A-type Antiferromagnetic and C-type Orbital-Ordered State in LaMnO$_3$
Using Cooperative Jahn-Teller Phonons

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The effect of Jahn-Teller phonons on the magnetic and orbital structure of LaMnO$_3$ is investigated using a combination of relaxation and Monte Carlo techniques on three-dimensional clusters of MnO$_6$ octahedra. In the physically relevant region of parameter space for LaMnO$_3$, and after including small corrections due to tilting effects, the A-type antiferromagnetic and C-type orbital structures were stabilized, in agreement with experiments.

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The theoretical understanding of manganese oxides is among the most challenging current areas of research in condensed matter physics. Experimental studies of manganites have revealed a rich phase diagram originating from the competition between charge, spin, and orbital degrees of freedoms. A simple starting framework for Mn-oxide investigations is contained in the double-exchange (DE) ideas, where ferromagnetism induced by hole doping arises from the optimization of the hole kinetic energy. In addition, recent results using the one-orbital model revealed a more complicated ground state, with phase separation tendencies strongly competing with ferromagnetism, leading to a potential explanation of the Colossal Magneto-Resistance effect.

However, to understand the fine details of the phase diagram of manganites the one-orbital model is not sufficient since the highly nontrivial A-type spin antiferro (AF) and C-type orbital structures observed experimentally in the undoped material LaMnO$_3$ cannot be properly addressed in such a simple context. Certainly two-orbital models are needed to consider the nontrivial state of undoped manganites. In this framework the two-band model without phonons has been studied before, and the results regarding the orbital order that coexists with the ferromagnetism, goal that provides the motivation for the present paper. The main result observed in this effort is that A-AF order, in combination with a C-type orbital arrangement, is indeed induced by JT-phonons in realistic parameter regions for LaMnO$_3$, namely large Hund-coupling between e$_g$-electrons and t$_{2g}$-spins, small AF interaction between t$_{2g}$-spins, and strong electron-lattice coupling. This shows that JT-based calculations can lead to correct qualitative predictions for manganites, actually improving on purely Coulombic approaches in the orbital sector.

To carry out the calculations note that experiments have revealed an orbital structure tightly related to the JT-distortion of the MnO$_6$ octahedron. If each JT-distortion would occur independently, optimal orbitals can be determined by minimizing the kinetic and interaction energy of the e$_g$-electrons, as in models with only Coulomb interactions. However, oxygens are shared between adjacent MnO$_6$ octahedra, indicating that the JT-distortions occurs cooperatively. Particularly in the undoped situation, all MnO$_6$ octahedra exhibit JT-distortions, indicating that such a cooperative effect is important. Thus, in order to understand the magnetic and orbital structures of LaMnO$_3$, the electron and lattice systems must be optimized simultaneously. However, not much effort has been devoted to the microscopic investigation of cooperative JT-phonons in manganites is carried out, focusing on the $n = 1$ density, where $n$ is the electron number per site.

The motion of e$_g$-electrons tightly coupled to the localized t$_{2g}$-spins and the local distortions of the MnO$_6$ octahedra is described by

$$H = - \sum_{i=1}^{N} \sum_{\gamma} \sum_{\sigma} t_{\gamma}^{\sigma} \gamma^{\dagger} \gamma^{\sigma} c_{i}^{\dagger} c_{i}^{\sigma} \gamma^{\dagger} \gamma^{\sigma} + JH \sum_{i,\gamma} \sum_{\sigma,\sigma'} S_{i} \cdot c_{i}^{\dagger} c_{i}^{\sigma} c_{i}^{\dagger} c_{i}^{\sigma'} + \lambda \sum_{i,\gamma,\gamma'} c_{i}^{\dagger} c_{i}^{\dagger} \gamma^{\dagger} \gamma^{\sigma} \gamma_{\gamma} \gamma^{\sigma} c_{i}^{\dagger} c_{i}^{\sigma} \gamma^{\sigma} c_{i}^{\dagger} c_{i}^{\sigma} \gamma^{\sigma}$$

$$+ J' \sum_{i,j} S_{i} \cdot S_{j} + (1/2) \sum_{i} (\beta Q^{2}_{i1} + Q^{2}_{i2} + Q^{2}_{i3}),$$

(1)

where $c_{i\alpha \sigma}$ ($c_{i\beta \sigma}$) is the annihilation operator for an e$_g$-electron with spin $\sigma$ in the $d_{x^2-y^2}$ ($d_{z^2}$) orbital at site $i$. The vector connecting nearest-neighbor (NN) sites is $\mathbf{a}$, $t_{\gamma}^{\sigma}$ ($c_{i\gamma}^{\dagger} c_{i\gamma}^{\sigma}$) is the hopping amplitude between $\gamma$- and $\gamma'$-orbitals connecting NN-sites along the $a$-direction via...
the oxygen 2p-orbital, \( J_\text{H} \) is the Hund coupling, \( S_i \) the localized classical \( t_{2g} \)-spin normalized to \([S_i] = 1\), and \( \sigma = (\sigma_1, \sigma_2, \sigma_3) \) are the Pauli matrices. The dimensionless electron-phonon coupling constant is \( \lambda \), \( Q_{11} \) denotes the dimensionless distortion for the breathing mode of the \( \text{MnO}_6 \) octahedron, \( Q_{31} \) and \( Q_{3i} \) are, respectively, JT distortions for the \((x^2−y^2)\)- and \((3z^2−r^2)\)-type modes, and \( \sigma_0 \) is the unit matrix. \( J' \) is the AF-coupling between NN \( t_{2g} \)-spins, and \( \beta \) is a parameter to be defined below.

To account for the cooperative nature of the JT-phonons, the normal coordinates for distortions of the \( \text{MnO}_6 \) octahedron are written as \( Q_{11} = (1/\sqrt{3})(L_{x1} + L_{y1} + L_{z1}) \), \( Q_{31} = (1/\sqrt{2})(L_{x1} − L_{y1}) \), and \( Q_{3i} = (1/\sqrt{6})(2L_{x1} − L_{x1} − L_{y1}) \), where \( L_{ni} \) denotes the distance between neighboring oxygens along the \( \mathbf{a} \)-direction, given by \( L_{ni} = L_a + (\sigma_n^a − \sigma_1^a) \). Here, \( L_a \) is the length between Mn-ions along the \( \mathbf{a} \)-axis and \( \sigma_n^a \) denotes the deviation of oxygen from the equilibrium position along the Mn-Mn bond in the \( \mathbf{a} \)-direction. In general, \( L_a \) can be different for each direction, depending on the bulk properties of the lattice. Since the present work focuses on the microscopic mechanism for A-AF formation in \( \text{LaMnO}_3 \), the undistorted lattice with \( L_x = L_y = L_z = 0 \) is treated first, and then corrections will be added. In the cubic undistorted lattice, the hopping amplitudes are given by \( t_{aa}^x = −\sqrt{3}t_{ab}^x = −\sqrt{3}t_{ba}^x = 3t_{bb}^x = t \) for the \( x \)-direction, \( t_{aa}^y = \sqrt{3}t_{ab}^y = \sqrt{3}t_{ba}^y = 3t_{bb}^y = t \) for the \( y \)-direction, and \( t_{aa}^z = 4t/3 \) with \( t_{ab}^z = t_{ba}^z = t_{ba} = 0 \) for the \( z \)-direction. The energy unit is \( t \). The parameter \( \beta \) is defined as \( \beta = (\omega_{br}/\omega_{JT})^2 \), where \( \omega_{br} \) and \( \omega_{JT} \) are the vibration energies for manganite breathing- and JT-modes, respectively, assuming that the reduced masses for those modes are equal. Using experimental results and band-calculation data for \( \omega_{br} \) and \( \omega_{JT} \), it can be shown that \( \beta \approx 2 \). However, the results presented here are basically unchanged as long as \( \beta \) is larger than unity.

To study Hamiltonian Eq. (1), two numerical techniques were here applied. One is the relaxation technique, in which the optimal positions of the oxygens are determined by minimizing the total energy. In this calculation, only the stretching mode for the octahedron, namely \( u_n^a + u_n^a = 0 \), is taken into account. Moreover, the relaxation has been performed for fixed structures of the \( t_{2g} \)-spins such as ferro (F), A-type AF (A-AF), C-type AF (C-AF), and G-type AF (G-AF), shown in Fig. 1(a). The advantage of this method is that the optimal orbital structure can be rapidly obtained on small clusters. However, the assumptions involved in the relaxation procedure should be checked with an independent method. Such a check is performed with the unbiased MC simulations used before by our group. The dominant magnetic and orbital structures are deduced from correlation functions. In the MC method, the clusters currently reachable are \( 2 \times 2 \times 2, \ 4 \times 4 \times 2, \) and \( 4 \times 4 \times 4 \). In spite of this size limitation, arising from the large number of degrees of freedom in the problem, the available clusters are sufficient for our mostly qualitative purposes.

In addition, the remarkable agreement between MC and relaxation methods lead us to believe that our results are representative of the bulk limit.

**FIG. 1.** (a) Magnetic structures in \( 2 \times 2 \times 2 \) clusters. (b) Total energy as a function of \( J' \) on a \( 2 \times 2 \times 2 \) lattice with \( J_\text{H} = 8 \) and \( \lambda = 1.5 \). The solid lines and circles indicate the relaxation and MC results, respectively. MC simulations have been performed at temperature 1/200. (c) Spin correlation function \( S(q) \) obtained by MC simulations as a function of \( J' \), at \( J_\text{H} = 8 \) and \( \lambda = 1.5 \). Solid and open symbols denote the results in \( 4 \times 4 \times 2 \) and \( 4 \times 4 \times 4 \) clusters, respectively. Circles, squares, diamonds, and triangles indicates \( S(q) \) for \( q = (0, 0, 0), (\pi, 0, 0), (\pi, \pi, 0) \), and \( (\pi, \pi, \pi) \), respectively. (d) Optimized orbital structure for each magnetic structure.
the two techniques are caused by temperature effects. As intuitively expected, with increasing $J'$ the optimal magnetic structure changes from ferro- to antiferromagnetic, and this occurs in the order $F\rightarrow A-AF\rightarrow C-AF\rightarrow G-AF$. To check size effects, the $t_{2g}$-spin correlation function $S(q)$ was calculated also in $4 \times 4 \times 2$ and $4 \times 4 \times 4$ clusters, where $S(q) = (1/N) \sum_{ij} e^{-i\mathbf{q}\cdot(\mathbf{S}_i-\mathbf{S}_j)}$, $N$ is the number of sites, and $\langle \cdots \rangle$ indicates the thermal average value. As shown in Fig. 1(c), with increasing $J'$ the dominant correlation changes in the order of $q = (0, 0, 0), (\pi, 0, 0), (\pi, \pi, 0), \text{and } (\pi, \pi, \pi)$. The values of $J'$ at which the spin structures changes agree well with those in Fig. 1(b).

The shape of the occupied orbital arrangement with the lowest energy for each magnetic structure is in Fig. 1(d). For the F-case, the G-type orbital structure is naively expected, but actually a more complicated orbital structure is stabilized, indicating the importance of the cooperative treatment for JT-phonons. For the A-AF state, only the C-type structure is depicted, but the orbital structure, obtained by a $\pi/2$-rotation of the upper $x$-$y$ plane of the C-type state, was found to have exactly the same energy. Small corrections will remove this degeneracy in favor of the C-type as described below. For C- and G-AF, the obtained orbital structures are G- and C-types, respectively. Although the same change of the magnetic structure due to $J'$ was already reported in the electronic model with purely Coulomb interactions, the orbital structures in those previous calculations were G-, G-, A-, and A-type for the F-, A-AF, C-AF, and G-AF spin states, respectively. Note that for the A-AF state, of relevance for the undoped manganites, the G-type order was obtained although in another treatment for the Coulomb interaction, the C- and G-type structures were found to be degenerate as in our calculation.

In Figs. 2 (a) and (b), the phase diagrams on the $(J', \lambda)$-plane are shown for $J_H = 4$ and 8, respectively. The curves are drawn by the relaxation method. As expected, the F-region becomes wider with increasing $J_H$. When $\lambda$ is increased at fixed $J_H$, the magnetic structure changes from $F\rightarrow A-AF\rightarrow C-AF\rightarrow G-AF$. This tendency is qualitatively understood if the two-site problem is considered in the limit $J_H \gg 1$ and $E_{JT} \gg 1$, where $E_{JT}$ is the static JT-energy given by $E_{JT} = \lambda^2/2$. The energy-gain due to the second-order hopping process of $e_g$-electrons is roughly $\delta E_{AF} \sim 1/J_H$ and $\delta E_F \sim 1/E_{JT}$ for AF- and F-spin pairs, respectively. Increasing $E_{JT}$, $\delta E_F$ decreases, indicating the relative stabilization of the AF-phase. In our phase diagram, the A-AF phase appears for $\lambda \gtrsim 1.1$ and $J' \lesssim 0.15$. This region does not depend much on $J_H$, as long as $J_H \gg 1$. Although $\lambda$ seems to be large, it is realistic from an experimental viewpoint: $E_{JT}$ is $0.25\ eV$ from photoemission experiments and $t$ is estimated as $0.2 \sim 0.5\ eV$ leading to $1 \lesssim \lambda \lesssim 1.6$. As for $J'$, it is estimated as $0.02 \lesssim J' \lesssim 0.1$. Thus, the location in parameter-space of the A-AF state found here is reasonable when compared with experimental results for LaMnO$_3$.

Let us now focus on the orbital structure in the A-AF phase. In the cubic lattice studied thus far, the C- and G-type orbital structures are degenerate, and it is unclear whether the orbital pattern in the $x$-$y$ plane corresponds to the alternation of $3x^2 - r^2$ and $3y^2 - r^2$ orbitals observed in experiments. To remedy the situation, some empirical facts observed in manganites become important: (i) The MnO$_6$ octahedra are slightly tilted from each other, leading to modifications in the hopping matrix. Among these modifications, the generation of a non-zero value for $t_{aa}^x$ is important. (ii) The lattice is not cubic, but the relation $L_x \approx L_y > L_z$ holds. From experimental results, these numbers are estimated as $L_x = L_y = 4.12\ \AA$ and $L_z = 3.92\ \AA$, indicating that the distortion with $Q_{3z}$-symmetry occurs spontaneously. Note that the hopping amplitude and $J'$ along the $z$-axis are different from those in the $x$-$y$ plane due to this distortion. Motivated by these observations, the energies for C- and G-type orbital structures were recalculated including this time a nonzero value for $t_{aa}^x$. Then, the results of Fig. 3(a) suggest that the C-type...
orbital structure should be stabilized in the real materials, and the explicit shape of the occupied orbitals is shown in Fig. 3(b). The experimentally relevant C-type structure with the approximate alternation of $3z^2 - r^2$ and $3y^2 - r^2$ orbitals is indeed successfully obtained by this procedure. Although the octahedron tilting actually leads to a change of all hopping amplitudes, effect not including in this work, the present analysis is sufficient to show that the C-type orbital structure is stabilized in the A-AF magnetic phase when $t^{z\alpha}_\lambda$ is a small positive number $\lambda$ that occurs in the real materials.

In this work the Coulomb interactions (intra-orbital Coulomb $U$, inter-orbital Coulomb $U'$, and inter-orbital exchange $J$) have been neglected. For Mn-oxides, they are estimated as $U = 7eV$, $J = 2eV$, and $U' = 5eV$, which are large compared to $t$. However, the result for the optimized distortion described in this paper, obtained without the Coulomb interactions, is not expected to change since the energy gain due to the JT-distortion is maximized when a single $e_g$-electron is present per site. This is essentially the same effect as produced by a short-range repulsion. In fact, it has been checked explicitly by using the Exact Diagonalization method that the JT- and breathing-distortions are not changed by $U'$ on a $2 \times 2$ cluster using the F-state in which $U$ and $J$ can be neglected. In addition, the MC simulations show that the probability of double occupancy of a single orbital is negligible where the A-type spin, C-type orbital state is stable. Based on all these observations, it is believed that that the effect of the Coulomb interaction is not crucial for the appearance of the A-AF state with the proper orbital order. Another way to rationalize this result is that the integration of the JT-phonons at large $\lambda$ will likely induce Coulombic interactions dynamically.

Finally, let us briefly discuss transitions induced by the application of external magnetic fields on undoped manganites. When the A-AF state is stabilized, the energy difference (per site) obtained in our study between the A-AF and F states is about $t/100$. As a consequence, magnetic fields of 20 $\sim$ 50T could drive the transition from A-AF to F order accompanied by a change of orbital structure, interesting effect which may be observed in present magnetic field facilities.

Summarizing, using numerical techniques at $n = 1$ it has been shown that the A-AF state is stable in models with JT-phonons, using coupling values physically reasonable for LaMnO$_3$. Our results indicate that it is not necessary to include large Coulombic interactions in the calculations to reproduce experimental results for the manganites. Considering the small but important effect of the octahedra tilting of the real materials, the C-type orbital structure (with the alternation pattern of $3z^2 - r^2$ and $3y^2 - r^2$ orbitals) has been successfully reproduced for the A-AF phase in this context.

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