at ($\pi, \pi, 0$) rather than ($\pi, \pi, \pi$).

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