Ferromagnetic polarons in La$_{0.5}$Ca$_{0.5}$MnO$_3$ and La$_{0.33}$Ca$_{0.67}$MnO$_3$

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Unrestricted Hartree-Fock calculations on La$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.5$ and $x = 0.67$) in the full magnetic unit cell show that the magnetic ground states of these compounds consist of 'ferromagnetic molecules' or polarons ordered in herringbone patterns. Each polaron consists of either two or three Mn ions separated by O$^-$ ions with a magnetic moment opposed to those of the Mn ions. Ferromagnetic coupling within the polarons is strong while coupling between them is relatively weak. Magnetic moments on the Mn ions range between 3.8 and 3.9 $\mu_B$ in the $x = 0.5$ compound and moments on the O$^-$ ions are -0.7 $\mu_B$. Each polaron has a net magnetic moment of 7.0 $\mu_B$, in good agreement with recently reported magnetisation measurements from electron microscopy. The polaronic nature of the electronic structure reported here is obviously related to the Zener polaron model recently proposed for Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ on the basis of neutron scattering data.

I. INTRODUCTION

The current paradigm for the electronic structure of manganites ($A_{1-x}B_x$MnO$_3$) with $x \geq 1/2$ is a lattice of Mn sites with $d^3$ or $d^4$ orbital occupancy, with the proportion of each decided by the value of $x$ and orbital ordering (OO) of the occupied $e_g$ orbital on $d^4$ sites. The corresponding double-exchange model Hamiltonian has been studied extensively\textsuperscript{1–3}. Manganites with $x \geq 1/2$ usually exhibit a phase transition\textsuperscript{4–9} which has been assumed to be charge ordering (CO) of the $d^3$ and $d^4$ sites at a temperature well below the paramagnetic transition temperature. The conventional picture of the orbital and charge ordered phase with the CE magnetic structure\textsuperscript{10} is shown schematically in Fig. 1a.

The validity of this picture for the manganites has been questioned recently\textsuperscript{11,12}; its contradictions were pointed out by Goodenough in 1955\textsuperscript{13}. An alternative picture, the Zener polaron\textsuperscript{14}, which challenges the ideas of double-exchange and CO in the manganites, was recently proposed to account for the structure of Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ determined by neutron scattering\textsuperscript{15}. In the conventional CO and OO picture, ordering of the $e_g$ electron on $d^4$ Mn sites is expected to induce a Jahn–Teller (JT) distortion; the long Mn–O bond distance in LaMnO$_3$ exceeds 2.15 Å\textsuperscript{10,16} while the Mn–O distance in cubic perovskite CaMnO$_3$ is 1.88 Å\textsuperscript{10}. The lesser modulations of bond length in doped manganites with $x \sim 1/2$ (1.92 and 2.06 Å in La$_{0.5}$Ca$_{0.5}$MnO$_3$\textsuperscript{5} and 1.98 and 2.01 Å in Pr$_{0.6}$Ca$_{0.4}$MnO$_3$\textsuperscript{15}) suggest an intermediate valence.
In this Communication we report results of Unrestricted Hartree-Fock (UHF) calculations on La$_{1-x}$Ca$_x$MnO$_3$ for $x = 1/2$ and $x = 2/3$. The UHF electronic structure for these compounds is interpreted in terms of ferromagnetic polarons containing two ($x = 1/2$) or three ($x = 2/3$) Mn ions. The main difference between results from UHF calculations and the conventional double exchange picture is that all Mn ions are essentially $d^4$. Consequently electrons must transfer from oxygen ions to every other Mn ion in the $x = 1/2$ compound, resulting in an ordered array of $O^-$ ions between pairs of Mn ions. The structures of the polaron phases for $x = 1/2$ and $x = 2/3$ are shown schematically in Figs. 1b and 2.

Mn-$O^-$-Mn and Mn-$O^-$-$Mn$-$O^-$-$Mn$ chains constitute the polarons for $x = 1/2$ and $x = 2/3$, respectively. Mn magnetic moments are in the range 3.8 to 3.9 $\mu_B$ for either compound while oxygen ions within the polarons have charges closer to $O^-$ than $O^{2-}$ and magnetic moments of -0.7 $\mu_B$. All other oxygen ions are essentially $O^{2-}$ ions. Each polaron has a net magnetic moment of 7.0 $\mu_B$, in good agreement with recently reported magnetisation measurements from electron holography and Fresnel imaging.

UHF calculations predict that magnetic coupling within polarons is strong and ferromagnetic (FM) while coupling between polarons is much weaker and can be antiferromagnetic (AF) or FM; these observations lead to a natural explanation for the observed CE or A-type AF magnetic ground states of manganites with $x = 1/2$ and the magnetic ground state of La$_{0.33}$Ca$_{0.67}$MnO$_3$, which contains polarons with the magnetic moment roughly aligned along the polaron axis. Given that the magnetic coupling within the polarons is strong and FM, the appropriate model Hamiltonian for these systems at low temperature is a Heisenberg Hamiltonian on a triangular lattice where each polaron is a single magnetic entity, rather than the conventional double exchange Hamiltonian.

Results of UHF our calculations are at odds with density functional theory (DFT) calculations in the local spin density approximation (LSDA) reported recently and with LSDA calculations done as part of this work using the same electronic structure code in that UHF calculations predict a magnetic moment on oxygen ions within the polarons whereas DFT calculations do not.

II. UHF CALCULATIONS

All electron UHF calculations were performed for La$_{0.5}$Ca$_{0.5}$MnO$_3$ and La$_{0.33}$Ca$_{0.67}$MnO$_3$ using the low temperature structures refined using x-ray data by Radaelli and coworkers in the full (80 and 120 atom) magnetic unit cells.

Spin densities of La$_{0.5}$Ca$_{0.5}$MnO$_3$ (Fig. 3) and La$_{0.33}$Ca$_{0.67}$MnO$_3$ (Fig. 4) in the ac planes of the crystal structures clearly show the polaronic nature of the electronic structures, including the magnetic moment of the $O^-$ ions opposed to those of the neighbouring Mn ions. The magnetic unit cells of either compound each contain four polarons in the ac planes shown.

Magnetic moments and Mulliken populations on Mn and oxygen ions in the polarons are given in Table I.

Electron holography and Fresnel imaging measurements show that below the AF Néel temperature the $x = 1/2$ compound actually consists of both FM and AF domains and that the magnetic moment per Mn ion in the FM domains was 3.4 ± 0.2 $\mu_B$. UHF calculations predict a net magnetic moment of 7.0 $\mu_B$ for the polaron, i.e. the polarons are fully spin polarised, in agreement with these measurements of the magnetisation of FM domains. Earlier neutron scattering data for this compound (Table I) indicated magnetic moments somewhat smaller than these fully polarised values but the trend, where larger moments are found on the sites denoted Mn$^{3+}$, is reproduced.
FIG. 4. UHF spin density plot for La$_{0.33}$Ca$_{0.67}$MnO$_3$ in AF state.

| Charges and magnetic moments in La$_{0.5}$Ca$_{0.5}$MnO$_3$ from Mulliken populations and experiment. |  |
|-------------------------------------------------|---|
| | Mn moment $\langle \mu_B \rangle$ | O moment $\langle \mu_B \rangle$ |
| UHF (CE-AF)$^a$ | 3.78, 3.91 | -0.67 |
| Expt.$^{ab}$ | 2.57, 2.98 | - |
| Expt.$^c$ | 3.4 ± 0.2 | - |
| | Mn charge | O charge |
| UHF (CE-AF)$^a$ | 2.18, 2.17 | -1.24 |

$^a$Two values for the Mn moment are quoted as the Mn ions in the polaron are inequivalent

$^b$Neutron scattering, Ref.5

$^c$Electron holography, value obtained for FM domain per Mn ion, Ref.17

Mulliken populations from UHF calculations on La$_{1-x}$Ca$_x$MnO$_3$ indicate total Mn ion populations in the range 2.25 (x = 0) to 2.13 (x = 1) with a monotonic variation for intermediate values of x. Mn d populations have an even smaller relative variation across the range of x with a d population of 4.66 in LaMnO$_3$, a range of d populations from 4.72 to 4.73 in La$_{0.5}$Ca$_{0.5}$MnO$_3$, and 4.70 in CaMnO$_3$. This is consistent with a bonding picture in which the $t_{2g}$ shell on each Mn ion is half-filled and a pair of $e_g$ orbitals is combined with a set of four empty sp$^3$ orbitals to form a set of equivalent d$^2$sp$^3$ octahedral hybrid orbitals for polar-covalent Mn-O bonding. The consistency of both the Mn ion population and d population across the range of values of x contradicts the conventional double exchange picture where Mn ions are assumed to have their formal Mn$^{3+}$ and Mn$^{4+}$ charges.

Total energies were calculated for the FM state and four different low energy AF states of the x = 1/2 compound. Low energy states are found by flipping entire polaron magnetic moments; flipping the spin of one of the Mn ions in a polaron results in an increase of the total energy by around 400 meV. Energies of the various low energy magnetic states of the x = 1/2 compound are well-fitted by an Ising-like, nearest-neighbour Hamiltonian of the form given in Eq. 1.

$$H = \sum_{<ij>} J_{ij} \hat{S}_{z_i} \hat{S}_{z_j}$$  \hspace{1cm} (1)

Labelling of exchange couplings is shown schematically in Fig. 5 and exchange constants obtained by fitting total energies of UHF calculations are given in Table II. The spin magnitude in Eq. 1 was chosen to be $S = 2$.

FIG. 5. Schematic illustration of exchange couplings between polarons in a Heisenberg Hamiltonian description.

Exchange couplings within the plane shown in Fig. 5 along zig-zag chains are FM and roughly equal in magnitude whereas they are AF perpendicular to the zig-zag chains. Exchange coupling between polarons in different planes is AF. The magnetic ground state is expected to be CE-type when $J_{AF1}$ exceeds $(J_{FM1} + J_{FM2})/2$ in magnitude and A-type otherwise. Both are observed to be the magnetic ground state for various x = 1/2 compounds, depending on the A and B ion types8.

TABLE II. Exchange coupling constants derived from La$_{0.5}$Ca$_{0.5}$MnO$_3$ UHF calculations.

| Exchange constant (meV) |  |
|------------------------|---|
| $J_{AF1}$ | 5 |
| $J_{AF2}^a$ | 8 |
| $J_{FM1}$ | -14 |
| $J_{FM2}$ | -12 |

$^a$Average value over two interplanar couplings in crystallographic unit cell

Our calculations actually predict an A-type AF ground state whereas the CE-AF structure is the ground state in La$_{0.5}$Ca$_{0.5}$MnO$_3$. However, in similar UHF calculations on LaMnO$_3$, it was found that AF couplings are significantly underestimated compared to either experiment or results of configuration interaction (CI) cluster calculations, whereas FM couplings are in better agreement with both.

III. DISCUSSION

The polaronic picture for manganites with x $\geq$ 1/2 which has been presented is consistent with a wide range
of experimental data and allows various observations, such as the unusual magnetisation in La$_{0.33}$Ca$_{0.67}$MnO$_3$, to be explained: it accounts for the observation of AF or CE-AF ground states for various combinations of counterion in A$_{0.5}$Ba$_{0.5}$MnO$_3$; it is consistent with full spin polarisation of Mn ions in La$_{0.5}$Ca$_{0.5}$MnO$_3$.

One must be cautious in using UHF calculations to estimate magnitudes of magnetic moments on the oxygen ions. An analogy can be drawn between electron transfer from the O ion in a polaron to a neighbouring Mn ion and separation of the electron pair in a hydrogen molecule as the proton-proton distance is increased above the molecular equilibrium bond length: UHF wave functions for hydrogen molecules at large bond distances consist of a spin-up electron on one proton and a spin-down electron on the other; the additional configuration in which a single spin configuration is a linear combination of several determinants with a magnetic moment on the central oxygen ion. The La$_{0.5}$Ca$_{0.5}$MnO$_3$ polaron electronic structure therefore resembles that in $\alpha'$-NaV$_2$O$_5$; it is unlike the electronic structure which results in FM coupling in LaMnO$_3$, which is very well described by a single spin configuration.

An obvious question which arises within the polaron picture is, 'What happens when electrons are added to the $x = 1/2$ phase?' That is, 'What is the electronic structure predicted to be in the FM region of the phase diagram with $0.2 < x < 0.5$?' Since the bottom of the conduction band in La$_{0.5}$Ca$_{0.5}$MnO$_3$ is comprised largely of vacant oxygen 2p states on the O$^-$ ion in the polaron, one would naturally expect to add the extra electron here. The spin density plots in Figs. 3 and 4 show that OO in the x = 1/2 compounds is parallel to the polaron axis, whereas it is T-shaped in LaMnO$_3$ (long Mn-O bonds in JT distorted octahedra in LaMnO$_3$ are perpendicular to each other). If the extra electron is added to the polaronic oxygen site, it is expected that there will be reorientation of $e_g$ orbitals (Fig. 1c) and adjustment of Mn-O-Mn bond lengths. OO in the vicinity of the added electron is expected to resemble that in LaMnO$_3$ and one might expect to nucleate a small FM patch as further electrons are added.

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