Jahn-Teller Effect and Superexchange in Half-Doped Manganites

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Abstract

We investigate the stability of the charge exchange (CE) phase within a microscopic model which describes a single plane as in La$_{0.5}$Sr$_{1.5}$MnO$_4$. The model includes Coulomb interactions (on-site and intersite), the Jahn-Teller term and the superexchange interactions due to $t_{2g}$ and $e_{g}$ electrons. By investigating the phase diagram at $T = 0$ in mean-field approximation we conclude that the superexchange interactions can stabilize the CE phase, but only if they are stronger than estimated from spectroscopy.

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The doped manganites belong to a very interesting class of transition metal oxides, with orbital degrees of freedom and several magnetic phases stable in various doping regimes. The so-called charge exchange (CE) phase, composed of one-dimensional (1D) ferromagnetic (FM) zigzag chains with an antiferromagnetic (AF) coupling between them, has attracted a lot of attention recently, and the origin of its stability is still under debate [1]. The charge and orbital ordering sets in La$_{0.5}$Ca$_{0.5}$MnO$_3$ at $T_{CO} \simeq 225$ K, and is followed by a magnetic transition at $T_N \simeq 155$ K [2]. The CE-phase was also observed in one-plane La$_{0.5}$Sr$_{1.5}$MnO$_4$ compound, with a similar sequence of phase transitions (a structural transition at $T_{CO} = 255$ K, a magnetic transition at $T_N \simeq 110$ K [3]), and a rather pronounced orbital order [4]. Recent experiments show that the charge order is particularly pronounced in this case, and the Jahn-Teller (JT) distortions around the occupied Mn$^{3+}$ centers are induced [5]. The reasons for appearing of the CE phase in La$_{0.5}$Sr$_{1.5}$MnO$_4$ are not yet fully understood.

We investigate the stability of the single-plane CE-type phase with respect to three other phases: the C phase with staggered linear FM chains, the G-type AF (G) phase, and the FM plane of the A-type AF (A) phase. These phases are characterized by different orbital structure, as shown in Fig. 1. The tight binding model without any interactions applied to the CE phase gives a band insulator due to a particular conflict of orbital phases which frustrates the kinetic energy [6]. This favors the observed zigzag CE phase with respect to the C phase. The CE phase is destabilized by large on-site Coulomb interactions $U$, and we have shown that either Coulomb intersite or the JT interaction can stabilize the CE phase [7]. This effect is enhanced when the superexchange energy is included. However, when we take into account A-AF phase or G-AF phase, the energy of CE phase is higher for $U$ not bigger then about 7$t$ and realistic values of other parameters. We have verified that the CE phase can be stabilized in the present model only by increasing the superexchange above that which follows from the spectroscopic parameters.

We consider below a model which describes the electronic properties of the single-plane compounds (La$_{0.5}$Sr$_{1.5}$MnO$_4$), and includes spin, orbital and charge degrees of freedom, as well as the cooperative JT distortions. We consider the Hamiltonian composed of four terms:

$$
\mathcal{H} = H_t + H_{int} + H_{JT} + H_{SE},
$$

where

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$$
\mathcal{H} = H_t + H_{int} + H_{JT} + H_{SE},
$$
where \( H_t \) refers to kinetic energy of \( e_g \) electrons hopping along FM bonds (the AF bonds cannot contribute as the kinetic energy is blocked by double exchange), \( H_{\text{int}} \) describes the Coulomb interactions, \( H_{\text{JT}} \) – the JT energy, and \( H_{\text{SE}} \) – the superexchange energy. The superexchange follows from \( d^n_i d^m_j \leftrightarrow d^{n+1}_i d^{m-1}_j \) charge excitations for the Mn\(^{3+}\)-Mn\(^{3+}\), Mn\(^{3+}\)-Mn\(^{4+}\), and Mn\(^{4+}\)-Mn\(^{4+}\) pairs [8].

The hopping Hamiltonian for CE phase is given by [6]:

\[
H_t = \sum_{i \in B, j \in C} \left[ (-1)^{\lambda_{ij}} t_1 b_i^\dagger a_{jx} + t_2 b_i^\dagger a_{jz} + \text{H.c.} \right],
\]

(2)

where \( B \) and \( C \) refer to the bridge and corner positions along the 1D zigzag chain, respectively, and \( t_1 = \frac{\sqrt{3}}{2} t, \ t_2 = \frac{1}{2} t \) are the hopping elements, with \( t \) standing for the hopping between two directional orbitals along the bond (e.g., two \( 3x^2-r^2 \) orbitals for \( \langle ij \rangle \parallel a \)) and being the energy unit (\( t \simeq 0.41 \text{ eV} \) was obtained from the charge-transfer model [9]). The phase factor \((-1)^{\lambda_{ij}}\) follows from the orbital phases. The minimal basis set includes a single orbital \( |3x^2-r^2\rangle \) at bridge positions \((b^\dagger_i)\), and two orbitals: \(|x\rangle \equiv |x^2-y^2\rangle \) and \(|z\rangle \equiv |3z^2-r^2\rangle \) at corner sites \((a^\dagger_{jx} \text{ and } a^\dagger_{jz})\), considered in the tight-binding model of Solovyev [10].

In our calculations we include the on-site Coulomb interaction \( \propto U \), and either the intersite Coulomb interaction \( \propto V \), or the energy of JT distortions \( \propto E_{\text{JT}} \):

\[
\begin{align*}
H_{\text{int}} & = U \sum_{j \in C} n_{jx} n_{jz} + V \sum_{\langle ij \rangle} n_i n_j, \\
H_{\text{JT}} & = E_{\text{JT}} \left[ \sum_{i,j(\chi)} q_i (n_{i\chi} - n_{i\bar{\chi}})(1 - n_j) + \frac{1}{2} \sum_i q_i^2 \right].
\end{align*}
\]

(3)

(4)

We treat the JT interactions as lattice polarons and thus introduce the local variables \( \{q_i\} \) which induce the charge-hole correlations \( \propto n_i (1 - n_j) \). They split the \( e_g \) orbitals around a hole, with the directional orbital \(|\chi\rangle\) oriented along the bond being favored with respect to the planar orbital \(|\bar{\chi}\rangle\) [11]. For instance, for a bond \( \langle ij \rangle \parallel c \) these orbitals are: \( 3z^2-r^2 \) and \( x^2-y^2 \).

We have solved the model (1) in the mean-field approximation (MFA). Fig. 2 shows electron densities and kinetic energy per site obtained for \( U = 6t \) and for different values of \( E_{\text{JT}} \). For the CE phase, the on-site Coulomb interaction \( U \) induces small charge ordering, which becomes much stronger when the JT (or nearest-neighbor Coulomb) interaction is included. In the C phase the charge distribution is symmetric for small values of interaction constants, while when the interactions increase, the electrons gradually localize. The absolute value of the kinetic energy of these two phases becomes lower with increasing \( V \) or \( E_{\text{JT}} \). The

Figure 1: Orbital ordering in considered magnetic phases of half-doped manganites: CE, C, A, and G phase.
Figure 2: Kinetic energy per site (a) and electron densities (b), as functions of the JT interaction at $U = 6t$; solid, dashed and dotted lines refer to the CE, A and C phase. In (b) the electron densities $n_i$ are plotted (from the top) for bridge, $|x\rangle$ and $|z\rangle$ orbital (CE phase); $|x\rangle$ and $|z\rangle$ orbitals (A phase), and two neighboring orbitals in the C phase. For G phase the kinetic energy is equal to zero and the orbital occupation is constant.

The kinetic energy of the A phase is much lower for all values of the JT interaction constant $E_{JT}$, and we conclude that neither Coulomb nor JT interactions can stabilize the CE phase.

In Table 1 we show the superexchange energy contributions for different phases. For anisotropic phases we show the values obtained for FM and AF bonds. As one can expect, the SE energy of the G phase has the biggest absolute value, and the SE contribution to the energy of the FM A phase is the smallest. Due to the orbital ordering (Fig. 1), the SE interactions favor the CE phase to the C phase (both phases have two AF and two FM bonds). Therefore, as long as the JT energy does not dominate in the G phase due to its orbital pattern (Fig. 1), the superexchange can stabilize the CE phase.

Table 1: Superexchange energy per one site in units of $10^{-3}t$ at $U = 6t$ and $E_{JT} = 1.2t$, as obtained using the spectroscopic parameters given in Ref. [9]. For the CE phase two anisotropic contributions: FM along the zigzag chain (||) and AF between two neighboring chains (⊥) are given separately. The FM bonds in the C phase do not contribute any superexchange energy.

| excitation | ion pair         | CE || | CE ⊥ | C ⊥ | G   | A  |
|------------|------------------|-----|-----|-----|-----|-----|-----|
| $e_g$      | Mn$^{3+}$-Mn$^{3+}$ | -7.1 | -10.4 | -6.9 | 0   | -21.1 |
| $e_g$      | Mn$^{4+}$-Mn$^{4+}$ | 0   | -17.5 | -13.1 | -72.4 | 0   |
| $t_{2g}$   | Mn$^{3+}$-Mn$^{3+}$ | 0   | -2.0  | -2.4 | 0   | 0   |
| $t_{2g}$   | Mn$^{4+}$-Mn$^{3+}$ | 0   | -4.4  | -5.2 | 0   | 0   |
| $t_{2g}$   | Mn$^{3+}$-Mn$^{4+}$ | 0   | -16.4 | -14.5 | -53.7 | 0   |
| total:     | -7.1            | -50.7 | -42.1 | -126.1 | -21.1 |

We compared the energies obtained for four phases of Fig. 1 as functions of either the JT interaction $E_{JT}$, or the intersite Coulomb interaction $V$, including the superexchange contributions scaled by a multiplicative factor $J/J_0$, with $J_0 = t^2/U \simeq 23$ meV [9]. We
have shown that if only the C and the CE phase is considered, for different values of $U$ the JT interactions cause very similar effects as the intersite Coulomb interaction with $V \approx 0.5E_{JT}$ [7]. Fig. 3 shows phase diagrams including also the A and the G phase and they are significantly different. For low values of interactions and without the superexchange, the A phase is stabilized by the kinetic energy. Increasing values of the $E_{JT}$ favor the G phase and it is the most stable phase above $E_{JT} \approx 0.7t$ for $J = J_0$. The superexchange interactions can stabilize the CE phase only for small values of JT interaction constant $E_{JT} < 0.4t$. In contrast, the intersite Coulomb interaction $V$ is not sensitive to the type of orbital occupied and the G phase is here less stable. It becomes the most stable phase only for very strong Coulomb interactions, but the range of stability range of the CE phase is much bigger then in the former case. We note that the sequence of phases: A, CE and G, obtained at increasing $J/J_0$ is the same as found by Dagotto et al. [12], showing that this result is robust and does not depend on the accurate form of $H_{SE}$. However, the C phase is never stable in our model, contrary to the model which includes the non-cooperative JT effect instead [12].

We conclude that the superexchange interactions play an important role in stabilizing the CE phase, but full understanding of microscopic reasons of its stability needs further investigation. It is expected that the CE phase could be more stable by going beyond the MFA and including the correlation effects for larger values of $U$.

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