Spin versus Lattice Polaron: Prediction for Electron-Doped CaMnO₃

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(October 29, 2018)

CaMnO₃ is a simple bi-partite antiferromagnet(AF) which can be continuously electron-doped up to LaMnO₃. Electrons enter the doubly degenerate $E_g$ subshell with spins aligned to the $S = 3/2$ core of Mn⁴⁺(T₁₂₃). We take the Hubbard and Hund energies to be effectively infinite. Our model Hamiltonian has two $E_g$ orbitals per Mn atom, nearest neighbor hopping, nearest neighbor exchange coupling of the $S = 3/2$ cores, and electron-phonon coupling of Mn orbitals to adjacent oxygen atoms. We solve this model for light doping. Electrons are confined in local ferromagnetic(FM) regions (spin polarons) where there proceeds an interesting competition between spin polarization (spin polarons) which enlarges the polaron, and lattice polarization (Jahn-Teller polarons) which makes it smaller. A symmetric 7-atom ferromagnetic cluster (Mn₇⁺) is the stable result, with net spin $S=2$ relative to the undoped AF. The distorted oxygen positions around the electron are predicted. The model also predicts a critical doping $x \approx 0.045$ where the polaronic insulator becomes unstable relative to a FM metal.

I. INTRODUCTION

CaMnO₃ is a bi-partite (G-type) antiferromagnetic(AF) insulator [1] with Néel temperature $T_N=125$K, and almost perfect cubic perovskite crystal structure. There is not a large literature on this material. It deserves attention because of the fascinating interplay of spin order, orbital order, and metallic versus insulating transport. “Colossal magnetoresistance” (CMR) occurring at concentration $x \approx 0.65$ and $T \approx 250$ K is the most dramatic manifestation [2]. For small $x$, magnetization and conductivity measurements [3] suggest local ferromagnetic(FM) regions or “spin polarons” in the range $0.02 < x < 0.06$. In this paper we use a model for pure CaMnO₃, the $x=0$ end member, and predict its behavior under light doping, $x \ll 1$. We keep $T$ equal to 0 and neglect lattice zero-point energy, but all other degrees of freedom are allowed and interact in interesting ways.

Our main question is, what is the ground state of an excess electron in CaMnO₃? The answer to this question will also apply to lightly doped CaMnO₃ provided the doped state is homogeneous. Our model has four parameters. (1) The bandwidth parameter $t$ governs the effective Mn $E_g$ electron hopping between Mn³⁺ and Mn⁴⁺ through the intervening oxygen. The spins of the two Mn ions must be parallel as in the usual “double exchange” model [4]. (2) The magnetic exchange parameter $J$ couples spins of first-neighbor Mn ions, due to virtual hopping of $T_{2g}$ electrons. (3) The electron-phonon coupling constant $g$ describes interactions between Mn $E_g$ orbitals and the 6 nearest oxygen atoms. (4) Oxygen displacements $u$ are opposed by the restoring force $-Ku$, where $\omega = \sqrt{K/M}$ is an Einstein frequency assigned to oxygen vibrations along the bonds. There are two important dimensionless parameters. Spin polarons are controlled by the ratio $\beta = t/JS^2$. Jahn-Teller (JT) lattice polarons are controlled by the parameter $\Gamma = g^2/Kt$ [5]. Balancing these competing effects, we find the most favorable local FM spin arrangement, lattice distortion and electron wavefunction. As doping increases, we predict a transition from polaronic insulator to FM metal.

II. MODEL HAMILTONIAN

The Mn⁴⁺ ion in CaMnO₃ has configuration 3d⁷, i.e., the three spin-aligned $T_{2g}$ states $(x, y, z, x)$ are filled with electrons, while the two spin-aligned $E_g$ states $(\psi_2 = (x^2 - y^2)/\sqrt{2}, \psi_3 = 3z^2 - r^2)$ are empty and lie above by the crystal field splitting. The empty opposite spin $T_{2g}$ states are split to even higher energy by the Hund term $J_H$. Light electron doping puts carriers into the doubly-degenerate $E_g$ level. Hopping of (dσ)-type occurs from $T_{2g}$ to $T_{2g}$, and of (dδτ)-type from $E_g$ to $E_g$, but no $E_g$ to $T_{2g}$ hopping matrix element exists because of the simple cubic structure. Virtual $T_{2g}$ hopping (at the cost of Hubbard energy $U$) gains delocalization energy if adjacent spins are antiparallel. This gives an $S = 3/2$ antiferromagnetic Heisenberg Hamiltonian with exchange coupling $J = 2(dd\pi)^2/U$ [6], $U$ being large compared with $(dd\pi)$ [7], and agrees with the experimentally observed magnetic structure of pure CaMnO₃. The ground state has $\uparrow$ spins on the A sublattice (when $\exp(i\vec{Q} \cdot \vec{l}) = 1$, where $\vec{l}$ labels the Mn sites), and $\downarrow$ spins on the B sublattice (when $\exp(i\vec{Q} \cdot \vec{l}) = -1$) with $\vec{Q} = (\pi, \pi, \pi)$.

Ignoring for now the electron-phonon terms, the Hamiltonian for an excess electron is $\mathcal{H} = \mathcal{H}_t + \mathcal{H}_r$. The first term contains hopping of Mn $E_g$ electrons to nearest neighbors,

$$\mathcal{H}_t = t \sum_{\vec{l}, \pm} |S(\vec{l}, \vec{l} \pm \hat{z})c_{\vec{l}}^\dagger(\vec{l} \pm \hat{z})c_{\vec{l}}(\vec{l}) + \text{rotations to } \hat{x}, \hat{y} \text{ directions},$$

(1)
cally rotating the axis of spin quantization for the $S(1,2) = \cos \theta_1^2 \cos \theta_2^2 + \sin \theta_1^2 \sin \theta_2^2 e^{-i(\phi_1 - \phi_2)}$ (2)

Here $c_3^\dagger(\bar{l})$ destroys an electron state $\psi_3(\bar{r} - \bar{l})$ on the Mn atom at $\bar{l}$; $\bar{l} = \bar{z}$ labels the Mn neighbors above and below the one at site $\bar{l}$; and $t$ is the $(\bar{dd})$ integral from Slater-Koster two-center theory [15]. We use a value $t = -0.75$ eV obtained from fitting the band structure of CaMnO$_3$ [16,17] (see Sec. III). The factor $Koster$ two-center theory [15]. We use a value $t = -0.75$ eV obtained from fitting the band structure of CaMnO$_3$ [16,17] (see Sec. III). The factor $S(1,2)$ comes from locally rotating the axis of spin quantization for the $i$th $E_g$ electron into the direction $(\theta_i, \phi_i)$ of the $i$th $S = 3/2$ core spin, treating the angles $(\theta_i, \phi_i)$ as classical parameters, and discarding from the Hilbert space the state with spin opposite to the core spin (i.e. assuming $J_H \rightarrow \infty$ [17,18]). In this paper, we usually take the spins to be perfectly ordered at $T = 0$, that is, $\theta = \theta_1 - \theta_2$ equals 0 or $\pi$, corresponding to $S(1,2)$ equal to 1 or 0 for FM or AF oriented neighbors. We will also consider uniformly canted states where a relative angle $\theta = \pi - \theta_0$ occurs, with $\phi = constant$, so that $S$ takes the value $\sin(\theta_0/2)$. These spin orientations are shown in Fig. 1.

\[
\begin{align*}
FIG. 1. \text{ Schematic spin structures for the antiferromagnetic G (AFG), ferromagnetic (FM), and antiferromagnetic C (AFC) structures, and interpolating canted structures.}
\end{align*}
\]

The rotation of $\psi_3$ to the $\hat{x}$ axis is $(-\psi_3 + \sqrt{3}\psi_2)/2 = 3x^2 - y^2$, and to the $\hat{y}$ axis is $(-\psi_3 - \sqrt{3}\psi_2)/2 = 3y^2 - x^2$. Using these, we rewrite $\mathcal{H}_t$ in the usual orthonormal basis ($\psi_2, \psi_3$),

\[
\mathcal{H}_t = t \sum_{l,\delta=x,y,z} \left( c_2^\dagger(\bar{l}) c_3(\bar{l}+\delta) \right) T_{\delta} \left( c_3^\dagger(\bar{l})+\delta \right),
\]

where it is understood that the hopping only operates between parallel spin Mn atoms. The hopping matrices are

\[
T_x = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \quad T_y = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \quad T_z = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}
\]

(3)

The $\mathcal{H}_J$ term is the AF nearest neighbor $T_{2g}$ exchange:

\[
\mathcal{H}_J = \sum_{\langle l,l' \rangle} J S(\bar{l}) \cdot S(\bar{l}')
\]

The exchange coupling $J$ is can be estimated from Mean Field theory (we use a quantum treatment for spin $3/2$, FM and AFM answers are equal) to be $J S^2 = 3.23$ meV, using the measured Neel temperature $T_N = 125 K$ [9]. However, for a given coupling $J$, a more accurate estimate from susceptibility expansions reduces the $T_C$ of the Heisenberg ferromagnet [20]

\[
\frac{T_C}{T_C(MF)} = \frac{5}{4 \epsilon} [1 + \frac{1}{6} z S(S + 1)],
\]

where $z = 6$ is the number of nearest neighbors. For a Heisenberg antiferromagnet [21,22] it is estimated that $T_N$ is slightly higher,

\[
\frac{T_N}{T_C} \simeq 1 + \frac{0.63}{z S(S + 1)}.
\]

Making these corrections, the coupling is found to be $J S^2 = 4.74$ meV, giving $t/J S^2 = 158$, with probable uncertainty of 10%. The phonon parts of the Hamiltonian are given in Sec. V.

III. UNIFORM SOLUTIONS

First consider the hypothetical case of a uniform FM spin order. Then a doped-in electron could hop without paying a Hund penalty, and extended Bloch states would form with wavefunctions

\[
\Psi_k = d_2 \frac{1}{\sqrt{N}} \sum_l e^{i\bar{k} \cdot \bar{l}} \psi_2(\bar{l}) + d_3 \frac{1}{\sqrt{N}} \sum_l e^{i\bar{k} \cdot \bar{l}} \psi_3(\bar{l}),
\]

where $d_2, d_3$ are coefficients. Diagonalizing Eq. (3), the resulting energy eigenvalue, taking into consideration that $t$ is negative, is

\[
\frac{E(\bar{k})}{|t|} = -\cos k_x - \cos k_y - \cos k_z
\]

\[
\mp(\cos^2 k_x + \cos^2 k_y + \cos^2 k_z)
\]

\[
- \cos k_x \cos k_y - \cos k_y \cos k_x - \cos k_z \cos k_x)^{1/2}.
\]

(9)

At $\cos k_x = \cos k_y = \cos k_z = 1$, the energy is minimum, $E(\bar{k} = 0) = -3|t|$, the state being doubly degenerate. Although the actual spin arrangement is not FM, the result $|3|t|$ sets a useful scale for the maximal energy gain from electron delocalization. Also, the dispersion relation E(k) can be fitted to a FM CaMnO$_3$ majority-spin band structure calculated in density-functional theory [10], determining the hopping energy $t = -0.75$ eV.

For light doping, the magnetic energy Eqn. (3) of antiferromagnetic order $(-z J N S^2/2$ for classical spins; $N$ is the number of Mn ions) is much larger than hopping energy. As discussed by deGennes [23], the best
uniform solution (for a one-band model) is a compromise where antiferromagnetic spins cant uniformly toward FM solutions. Start from the Néel AF structure and let all spins tilt towards the direction with angle $\theta/2$, as shown in Fig. 1. This costs magnetic energy $\Delta E_J = zNJS^2(1 - \cos \theta)/2$. A doped-in electron can now delocalize, reducing its energy by $-3|t| \sin(\theta/2)$. For small doping $x = n/N \ll 1$, the total hopping energy is $\Delta E_t = -3n|t| \sin(\theta/2)$. Therefore when $\sin(\theta/2) = x|t|/4JS^2$, the total energy $\Delta E = \Delta E_J + \Delta E_t$ is minimum, $-3N|t|^2/8JS^2$. From this estimate, the system cant all the way to FM when the optimal $\theta$ equals $\pi$, which occurs at $x = 4JS^2/|t| \approx 0.025$.

Because the doubly-degenerate $E_g$ electrons hop anisotropically, a better canted solution exists. Let all spins with $\exp(i\vec{K} \cdot \vec{r}) = 1$ ($\vec{K}$ is $(0, \pi, \pi)$) tilt towards $+\hat{x}$ and all spins with $\exp(i\vec{K} \cdot \vec{r}) = -1$ tilt towards $-\hat{x}$ with angle $\theta/2$, as shown in Fig. 1. The magnetic energy cost is reduced to $\Delta E_J = zNJS^2(1 - \cos \theta)/6$, but the delocalization energy lowering is also reduced to $\Delta E_t = -2n|t| \sin(\theta/2)$. This type of canting terminates in C-type antiferromagnetism when $x = 2JS^2/t$, as shown in Fig. 1. Fig. 2 summarizes our results for the energies of uniform solutions versus $x$.

**IV. PURE SPIN POLARON EFFECT**

Experimentally, CaMnO$_3$ is insulating at small doping $x$. This rules out uniform solutions with electrons doped into delocalized states. The simplest picture is that each doped electron is localized on one Mn site, creating a local Mn$^{3+}$ with spin $S = 2$ in an AF background, for a spin excess of $1/2$. This does not agree with the measured saturated magnetization, which has been interpreted in terms of local spin flipping (net excess spin of $2$) in the region $0.02 < x < 0.08$. Local spin flipping leads to local FM regions (called spin polarons) around doping centers, allowing the doped electron to gain delocalization energy. In this section we discuss candidate localized ground states of a single $E_g$ electron, using the same Hamiltonian $H = H_t + H_J$.

First, we make a continuum (effective mass) approximation in the spirit of Nagaev. Inside the local FM region, electrons hop like free electrons with inverse band mass $1/m^* = (a/\hbar)^2|t|$ given by Eqn.(10). With $a$ the perovskite lattice constant, $a \approx 3.73$. A electron sits in a spherical well with infinite walls at radius $R$, whose depth is $-3|t|$. G-type antiferromagnetism resumes for $r > R$. The ground state energy of the electron in this polarized region is then

$$\Delta E_t = |t|(3 + \pi^2 a^2/2R^2),$$

where the second term is the zero-point energy in the well. The magnetic energy cost from spin-canting is

$$\Delta E_J = zJS^2(4\pi R^3/3a^3),$$

where the last factor is the number of Mn atoms in the cluster. Optimizing $\Delta E = \Delta E_t + \Delta E_J$ over $R$, the optimal size cluster has a number of Mn atoms inside the sphere equal to

$$\frac{4}{3} \pi \left(\frac{R}{a}\right)^3 = \frac{4}{3} \pi \left(\frac{|t|}{4\pi JS^2}\right)^{3/5} \approx 26.$$

This is close to the optimum 25-site symmetric cluster which we will find by exact diagonalization and show in Table I. However, we will also find a smaller asymmetric cluster of lower energy.

It is interesting that continuum theory gives a lower energy if the region $r < R$ is canted rather than fully FM. The A sublattice is fixed for all $r$, but the B sublattice is tilted toward the A sublattice by angle $\theta$ for $r < R$. Then the optimum tilting angle is $180^\circ$ (FM) for $\beta = t/JS^2 > \beta_c = (7\pi^2/18)^{-5/2}42\zeta/\pi \approx 220$, while for smaller $\beta$, the optimal tilting angle is $\sin(\theta/2) = \beta/\beta_c$. Our estimated value is $\beta \approx 158$, which gives $\beta/\beta_c \approx 0.72$. So the spins inside radius $R$ are approximately $90^\circ$ apart, and the optimum cluster increases to $31$.

Now we repeat the calculation using the true discrete Hamiltonian. First consider flipping only one spin. In this way, the spin-flipped Mn (the central site), along
with its 6 nearest neighbors, form a 7-site cluster with all 7 spins parallel. The cluster is invariant under transformations of the point group $O_h$. If the central Mn spin is kept unflipped, but instead the spins of those 6 nearest neighbors are flipped, a 25-site $O_h$-symmetric cluster is formed. Similar steps can be taken to obtain larger and larger symmetric clusters. We will not look at candidate states with canted spins except for one special case to be mentioned later.

Each spin flip costs magnetic energy $6 \times 2JS^2$. Since spins are parallel inside the cluster, the electron can hop among the $E_g$ orbitals of all the spin-aligned Mn ions, with a corresponding energy lowering from delocalization. Table I shows numerical values of ground state energy found by exact diagonalization of $2M \times 2M$ Hamiltonian matrices for symmetric clusters of $M$ Mn atoms, ranging in size from $M=1$ to 63. The ground states are all doubly degenerate ($E_g$ representation) because of the $O_h$ symmetry of the cluster.

Asymmetric clusters are also possible. If we flip one spin at site $\vec{l}$ and another one at site $\vec{l} + \hat{x} + \hat{y}$, a 12-site cluster is formed. Starting from this 12-site cluster, there are four different ways to create a larger cluster with one more flipped spin, as shown in Fig. 3. Other possibilities are less closely packed, such as the 13-site cluster shown in the figure, and other 3-spin-flipped cases not shown here. The ground state energy of these examples are calculated, as shown in Table II. For our chosen values of $t$ and $2JS^2$, the most favorable spin polaron is an asymmetric 17-site cluster with three flipped spins.

**TABLE I.** Ground state energy of symmetric clusters, with only spin polaron effects included. The last column uses $t = -0.75$ eV and $JS^2 = 4.74$ meV.

| cluster size | number of spins flipped | energy gain from hopping ($|t|$) | ground state energy (eV) |
|--------------|-------------------------|----------------------------------|--------------------------|
| 1            | 0                       | 0                                | 0                        |
| 7            | 1                       | $-\sqrt{3} = -1.732$            | -1.242                   |
| 25           | 6                       | -2.330                           | -1.406                   |
| 51           | 13                      | -2.449                           | -1.097                   |
| 57           | 14                      | -2.380                           | -0.989                   |
| 63           | 19                      | -2.600                           | -0.869                   |

**TABLE II.** Ground state energy of asymmetric clusters, with pure spin polaron effect.

| cluster size | number of spins flipped | energy gain from hopping ($|t|$) | ground state energy (eV) |
|--------------|-------------------------|----------------------------------|--------------------------|
| 12(as2-1)    | 2                       | -1.936                           | -1.338                   |
| 13(as2-2)    | 2                       | -2                               | -1.386                   |
| 16(as3-2)    | 3                       | -2.015                           | -1.341                   |
| 17(as3-1)    | 3                       | -1.936                           | -1.281                   |
| 17(as3-3)    | 3                       | -1.984                           | -1.317                   |
| 17(as3-4)    | 3                       | -2.145                           | -1.438                   |

FIG. 3. Different asymmetric clusters: as2 is the only one with two spins flipped; there are four types of as3 which have 3 spins flipped.
There are many possible variations with inhomogeneously canted spins, of which we considered only one, a 25-site cluster with the 7 inner atoms canted rather than ferromagnetically aligned with the outer 18 atoms. This interpolates between the 7 and the 25 atom cluster. Without canting, the 7 and 25 atom cluster become equal in energy for the value \( |t|/JS^2 \approx 100 \), smaller than our preferred value of 158. It turned out that in the range \( 94 < |t|/JS^2 < 104 \), the locally canted state was lower in energy than either the 7 or the 25 atom pure ferromagnetic cluster.

V. LATTICE POLARON EFFECT

The degenerate ground state, found in the previous section for symmetrical spin polarons, is Jahn-Teller (JT) unstable [24]. We now add to our Hamiltonian lattice distortions, controlled by the electron-phonon interaction. The only lattice degrees of freedom included are oxygen distortions, which points toward the oxygen (that is, the \( 3z^2 - r^2 \) state if oxygen motion in the \( z \)-direction considered.) We use adiabatic approximation (oxygen mass \( \to \infty \)) and treat the oxygen distortions as classical parameters. Each Mn ion is surrounded by six oxygen whose distortion amplitudes \( u_\delta (\pm \delta/2, \delta = \hat{x}, \hat{y}, \hat{z}) \) form basis vectors for a representation of \( O_h \), namely, \( a_{1u} \otimes e_g \otimes t_{1u} \). The vector representation \( t_{1u} \) contains the distortions \( u_\delta (\hat{l} + \hat{z}/2) + u_\delta (\hat{l} - \hat{z}/2) \), etc. The remaining 3 degrees of freedom \( Q_z = u_z (\hat{l} + \hat{z}/2) - u_z (\hat{l} - \hat{z}/2) \), etc. form basis vectors of \( a_{1g} \) \((Q_1 = (Q_x + Q_y)/\sqrt{6})\) and \( e_g \) \((Q_2 = Q_x - Q_y)/2\), \( Q_3 = (2Q_z - Q_x - Q_y)/\sqrt{12}\), in Van Vleck notation [25]. The oxygen distortions are limited by a harmonic restoring force, e.g., \(-KK_u (\hat{l} + \hat{z}/2)\).

The lattice elastic energy and electron-phonon interaction terms of the Hamiltonian are [26]

\[
\mathcal{H}_L = \frac{K}{2} \sum_i \left[ u_x (\hat{l} + \frac{1}{2} \hat{x})^2 + u_y (\hat{l} + \frac{1}{2} \hat{y})^2 + u_z (\hat{l} + \frac{1}{2} \hat{z})^2 \right],
\]

\[
\mathcal{H}_{ep} = -\frac{4g}{\sqrt{3}} \sum_i \left[ c^\dagger_i (\hat{l}) c_i (\hat{l}) Q_z (\hat{l}) \right] + \text{rotations to \( \hat{x}, \hat{y} \) directions}. \tag{14}
\]

\( \mathcal{H}_{ep} \) can be split into two parts, JT and “breathing”:

\[
\mathcal{H}_{ep} = \mathcal{H}_{JT} + \mathcal{H}_{br} \tag{15}
\]

where, in Van Vleck notation,

\[
\mathcal{H}_{JT} = 2g \sum_i \left( c_i^\dagger (\hat{l}) c_i (\hat{l}) \right) \left( \begin{array}{cc} Q_3 (\hat{l}) & Q_2 (\hat{l}) \\ Q_2 (\hat{l}) & -Q_3 (\hat{l}) \end{array} \right) \left( \begin{array}{c} c_2 (\hat{l}) \\ c_3 (\hat{l}) \end{array} \right).
\]

\[
\mathcal{H}_{br} = -2\sqrt{2} g \sum_i Q_1 (\hat{l}) \left( c_2^\dagger (\hat{l}) c_2 (\hat{l}) + c_3^\dagger (\hat{l}) c_3 (\hat{l}) \right). \tag{16}
\]

The vector distortions (\( t_{1u} \)) do not couple to \( E_g \) electron states and therefore do not appear.

A simple case shows how \( \mathcal{H}_{JT} \) splits energy degeneracy. Suppose a doped electron is localized at a single Mn site, with no hopping or spin flipping considered. The two \( E_g \) states at that Mn are the only degrees of freedom for the electron and are originally degenerate. When the six surrounding oxygen distortions are considered, the degeneracy is lifted in \( \mathcal{H}_{JT} \):

\[
\mathcal{H}_{JT} = 2g \left( c_2^\dagger c_3 \right) \left( \begin{array}{cc} Q_3 & Q_2 \\ Q_2 & -Q_3 \end{array} \right) \left( \begin{array}{c} c_2 \\ c_3 \end{array} \right) \tag{17}
\]

\[
= 2g \left( \alpha^\dagger \beta^\dagger \right) \left( \begin{array}{c} Q \end{array} \right) \left( \begin{array}{c} \alpha \\ \beta \end{array} \right) \tag{18}
\]

where

\[
\left( \begin{array}{c} \alpha^\dagger \\ \beta^\dagger \end{array} \right) = \left( \begin{array}{cc} \cos \frac{\phi}{2} & -\sin \frac{\phi}{2} \\ \sin \frac{\phi}{2} & \cos \frac{\phi}{2} \end{array} \right) \left( \begin{array}{c} c_2^\dagger \\ c_3^\dagger \end{array} \right)
\]

and \((Q_2, Q_3) = Q(\sin \phi, \cos \phi)\). The change in energy due to \( \mathcal{H}_{JT} + \mathcal{H}_{br} + \mathcal{H}_L \) is \( \Delta E = -2\sqrt{2} g Q_1 \pm 2gQ + 12(Q_1^2 + Q_2^2)/2 \). The energy splitting \( \pm 2gQ \) comes only from the JT term. The optimal distortions are \( Q_1 = 4\sqrt{2}g/K \) and \( Q = 4g/K \), which give the maximum energy lowering of ground state \( \Delta E = -6g^2/K \).

The angle \( \phi \) does not enter \( \Delta E \). This continuous degeneracy can be lifted either by adding kinetic energy and quantization of lattice degrees of freedom (dynamic JT effect), or else by introducing higher order anharmonic terms in \( \mathcal{H}_{ep} \) [27, 28]. However, later in the discussion of the 7-site cluster, we shall show how this continuous degeneracy is naturally removed by the increase of electronic and lattice degrees of freedom.

It is interesting to consider what would happen if spins were ferromagnetically ordered, so that magnetism does not assist localization. Then polaron formation can only occur through lattice distortion and is prohibited when the delocalization energy per electron is larger than the polaron energy, i.e., when \( \Gamma = g^2/K|t| \) is less than a critical value close to 0.5. We believe that \( \Gamma \) is close to 0.25, so that in the hypothetical ferromagnetic case, polarons would not form. Antiferromagnetic confinement is needed before a lattice polaron effect occurs. LaMnO\(_3\) is different in this respect; its cooperative Jahn-Teller ground state makes polaron formation easier [11].

VI. THE 7-SITE CLUSTER: SPIN AND LATTICE POLARON

With the full Hamiltonian considered, the 7-site cluster turns out to be the most important one, as shown later in this section. Only a single spin is flipped. Inhomogeneous canting will not be favored for this state.
By understanding its ground state algebraically, we learn several interesting aspects of the influence of $H_{ep}$ in the Hamiltonian. The dimensionless parameter $\Gamma \equiv q^2/Kt$ characterizing the strength of electron-phonon coupling has a value near 0.25 for LaMnO$_3$, and we assume that the value for for CaMnO$_3$ is similar, i.e. $0.20 < \Gamma < 0.30$ [21, 29]. We will measure energies in units of $|t|$, using dimensionless lattice variables $Q' = \sqrt{K/|t|}Q$. The prime in $Q'$ is suppressed from here on.

To study the ground state of a single electron in the 7-site cluster, a 14-dimensional Hilbert space is used, consisting of atomic $E_g$ orbitals from each of the 7 Mn atoms. Later when we turn on $H_{ep}$, we will find that for $\Gamma$ small, fewer than 14 basis functions are needed for the ground state calculation. The 14-dimensional space can be decomposed into 7 irreducible representations of point group $O_h$, namely, $A_{1g} \oplus A_{2g} \oplus T_{1u} \oplus T_{2u} \oplus 3E_g$. When lattice distortions are absent ($\Gamma = 0$, $H_{ep} = H_t = 0$), these functions diagonalize $H_t$. The 3 $E_g$-type basis functions $(\psi_1^+, \psi_3^+)$, $(\psi_2^0, \psi_3^0)$ and $(\psi_2^-, \psi_3^-)$ are degenerate separately with eigenvalues $+\sqrt{3}|t|$, 0, and $-\sqrt{3}|t|$. These 6 states, along with the $A_{1g}$ state (with eigenvalue 0), will be the main states of interest when $\Gamma \neq 0$. All other states stay absent as long as $\Gamma$ is small.

When $\Gamma \neq 0$, $H_{ep}$ and $H_t$ are turned on. Amplitudes of lattice distortions appear linearly in the matrix representation of $H_{ep}$, and quadratically in that of $H_t$. Since these lattice distortions are of order $\sqrt{\Gamma}$ when $\Gamma \ll 1$, $H_{ep}$ and $H_t$ can be treated as perturbations to $H_t$. In the following, all lattice distortion modes will be introduced. Then second order perturbation of the original ground states $(\psi_2^-, \psi_3^-)$ can be expressed in terms of these modes and shows that most of these modes do not participate in the ground state lattice distortion. This will in turn eliminate the need for considering electron states of symmetries which couple to the absent modes only. Finally, from the form of the perturbed ground state energy, the pattern of its optimized lattice distortion will be derived and compared to the exact numerical result.

There are 36 oxygens adjacent to one or more Mn atoms in the 7-atom cluster, so there are 36 distortion parameters in $H_{ep}$. These can be organized into sets of basis vectors for irreducible representations of the point group $O_h$, namely, $3a_{1g} \oplus a_{2g} \oplus 5t_{1u} \oplus 3t_{2u} \oplus 4e_g$. The $a_{1g}$-type modes are denoted as $(q_{1i},$ where $i = 1, 2, 3)$, and the $e_g$-type modes are denoted as $(q_{2j}, q_{4j}),$ where $i = 1, 2, 3, 4$. The matrix elements of $H_{ep}$ can be reexpressed in terms of these modes, and $H_t$ is simply $\sum_{\text{modes}} q_{\text{modes}}^2/2$.

Second order perturbation theory shows that for small $\Gamma$, many of these modes appear only quadratically with positive coefficients and hence should be optimized to 0. For larger $\Gamma$, these coefficients start to turn negative, and the corresponding distortions start to develop. The critical values are $\Gamma = 0.443$ for the appearance of the $t_{1u}$ and $q_{43}$ distortion, $\Gamma = 1.30$ for $t_{2u}$, $\Gamma = 0.819$ for $a_{2g}$ and $q_{42}$. It will thus happen that as $\Gamma$ increases, the symmetry of the ground state electron wavefunction and lattice distortion pattern is gradually lowered by the successive appearance of these distortions.

We therefore ignore the above modes for the actual range $\Gamma \approx 0.25 \pm 0.05$. This eliminates the presence of electron states of $A_{2g}$, $T_{1u}$ and $T_{2u}$ symmetry. The remaining modes are 3 sets of $(q_{1i}, q_{4i}, q_{3i})$, with $i = 1, 2, 3$, of the inner, intermediate and outer oxygen layers, respectively. Degenerate first-order perturbation theory for $(\psi_2^-, \psi_3^-)$ shows that the ground state energy of $H_t$ splits into

$$E^{(1)}(\Gamma) = -\sqrt{3} - \sqrt{\Gamma}(\sqrt{2} Q_1 + \sqrt{Q_2^2 + Q_3^2})$$

$$Q_1 = \frac{1}{3} q_{11} + \frac{1}{6} q_{21} + \frac{1}{12} q_{31},$$

$$Q_2 = \frac{1}{3} q_{12} + \frac{1}{6} q_{22} + \frac{1}{12} q_{32},$$

$$Q_3 = \frac{1}{3} q_{13} + \frac{1}{6} q_{23} + \frac{1}{12} q_{33}.$$  (19)

Thus at first order, there is still a continuous degeneracy, in the sense that the energy JT splitting depends only on $Q = \sqrt{Q_2^2 + Q_3^2}$, not on $\phi \equiv \tan^{-1}(Q_3/Q_2)$.

To include 2nd order perturbations, for simplicity, we treat analytically only the distortion modes from the inner oxygen layer, $(q_{1i}, q_{2i}, q_{3i})$. The number of related electronic states is now reduced to 5, namely, they are $(A_{1g}, \psi_2^+, \psi_3^+)$ and $(\psi_2^-, \psi_3^-)$. In this 5-dimensional subspace, the Schrödinger equation to be solved can be expressed as follows (not including $H_t$, which is always proportional to the identity matrix):

$$\left( H_{ep}^{II} - \frac{h_{ep}}{h_{ep}^2} H_t^{II} + \frac{h_{ep}}{h_{ep}^2} H_t^{II} - E \right) \left( \begin{array}{c} \Psi_{II} \\ \Psi \end{array} \right) = \left( \begin{array}{c} \Psi_{II} \\ \Psi \end{array} \right) = 0$$  (20)

where $\Psi = (\psi_2^-, \psi_3^-)$, $\Psi_{II} = (A_{1g}, \psi_2^+, \psi_3^+)$. We obtain an effective Hamiltonian $H_{eff} = H_t^{II} + H_{ep}^{II} - \frac{h_{ep}}{h_{ep}^2} (H_t^{II} + H_{ep}^{II} - E)^{-1} h_{ep} \Psi$. Since $E$ should be very close to $-\sqrt{3}|t|$ for small perturbation, we take $E$ as $-\sqrt{3}|t| \times 1_{(3 \times 3)}$ and ignore $H_{ep}^{II}$ in the denominator. The $H_{eff}$ obtained this way shows that the degeneracy of $(\psi_2^-, \psi_3^-)$ is now lifted to become (including $H_t$)

$$E^{(2)}(\Gamma) = -\sqrt{3} - \sqrt{2} A - \left( \frac{4\sqrt{3}}{3} - \frac{9}{2T} \right) (A^2 + \rho^2)^{1/2}$$

$$\epsilon \equiv \frac{4}{3}\rho^2 + \frac{32}{3} A^2 \rho^2 + \frac{8\sqrt{6}}{3} A \rho^2 + \rho^2 + 4 \rho^2 \left( 4\sqrt{2} A + \sqrt{3} \right) \cos(3\theta),$$  (21)

where we introduce the notation

$$A \equiv \frac{\sqrt{3}}{3} q_{11}, \quad \rho \equiv \sqrt{B^2 + C^2}$$

$$B \equiv \frac{\sqrt{3}}{3} q_{12} \equiv \rho \sin \theta, \quad C \equiv \frac{\sqrt{3}}{3} q_{13} \equiv \rho \cos \theta$$
We see that \( \cos 3\theta \) should be +1 to minimize the ground state energy. Hence the degeneracy of ground states is not continuous anymore and has become 3-fold. This feature agrees with the numerical result. The ground state electronic wavefunction of \( \theta = 0 \) is shown in Fig. 4. A rotation which brings \( \hat{z} \) to \( \hat{x} \) (or \( \hat{y} \)) will generate the wavefunctions of \( \theta = 2\pi/3 \) (or \( \theta = 4\pi/3 \)).

![FIG. 4. One of the possible ground state wavefunctions in the 7-site cluster. The corresponding lattice distortion pattern has \( q_1 \) and \( q_3 \) components.](image)

**VII. NUMERICAL RESULTS**

Now we consider the full Hamiltonian \( \mathcal{H} = \mathcal{H}_t + \mathcal{H}_J + \mathcal{H}_{ep} + \mathcal{H}_L \) for all clusters examined in Sec. IV. FM spin alignment facilitates hopping and causes energy lowering from delocalization, therefore encourages the polaron to grow. However, as \( \Gamma \) increases, the JT splitting will become the dominating influence on ground state energy. Greater localization enhances the JT energy lowering, which increases localization of the electron. On the other hand, \( \mathcal{H}_J \) and \( \mathcal{H}_L \) serve as penalties for spin misalignment and lattice distortions. Our numerical studies find the optimal resolution of the competition between these effects. The 7-site cluster becomes favored from \( \Gamma > 0.18 \), as shown in Fig. 5, and Fig. 6. For all clusters considered, when \( \Gamma \) becomes large enough, the size of the ground state wavefunction shrinks to become that of the 7-site polaron, as shown in Fig. 5. Enlarging the size of the FM cluster to enhance delocalization energy is then disfavored by the strong lattice polaron effect. It is also clear that for extremely large \( \Gamma \), the 1-site lattice polaron will be the only form of electron state which exists.

Our numerical calculation predicts the lattice distortion pattern of the 7-site ground state. For \( \Gamma = 0.25 \), \( t = 0.75 \) eV, and \( K = 27.2 \) eV/\( \text{Å}^2 \) (obtained from Raman scattering in LaMnO\(_3\)), the ground state shown in Fig. 4 has oxygen displacement parameters \( q_{11} \simeq 1.1 \), \( q_{13} \simeq 0.78 \) and \( q_{12} = 0 \), which gives an outward displacement of 0.38\( \text{Å} \) in the \( \hat{z} \) direction, and smaller outward displacements of 0.036\( \text{Å} \) in both \( \hat{x} \) and \( \hat{y} \) directions, for the 6 oxygens surrounding the central Mn. Displacements of oxygens in the intermediate and outer layers are at least 10 times smaller. As predicted perturbatively, \( t_{1u}, t_{2u}, a_{2g}, q_{42} \) and \( q_{43} \) distortions are absent.

![FIG. 5. Numerical results for ground state energy(\( E_{gs} \)) of symmetric clusters](image)

![FIG. 6. Numerical results for ground state energy(\( E_{gs} \)) of asymmetric clusters](image)
VIII. DISCUSSION

When doping $x$ is non-zero, one should ask whether localized polaron solutions will distribute homogeneously or will attract, causing phase separation [31]. We have not addressed this issue, which requires a more complicated calculation with additional Coulomb parameters in the Hamiltonian. Experiment is consistent with a concentration interval up to $x \approx 0.08$ where polarons are homogeneously distributed. Our model shows that at concentrations $x > 0.045$, polarons should be unstable relative to an undistorted ground state with FM spin order and metallic conduction by the doped electrons. This effect is not seen in experiments. Apparently alternate ground states, possibly involving organization of polaronic distortions, occur and enable the system to remain non-metallic.

Without additional physics (such as defects), our model cannot account for the observation [3] that La concentrations $x$ less than 0.02 yield less excess moment than expected from 7-site polarons.

Our model describes the competing spin and lattice polaron effects. We believe that it contains the main features needed to describe the system. A test would be measurement of the oxygen displacements which our model predicts. The model omits non-adiabatic phonon effects, spin quantization, temperature, and polaron-polaron interactions [12]. For higher doping levels or $T > 0$, these may have a larger influence and present challenges which could be worth pursuing if experimental guidance improves.

ACKNOWLEDGMENT

We thank J. J. Neumeier for suggesting this investigation; J. J. Neumeier and J. L. Cohn for comments on the manuscript, and V. Perebeinos and A. Abanov for discussions. This work was supported by NSF grant No. DMR-0089492.

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FIG. 7. Numerical results for ground state radius of symmetric clusters. The radius is measured in unit of lattice constant $a$ (the Mn-Mn separation distance), and is defined to be $\left(\sum_i (\vec{r}_i - \langle \vec{r} \rangle)^2 \psi_i^2 \right)^{1/2}$, where the index $i$ runs over all Mn sites inside the cluster, and $\langle \vec{r} \rangle \equiv \sum_i \vec{r}_i \psi_i^2$. 

\[ \sum_i (\vec{r}_i - \langle \vec{r} \rangle)^2 \psi_i^2 \]
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