Recent computational studies of models for manganese oxides have revealed a rich phase diagram, not anticipated in early calculations in this context performed in the 1950’s and 60’s. In particular, the transition between the antiferromagnetic insulator state of the hole-undoped limit and the ferromagnetic metal at finite hole-density was found to occur through a mixed-phase process. When extended Coulomb interactions are included, a microscopically charge inhomogeneous state should be stabilized. These phase separation tendencies, also present at low electronic densities, influence the properties of the ferromagnetic region by increasing charge fluctuations. Experimental data reviewed here using several techniques for manganites and other materials are consistent with this scenario. Similarities with results previously discussed in the context of cuprates are clear from this analysis, although the phase segregation tendencies in manganites seem stronger.

I. Introduction

Hole-doped manganese oxides with a perovskite structure have stimulated considerable scientific and technological interest due to their exotic electronic and magnetic properties [1]. These manganites have a chemical composition $\text{R}_{1-x}A_x\text{MnO}_3$, with $\text{R}$ a rare-earth ion and $A$ a divalent ion such as Ca, Sr, Ba, or Pb. They present an unusual magnetoresistance (MR) effect, whereby magnetic fields induce large changes in their resistivity $\rho$, a property that may find applications in sensor technologies such as that utilized in magnetic storage devices. For example, in La-Ca-Mn-O thin films, the ratio $(\rho(0) - \rho(\text{H}))/\rho(\text{H})$, with $\rho(\text{H})$ the resistivity in a magnetic field $\text{H}$, can be as large as $10^4$ at 77K ($\text{H}=6\text{T}$). The term “colossal” magnetoresistance (CMR) has been coined to describe this effect [2].

The unusual properties of manganese oxides challenge our current understanding of transition-metal oxides, and define a basic research problem that involves an interplay between the charge, spin, phononic, and orbital degrees of freedom. Manganites have a rich phase diagram [3] that includes a well-known ferromagnetic (FM) phase that spans a robust range of electronic densities. The CMR effects have been observed particularly at small hole densities $x$ but also at $x\sim0.5$, which are the density limits of the FM-phase. The strength of the MR effect increases as the electronic bandwidth is decreased through chemical substitution [1], which also reduces the Curie critical temperature $T_C$. At hole concentrations $x\sim0.5$, an antiferromagnetic (AF) charge-ordered (CO) insulating state, discussed by Goodenough [4], is involved in the CMR effect, which at these densities is extraordinarily large [5].

In the undoped limit, the Mn$^{3+}$ ions have four electrons in the 3d-shell, and they are surrounded by oxygens O$^{2-}$ forming an octahedron. This crystal environment breaks the full rotational invariance, causing the two $e_g$- and three $t_{2g}$-orbitals to split. The strong Hund coupling ($J_H$) in these systems favors the spin alignment of the four electrons in the active shell; on average three electrons populate the $t_{2g}$-orbitals and one occupies the $e_g$-states. The $t_{2g}$-electrons are mainly localized, whereas the $e_g$-electrons are mobile and use O p-orbitals as a bridge between Mn ions. When the manganites are doped with holes through chemical substitution, Mn$^{4+}$-ions with only three $t_{2g}$-electrons are formed. In addition, in the undoped limit the $e_g$-degeneracy is split due to Jahn-Teller (JT) distortions; as a consequence, a one-orbital approximation has been frequently used since the earliest theoretical studies [6]. For these reasons, typical electronic models for the manganites include at least a kinetic energy contribution for the $e_g$-electrons, regulated by a hopping amplitude $t$, and a strong $J_H$ coupling contribution between the $e_g$- and $t_{2g}$-spins. The localized spin is large enough $(3/2)$ to be approximated by a classical spin, which simplifies the calculations. Here this model will be simply referred to as the “one-orbital” model, although other names are sometimes used, such as FM Kondo model.

This formalism leads to a natural explanation for the FM-phase of the manganites, because carriers energetically prefer to polarize the spins in their vicinity. When an $e_g$-electron jumps between nearest-neighbor ions, it does not pay an energy $J_H$ if all of the spins involved are parallel. The hole-spin scattering is minimized in this process, and the kinetic energy of the mobile carriers is optimized. This mechanism is usually referred to as double-exchange (DE) [6,7]. As the carrier density grows, the FM distortions around the holes start overlapping and the ground state becomes fully ferromagnetic.

Currently there is not much controversy about the qualitative validity of DE to stabilize a FM-state. However, several experimental results suggest that more com-
plex ideas are needed to explain the main properties of manganese oxides. For instance, above $T_c$ and for a wide range of densities, several manganites exhibit insulating behavior of unclear origin that contributes to the large MR results. The low-temperature ($T$) phase diagram of these materials has a complex structure [3], not predicted by DE, that includes insulating AF- and CO-phases, orbital ordering, FM-insulating regimes, and, as discussed extensively below, tendencies toward the formation of charge inhomogeneities, even within the FM-phase. To address the strong MR effects and the overall phase diagram of manganites, the DE framework must be supplemented with more refined ideas.

II. Phase Separation in the One-Orbital Model

Motivated by new experimental research on manganese oxides, there has been considerable theoretical work in the analysis of models for these materials. Several many-body techniques for modeling strongly correlated electron systems were developed and improved during recent efforts to understand high-temperature superconductors, and thus it is natural to apply some of these methods to manganite models. Of particular relevance here are the computational techniques that allow for an unbiased analysis of correlated models on finite clusters [8]. The first comprehensive computational analysis of the one-orbital model was presented by Yunoki et al. [9] using classical spins for the $t_2g$-electrons and the Monte Carlo (MC) technique. Several unexpected results were found in this study. In particular, when calculating the density of $e_g$-electrons $\langle n \rangle = (1 - x)$ as the chemical potential $\mu$ was varied, it was surprising to observe that some densities could not be stabilized; in other words, $\langle n \rangle$ was found to change discontinuously at special values of $\mu$. These densities are referred to as “unstable.” Alternative calculations in the canonical ensemble [9,10] where the density is fixed to arbitrary values, rather than being regulated by $\mu$, showed that at unstable densities, the resulting ground state is not homogeneous, but it is separated into two regions with differing densities. The two phases involved correspond to those that bound the unstable range of densities [9-11]. This phenomenon, which has been given the name of “phase separation” (PS), appears in many contexts, such as the familiar liquid-vapor coexistence in the phase diagram of water, and it is associated with the violation of the stability condition $\kappa^{-1} = (n)^2 \partial^2 E / \partial (n)^2 > 0$, with $E$ the energy of the system per unit volume, and $\kappa$ the compressibility.

In the realistic limit $J_H/t \gg 1$, phase separation occurs between hole-undoped $\langle n \rangle = 1$ and hole-rich $\langle n \rangle < 1$ phases [9-11]. Although the $e_g$- and $t_{2g}$-spins of the same ion tend to be parallel at large $J_H$, their relative orientation at one lattice-spacing depends on the density. At $\langle n \rangle = 1$, an AF arrangement results because the Pauli principle precludes movement of the electrons if all spins are aligned. However, at stable $\langle n \rangle < 1$ densities, DE forces the spins to be parallel, as computer studies have indicated [9-11]. Yunoki and Moreo [11] have shown that if an additional small Heisenberg coupling among the localized spins is introduced, PS occurs also at small $\langle n \rangle$, this time involving FM- $\langle n \rangle > 0$ and electron-undoped AF-states. Phase segregation near the hole-undoped and fully-doped limits implies that a spin-canted state [6] for the one-orbital model is not stable. Other authors arrived to similar conclusions after observing phase segregation tendencies using several analytical techniques [12-14]. If a spin-canted state is unequivocally found in experiments, mechanisms other than DeGennes’ [6] may be needed to explain it. Note also that a canted state is difficult to distinguish experimentally from a mixed AF-FM state.

It is interesting that PS behavior is not unique to manganese oxides. Indeed, the existence of PS in AF rare-earth compounds has been addressed by Nagaev for many years [15]. In these materials, there is a small density of electrons interacting with localized spins. Actually, Eu$_{1-x}$Gd$_x$Se has a very large MR effect similar to that observed in manganites [16,17]. Calculations in this context were performed using the one-orbital model mainly in the limit where the localized-conduction spin-spin coupling is smaller than the bandwidth (equivalent to $J_H \ll t$) and at small $\langle n \rangle$. Nevertheless, some of these results have been discussed also in the context of manganites [18]. Note that in the recently established phase diagram of the one-orbital model, PS occurs at both high- and low-electronic density [11]. Because the $\langle n \rangle \ll 1$ limit corresponds to the dilute AF semiconductors mentioned above, the computational studies confirm that these materials should also exhibit PS tendencies. A broad distribution of FM cluster sizes should be expected, with a concomitant distribution of electrons trapped in those clusters [19]. Gavilano et al. [20] have recently reported a two-phase mixed regime in these materials that may be related to intrinsic PS tendencies. Analogous results were also observed in other diluted magnetic semiconductors [21]. The analysis of experimental data in this context should certainly allow for the possibility of large-scale inhomogeneous states.

III. Phase Separation in the Two-orbitals Model

Most of the theoretical studies for manganites have been carried out using the one-orbital model, which certainly provides a useful playground for the test of qualitative ideas. However, quantitative calculations must necessarily include two active $e_g$-orbitals per Mn-ion to reproduce the orbital-ordering effects known to occur in these materials [22]. In addition, it has been argued that dynamical JT effects cannot be neglected [23], and the electron-JT-phonon coupling $\lambda$ should be important for the manganites.
FIG. 1. Phase diagram of the two-orbital model for manganites in one-dimension and $T \sim 0$ including Jahn-Teller phonons, obtained with Monte Carlo techniques [24]. S-F labels a spin-ferromagnetic configuration. O-F, O-AF, and O-D denote a state where the orbital degrees of freedom are ordered uniformly, staggered or they are disordered, respectively; PS indicates a phase separated state, and AF is an antiferromagnetic state. The Hund-coupling is $J_{\text{H}} = 8$, the Heisenberg coupling between localized classical spins $J' = 0.05$, both in units of the hopping among the same orbitals. The meaning of the dashed line is explained in the text.

Although computational studies accounting for JT-phonons are at their early stages, some illustrative results are already available. Yunoki et al. [24] recently reported the low-temperature phase diagram of a two-orbital model using the Monte Carlo method, and analyzed the results in a manner similar to the one-orbital case. The results are reproduced in Fig.1 for a one-dimensional (1D) system at large Hund coupling. The phase diagram is rich and includes a variety of phases such as metallic and insulating regimes with orbital order. The latter can be uniform, with the same combination of orbitals at every site, or staggered, with two combinations alternating between the even- and odd-sites of the lattice at $\langle n \rangle = 1$. Recently, our group observed that the density of states exhibits pseudogap behavior caused by the PS tendencies, both in the one- and two-orbital cases, in agreement with photoemission experiments for layered manganites [25]. Of special importance for the discussion here are the regions of unstable densities. Phase separation appears at small $c_{\text{e}}$-densities between an electron-undoped AF-state and a metallic uniform-orbital-ordered FM-state. The latter phase itself coexists at larger densities and intermediate values of $\lambda$ with an insulating $(\langle n \rangle = 1)$ staggered-orbital-ordered FM-state, in an orbital-induced PS process [24]. The overall results are qualitatively similar to those obtained with other model parameters, and in studies of 2D and 3D systems. Overall, PS tendencies are strong both in the one- and two-orbital models, and over a wide range of couplings. Similar tendencies have been recently observed including large on-site Hubbard interactions [26], which is reasonable because at intermediate and large electron-phonon coupling a negligible probability of on-site double-occupancy was found [24].

The macroscopic separation of two phases with different densities, and thus different charges, should actually be prevented by long-range Coulombic interactions, which were not incorporated into the one- and two-orbital models discussed thus far. Even including screening and polarization effects, a complete separation leads to a huge energy penalty. This finding immediately suggests that the two large regions involved in the process will break into smaller pieces to spread the charge more uniformly. These pieces are hereafter referred to as polarons if they consist of just one-carrier in a local environment that has been distorted by its presence. This distortion can involve nearby spins (magnetic polaron), nearby ions (lattice polaron), or both, in which case this object will be simply referred to as a “polaron.” However, the terms “clusters” or “droplets” are reserved for extended versions of the polarons, characteristics of a PS regime, containing several carriers inside a common large magnetic distortion or lattice distortion or both.

The present discussion suggests that in the regime of unstable densities the inclusion of extended Coulomb interactions will lead to a stable state, with clusters of one phase embedded in the other [see also (15)]. It is expected that the competition between the attractive DE tendencies among carriers and the Coulomb forces will determine the size and shape of the resulting clusters. Either sizable droplets or polarons may arise as the most likely configuration [27]. The stable state resulting from the inclusion of extended Coulomb interactions on an otherwise PS unstable regime will be referred to as a charge-inhomogeneous (CI) state. However, the ideas presented here will still be described as the “PS scenario,” with the understanding that only microscopic phase segregation is the resulting net effect of the DE-Coulomb competition. Related ideas have been previously discussed in the context of the cuprates [28], with attractive interactions generated by antiferromagnetism or phonons. An exception to the existence of only purely microscopic effects occurs if the competing phases have approximately the same density, as observed experimentally at $x = 0.5$ (discussed below). In this case, large-scale PS can be expected. Note also that the CI-state is certainly different from the metastable states that arise in a standard first-order transition. Figure 2 contains a cartoon-like version of possible charge arrangements in the CI-state, which are expected to fluctuate in shape, especially at high temperature where the clustering is dynamic. Unfortunately, actual calculations supporting a particular distribution are still lacking. Nevertheless, the presently available re-
sults are sufficient to establish dominant trends and to allow a qualitative comparison between theory and experiment, as shown below.

Phase separation in manganese oxides has clear similarities with the previously discussed charge inhomogeneities observed in copper and nickel oxides [28]. Actually, studies of 1D generalizations of the t-J model by Rivera et al. [29] showed that as the localized spin magnitude S grows, the phase diagram is increasingly dominated by either FM or PS tendencies. The importance of PS arises from the dominance of the Heisenberg interactions over the kinetic energies as S increases, which causes holes to be expelled from the AF-regions because they damage the spin environment. The tendency toward phase segregation decreases across the transition-metal-row, from a strong tendency in Mn, to a weak tendency in Cu [29]. The stripes observed in cuprates [28] could certainly appear in manganites as well through the competition of the DE attraction and Coulomb repulsion among clusters.

**IV. Influence of Phase Separation on the Ferromagnetic Phase**

A critical aspect of the scenario discussed here is the influence that the low-temperature PS regime exerts on the behavior of electrons at higher temperatures, and especially on the ordered phases which neighbor PS regimes. As an illustration, consider the lines of constant $\kappa(n)^2 = \langle n \rangle / \langle n^2 \rangle$ of the 1D one-orbital model at large $J_H$ (Fig. 3A). Because PS occurs through the divergence of $\kappa$, naturally this quantity is the largest at those densities where PS is observed (see above). A large $\kappa$ implies that strong charge fluctuations occur, because $\kappa \propto (N^2 - \langle N \rangle^2)$, with N the total number of particles. A characteristic crossover temperature for ferromagnetism $T_C^*$ occurs where the zero-momentum spin structure factor starts growing very rapidly as the temperature is reduced. $T_C^*$ is expected to become truly critical in higher dimensional systems, where also a finite critical temperature for PS is expected to exist. Figure 3A shows that the PS tendencies influence the neighboring FM-state because the compressibilities close to the PS regime, located at $0.8 \leq \langle n \rangle \leq 1.0$, are much larger than those at, e.g., $\langle n \rangle = 0.5$. This result implies that even within the FM-phase, which is uniform when time-averaged, there is a dynamical tendency toward cluster formation because $\kappa$ is large. The same situation occurs for $T > T_C^*$ and at low hole-densities.

This effect should influence transport properties, including resistivity. Although it is difficult to evaluate $\rho$ with finite-cluster techniques, crude estimations can be made using the inverse of the zero-frequency Drude weight found from the optical conductivity [11]. As an example, results are shown in Fig. 3B for the one-orbital model. This estimation of $\rho$ produces the qualitatively expected results, namely, it behaves as an insulator at small $x$ and rapidly decreases as $x$ increases, turning smoothly into a metal. Studies by our group using more sophisticated techniques connecting the cluster with ideal metals have recently been found to produce qualitatively similar data. The results compare well with experiments for Sr-doped compounds [30]. Starting from a regime with dynamical cluster formation above $T_C^*$, the metallic state can be obtained if the clusters grow in size as $T$ is reduced, eventually reaching the limit where percolation is possible. At this temperature, the carriers move over long distances and the metallic state is reached. The
same mechanism arises in polaronic theories [31] [see also (32)].

V. Comparing Theory with Experiments: the Phase Diagrams

The computational results are consistent with several experiments on a variety of manganese oxides. Consider, for example, La$_{1-x}$Sr$_x$MnO$_3$. The experimentally observed sharp increase in $\rho$ as $x$ decreases towards the undoped limit, both above and below $T_C$ [30], is difficult to explain if the only effect of the correlations were to induce a reduced effective electronic hopping $t_{\text{eff}} = t(\cos(\theta/2))$, where $\theta$ is the angle between nearest-neighbor sites [6]. In addition, the insulating properties of the intermediate region $0.0 < x < 0.16$ [30] do not fit into the simpler versions of the DE ideas. This regime is important because the CMR effect is maximized at the lowest $T_C$, that is, at the boundary between the metallic and insulating regions. Note also that recent experiments [33,34] for hole-densities slightly above $x=0.5$ showed that the ground state of the (La, Sr)-based manganese oxide is an A-type AF-metal with uniform $d_{x^2-y^2}$ orbital-order (Fig.4A). This phase, as well as the orbital-ordered $x=0$ A-type AF-insulator, does not appear in the one-orbital model [9]. For these reasons, La$_{1-x}$Sr$_x$MnO$_3$ does not seem a typical DE material when considered including all available densities, although at $x \sim 0.3$ Furukawa [35] showed that it has DE characteristics.

However, the experimental results mentioned above can be more naturally accounted for once PS tendencies and the coupling with JT-phonons are considered (narrower band materials are more complicated because of their $x=0.5$ CO-state, and they will be discussed below). Actually, it has already been argued that $\rho$ should rapidly grow as $x$ decreases due to the strong charge fluctuations at small $x$ caused by the nearby phase segregation regime (Fig.3B). In this context, the insulating state above $T_C$ of the lightly hole-doped (La, Sr)-compound can be rationalized as formed by clusters of one phase (FM or AF) embedded into the other. Even the experimentally observed A-type AF-metallic $d_{x^2-y^2}$-ordered phase at $x \sim 0.5$ (Fig.4A) can be related to the phase with similar characteristics near $x=0.5$ found in the theoretical calculations (Fig.1). Although simulations with the realistic hopping amplitudes needed to stabilize an A-type AF-state in a 3D environment have not been performed yet, at least the 1D and 2D FM tendencies, as well as the stabilization of a uniform orbital-ordering (Fig.1), are clear. If phenomenologically one assumes that $\lambda/t$ decreases with hole doping, the dashed-line in Fig.1 runs through the proper series of experimentally observed phases [33], namely, an insulating staggered orbital-ordered state at $x=0$, a charge-segregated regime at small $x$, a metallic orbital-disordered FM-phase at a higher density, and finally the $x \sim 0.5$ orbitally ordered FM-state compatible with A-type AF-order in dimensions $D < 3$ [36]. If it were possible to complete the phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ by synthesizing $x>0.6$ samples, the calculations predict a new mixed-phase, involving the A-type AF-metal with $x < 1$ and a G-type AF-insulator with $x = 1$, where large MR effects could potentially occur.

![FIG. 4. (a) Phase diagram of La$_{1-x}$Sr$_x$MnO$_3$, courtesy of Prof. Y. Tokura and Dr. Y. Tomioka, prepared with data taken from Ref. [30] and from Ref. [68]. The “AFM” phase at large $x$ is an A-type AF-metal with uniform orbital-order. In this material there is no charge-ordered AF-state near $x=0.5$. PM, PI, FM, FI and CI denote paramagnetic metal, paramagnetic insulator, ferromagnetic metal, ferromagnetic insulator, and spin-canted insulator states, respectively. $T_C$ is the Curie temperature and $T_N$ the Néel temperature; (b) Schematic version of the phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ to illustrate the experimental observation of the tendencies for charge inhomogeneities in this material. The language used to describe these tendencies, and the experimental techniques employed, are indicated at the proper densities and temperatures. Additional details and references can be found in the text.](image)

VI. Experimental Evidence of Charge Inhomogeneities

Independently of the development of the theoretical ideas on PS, a large body of experimental evidence has accumulated that suggests the existence of charge inhomogeneities in manganese oxides either in macroscopic form or, more often, through the presence of small clusters of one phase embedded into another. The results have been obtained on several materials, at a variety of temperatures and densities, and using a large array of microscopic and macroscopic experimental techniques. These studies have individually concentrated on particular parameter regions, and the results have rarely been discussed in comparison to similar results obtained in other phase regimes. However, once all of these experimental data are combined, it appears that the manganite metallic FM-phase is surrounded both in temperature and density by charge inhomogeneous regions involving...
FM clusters coexisting with another phase, which in some cases is AF. It would be unnatural to search for special justifications for each one of these experimental results.

The most economical hypothesis is to explain the data as arising through a single effect, such as tendencies to PS that compete strongly with ferromagnetism both at large and small x, as well as above Tc. The experimental details are the following:

**VI.1 Sr-doped Manganese Oxides**: Part of the phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ is schematically shown in Fig.4B, including at their proper location in T and (n) some of the descriptions of charge inhomogeneity found in the literature, along with the experimental techniques that have reported such inhomogeneity. They include results by Egami et al. [31], where evidence for an inhomogeneous FM-state and small polarons both at high- and low-T was reported using pair-density functional (PDF) techniques. In addition, a recent analysis of the optical conductivity of La$_{7/8}$Sr$_{1/8}$MnO$_3$ by Jung et al. [37] observed PS features in the data. Magnetic, transport, and neutron scattering experiments by Endoh et al. [26] on La$_{0.8}$Sr$_{0.12}$MnO$_3$ revealed PS tendencies between two FM-phases, one metallic and the other insulating. Other authors have also reported inhomogeneities in Sr-doped compounds [38].

**VI.2 Ca-doped Manganese Oxides**: In Fig.5, the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ is sketched. Although previous reports [3] contain more details, for the present discussion just the dominant qualitative aspects are needed. The list is not exhaustive but it is sufficient to illustrate the notorious presence of charge inhomogeneities in this compound near the FM-phase, and even inside it. Overall, the analysis of available data for Ca-doped LaMnO$_3$ leads to conclusions similar to those presented for their Sr-doped counterpart.

The details are the following (postponing the analysis for x~0.5, which requires special discussion). Consider first the small-angle neutron scattering (SANS) results at x=0.05 and 0.08 and low-T by M. Hennion et al. [39]. They revealed the existence of a liquid-like distribution of FM droplets with a density 1/60 that of holes. In a similar regime of parameters, nuclear magnetic resonance (NMR) experiments by Allodi et al. [40] reported the coexistence of FM and AF features and the absence of spin-canting [41]. SANS results at x=1/3 and T > Tc by Lynn et al. [42] and De Teresa et al. [43] observed a short (weakly T dependent) FM correlation length, attributed in [43] to magnetic clusters 10 to 20Å in diameter. Other experimental results, not reviewed here, agree with this conclusion. Even within the metallic FM-phase (T < Tc), indications of charge inhomogeneities have been reported. Transport measurements by Jaime et al. [44] were analyzed using a two-fluid picture involving polarons and free electrons. µ-Spin relaxation and resistivity data by Heffner et al. [45] were interpreted as produced by a multidomain sample. X-ray absorption results by Booth et al. [46] provided evidence of coexisting localized and delocalized holes below Tc [47]. Using Raman and optical spectroscopies, S. Yoon et al. [17] found localized states in the low-T metallic FM-phase of several manganese oxides. Neutron scattering experiments [42] reported an anomalous diffusive component in the data below Tc, which could be explained by a two-phase state. Fernandez-Baca et al. [48] have shown that this diffusive component is enhanced as the Tc of the considered manganite decreases. Actually, the low-energy component of the two-branch spin-wave spectrum observed at small x [49] has similarities with the diffusive peak at x=1/3 [42].

For the large hole-density regime, neutron scattering by Bao et al. [50] at x~0.8 using Bi$_{1-x}$Ca$_x$MnO$_3$, which behaves similarly to La$_{1-x}$Ca$_x$MnO$_3$, found FM-AF features coexisting between 150 and 200K. Optical measurements at x>0.5 by Liu et al. [51] reported similar features. Cheong and Hwang in [3] found a finite magnetization at low-T and x ≥ 0.83 in the (La, Ca)-compound [see also (52)]. The system remains insulating, and the results could be compatible with spin-canted or mixed-phase states. More work at small electronic density is needed to clarify if the phase segregation predicted by the theoretical calculations indeed appears in experiments.

**VI.3 Manganese Oxides with a Charge-Ordered State Near x=0.5**: Results involving the “charge-ordered” AF-state at x~0.5 require special discussion. Here, the extraordinarily large CMR effect involves the abrupt destabilization of the CO-state by a mag-
nentic field [5]. Evidence for PS tendencies is rapidly accumulating in this region of the phase diagram of narrow band manganese oxides. Several experiments for La$_{1-x}$Ca$_x$MnO$_3$ have already reported coexisting metallic FM and insulating CO-AF clusters near $x=0.5$ (Fig.5) [53]. Another compound at the FM-CO boundary at low-$T$ is Pr$_{0.7}$Ca$_{0.3}$MnO$_3$. Here x-ray synchrotron and neutron-powder diffraction results [54,55] were attributed to the presence of FM clusters in the CO-phase. Exposure to x-rays produces a nonuniform PS phenomenon characteristic of two competing states, with an increasing size of the FM droplets and no evidence of spin-canting. This phenomenon is expected to appear at other hole densities as well. Related manganese oxides exhibit similar features. For example, the absorption spectra of thin films of Sm$_{0.6}$Sr$_{0.4}$MnO$_3$ have been attributed [32] to the formation of large clusters of the CO-state above its ordering temperature. In (La$_{0.8}$Nd$_{0.2}$)$_{2/3}$Ca$_{1/3}$MnO$_3$, insulating CO and metallic FM regions coexist [56].

However, consider $\rho$ at 300 K for La$_{1-x}$Ca$_x$MnO$_3$ [3]. A smooth connection between the undoped, lightly-doped, and heavily-doped compounds seems to exist even in this narrow-band material. No obvious precursors for $x>0.5$ of the low-T CO-state have been reported. The same occurs for Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, which is metallic above $T_C$, becomes FM upon cooling, and reaches the CO-state through a first order transition upon further decreasing $T$ [57]. These results establish a possible qualitative difference between the MR effect at small $x$ and $x=0.5$. In the former, charge inhomogeneities appear above and below the critical temperatures, and the mutual influence of neighboring phases (notably FM and PS) is important. However, at $x \approx 0.5$, the CO- and FM-states do not seem to have much influence on each other. It could even be that the low-T microscopic PS tendencies at $x=0.5$ may be caused by metastabilities rather than a stable CI-state. However, since the competing states at $x \approx 0.5$ have similar (n) charge inhomogeneities involving large clusters are possible because Coulomb interactions will not prevent it (see above). Further experimental work is needed to clarify this situation. The theoretical study of competing FM and CO-AF states of narrow band manganese oxides in a single formalism also represents a challenge for computational studies. Preliminary results are promising since a CE-type CO state has been recently stabilized in computer simulations carried out at large electron-phonon coupling [58].

VI.4 Layered Manganites: Tendencies toward PS in layered manganites have also been observed. Neutron scattering results [59] for the bilayered La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ revealed a weak peak at the AF-momentum of the parent compound that coexists with the dominant FM signal [60]. Recently, PS between A-type metallic and CE-type insulating CO-states was reported for La$_2$Sr$_2$Mn$_2$O$_7$ [61]. In addition, studies of the one-layer material Sr$_2-x$La$_x$MnO$_4$ [62] observed direct evidence for macroscopic PS at small electronic density [63].

VII. The PS scenario compared with other theories for manganites.

The PS scenario is qualitatively different from other theories proposed to explain the CMR effects in manganese oxides. It improves on the simpler versions of the DE ideas [6] by identifying charge inhomogeneities as the main effect competing with ferromagnetism, and by assigning the insulating properties above $T_C$, fundamental for the low-hole-density CMR effect, to the influence of those competing phases. In particular, the compressibility increase above $T_C$ caused by PS leads to dynamical cluster formation.

The ideas presented here also differ qualitatively from those by Millis et al. [23], although there are common aspects. In the PS scenario, charge inhomogeneities over several lattice spacings, not contained in local mean-field approximations [23], are believed to be relevant for the description of the insulating state above $T_C$. In addition, the orbital ordering plays a key role in the results presented in Fig.1. Although the importance of the JT-coupling introduced by Millis et al. [23] is shared in both approaches, in the PS scenario a state formed by independent local polarons is a special case of a more general situation where clusters of various sizes and charges are possible. These fluctuations increase as $T_C$ decreases explaining the optimization of the MR effect at the boundary of the FM-phase. Note that the regime of small $x$ is crucial to distinguish between the PS scenario and other polaronic theories based on more extended polarons and percolative processes [31].

Other theories are based on the electronic localization effect using the off-diagonal disorder intrinsic to the DE model [64], and nonmagnetic diagonal disorder caused by the chemical substitutions. These effects lead to a large MR under some approximations [65]. However, the calculations are difficult because they involve both strong couplings and disorder, and the prominent cluster and polaron formation found in experiments has not been addressed in this framework. A better starting point for manganites may need a formalism that accounts for the tendency to develop charge inhomogeneities before including disorder.

VIII. Conclusions

A variety of recent calculations have found PS tendencies in models for manganites, usually involving FM and AF phases. These tendencies, which should lead to a stable but microscopically inhomogeneous state upon the inclusion of Coulomb interactions, compete strongly with ferromagnetism in the phase diagrams and are expected to increase substantially the resistivity. Particularly, when two-orbital models are studied, the results are in good agreement with a large list of experimental observations reviewed here. Tendencies toward charge inhomogeneous states exist in real manganese oxides all around the FM-phase in the temperature-density phase.
diagram. The computer simulations have shown that the region with PS tendencies substantially influences the stable FM-phase by increasing its compressibility, an aspect that can be tested experimentally. This provides a rationalization for the experimental observation of a large MR effect at the boundaries of the FM-phase. The presence of short-range charge correlations is certainly a crucial feature of the PS scenario.

However, considerable work still remains to be done. The inclusion of extended Coulomb interactions and the stabilization of the x=0.5 charge-ordered state are the next challenges for computational studies. Analytical techniques beyond the local mean-field approximations are needed to capture the essence of the charge inhomogeneous state. Macroscopic phenomenological approaches should be used to obtain predictions for transport properties and the shapes of the clusters that arise from the competition of the DE attraction and Coulomb repulsion. These resulting clusters are surely not static but fluctuating, specially above Tc.

In related problems of nuclear physics at high density, several geometries have been found including spherical drops, rodlike structures (stripes [28] or “spaghetti”) and plate-like ones (“lasagna”) [66]. Similar rich phenomena may occur in manganites. On the experimental front it is crucial to establish if the various regimes with charge inhomogeneities (Figs.4B and 5) are related, as predicted by the theoretical calculations. For example, work should be carried out to link the small x regime of (La,Ca)-manganites where FM-droplets appear, with the polarons reported at the x=1/3 density, and beyond into the highly hole-doped regime. In addition, phase segregation tendencies should also be studied close to the fully doped limit (n) ≪1 of manganese oxides, as well as in related compounds such as doped AF semiconductors [67].

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