Charge-order in the quasi-cubic manganites

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Abstract. The CE phase of La$_{1-x}$Ca$_x$MnO$_3$ displays long-range magnetic, charge and orbital order. The magnetic order of the Mn spins arises from the competition of the superexchange and double-exchange interactions. 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, we obtain the phase diagram including the A, B, C, CE and G phases.

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 phase 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 phase diagram for the A, B, C and G phases to include the CE phase.

2. The model
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$^{4+}$ 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.
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 $H_{mag}$, which is the magnetic energy arising from the superexchange between the $t_{2g}$ spins [13],

$$H_t = -\mu \sum_{jM^+m} |jS^+M^+m\rangle \langle jS^+M^+m| - t \sum_{\langle jl \rangle m_\sigma M_j m_\sigma M_j^+m_\sigma} \left( SM_j, \frac{1}{2}\sigma | S\frac{3}{2}S^+M_j^+ \right) \times$$

$$\left(SM_j, \frac{1}{2}\sigma | S\frac{3}{2}S^+M_j^+ \right) \left( |jSM_j\rangle \langle jSM_j^+m_j| \hat{M}_{m_j m_l}(R_{jl}) |lSM_l\rangle \langle lSM_l| + H.c. \right),$$

$$H_{mag} = -\alpha JS^2N$$

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 $S^+ = S + \frac{1}{2}$ 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

$$\sum_{M^+m} |jS^+M^+m\rangle \langle jS^+M^+m| + \sum_M |jSM\rangle \langle jSM| = 1,$$

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

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 $M_j^+ = \pm S + \sigma$ 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 0 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], $b_{j\pm S}^\dagger$ and $b_{j\pm S}$, which act as projectors onto the states of the Mn$^{4+}$ configuration at site $j$, and fermion operators for the Mn$^{3+}$ states at the site $j$, $d_{j\rho,m}^\dagger$ and $d_{j\rho,m}$. The Hamiltonian $H_t$ 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].

3. The CE phase and the phase diagram
The CE phase has a checkerboard charge order in addition to the complex magnetic and orbital order in the $x$-$y$ plane shown in Fig. 1. The dashed lines denote the unit cell. All spins are
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 bows indicate the $3x^2 - r^2$ and $3y^2 - r^2$ orbital order of the nearly trivalent sites. The dashed lines denote the unit cell containing altogether 16 sites in two planes.

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 charge order requires two different boson expectation values, $b_1$ and $b_2$, one for each sublattice. The completeness condition (3) is incorporated via two Lagrange multipliers, $\lambda_1$ and $\lambda_2$, for sublattice 1 and 2, respectively. To drive the charge imbalance between sublattices an additional interaction $H_W$ is needed. $H_W$ is mediated by the Jahn-Teller effect involving the $Q_1$-mode, rather than a Coulomb repulsion between nearest neighbor Mn sites. The $Q_1$-mode modifies the volume of each MnO$_6$ octahedron without changing its symmetry. The effective interaction between the sublattices is

$$H_W = (2Ng^2/C)(b_1^2 - b_2^2)(n_1 - n_2) = (W/4)N(b_1^2 - b_2^2)(n_1 - n_2),$$

(4)

where $g$ is the electron-phonon coupling, $C$ the lattice harmonic potential corresponding to $\vec{Q} = (\pi, \pi, 0)$, and $n_1$ and $n_2$ the sublattice charges per site. Here $W$ is assumed $x$-dependent. If $x > 1/2$ there are more $e_g$ holes than for half-filling and the lattice is expected to soften, since the $e_g$ electrons can move more freely. This corresponds to a decrease in $C$ and an increase of $g$. The contrary occurs for $x < 1/2$. This can be described by parametrizing $W = W_0[1 + \alpha(x - 1/2)]$, where $\alpha > 0$ is a constant of the order of unity.

Figure 2. (a) Solution for $W/t$ vs. the relative charge imbalance $(n_1 - n_2)/(n_1 + n_2)$. For $x = 1/2$ the solutions correspond to a narrow interval of $W$, while for $x \neq 1/2$ the range is much larger. The curves for $x < 1/2$ are shown as dashed lines. (b) Ground state phase diagram obtained by comparing the energies of the different phases. For the CE phase we used $W_0 = 3.32$ and $\alpha = 1.6$. For these parameters the CE phase is only stable up to $x \sim 0.59$. Note the strong asymmetry for the CE-phase about $x = 1/2$.

A complete description should as well include the Jahn-Teller distortions due to the $Q_2$ and $Q_3$ modes [19, 20], which distort the octahedra without changing the volume and lift the degeneracy of the $e_g$ orbitals. Long-range order of these modes gives rise to orbital order [21].
The $e_g$ bands are obtained by Fourier transforming and diagonalizing the mean-field Hamiltonian using the spin configuration of the CE phase. The total energy is then calculated and minimized with respect to $b_1, b_2, \lambda_1$ and $\lambda_2$. This yields transcendental equations, which are solved selfconsistently. The solution for $W/t \gamma (n_1 - n_2)/(n_1 + n_2)$ is shown in Fig. 2(a). Note that for $x = 0.5$ the range of $W$ for which there are solutions is rather narrow. This range is expected to increase if the interaction mediated by the $Q_2$ and $Q_3$ modes is also included.

The phase diagram is obtained by comparing the ground state energies of the different phases. The energies of the phases other than CE have been obtained in Ref. [13]. For a given $x$ the energies of all phases except the CE phase depend only on one parameter: $J/t$. A value of $J/t \sim 0.03$ seems realistic for LCMO. The A phase is only stable for small $x$. For $W_0 = 3.32$ and $\alpha = 1.6$ the CE phase is the ground state only for $0.5 \leq x < 0.59$ due to the limited range of $W$ for which solutions exist and energy considerations. This boundary is shifted to $x \sim 0.58$ for $\alpha = 1.2$. For $\alpha \sim 1$ and $x < 1/2$ there is no physical solution, producing a strong asymmetry in the phase diagram. For larger $x$ again the C and G phases are the stable ones.

The band-structure of the CE phase has 32 bands (two $e_g$ 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. Within each group of 16 bands they are further grouped into four sets of four bands.[22] Since for $x = 0.5$ there is in average 0.5 $e_g$ electron per site, only the lower four bands are occupied. The charge order gap then plays no direct role neither for the ground state nor the low-energy excitations. With sufficient strength, the Jahn-Teller coupling to the $Q_2$ and $Q_3$ modes would induce orbital order and open a gap at the Fermi level, separating the lowest 4 bands from the next 12 bands. For $x = 0.5$ the CE phase is then an insulator, mostly due the orbital order and only indirectly due to the charge order. Although the present calculation reproduces the main features of LCMO, it is necessary to include the Jahn-Teller coupling to the $Q_2$ and $Q_3$ modes for a more complete understanding of the phase diagram.

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References
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