Competing Ferromagnetic and Charge-Ordered States in Models for Manganites: the Origin of the CMR Effect

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The one-orbital model for manganites with cooperative phonons and superexchange coupling $J_{AF}$ has been investigated via large-scale Monte Carlo (MC) simulations. Results for two-orbitals are also briefly discussed. Focusing on electronic density $n=0.75$, a regime of competition between ferromagnetic (FM) metallic and charge-ordered (CO) insulating states was identified. In the vicinity of the associated bicritical point, colossal magnetoresistance (CMR) effects were observed. The CMR is associated with the development of short-distance correlations among polarons, above the spin ordering temperatures, resembling the charge arrangement of the low-temperature CO state.

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Introduction: The colossal magnetoresistance of the manganites is an example of the complex behavior and nonlinearities that can emerge in materials where several degrees of freedom are simultaneously active [1, 2]. Understanding theoretically the CMR effect is important not only for its intrinsic value in the Mn oxide context, but also to provide a framework for rationalizing a plethora of related complex phenomena unveiled in several other transition metal oxides in recent years [3]. The current scenarios to understand the CMR behavior rely on the existence of competing states and the emergence of nanometer-scale electronic structures [2]. Using simple models of phase competition (valid at large length scales) and resistor-network approximations, CMR behavior was observed [4]. However, for a deeper understanding, it is imperative to unveil the CMR effect in more fundamental microscopic models, using fully unbiased many-body techniques to handle the strong interactions. Along this line, considerable progress was recently made with the report of large magnetoresistance effects in Mn-oxides models in the case where the double-exchange (DE) induced FM metal competes with a FM insulator made out of randomly localized polarons [2, 5, 6]. However, a reduced FM metal competes with a FM insulator made of nanometer-scale electronic structures [2]. The comprehensive investigation reported here was possible by using hundreds of nodes of the Cray XT3 supercomputer operated by the National Center for Computational Studies, at Oak Ridge National Laboratory (ORNL). The same effort on conventional PC clusters would have demanded several years for completion.

Models and Techniques: The models and methodology used in this effort have been extensively discussed before [2]. Then, only a brief description is here included. The one-orbital Hamiltonian is given by $H=H_{1b}+H_{AF}$, where $H_{1b}$ contains the standard fermionic nearest-neighbor (NN) hopping term at infinite Hund’s coupling, plus the interaction with the oxygen phonons which are assumed classical. The full $H_{1b}$ term, including on-site disorder, is explicitly defined in Eq.(2) of Ref. [7]. The two-orbital model, also used here, is identical to Eq.(4) of Ref. [7]. The electron-phonon coupling is denoted by $\lambda$, the strength of the on-site quenched disorder is $\Delta$, the chemical potential $\mu$ regulates the density $n$, and the hopping $t=1$ is the energy unit [8]. In this study, the second term $H_{AF}=J_{AF}\sum_{(ij)}\vec{S}_{i}\cdot\vec{S}_{j}$ plays a key role. This interaction represents the NN superexchange, with coupling $J_{AF}$, between the (assumed classical) $t_{2g}$ spins $\vec{S}_{i}$. The study of this model involves the standard exact diagonalization of the fermionic sector for a given classical phononic and $t_{2g}$ spins configuration, updated via a MC procedure [2]. The charge-charge correlations were evaluated using $C(j)=(1/N)\sum_{i}(\langle n_{i}n_{i+j}\rangle-\langle n_{i}\rangle^{2})$ with $n_{i}$ the electronic density at site $i$, and $N$ the total number of sites. The resistivity $\rho$ has been calculated by taking the inverse of the mean conductivity $\sigma$, where the

\[
H_{AF} = \sum_{(ij)} J_{AF} \vec{S}_{i} \cdot \vec{S}_{j}
\]

\[
C(j) = \frac{1}{N} \sum_{i} (\langle n_{i} n_{i+j} \rangle - \langle n_{i} \rangle^{2})
\]

\[
\rho = \frac{1}{\sigma}
\]

\[
\sigma = \frac{1}{\sum_{i} \sum_{j} C(j)}
\]

\[
J_{AF} = \text{coupling is shown to be crucial for the magnitude of the effect. A simple picture for the origin of the CMR effect is discussed, that relies on nanometer-scale short-range order above the Curie temperature $T_{C}$, in qualitative agreement with previously proposed mixed-phase scenarios.}

\[
H_{1b} = t \sum_{\langle i,j \rangle} c_{i}^{\dagger} c_{j} + \mu \sum_{i} n_{i} + \sum_{i} \left( \Delta n_{i}^{2} - \lambda \sum_{j} \langle n_{i} n_{i+j} \rangle - \langle n_{i} \rangle^{2} \right)
\]

\[
J_{AF} = \text{between the (assumed classical) } t_{2g} \text{ spins } \vec{S}_{i}.
\]

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latter is related to the conductance \( G \) by \( G = \sigma L^{d-2} \), \( d \) being the dimension, and \( L \) the linear size of the lattice. The conductance \( G \) was obtained using the Kubo formula \[3\]. For further details, the reader should consult Sec. II of Ref. \[3\]. Finally, note that finite clusters do not lead to true singularities, such as a critical temperatures. However, decades of investigations in a wide variety of contexts have shown that finite systems can accurately capture the rapid growth of correlation lengths in narrow temperature ranges expected from criticality. These temperatures can be safely associated with true critical temperatures, and this is the convention followed here and in many previous studies \[2, 4, 5, 6, 7\].

**Clean-Limit Phase Diagram:** The key novelty of this investigation is the existence of an insulating CO/AF state competing with the FM metal to generate the CMR. In Fig. 1, the clean-limit \( \Delta = 0 \) one \( e_g \)-orbital model phase diagram is presented, at an experimentally realistic density \( n = 0.75 \) and intermediate \( \lambda = 1.2 \). At \( J_{AF} = 0 \), the ground state is a DE generated standard FM metal, with charge uniformly distributed. With increasing \( J_{AF} \), a first-order transition occurs to a CO/AF state schematically shown in Fig. 1 \[10\]. The holes are arranged regularly, separated by distances 2 and \( \sqrt{5} \). This state is degenerate with a state rotated in 90°. The spins are also indicated. This type of states are the analog of the more realistic CO/AF states that exist in two-orbital Mn-oxide models, such as the CE state \[2\].

**Clean-limit CMR:** The most important result of these investigations is shown in Fig. 2 where the \( \rho \) vs. temperature \( T \) curves are shown. Consider Fig. 2(a): here \( \rho \) vs. \( T \) presents the expected insulating behavior at large \( J_{AF} \), and the canonical bad-metal DE form at small \( J_{AF} \) (or reducing \( \lambda \)). The remarkable result appears in between, mainly in the narrow \( J_{AF} \) interval approximately between 0.02 and 0.0325. In this regime, \( \rho \) vs. \( T \) presents a canonical CMR shape, with insulating behavior at large \( T \), transforming into a broad high peak upon cooling (logarithm scale used), followed by metallic behavior at low \( T \). The \( T_C \) is approximately located at the resistivity peak. This is in agreement with the experimental phenomenology of CMR manganites, and with the theoretical scenarios \[2, 4\] based on a CMR emerging from phase competition between a FM metal and a CO-AF insulator. The result is particularly remarkable considering the relatively small clusters used in our studies: the origin of the CMR effect unveiled here must lie in phenomena occurring at the nanometer scale, as recently remarked \[11\]. The only “price” to pay is the tuning of couplings: the CMR shape is obtained in narrow intervals \( \Delta \lambda \sim 0.1 \) (inset Fig. 2(a)) and \( \Delta J_{AF} \sim 0.02 \). However, this delicate tuning is removed by adding quenched disorder, as shown before \[1, 7\], and also below in the present effort.

In Figs. 2(b,c), the effects of magnetic fields \( H \) are shown. In agreement with experiments, the peak in \( \rho \) is strongly suppressed by magnetic fields that are small in the natural units \( t = 1 \). The concomitant CMR ratios \( [(\rho(0) - \rho(H))/\rho(H)] \times 100\% \) are as large as 10,000%. The comparison between \( 8 \times 8 \) and \( 12 \times 12 \) clusters also show that size effects are mild in these investigations.

**Influence of Quenched Disorder, Dimensionality, and Number of Orbitals:** Fig. 3(a) shows typical \( \rho \) vs. \( T \) curves in the presence of on-site-energy quenched disorder. As discussed before \[6, 7\], the disorder enhances the tendency toward having \( \rho \) vs. \( T \) curves with the canonical CMR shape, and the fine tuning problem is avoided. This is important to rationalize the universality of the CMR effect, present in so many Mn oxides that they cannot all be finetuned to the same couplings.

To complete our investigations, the effects of dimensionality and orbital number were also addressed. In Fig. 3(b) results are shown using a \( 4 \times 4 \times 4 \) cluster, as a representative of a 3D lattice, in the clean limit. The \( \rho \) vs. \( T \) curves are very similar to those found in 2D sys-
for La0.7Ca0.3MnO3 was shown together with the neutron scattering (1/4, 1/4, 0) polaron peak that describes short-distance polaron correlations. Such a “correlated polaron” signal is the analogous of short-range CO in our one-band model, a precursor of the CO state stabilized at low T in parameter space. Figure 3(a) shows that the short-distance charge order is reduced at low T but does not disappear: in this regime the FM polaron formation. The resistivity becomes nearly flat above T*. In our investigations, a pseudogap (PG) in the density-of-states N(\omega) was also observed, and its inverse at \mu is shown in Fig. 3(a). The PG disappears at a higher temperature T^pl, probably related to polaron formation. The resistivity is not affected by T^pl, but upon further cooling to T* those polarons become correlated and \rho dramatically increases.

Finally, while averaged quantities are certainly crucial for quantitative studies, the “by eye” examination of MC snapshots is also illustrative. In Fig. 3(b), a typical snapshot in the CMR regime is shown. Pairs of holes located at the distances \sqrt{5} and 2 are highlighted. Clearly, MC equilibrated configurations do not have randomly distributed holes (i.e., it is not a gas of heavy polarons), but special distances are preferred over others: the polarons are correlated. Those distances are the same that

![FIG. 2: (Color online) Resistivity \( \rho \) vs T curves for various parameters: (a) Fixing \( \lambda=1.2 \) and varying \( J_{AF} \). Arrows indicate Tc’s. Results at \( \lambda=0.8 \) and \( \lambda=1.0 \), with \( J_{AF}=0.0 \), are also shown. Inset: results fixing \( J_{AF}=0.03 \) and varying \( \lambda \). (b) Effect of magnetic fields (indicated, in t units) on \( \rho \) using \( J_{AF}=0.0325 \), on an 8x8 lattice. (c) Same as (b) but for \( J_{AF}=0.035 \), on a 12x12 lattice. In (a) and (b), MC steps and the starting configurations are the same as in Fig. 1. In (c), 7500 thermalization and 5000 measurement steps were used. Typical error bars are indicated in (a).](image2)

![FIG. 3: (Color online) (a) \( \rho \) vs. T in the presence of quenched disorder \( \Delta \). Up to ten different disorder realizations were used in calculations with quenched disorder. Only small changes between configurations were observed. MC steps and starting configurations are as in Fig. 1. (b) \( \rho \) vs. T using a 4x4x4 lattice, parametrized with \( \lambda \), at \( J_{AF}=0.03 \). (c) Two orbitals \( \rho \) vs. T results using an 8x8 lattice for \( J_{AF}=0.05 \). In (b) and (c), 4000 thermalization and 4000 measurement MC steps were used, \( n=0.75 \), and the clean limit \( \Delta=0 \) was studied.](image3)
characterize the low-T CO state (Fig. 1). Also, in the MC snapshots the $t_{2g}$ spins at the hole locations and their four neighbors were found to be polarized similarly to that shown in Fig. 1. Thus, puddles of the CO-AF state appear in the MC snapshots, and their existence is correlated with the shape of the $\rho$ vs. $T$ curves.

Conclusions: The results reported here show that realistic models for manganites – with the DE, electron-phonon, and $J_{AF}$ interactions – can explain the CMR effect and its magnitude. The coupling $J_{AF}$ is crucial, since it is needed to stabilize the CO-AF state that competes with the FM metal. The origin of the CMR is the formation of nano-scale regions above $T_C$, with the same charge and spin pattern as the low-T insulating CO-AF state. To obtain CMR effects, clusters of just a few lattice spacings in size appear sufficient [11]. Our results show that the CMR effect is much larger when the insulating competing state has charge ordering tendencies, as opposed to having merely randomly localized polarons. The latter state has been recently identified using STM techniques, in a bilayered $x=0.3$ manganite with mild in-plane magnetoresistance [17]. If the same STM experiment is repeated at $x=0.4$, where the CMR is much stronger, it is predicted that aggregates of polarons resembling a CO state should be observed above $T_C$.

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FIG. 4: (Color online) (a) MC averaged $C(\sqrt{5})$ vs. $T$, showing a qualitative similarity with the rescaled resistivity (also shown). This agreement occurs below the $T^*$ indicated. At higher $T$, $\rho$ is flat and $C(\sqrt{5})$ nearly vanishes. Also shown is the inverse of $N(\omega = \mu)$, to indicate the PG formation at $T''$.
(b) Typical MC snapshot with the radius of the circles proportional to the local charge density. Also shown are the hole-hole distances $\sqrt{5}$ and 2 of relevance (see text).