Giant Cluster Coexistence in Doped Manganites and Other Compounds

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Computational studies of models for manganese oxides show the generation of large coexisting metallic and insulating clusters with *equal* electronic density, in agreement with the recently discovered micrometer-sized inhomogeneities in manganites. The clusters are induced by disorder on exchange and hopping amplitudes near first-order transitions of the nondisordered strongly coupled system. The random-field Ising model illustrates the qualitative aspects of our results. Percolative characteristics are natural in this context. The conclusions are general and apply to a variety of compounds.

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Considerable work is currently being focused on the experimental and theoretical study of manganese oxides, triggered by the discovery of the colossal magnetoresistance (CMR) effect [1]. Theoretical investigations of simple manganite models have already reproduced several of the complex spin-, orbital-, and charge-ordered phases observed experimentally [2]. However, the curious magneto-transport properties of manganites have resisted theoretical understanding and a proper explanation of the CMR phenomenon is still lacking.

Recently, important new experimental information about the microscopic properties of manganites has been reported. Electronic diffraction and transport techniques were applied to $La_{5/8-y}Pr_yCa_{3/8}MnO_3$, material that changes from a ferromagnetic (FM) metal to a charge-ordered (CO) insulating state at $y \sim 0.35$ [3]. At low temperatures in this regime the unexpected coexistence of giant clusters of FM and CO phases was observed [3]. Similar results were also reported using scanning tunneling spectroscopy applied to $La_{0.7}Ca_{0.3}MnO_3$ [4]. The clusters found in both these experiments were as large as 0.1 μm = 1000 Å $\sim 250a$, with $a \sim 4$ Å the Mn-Mn distance. These experimental results are *not* caused by chemical inhomogeneities, and the results are believed to correspond to equilibrium properties [3,4]. The metal-insulator FM-CO transition occurs percolatively, varying either temperature or magnetic fields. These results rule out the picture of homogeneously distributed small polarons to describe manganites in the CMR region.

The discovery of huge coexisting FM-CO clusters in manganite single crystals is puzzling. The only theoretical framework with similar characteristics is the phase separation (PS) scenario involving phases with different electronic densities [5]. The PS ideas could be successful in describing manganites at, e.g., small hole density, where nanometer size inhomogeneities have been reported [5], and at high densities $x \sim 1$ [6]. However, the micrometer clusters at intermediate densities [3,4] appear to require an alternative explanation since the energy cost of charged μm-sized domains is too large to keep the structure stable. The random location and shape of the clusters observed experimentally [3,4] also differ from the regularly spaced charge arrangement observed in PS regimes when long-range interactions are included [7]. A novel framework involving *equal-density* large clusters is needed to rationalize the results of Refs. [3,4].

Searching for an explanation of the coexistence of large clusters in manganese oxides, here a study is reported combining (i) strong coupling interactions, necessary to produce the ordered phases, and (ii) quenched disorder. The latter is caused by the random chemical replacement of ions, such as La and Pr, with different sizes. This replacement affects the hopping of e_g electrons and the exchange $J_{\rm AF}$ between the t_{2g} spins due to the buckling of the Mn-O-Mn bonds near Pr [8]. Considering hopping and exchange couplings fluctuating about nondisordered values of interest, here is reported the appearance of coexisting giant clusters of equal-density FM and AF (antiferromagnetic) phases in realistic manganite models.

To present our main results first consider the two-orbital model, described extensively in previous work [9]. It contains (i) a hopping term, regulated by t_{ab}^{α}, with $a, b = 1, 2$ labeling the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, $\alpha = x, y, z$ being the axes directions, and $t_{11}^{x} = t$ the energy scale, (ii) a strong FM coupling between the localized t_{2g} and mobile e_g fermions, regulated by J_H, (iii) an antiferromagnetic exchange among the localized spins with strength $J_{\rm AF}$, and (iv) an electron-phonon coupling between the Q_2 and Q_3 Jahn-Teller modes and the mobile electrons, with strength λ. The phase diagram of the nondisordered model was studied by Monte Carlo (MC) simulations [2,9]. Similar results were obtained including Coulombic repulsions [2]. The rationalization of the results described below suggests that the main conclusions are independent of the detailed properties of the competing states. Whether the phases are generated by phononic, magnetic, and/or Coulombic interactions is unimportant.

The focus of our studies will be on *first-order* transitions, which in the two-orbital model occur in several locations in parameter space in any dimension [2,5,9]. Let us start with 1D systems. Among the possible 1D first-order transitions, efforts are here focused on the FM-AF transition at fixed $x = 0.5$ and large λ, as a function of $J_{\rm AF}/t$ (similar results were found at other densities). The AF

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phase studied has a four-spin unit cell ↑↑↓↓ [2,10]. The state is insulating, with vanishing Drude weight. Nearest-neighbor correlations among the t_{2g} spins are used to distinguish among the FM and AF phases. In Fig. 1a the energy per site (E) vs $J_{\rm AF}/t$ for the nondisordered model is shown. The $dE/d(J_{\rm AF}/t)$ discontinuity indicates the first-order character of the transition at $J_{\rm AF}/t|_c \approx 0.21$. Disorder is introduced in t_{ab}^{α} and $J_{\rm AF}$ such that $J_{\rm AF}/t$ becomes effectively random in the interval $J_{\rm AF}/t|_c - \delta$ to $J_{\rm AF}/t|_c + \delta$. Results for one fixed set of couplings are shown at $\delta = 0.01$ in Fig. 1b (other sets lead to similar results). The MC averaged correlations in Fig. 1b already show one of the main results of this paper, namely, the remarkable formation of coexisting large FM and AF clusters in the ground state, of order $10a$ each for $\delta = 0.01$ (a is the lattice spacing). This occurs even though $J_{\rm AF}/t$ at each link rapidly changes at the a scale since different sites are *uncorrelated* in the disorder. Naively it may have been expected that at every link either the FM or AF phases would be stable depending on the local $J_{\rm AF}/t$, as it occurs for strong disorder. However, at weak disorder this would produce a large interface energy and the order parameter cannot follow the rapid $J_{\rm AF}/t$ oscillations from site to site. As a consequence, structures much larger than the lattice spacing emerge, with a size regulated by δ (compare the results in Fig. 1c at $\delta = 0.05$ with Fig. 1b). The effect occurs only near first-order transitions; i.e., the same weak disorder in other regions is not important [11]. Qualitatively similar results were found to appear also in other first-order transitions of the two-orbital model, such as for the FM-CO(CE state) level crossing [2] using 4×4 and $4 \times 4 \times 2$ clusters. Note also that here and in all the discussion below it has been checked that the MC results correspond to *equilibrium* properties: a variety of different starting configurations leads to the same results.

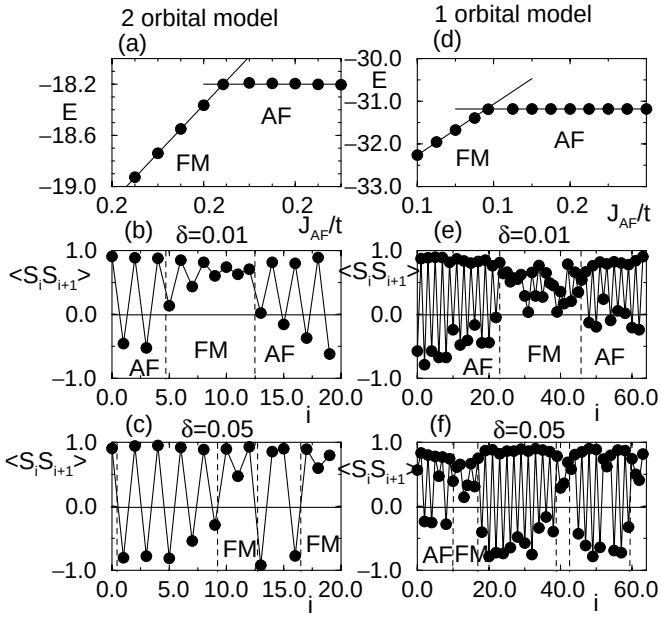

FIG. 1. (a)–(c) are MC results for the two-orbital model with $\langle n\rangle = 0.5$, $T = 1/100$, $J_{\rm H} = \infty$, $\lambda = 1.2$, $t = 1$, PBC, and $L = 20$. (a) is the energy per site vs $J_{\rm AF}/t$ for the nondisordered model; (b) MC averaged nearest-neighbor t_{2g}-spin correlations vs position along the chain (denoted by i) for one set of random t_{ab}^{α} and $J_{\rm AF}$ couplings ($J_{\rm AF}/t$ at every site is between $0.21 - \delta$ and $0.21 + \delta$, with $\delta = 0.01$). FM and AF regions are shown; (c) same as (b) but with $\delta = 0.05$; (d)–(f) results for the one-orbital model with $\langle n\rangle = 0.5$, $T = 1/70$, $J_{\rm H} = \infty$, $t = 1$, OBC, and $L = 64$. (d) is energy per site vs $J_{\rm AF}$ for the nondisordered model, showing the FM-AF states level crossing at $J_{\rm AF} \sim 0.14$; (e) are the MC averaged nearest-neighbor t_{2g}-spin correlations vs position for one distribution of random hoppings and t_{2g} exchanges, such that $J_{\rm AF}/t$ is between $0.14 - \delta$ and $0.14 + \delta$, with $\delta = 0.01$; (f) same as (e) but with $\delta = 0.05$.

The well-known one-orbital model [5] presents the same behavior as the two-orbital one, and larger lattices can be studied. This model contains hopping for only one species of e_g electrons (regulated by t), a FM Hund coupling $J_{\rm H}$ linking the e_g and (classical) t_{2g} spins, and a direct exchange $J_{\rm AF}$ among the t_{2g} spins. This model also has a first-order transition at $x = 0.5$ as $J_{\rm AF}/t$ varies [10]. It involves equal-density metallic FM and insulating AF states, the latter with a similar spin structure as the AF state of Figs. 1a–1c. To investigate disorder effects, $J_{\rm AF}$ at every site is randomly selected in the interval $[J_{\rm AF}^c - \delta, J_{\rm AF}^c + \delta]$ [12], where $J_{\rm AF}^c \sim 0.14$ is the critical first-order transition coupling at $J_H = \infty$, $t = 1$, and $T = 1/70$ in the nondisordered limit (Fig. 1d). In Fig. 1e, results of a MC simulation corresponding to a representative set of random couplings $(t, J_{\rm AF})$ centered at 0.14 are shown. As in the two-orbital case, FM and AF clusters, this time as large as $20a$, are obtained. If the range of possible $(t, J_{\rm AF})$ increases, the cluster size decreases (Fig. 1f) [13].

The nondisordered one-orbital model has another prominent first-order transition corresponding to a discontinuity in the density $\langle n\rangle$ vs chemical potential μ [5]. The direct interpretation of such a result is the presence of PS between competing FM-AF states [5]. However, in the context emphasized here the focus shifts from the transition properties to the effect of disorder on the $\langle n\rangle$ discontinuity itself. Disorder is here naturally introduced as a site-dependent chemical potential of the form $\sum_i \phi_i n_i$, where ϕ_i is randomly selected in the interval $[-\frac{W}{2}, +\frac{W}{2}]$, and n_i is the number operator at site i. Results of a standard MC simulation (averaged over 100 disorder configurations) for a $L = 20$ sites chain of the disordered one-orbital model are in Fig. 2a. For the values of W studied here, $\langle n\rangle$ is now continuous. For small W, the first-order transition is replaced by a rapid crossover, where the compressibility remains high, suggesting the formation of large clusters. This is confirmed in Fig. 2b where the nearest-neighbor t_{2g}-spin correlations are shown for a long chain, two disorder configurations, and one (typical) MC snapshot for each [14]. Once again, reducing W increases the cluster sizes. It was also observed that the mixed-phase ground state leads to a *pseudogap* in the $T \sim 0$ density of states (DOS) (Fig. 2c) [15]. An analogous pseudogap was also

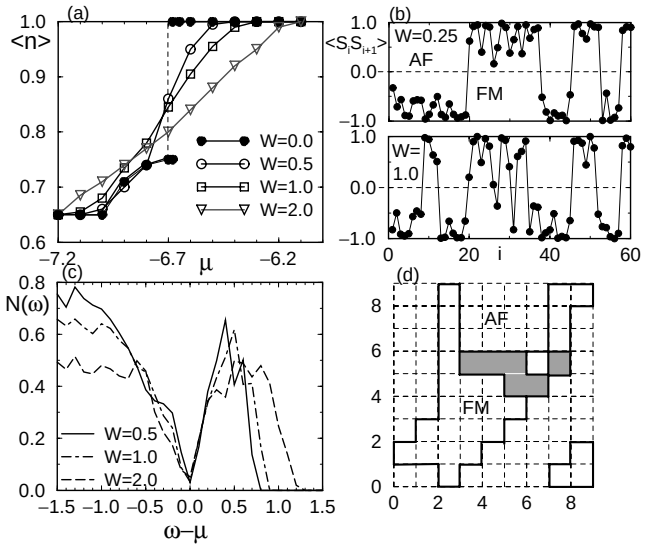

FIG. 2. Results of a MC simulation of the one-orbital model with a random chemical potential, PBC, $J_{\rm H} = 8.0$, and $J_{\rm AF} = 0.0$, in units of $t = 1$. (a) $\langle n \rangle$ vs μ for a $L = 20$ chain at $T = 1/75$ using 24 000 MC sweeps per $\{\phi_i\}$ set. Results are averages over $\sim$100 of $\{\phi_i\}$ configurations for the W's shown; (b) nearest-neighbors t_{2g}-spin correlations vs location along a $L = 60$ chain with $\mu = -6.7$ and $T = 1/75$. Shown are results for one representative MC snapshot, $W = 0.25$ (upper panel) and $W = 1.0$ (lower panel). Other snapshots differ from this one only by small fluctuations. The clusters remain pinned as the simulation evolves; (c) DOS at $T = 1/75$, $L = 20$, and $\mu = -6.7$. The average density is $\langle n \rangle \sim 0.87$; (d) results of a representative MC snapshot for an 8×8 cluster, $T = 1/50$, $\mu = -6.2$ (close to critical value), and $W = 1.0$. Regions with FM or AF nearest-neighbor t_{2g}-spin correlations are shown. The shaded area is an AF region in the absence of external magnetic fields, which becomes FM with a small field $h = 0.01$.

observed working with the two-orbital model. Similar results as in Figs. 2a–2c were also found in two dimensions (2D) (Fig. 2d) and thus the large cluster formation does not depend on pathological properties of 1D systems [16]. Figure 2d also illustrates an important effect of a clustered state: a weak magnetic field as small as 0.01 can link separated FM clusters through a percolative process, as observed experimentally.

The universality of the MC simulation results suggest that there is a general principle behind them. To understand this effect let us briefly review the phenomenology of the random-field Ising model (RFIM) [17] defined by $H = -J \sum_{\langle ij \rangle} S_i S_j - \sum_i h_i S_i$, where $S_i = \pm 1$, and the rest of the notation is standard. The random fields $\{h_i\}$ have the properties $[h_i]_{\rm av} = 0$ and $[h_i^2]_{\rm av} = h^2$, where h is the width of the distribution, and $[\ldots]_{\rm av}$ is the average over the fields. In manganites, $S_i = \pm 1$ would represent the competing metallic and insulating states on a small region of space centered at i. The random field mimics the t_{ab}^{α} and $J_{\rm AF}$ fluctuations locally favoring one state over the other. Without disorder, the $T = 0$ Ising model has a first-order transition located at zero magnetic field between the two fully ordered states, analogous to the first-order transitions of nondisordered manganite models [2]. However, at $h \neq 0$ the Ising transition is drastically modified [17]. Key arguments guiding RFIM investigations [18] can be restated for manganites. Working close to a first-order transition, consider that in a region of phase I (either AF or FM), a phase-II bubble of radius R is created. The energy cost is proportional to the domain wall area. To stabilize the bubble an energy compensation originating in the $(t, J_{\rm AF})$ disorder is needed. Consider the average hopping inside the bubble using $S_R = \sum_l t_l$, where l labels bonds and t_l is the hopping deviation at bond l from its nondisordered value, the latter fixed at the critical coupling of the first-order transition without disorder. Although the random hopping deviations mostly cancel inside the bubble, important fluctuations survive. In particular, the S_R standard deviation is $\sigma_{S_R} = (\Delta t) R^{d/2}$ (d is the spatial dimension) since $[t_l t_{l'}]_{\rm av} = (\Delta t)^2 \delta_{ll'}$, with (Δt) the width of the random hopping distribution about the nondisordered value. Similar expressions hold for the $J_{\rm AF}$ fluctuations. Even though individual random deviations t_l cannot exceed a (small number) Δt, the strength of the overall fluctuations can be fairly large.

To provide qualitative guidance to manganite experts, standard MC simulations of the RFIM were performed. In Fig. 3a, low temperature results are shown for one representative set $\{h_i\}$, individually taken from $[-W, +W]$ with $W = 3.0$ ($J = 1, W = \sqrt{3}\, h$). The formation of large coexisting clusters is clear, even with uncorrelated random fields at neighboring sites. Using the same set $\{h_i\}$ as in Fig. 3a but rescaling its intensity with W, Fig. 3b shows that as W is reduced the typical cluster sizes rapidly grow. These clusters can be made as large as those found in experiments ($250a$) adjusting W (Fig. 3c). This figure also illustrates the influence of an external field $H_{\rm ext} \sum_i S_i$. As $H_{\rm ext}$ grows, the region most affected by the field is the surface of the clusters. This suppresses the narrowest portions of the spin-down regions (Fig. 3c), inducing a connection among separated spin-up domains (as in Fig. 2d). Then, as $H_{\rm ext}$ increases, a percolative transition is to be expected. Similar results were here found at zero field, decreasing the temperature.

Based on the RFIM-manganite analogy, the picture described here predicts a metal-insulator percolative transition in manganites as chemical compositions, temperatures, or magnetic fields are varied near first-order transitions. However, even though manganite models and the RFIM have qualitatively similar behavior, subtle manganite properties such as critical exponents at the metal-insulator transition cannot be easily predicted (the transition is continuous after disorder is included). For instance, critical properties may be affected by the 1D character of the zigzag chains of the planar CE state [19]. The critical dimension d_c, related with long-distance properties, may be different between realistic manganite models and simple spin systems: whether both models

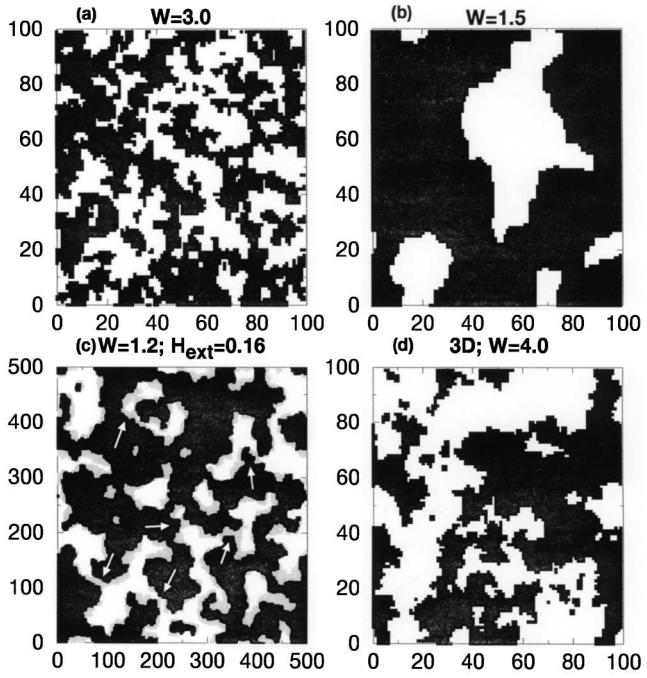

FIG. 3. Results of a MC simulation of the RFIM at $T = 0.4$ ($J = 1$), with PBC. The dark (white) small squares represent spins up (down). At $T = 0.4$ the thermal fluctuations appear negligible and the results shown are those of the lowest energy configuration. (a) was obtained for $W = 3$, $H_{\text{ext}} = 0$ using a 100×100 cluster and one set of random fields $\{h_i\}$; (b) same as (a) but with $W = 1.5$. The cluster sizes are now larger; (c) results using a 500×500 cluster with $W = 1.2$ and for one configuration of random fields. The dark regions are spins up in the $H_{\text{ext}} = 0$ case, the grey regions are spins down at zero field that have flipped to up at $H_{\text{ext}} = 0.16$, while the white regions have spins down with and without the field. The percolativelike features of the giant clusters are apparent in the zero field results. Special places are marked by arrows where narrow spin-down regions have flipped linking spin-up domains; (d) results for the RFIM on a 100^3 cluster with disorder. A representative slice at constant z-coordinate is shown.

belong to the same universality class is a subtle question beyond the scope of this effort. Moreover, Fig. 3d shows that even at the RFIM critical dimension large coexisting clusters *still* exist. Clearly the RFIM and electronic models share a common local tendency to large cluster formation in *any* dimension.

Summarizing, the giant clusters in manganites [3,4] are conjectured to be caused by quenched disorder in the couplings (t_{ab}^{α} and J_{AF}), induced by chemical substitution, and which affect transitions that otherwise would be of first order without disorder. The mixed-phase state presented in Figs. 1a–1f involves clusters with equal electronic density, complementing the PS scenario which involves regions with different densities [5]. Although nondisordered models remain crucial to determining the competing tendencies in manganites, disordering effects appear necessary to reproduce the subtle percolative nature of the metal-insulator transition and the conspicuous presence of μm domains in these compounds [3,4]. The present observations are very general, and the formation of coexisting giant clusters when two states are in competition through first-order transitions should be a phenomenon frequently present in transition-metal oxides and related compounds [20].

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[11] At this early stage in the calculations it is difficult to quantify how close to the first-order transition one must be in real manganites to observe the effect.
[12] Simulations with other distributions of random numbers lead to similar results.
[13] Open boundary conditions (OBC) were used in Figs. 1d–1f, and periodic boundary conditions (PBC) in Figs. 1a–1c, to show that large cluster formation occurs in both cases.
[14] These results are very similar if MC averages are made, i.e., the system is basically frozen into an inhomogeneous ground state with large AF and FM clusters of size $\sim 10-20a$, as in Figs. 1b and 1e.
[15] As it occurs in nondisordered models at particular densities [A. Moreo *et al.,* Phys. Rev. Lett. **83**, 2773 (1999)].
[16] In the example studied in Figs. 2a–2d, the AF-FM regions have different electronic densities, complementing the results of Figs. 1a–1f with equal-density clusters.
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