Competing crystal structures in La$_{0.5}$Ca$_{0.5}$MnO$_3$: conventional charge order versus Zener polarons

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Equilibrium crystal structures for La$_{0.5}$Ca$_{0.5}$MnO$_3$ have been calculated using hybrid exact exchange and density functional methods. Two distinct ground states with either conventional checkerboard charge ordering or Zener polaron formation are found depending on the proportion of exact exchange used. The checkerboard state has mixed $d_{x^2-y^2}$, $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbital ordering and CE-type magnetic order while the Zener polaron state has $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ ordering and A-type magnetic order.

INTRODUCTION

Low temperature charge ordering (CO) transitions in manganites such as La$_{1-x}$Ca$_x$MnO$_3$ are generic for doping in the range $0.4 < x < 0.9$. They are observed as commensurate or incommensurate changes in unit cell dimension parallel to the crystallographic $b$ axis. Commensurate structures are found when $x$ is a rational fraction such as 1/2, 2/3 or 3/4. Half-doped manganites, $A_{0.5}B_{0.5}$MnO$_3$ with $A =$ La, Nd, Pr and $B =$ Ca, Sr, have been widely studied as the CO phase is believed to consist of a checkerboard (CB) pattern of Mn$^{3+}$ and Mn$^{4+}$ ions in which Mn$^{3+}$ ions are Jahn-Teller (JT) distorted while Mn$^{4+}$ ions are not. However, there is evidence from Hartree-Fock calculations on La$_{0.5}$Ca$_{0.5}$MnO$_3$ for a Zener polaron (ZP) electronic structure in which all Mn ions have a valence of 3.5 and a recent single-crystal neutron scattering study found a ZP crystal structure for Pr$_{0.60}$Ca$_{0.40}$MnO$_3$ where all Mn ions have an intermediate JT distortion. There is conflicting experimental evidence from resonant XRD experiments on La$_{0.5}$Ca$_{0.5}$MnO$_3$ for a CB CO pattern in Pr$_{0.60}$Ca$_{0.40}$MnO$_3$ and a recent refinement of the structure of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ using high resolution x-ray and neutron powder data favored a CB structure. Both CB and ZP phases have been proposed to exist in a phase diagram for half-doped manganites in which the tolerance ratio for the rare earth and alkaline earth ions is varied.

In this Letter we use hybrid Hartree-Fock/density functional theory ab initio energy minimization calculations and show that the ground state CO crystal structure switches between CB and ZP as the percentage of Hartree-Fock (exact) exchange is varied. These two states are therefore similar in energy and the actual ground state may depend on specific $A$ and $B$ ions, or even sample preparation, history and ambient conditions. The predominant difference in charge populations of the two states is in charge on O ions rather than Mn ions and so CO may be associated with O ions rather than Mn ions. Furthermore, we find that the lowest energy structure for either CO pattern has a different space group from those proposed for the CB or ZP structures. The structure that we find has modulations of Mn and O ions in the checkerboard state by a filled circle. Mn and O ion positions in the ZP state by a shaded circle and O$^-$ ions by large dashed circles. Directions of transverse displacements of Mn ions from their ideal perovskite positions are indicated by arrows. Labels on ions refer to Tables I to III.

![FIG. 1: ab plane atomic positions for La$_{0.5}$Ca$_{0.5}$MnO$_3$ shown to scale. (a) Pn2$_1m$ structure. Mn ion positions in the ZP state (Table I) are indicated by small circles, O$^-$ ions by shaded circles and O$^-$ ions in the ZP state by a filled circle. Mn and O ion positions in the checkerboard state (Table II) are indicated by small and large dashed circles. (b) P2$_1$nm ZP structure (Table II). Directions of transverse displacements of Mn ions from their ideal perovskite positions are indicated by arrows. Labels on ions refer to Tables I to III.](https://example.com/fig1)
ing mechanism for the CO transition would explain the observation of incommensurate order with wavevector \( q = (1-x)b^* \) and may also be relevant to colossal magnetoresistance (CMR) phases of manganites where diffuse satellites in x-ray scattering have been observed \[21, 22\] and attributed to polarons with transverse displacements of ions \[22\] similar to those in Fig. 1(a).

Structure optimizations were performed using the CRYSTAL program \[23\]. A \( \sqrt{2}x\sqrt{2}x \) unit cell (Fig. 1) containing eight formula units with ferromagnetic (FM) order was used for optimizations while total energies of \( \Lambda \) and CE-type magnetically ordered structures were compared using \( 2\sqrt{2}x\sqrt{2}x \) unit cells. A single force evaluation was carried out for CE-type magnetic order for a structure which had been optimized with FM magnetic order in order to estimate the importance of magnetoelectronic effects on the crystal structure; these were found to be small. No simultaneous relaxation of unit cell dimensions was performed as the calculations are expensive in computer time; unit cell dimensions were taken from experiment \[2\] (\( a = 5.4763 \) Å, \( b = 10.8932 \) Å, \( c = 7.5247 \) Å). Structure optimizations were performed for 60%, 80% and 100% exact exchange (the latter is simply an unrestricted Hartree-Fock (UHF) calculation); both 60% and 80% exact exchange calculations resulted in CB CO for all space groups investigated while 100% exact exchange resulted in ZP CO structures. Initial atomic configurations were taken from Table II in Ref. \[2\] (\( P11_2/m \) symmetry) or were generated by hand. As noted by Daoud-Aladine and coworkers \[14\], the isotropy subgroups of the parent high temperature \( Pbnm \) phase that have a doubled unit cell along the \( b \) axis are: \( P11m, P2_1/nm, P112_1/m, P112_1/b, P2_1nb \) and \( P11b \). The relevant isotropy subgroups for ZP CO are \( P2_1nm \) and \( P11m \) and for CB CO they are \( P112_1/m \) \[2\] and \( P11m \).

Hessian matrices for energy minimized CB or ZP CO structures with these space groups had at least one negative eigenvalue, which indicates that they are saddle points on the potential energy surface. A further energy minimization was performed using \( P112_1/m \) symmetry and 100% exact exchange. The screw axis parallel to the \( b \) axis naturally incorporates transverse Mn displacements found in experiment. All Hessian matrix eigenvalues were positive for this ZP CO structure and it was lower in energy than the other structures (\( P11m +7 \) meV/Mn ion; \( P2_1nm +14 \) meV/Mn ion). A structure optimization with 60% exact exchange and \( Pn2_1m \) symmetry resulted in a stable CB CO structure which was 31 meV/Mn ion lower than the optimized structure with \( P112_1/m \) symmetry. Fractional coordinates for the lowest energy CB and ZP CO structures found, which have \( Pn2_1m \) symmetry, are given in Table II. Fractional coordinates for the \( La_{0.5}Ca_{0.5}MnO_3 \) ZP CO structure are compared to those determined by neutron scattering for \( Pr_{0.60}Ca_{0.40}MnO_3 \) \[14\] in Table II.

Fig. 1(a) shows atomic positions for nearly coplanar

| Atom | Wyck. | x | y | z | x | y | z |
|------|-------|---|---|---|---|---|---|
| Ca1  | 2a    | 0.4779 | 0.9021 | 0.0000 | 0.5121 | 0.8936 | 0.0000 |
| La2  | 2a    | 0.4783 | 0.3723 | 0.5000 | 0.4784 | 0.3614 | 0.5000 |
| La3  | 2a    | 0.9832 | 0.1286 | 0.0000 | 0.9977 | 0.1426 | 0.0000 |
| Ca4  | 2a    | 0.9741 | 0.6093 | 0.5000 | 0.9905 | 0.6088 | 0.5000 |
| Mn1  | 4b    | 0.2463 | 0.0069 | 0.2109 | 0.2352 | 0.9977 | 0.2109 |
| O1   | 4b    | 0.2556 | 0.7600 | 0.2112 | 0.2676 | 0.7600 | 0.2144 |
| O3   | 4b    | 0.1813 | 0.2315 | 0.2942 | 0.2118 | 0.2433 | 0.2146 |
| O4   | 4b    | 0.7479 | 0.9891 | 0.2753 | 0.7539 | 0.9970 | 0.2717 |
| O1'  | 2a    | 0.4298 | 0.1255 | 0.5000 | 0.4320 | 0.1055 | 0.5000 |
| O2'  | 2a    | 0.5550 | 0.1309 | 0.0000 | 0.5430 | 0.1337 | 0.0000 |
| O3'  | 2a    | 0.0443 | 0.3645 | 0.5000 | 0.0316 | 0.3611 | 0.5000 |
| O4'  | 2a    | 0.9054 | 0.3770 | 0.0000 | 0.9012 | 0.3625 | 0.0000 |

Mn and O ions projected onto the \( ab \) plane in the \( Pn2_1m \) energy minimized structure. Positions of ions in the ZP CO structure are indicated by shaded or filled circles and positions of ions in the CB CO structure are indicated by dashed lines (Table II). The structures are coincident at the Mn1 ion positions and so this figure facilitates
comparison of distortions in the ab plane. The main differences in ion position occur at the Mn2 and O3 positions to accommodate the switch between ZP and CO JT distortion patterns. Transverse wavelike positions of Mn and O ion positions about ideal perovskite positions can be identified in Fig. II a). Modulations of either ion type have wavelength equivalent to the unit cell dimension along the b axis and are out of phase by $\pi/2$ and are similar to modulations of MnO6 proposed in manganites with $x > 0.5$ and $x < 0.5$.

Positions of ions in the energy minimized $P2_1nm$ structure with ZP CO are shown in Fig. II b). The main differences in atomic positions in the plane between this ZP CO structure and the $Pn2_1m$ ZP CO structure occur at the O2 and O3 positions. Fractional coordinates for the $P2_1nm$ structures for both La0.5Ca0.5MnO3 (this work) and for Pr0.60Ca0.40MnO3 [14] are compared in Table III and the agreement is remarkable. The starting guess for the La0.5Ca0.5MnO3 structure in ab initio calculations was not the Pr0.60Ca0.40MnO3 structure and the coordinates obtained via ab initio calculations are not simply a relaxation of the Pr0.60Ca0.40MnO3 structure. There are bonds of intermediate length along the ZP axis ranging from 1.99 to 2.09 Å in ab initio calculations and from 1.98 to 2.05 Å in experiment [13] (Table III). Bond valence sums [24] (calculated using $R_{\text{ZP}}$ structures, which is indicative of an intermediate valence. The Mn-O$^-$-Mn bond angle is $160^\circ$ or less in both La0.5Ca0.5MnO3 and Pr0.60Ca0.40MnO3.

![Figure 2: Spin density and charge density difference for La0.5Ca0.5MnO3 in the ZP state with A-type magnetic order and $Pn2_1m$ symmetry obtained using 100% exact exchange. (left) Spin density. The unit cell shown in Fig. II a) is outlined. (right) Charge density difference.](image)

The spin density and charge density difference of the ZP CO structure are shown in Fig. 2. Charge density difference plots are generated by subtracting densities of isolated O$^2-$ and Mn$^{4+}$ ions from the total charge density of the crystal structures and therefore show deformations of charge density at O ion sites and $e_g$ orbital order at Mn ion sites. Each Mn ion in the ZP CO state has a d$^4$ configuration, O$^-$ ions order in Mn(d$^4$)-O$^-$-Mn(d$^4$) dimers (Zener polarons) in ab planes and the magnetic ground state is A-type [12]. UHF calculations [12] predict a magnetic moment of 0.7 $\mu_B$ on the O$^-$ ion in the center of each ZP, which is opposed to the moments of neighboring ZP Mn ions. On the other hand, cluster configuration interaction (CI) calculations [27] show that the moment on O$^-$ ions is much less than 0.7 $\mu_B$. However they show that the charge on these ions is approximately -1.0e, in agreement with UHF calculations and that the ZP are strongly bound in a FM state. In both UHF and CI calculations the total magnetic moment on each ZP is 7/2 $\mu_B$ in agreement with experiment [8]. The reason for the discrepancy between spin distributions in CI and UHF calculations is simply that the UHF spin function for the Mn-O$^-$ bond is $\alpha\beta$ whereas it should be $(\alpha\beta - \beta\alpha)/\sqrt{2}$. $d_{3z^2-r^2}$ and $d_{3p^2-r^2}$ orbital order in the ZP state can clearly be seen in Fig. 2 in both spin density and charge density difference plots.

Bond lengths, the Mn1a-O3a-Mn2 bond angle and bond valence sums for the CB state with $ab$ initio energy minimization and for PCMO from single crystal neutron diffraction [14] and bond valence sums (BVS). Ion labels refer to atomic positions given in Fig. I. The bond angle given is the Mn1a-O3a-Mn2 angle at the center of the ZP or adjacent to a JT distorted Mn ion. The structure and space group are indicated at the top of each column.

| Bond                  | CB   | ZP   | Bond                  | ZP   | ZP   |
|-----------------------|------|------|-----------------------|------|------|
| Mn1a-O1a              | 1.92 | 1.99 | Mn1a-O1a              | 2.01 | 2.05 |
| Mn1a-O4               | 1.86 | 1.87 | Mn1a-O1b              | 1.86 | 1.88 |
| Mn1a-O2               | 1.91 | 1.89 | Mn1a-O2               | 1.91 | 1.91 |
| Mn1a-O3a              | 1.84 | 2.05 | Mn1a-O3a              | 2.08 | 1.98 |
| Mn2-O2                | 1.91 | 1.89 | Mn2a-O2               | 1.90 | 1.90 |
| Mn2-O3a               | 2.14 | 2.09 | Mn2a-O3a              | 2.09 | 2.01 |
| Mn2-O1a               | 1.92 | 1.86 | Mn2n-O4               | 1.88 | 1.90 |
| Mn2-O4a               | 2.15 | 2.03 | Mn2n-O4a              | 2.02 | 2.03 |

- La0.5Ca0.5MnO3 $Pn2_1m$ symmetry, 60% exact exchange
- La0.5Ca0.5MnO3 $Pn2_1m$ symmetry, 100% exact exchange
- La0.5Ca0.5MnO3 $Pn2_1m$ symmetry, 100% exact exchange
- Pr0.60Ca0.40MnO3 $P2_1nm$ symmetry, expt. (Ref. [14])

![Table III: Selected bond distances in å, bond angles for LCMO from ab initio energy minimization and for PCMO from single crystal neutron diffraction (14) and bond valence sums (BVS). Ion labels refer to atomic positions given in Fig. I. The bond angle given is the Mn1a-O3a-Mn2 angle at the center of the ZP or adjacent to a JT distorted Mn ion. The structure and space group are indicated at the top of each column.](image)
lengths of Mn-O bonds in CaMnO$_3$ and LaMnO$_3$ [11, 26]. The magnetic moments on these ions are 3.23$\mu_B$ (Mn1) and 3.85$\mu_B$ (Mn2) and bond valence sums are 3.28 and 4.08. All of these are characteristic of conventional CO, although charges on Mn ions as measured by Mulliken populations are essentially identical, with values of +2.02 (Mn1) and +2.02 (Mn2). A small difference in Mn ion charge has been noted in several experimental papers [17, 18] in apparently CO states.

In summary, we have shown that the equilibrium structure for La$_{0.5}$Ca$_{0.5}$MnO$_3$ which is predicted by hybrid Hartree-Fock/density functional theory depends on the percentage of exact exchange used in the calculation. The CB CO state consists of FM zig-zag chains in which corner (Mn1) ions have short bonds (1.85\(\AA\)) while JT distorted (Mn2) ions have long bonds (2.15\(\AA\)) to neighboring O ions. A preliminary calculation of the RXD spectrum using this structure is in reasonably good agreement with experimental RXD spectra for Pr$_{0.66}$Ca$_{0.40}$MnO$_3$ [27]. The ZP CO state consists of FM planes tiled with polarons which have Mn-O bonds of intermediate length along the polaron axis and this structure is in reasonable agreement with that found for Pr$_{0.66}$Ca$_{0.40}$MnO$_3$ by neutron scattering [14]. Transformation from the CB to the ZP state requires rehybridization at Mn1 and O3 sites together with relatively minor displacements shown in Fig. 1(a). Effective magnetic moments from magnetic susceptibility data for at least two mixed valence manganites display marked increases in effective magnetic moment on cooling below the CO transition temperature to 6.1 or 7.9 $\mu_B$ [14]. These magnitudes are similar to the ZP magnetic moment of 7 $\mu_B$. Dimerization of CE zig-zag chains to form a ZP state may produce this large effective moment.

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