P H Y S I C A L   R E V I E W   L E T T E R S

Coulomb Interactions and Nanoscale Electronic Inhomogeneities in Manganites

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We study electronic inhomogeneities in manganites using simulations on a microscopic model with Coulomb interactions amongst two electronic fluids—one localized (polaronic), the other extended—and dopant ions. The long range Coulomb interactions frustrate phase separation induced by the large on site repulsion between the fluids. A single phase ensues which is inhomogeneous at a nanoscale, but homogeneous on mesoscales, with many features that agree with experiments. This, we argue, is the origin of nanoscale inhomogeneities in manganites, rather than phase competition or disorder effects.

A generic characteristic of complex solids such as doped manganites [1–3], cuprates [4], and cobaltates [5] seems to be the coexistence of patches of metallic and insulating regions (often called "phases"). This "electronic inhomogeneity" can vary from nanometers to microns and can be static or dynamic [1–5]. Questions as to whether this can be characterized as "electronic softness" [6] and is a defining feature of these materials, its origins, and role in determining their electronic properties, etc., are among the most actively explored issues. However, proposed mechanisms [2,7] are based on simplified models that ignore important quantum degrees of freedom and do not appeal to realistic physical parameters, and, therefore, do not adequately address the specifics of the scale and nature of inhomogeneities in the actual systems.

Motivated by the fact that phenomena of electronic inhomogeneities came to prominent attention first in manganites [1], in this Letter we address these issues using simulations of a new microscopic model for manganites with realistic physical parameters. Our model for doped manganites ($Re_{1-x}Ak_x MnO_3$, Re is rare earth, Ak is alkaline earth) is obtained by adding two new and critical ingredients, namely, the long range Coulomb interaction and dopant ion disorder to the recently proposed ℓb model for manganites [8,9].

The ℓb model [8,9] uses the idea that under the conditions prevailing in the doped manganites, the electrons populating the doubly degenerate e_g states centered at the Mn sites spontaneously reorganize themselves into two types of coexisting electron fluids. One is obtained by populating essentially site localized states labeled ℓ which are polaronic, with strong local Jahn-Teller (JT) distortions of the oxygen octahedra, an energy gain $E_{JT} \sim 0.5$ eV [10] and exponentially reduced intersite hopping. The other, labeled b, is a fluid of broadband, nonpolaronic electrons, with no associated lattice distortions, and undiminished hopping amplitudes. For a generic x in the regime ($0.1 \lesssim x \lesssim 0.4$) of interest to us in this Letter, manganites do not exhibit orbital long-range order and can be regarded as

"orbital liquids". Hence one can characterize the hopping of the b electrons by a single orbitally averaged number $t(\sim 0.2)$ eV and ignore the e_g orbital index. There is a strong local repulsion between the two fluids, as double occupancy on a site costs an extra Coulomb energy $U(\sim 5$ eV). The spins of ℓ and b are enslaved to the Mn-t_{2g} spins ($S = 3/2$) on site due to the large ferromagnetic Hund's coupling $J_H(\sim 2$ eV). Furthermore, there is a new, occupancy dependent, ferromagnetic nearest neighbor exchange coupling [9] between the t_{2g} core spins, of order $x(1 - x)t^2/E_{JT}$, referred to as "virtual double exchange," which overwhelms the normal superexchange for $x \gtrsim 0.1$. Hence, as is seen in manganites over the above mentioned range of doping x, the ground state is ferromagnetic (insulating or metallic). In the simplest picture, assuming all the t_{2g} spins and the e_g spins to be aligned parallel, the ℓ and b electrons can be regarded as spinless, leading naturally to the Falicov-Kimball-like [11] ℓb Hamiltonian

$$H_{\ell b} = -E_{JT}\sum_i n_{\ell i} - t\sum_{\langle ij \rangle}(b_i^\dagger b_j + \text{H.c.}) + U\sum_i n_{\ell i}n_{bi}$$

(1)

Here $\ell_i^\dagger$ and $b_i^\dagger$ create ℓ polarons and b electrons, respectively, at the sites i of a cubic Mn lattice, and $n_{\ell i} \equiv \ell_i^\dagger \ell_i$ and $n_{bi} \equiv b_i^\dagger b_i$ are the corresponding number operators.

While the ℓb model successfully describes many puzzling phenomena (including colossal magnetoresistance) in manganites, it is unable to address the issue of electronic inhomogeneities. In this Letter we introduce the long range Coulomb interactions and dopant ion disorder that are necessarily present in the doped manganites, and indeed, in other correlated oxides, and show below that these are crucial to obtain electronic inhomogeneities. This is done at the simplest level by associating quenched (spatially fixed) charges $-|e|$ (with respect to the Re^{3+} background) at a fraction x of random, body centered, "Ak sites," and annealed charges $+|e|$ with the corresponding deficits in

the Mn-e_g electron occupancy (overall reduced to $(1 - x)$ per site). In terms of the hole operator ($h_i^\dagger \equiv \ell_i$ which removes an ℓ polaron at site i), and the electron charge operator $q_i \equiv h_i^\dagger h_i - b_i^\dagger b_i$, which has the average value x per site because of overall charge neutrality, the extended model Hamiltonian is

$$H = H_{\ell b} + H_C; \qquad H_C = \sum_i \Phi_i q_i + \frac{V_0}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}. \quad (2)$$

The Coulomb term H_C has two parts; the charge at site i has energy $q_i \Phi_i$, where Φ_i is the electrostatic potential there due to dopant ions (Ak^{2+} ions), and the interaction between the charges at site i and j leads to an energy $V_0 \frac{q_i q_j}{r_{ij}}$.

We now describe the results of numerical simulations of the above model (2) on finite $3d$ periodic lattices of sizes up to 20^3. The electrostatic interaction is treated in the Hartree approximation, using the mean b electron charge at site i; i.e., q_i is approximated by $\langle q_i \rangle = h_i^\dagger h_i - \langle b_i^\dagger b_i \rangle$. All electrostatic energies and potentials are accurately calculated via the Ewald technique [12]. Furthermore, since U is large, for simplicity we take the $U \rightarrow \infty$ limit, i.e., assume that b electrons do not hop to sites occupied by ℓ, so the two kinds of electrons form disjoint clusters. On a hole-cluster, which has two or more h sites, each accessible to the other by electron hops, which we will refer to as a "clump," the b electron energy levels are determined exactly by solving the intersite Hamiltonian $H_b = -t \sum_{ij} (b_i^\dagger b_j + \text{H.c.})$. The ground state (i.e., at zero temperature) is obtained by starting from an overall charge neutral trial configuration of random ℓ polaronic sites, and performing electron transfers that lower energy, till none such exist. Some of these are of the type $\ell - h$ as in a classical Coulomb glass [13], in which an ℓ electron is moved to a hole site. In addition, there are $\ell - b$ and $b - b$ transfers involving one or two b states whose energy is quantum mechanically obtained for a particular clump structure. At each iteration then, we find the best possible transfer, i.e., the one which lowers most the (occupied) single particle levels whose energies include Coulomb interactions. Then we perform the transfer, and update the clump structure, if necessary, i.e., redistribute the b electrons in the new clumps. The process is repeated until the final b-clump–ℓ-polaron structure is stable against all further electron transfers. This is a new generalization of the common Coulomb glass simulation [13], which includes the quantum mechanically obtained b states within their clump or puddle.

In the discussion below, all length scales are normalized by the lattice parameter a, and we use dimensionless energy parameters E_{JT} and V_0, scaled by the hopping amplitude t. Realistic values [10] for manganites are $2.0 \leq E_{JT} \leq 3.0$ and $0.01 \leq V_0 \leq 0.1$ with $t \approx 0.2$ eV. In the absence of V_0 (i.e., in the ℓb model), the system "phase

separates"; i.e., holes move to one side of the box and several ℓ polarons are converted to b electrons that occupy the low energy band states with energies below $-E_{JT}$ in this large clump (see inset, Fig. 1). This phase separation is due to strong local correlations (large U between ℓ s and b s) and is in agreement with known results [11]. The presence of V_0 renders this phase separation energetically unfavorable, and intermixes the phases as expected [14]. The favored electronic configurations strongly depend on the JT energy E_{JT} and the doping x. Two examples are shown in Fig. 1. For a given E_{JT}, there are two critical values of doping, x_{c1} and x_{c2}, as shown in Fig. 2. For $x < x_{c1}$, there are no occupied b-electron states in the system, and the holes form an insulating [15] Coulomb glass [13]. For doping larger than x_{c1}, some occupied b-electron puddles appear [Fig. 1 (left)]. On further increase of doping, clumps interconnect and percolate through the simulation box [Fig. 1 (right)], giving rise to the possibility of occupancy of b states extended throughout the system, and hence metallicity. The results for x_{c1} and x_{c2} are insensitive to V_0 for $V_0 \leq 0.5$ (the typical value of $0.01 \leq V_0 \leq 0.1$ in manganites falls in this range). For larger values of V_0, the clumps are never occupied by electrons, and the system is an insulator for all $x < 0.5$.

These results are better understood by a study of the density of states (DOS) of the ℓ polarons and b electrons shown in Fig. 3. We find that the chemical potential μ (Fig. 3) goes essentially as $\mu = -E_{JT} + V_0$. The polarons form a Coulomb glass with a soft gap (Fig. 3, inset) at the chemical potential, as in the classical Coulomb glass [13]. Furthermore, the polarons have their energies spread over an energy scale of order V_0 [16]. The b electrons have a bandlike DOS with a bandwidth that depends on the doping x. In fact, we find that the effective half-bandwidth of
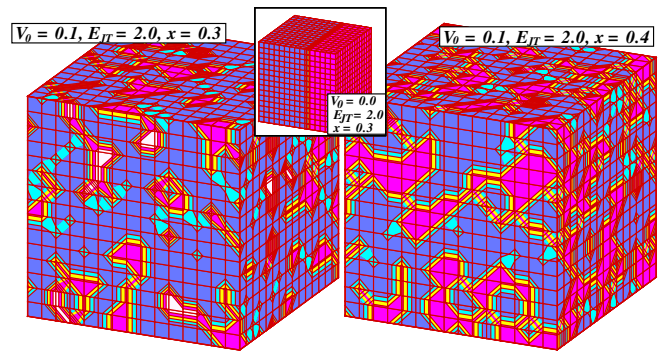

FIG. 1 (color online). Real space electronic distribution obtained from simulations on a 16^3 cube. Magenta (darkest) denotes hole clumps with occupied b electrons, white (lightest) denotes hole clumps with no b electrons, cyan (2nd lightest) denote singleton holes, and light blue (2nd darkest) represents regions with ℓ polarons. Left: Isolated clumps with occupied b electrons (b-electron puddles). Right: Larger doping; percolating clumps. Inset: "macroscopic phase separation" absence of long range Coulomb interaction ($V_0 = 0.0$).
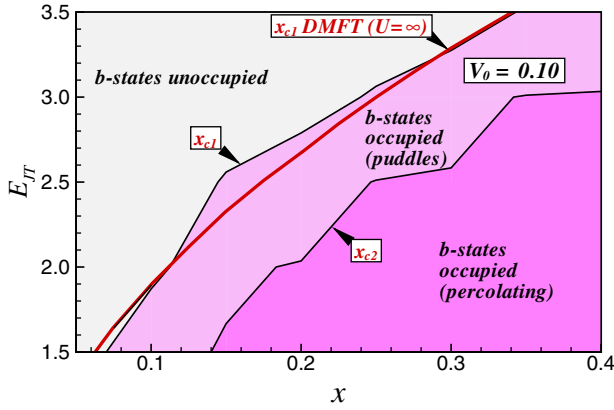
FIG. 2 (color online).   Critical doping levels x_{c1} and x_{c2}. x_{c1} separates the lightest region, where no b states are occupied, from the intermediate shade region, which has b states occupied in puddles. The darkest shaded region, with $x > x_{c2}$, has some occupied b states that percolate through the 10^3 box. Results shown are averages over 100 realizations of the Ak ions. The solid line corresponds to the DMFT result [8] for x_{c1}.

the b electrons scales as $D_{\text{eff}} = D_0\sqrt{x}$ (D_0, the bare half-bandwidth, $= 6t$ for the cubic lattice), in remarkable agreement with an earlier [8] single site dynamical mean field theory (DMFT) result obtained for (1). Furthermore, the simulation results show that the b band center (marked by E_b in the figure) is not affected by doping, and scales as $E_b \approx V_0$ (for small $V_0 \lesssim 0.5$).

The behavior of the chemical potential and the band center arises from the random distribution of Ak ions that plays an important role in determining the real space structure. From a study of the positional correlation function between two holes, and a hole and an Ak ion, we

FIG. 3 (color online).   DOS of ℓ polarons and b electrons (average over 100 random initial conditions, size: 10^3). The occupied states are shaded. The chemical potential μ and the b band center E_b are marked. Results shown are averages over 100 realizations of the Ak ions. Inset: soft Coulomb gap of the polarons.

find that the holes tend to cluster around the Ak ions. Furthermore, the electrostatic screening is quite strong in this system in that these correlation functions (both hole-hole and hole-Ak ion) reach a plateau within a few lattice spacings. Since the holes cluster around the (oppositely charged) Ak ions, it is clear that a typical ℓ polaron will have a larger number of ℓ-polaron neighbors than hole sites. Thus, the ℓ-polaron sites see, on an average, an electrostatic potential of order V_0, and the average energy of an ℓ polaron is increased from $-E_{\text{JT}}$ to $-E_{\text{JT}} + V_0$. Since the chemical potential of a Coulomb glass is the average energy of the states [13], it follows that the chemical potential is $-E_{\text{JT}} + V_0$. Similarly, every hole site sees an electrostatic potential of V_0, implying that the b band center is placed at V_0. These observations and the fact that the b bandwidth scales as $\sqrt{x}$, suggests that the minimum doping for the b-band bottom to touch the chemical potential (i.e., for b-state occupancy) is $x_{c1} = (\frac{E_{\text{JT}}}{D_0})^2$, the same as the DMFT prediction [8] for (1).

However, we note that the simulation results include important new physics not contained in the DMFT [8], namely, that b state occupancy does not by itself make the system a metal, as these states are localized inside the clumps. Based on inverse participation ratio, geometric percolation of the clumps and Kubo conductivity calculations, we have good estimates for a second, higher, critical doping level, x_{c2}, at which the system actually becomes a metal (Fig. 2), for which the occupied b states should extend across the simulation box. Our results suggest that for $x < x_{c1}$, electrical transport should be that of a classical Coulomb glass ($\sigma \sim e^{-A/\sqrt{T}}$). For $x_{c1} < x < x_{c2}$, the transport should have two contributions—the first a Coulomb glass contribution of the ℓ polarons and the second a variable range type interpuddle hopping of the electrons in the b puddles, as is indeed observed in doped manganites [17]. For $x > x_{c2}$ we find a highly resistive metal.

Another interesting aspect is the clump size R, and its dependence on V_0. For a (fictitious) uniform distribution of Ak ions, one can show by an approximate analytical calculation that $R \sim \frac{1}{\sqrt{V_0}}$, corresponding, for $E_{\text{JT}} = 2.5$ and $x = 0.3$, to clump sizes between 10 and 5 lattice spacings for V_0 between 0.01 and 0.1. The clump sizes for the more realistic, random, distribution of Ak ions obtained from our simulations are much smaller; even a very small V_0 produces clumps that are four to five lattice spacings that arises from the "screening cloud" of holes or b electrons around the clusters of dopant Ak ions. This clump size is essentially independent of V_0 for realistic values of V_0—in stark contrast to the analytical result above. Thus, the long range Coulomb interaction is a "singular perturbation" that prevents macroscopic phase separation, but the sizes and the distribution of the clumps are determined by the random distribution of the Ak ions. Thus we conclude that doped manganites as modeled by (2) are necessarily and
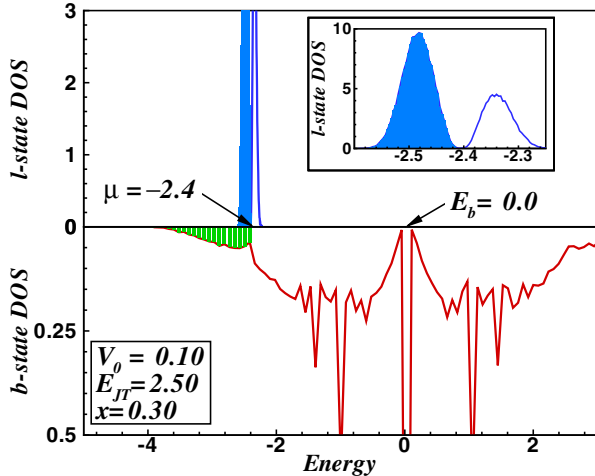
intrinsically electronically inhomogeneous, on a nanometric scale.

Our Hamiltonian and energy parameters are very realistic especially in low bandwidth manganites with a large ferromagnetic region in their phase diagram. In sharp contrast to some of the earlier scenarios proposed in manganites, the nanoscale inhomogeneities we obtain are not due to "phase competition" induced "phase separation" between "insulating" and "metallic" phases frustrated by disorder as suggested by studies on simple models (without appeal to realistic physical parameters), such as spin Hamiltonians [2] or Hamiltonians with two localized states and electron lattice coupling [7]. Rather, they arise due to the long ranged Coulomb interactions frustrating the phase separation induced by strong local correlations. The mechanism itself has been discussed before [2,14], but to the best of our knowledge, ours is the first quantitative study on a realistic model for any correlated oxide.

We emphasize that the nanoscale inhomogeneities we obtain are present in both the insulating and metallic phases of doped manganites between which one has a transition as a function of doping, at x_{c2}, and furthermore, as is clear from Figs. 1 and 2, each of these constitutes a valid, single, thermodynamic phase that is homogeneous on mesoscales. These results are in conformity with the electron holography results of Loudon et al. [18], where even the ferrometallic state is seen to have interspersed in it nanoscale "insulating regions," which in the context of the present simulation are just the ℓ clusters [19].

Furthermore, our work suggests that mesoscale phase separation [2], or proximity to multicriticality [20], are not essential for explaining CMR in manganites. Given the correspondence between the simulation results for the extended ℓb model and the (homogeneous) DMFT results for the simple ℓb model, the single metallic phase obtained here will show a ferrometal to parainsulator transition as well as CMR due to strong Hund's coupling between the Mn t_{2g} core spins and the b electrons and thermal fluctuations. As shown elsewhere [9], the CMR arises from small field induced changes in the energetics of the extended b states which are responsible for charge transport, and the consequent exponential changes in their occupancy. Indeed, there are many manganites without mesoscale inhomogeneities that show colossal responses [21]. Finally, our work reinforces suggestions that the mesoscale patterns seen in experiments arise from other sources such as long range elastic strains, possibly due to defects [3,22]. In our model, they can be generated from the strain dependence of the local energy parameters such as E_{JT} and t.

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