Theory of the Reentrant Charge-Order Transition in the Manganites

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A theoretical model for the reentrant charge-order transition in the manganites is examined. This
transition is studied with a purely electronic model for the $\epsilon_g$ Mn electrons: the extended Hubbard
model. The electron-phonon coupling results in a large nearest-neighbor repulsion between $\epsilon_g$
 electrons. Using a finite-temperature Lanczos technique, the model is diagonalized on a 16-site periodic
cluster to calculate the temperature-dependent phase boundary between the charge-ordered and
homogeneous phases. A reentrant transition is found. The results are discussed with respect to the
specific topology of the 16-site cluster.

The manganites have a very rich phase diagram that
includes ferromagnetic, antiferromagnetic, and charge-
ordered phases [1,3]. Various theoretical models have
been used to explain different aspects of this phase dia-
gram [1,3].

In its simplest incarnation, the charge-ordered (CO)
phase occurs at hole doping $x = 1/2$ with equal amounts
of Mn$^{3+}$ and Mn$^{4+}$ ordered in real space in a checker-
board pattern. The oxygens relax away from the Mn$^{3+}$
ions and towards the Mn$^{4+}$ ions, thus providing a re-
pulsive potential between Mn$^{3+}$ ions (or equivalently be-
tween Mn$^{4+}$ ions). The potential energy gain exceeds the
kinetic energy loss due to the formation of this insulating
state [8].

When observed, the CO is generally the lowest
temperature phase, but recently the CO phase has been
seen to melt with decreasing temperature in Pr$_{0.65}$(Ca$_{0.7}$Sr$_{0.3}$)$_{0.35}$MnO$_3$ [4] and LaSr$_2$Mn$_2$O$_7$ [5].
The lowest temperature phase is metallic, and the CO in-
sulator is only observed at intermediate temperatures. A
reentrant transition has been obtained theoretically using
extended Hubbard models both with electron-phonon in-
teractions [1] and without electron-phonon interactions
[12].

In this paper, we study the charge-order transition in
the extended Hubbard model (without electron-phonon
interactions) on the two-dimensional square lattice. Pre-
vious work [12] solved this model in infinite spatial di-

The Hamiltonian is given by

$$
H = t \sum_{\langle ij \rangle \sigma} (c^\dagger_{i\sigma} c_{j\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_i n_j,
$$

(1)

where $c^\dagger_{i\sigma}$ ($c_{i\sigma}$) creates (annihilates) an electron with spin
$\sigma$ on site $i$, $n_{i\sigma}$ is the number operator with spin $\sigma$ on site
$i$, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. The hopping amplitude is $t$, $\langle ij \rangle$
enumerates nearest neighbor sites on the two-dimensional
square lattice, $U$ is onsite repulsion, and $V$ is the nearest-
neighbor repulsion. The non-interacting bandwidth on
the two-dimensional square lattice is given by $W = 8|t|$;
we set $U = W$ and vary $V$ at quarter filling (one electron
for every two sites). For small $V$, we expect the ground
state will be a homogeneous Fermi liquid. For large $V$,
the electrons will crystallize in a checkerboard liquid to
avoid occupying neighboring sites.

We solve the Hamiltonian (1) on a $4 \times 4$ cluster using a
recently developed finite-temperature Lanczos technique
[13,14]. We choose periodic boundary conditions result-
ing in a closed Fermionic shell in the non-interacting limit
[13]. In each symmetry sector, we perform $N_L = 4000$
Lanczos steps. We eliminate spurious eigenvalues [16],
leaving more than 2000 real eigenvalues in each sector,
but not all of these will be converged. The extreme
eigenvalues (lowest and highest) converge first [14]. From
these eigenvalues, we compute the susceptibility

$$
\chi = \frac{1}{N} \frac{\partial E}{\partial V},
$$

(2)

where $N = 16$ is the number of sites. The susceptibility
$\chi$ is equivalent to the nearest-neighbor pair correlation
function by the Kubo formula. In the homogeneous phase
$\chi$ is large, but in the CO phase where there is only a small
probability of finding electrons on neighboring sites, $\chi$ is
small.

The susceptibility (2) for five different temperatures is
plotted in Fig. 1. For all temperatures shown, $\chi$ is large
at small $V$ in the homogeneous phase, decreases contin-
uously with increasing $V$, and flattens out at a small
value in the CO phase at large $V$. To determine the
boundary between the homogeneous and CO phases, we
pick a critical value of $\chi_c = 0.1$ for the phase boundary.
We choose this value to coincide approximately with the
maximum of $\partial^2 \chi / \partial V^2$. A different value of $\chi_c$ results in
a phase boundary that is qualitatively the same: for all
reasonable values of $\chi_c$, the phase boundary first shifts
to smaller $V$ as the temperature is raised from zero and
then moves to larger $V$ in the high-temperature regime,
characteristic of a reentrant transition.
The phase diagram calculated from the point where \( \chi(V, T) = \chi_c = 0.1 \) is shown in Fig. 2. Reentrant behavior is seen for \( 0.31 \leq V/W \leq 0.37 \). For \( V \) in this range, the ground state is homogeneous, but a CO phase exists at intermediate temperatures.

The 4×4 system has no entropy in either the homogeneous or the CO phases, so the phase boundary in Fig. 2 has infinite slope in the \( T \to 0 \) limit. However, the CO phase has more low-lying excitations than the homogeneous phase, so in the reentrant region the CO phase becomes favored at intermediate temperatures.

The greater number of low-lying excitations in the CO phase may be at least partially due to the topology of the 4×4 periodic cluster used. The homogeneous phase will have the usual Fermi-liquid excitations. In the CO phase, the electrons order in a checker-board pattern. The spins interact via a fourth order superexchange process [17,18]. A given spin can interact both with its diagonal neighbor and with its neighbor two steps away either horizontally or vertically. On the infinite lattice, the interaction with the diagonal neighbor is 4 times as strong as the interaction with the horizontal/vertical neighbor because there are 4 times as many diagonal superexchange paths. Thus the spin system is equivalent to the extended antiferromagnetic Heisenberg model on a square lattice with \( J_1 = 4J_2 \), where \( J_1 \) is the nearest-neighbor interaction and \( J_2 \) is the next-nearest-neighbor interaction. Extensive numerical calculations have shown that this Heisenberg model forms a Néel state at \( T = 0 \) [19,20]. Because two steps to the left is the same as two steps to the right (and the same for up and down), the 4×4 periodic cluster is equivalent to a hypercubic 2\(^4\) cluster [21]. Thus the diagonal superexchange coupling is the same as the horizontal/vertical coupling. So the CO Néel state on this particular cluster is strongly frustrated and may not form. This could contribute to the greater density of low lying states in the CO phase than in the homogeneous phase.

Smaller periodic clusters have even more severe finite-size problems. We decided to work with the 4×4 cluster because it is the largest system with a manageable Hilbert space. Even with all symmetries applied, the largest Hamiltonian matrices were larger than \( 2.0 \times 10^5 \) (the matrices are very sparse, with only about 30 non-zero elements in each row or column). The Hilbert space diverges exponentially with the number of sites in the cluster. The next largest cluster with an even number of electrons has 20 sites and has irreducible sectors with Hilbert spaces larger than \( 2.4 \times 10^8 \), more than 1000 times larger than those of the 16-site system.

In summary, we have examined the reentrant charge order transition in a simple model for the manganites, the extended Hubbard model in two dimensions. We computed the low-lying eigenvalues of the model on a 16-site periodic cluster, and used the susceptibility with respect to the nearest-neighbor repulsion to compute the low-temperature phase boundary between the homogeneous and charge-ordered phases. Like previous results on this model in infinite dimensions, we find a parameter region where the model shows reentrant behavior. The reentrant region may be partially an artifact of the small cluster used, which frustrates the formation of Néel spin...
order in the charge ordered state.

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