Phase Separation in Electronic Models for Manganites

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(Received 2 June 1997)

The Kondo lattice Hamiltonian with ferromagnetic Hund's coupling as a model for manganites is investigated. The classical limit for the spin of the (localized) t_{2g} electrons is analyzed on lattices of dimension 1, 2, 3, and ∞ using several numerical methods. The phase diagram at low temperature is presented. A regime is identified where phase separation occurs between hole undoped antiferromagnetic and hole-rich ferromagnetic regions. Experimental consequences of this novel regime are discussed. Regions of incommensurate spin correlations have also been found. Estimations of the critical temperature in 3D are compatible with experiments. [S0031-9007(97)05072-2]

PACS numbers: 75.10.–b, 75.30.Mb, 75.30.Kz

The phenomenon of colossal magnetoresistance in metallic oxides such as $La_{1-x}Sr_xMnO_3$ has recently attracted considerable attention [1] due to its potential technological applications. A variety of experiments have revealed that oxide manganites have a rich phase diagram [2] with regions of antiferromagnetic (AF) and ferromagnetic (FM) order, as well as charge ordering, and a peculiar insulating state above the FM critical temperature, T_c^{FM}. Recently, *layered* manganite compounds $La_{1.2}Sr_{1.8}Mn_2O_7$ have also been synthesized [3] with properties similar to those of their 3D counterparts.

The appearance of ferromagnetism at low temperatures can be explained using the double exchange (DE) mechanism [4,5]. However, the DE model is incomplete to describe the entire phase diagram observed experimentally. For instance, the electron-phonon coupling may be crucial to account for the insulating properties above T_c^{FM} [6]. The presence of a Berry phase in the large Hund coupling limit also challenges predictions from the DE model [7]. In this paper we remark that another phenomenon occurring in manganites which is not included in the DE description, namely, the charge ordering effect, may be contained in a more fundamental Kondo model where the t_{2g} (localized) electrons are ferromagnetically (Hund) coupled with the e_g (mobile) electrons. More precisely, here we report the presence of *phase separation* (PS) between hole undoped antiferromagnetic and hole-rich ferromagnetic regions in the low temperature phase diagram of the FM Kondo model. Upon the inclusion of long-range Coulombic repulsion, charge ordering in the form of nontrivial extended structures (such as stripes) could be stabilized, similarly as discussed for the cuprates [8–11] but now also including ferromagnetic domains. The analysis reported in this paper suggests that phenomena as rich as observed in the high-T_c superconductors may exist in the manganites.

The FM Kondo Hamiltonian [4,12] is defined as

$$H = -t \sum_{\langle ij\rangle\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + \mathrm{H.c.}) - J_H \sum_{i\alpha\beta} c_{i\alpha}^{\dagger} \boldsymbol{\sigma}_{\alpha\beta} c_{i\beta} \cdot \mathbf{S}_i , \quad (1)$$

where $c_{i\sigma}$ are destruction operators for one species of e_g fermions at site i with spin σ, and $\mathbf{S}_i$ is the total spin of the t_{2g} electrons, assumed localized. The first term is the e_g electron transfer between nearest-neighbor Mn ions, $J_H > 0$ is the Hund coupling, the number of sites is L, and the rest of the notation is standard. The density is adjusted using a chemical potential μ. In this paper the spin $\mathbf{S}_i$ will be considered classical (with $|\mathbf{S}_i| = 1$), unless otherwise stated. Although models beyond Eq. (1) may be needed to fully understand the manganites, it is important to study the properties of simple Hamiltonians to clarify if part of the experimental rich phase diagram can be accounted for using purely electronic models.

To study Eq. (1) in the t_{2g} spin classical limit a Monte Carlo (MC) technique was used: first, the trace over the e_g fermions in the partition function was carried out exactly diagonalizing the $2L \times 2L$ Hamiltonian of electrons in the background of the spins $\{\mathbf{S}_i\}$, using library subroutines. The fermionic trace is a positive function of the classical spins, and the resulting integration over the two angles per site parametrizing the $\mathbf{S}_i$ variables can be performed with a standard MC algorithm without "sign problems." In addition, part of the calculations were also performed with the dynamical mean-field approximation ($D = \infty$) [12], the density-matrix renormalization group (DMRG), and the Lanczos method. Special care must be taken with the boundary conditions (BC) [13,14].

Our results are summarized in the phase diagrams of Fig. 1. In both 1D and 2D and at low temperatures clear indications of (i) ferromagnetism, (ii) incommensurate (IC) correlations, and (iii) phase separation were identified. For $D = 1$ and 2, finite size effects were small, although the PS-IC boundary in 2D was difficult to obtain accurately. Results are also available in small 3D clusters and qualitatively they agree with those in Figs. 1(a) and 1(b). In 1D we also obtained results with quantum t_{2g} spins $S = 3/2$. In this case the PS regime was studied calculating the compressibility using DMRG, and the FM regime monitoring the ground state spin quantum number with a Lanczos procedure. A good agreement with results

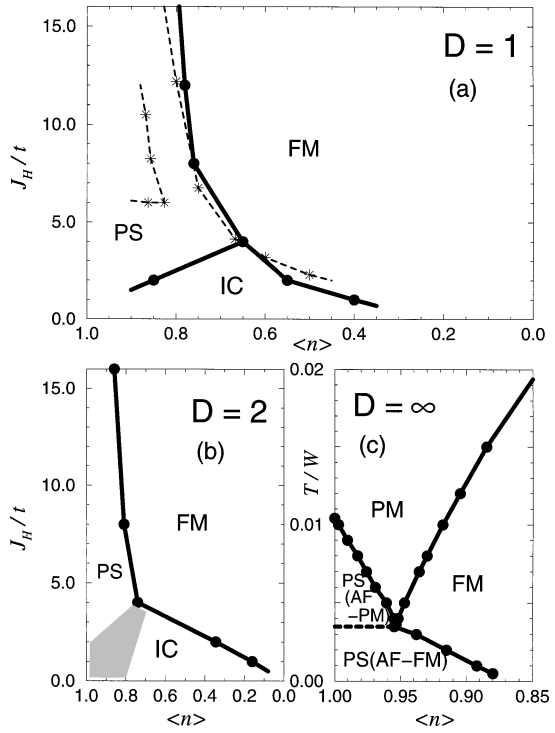

FIG. 1. Phase diagram of the FM Kondo model reported here. FM, IC, PM, and PS denote regimes with FM correlations, incommensurate correlations, paramagnetic correlations, and with phase separation between undoped AF and hole-rich FM regions, respectively. (a) was obtained with MC simulations at $T = t/75$ using chains with $L = 20$, 30, and 40 sites. Full circles correspond to classical spins. The stars and dashed lines are DMRG results obtained with t_{2g} spins $S = 3/2$ on chains with up to $L = 16$ sites keeping 48 states, and using $(2/3)J_H$ as coupling in the Hund term; (b) are MC results for classical spins at $T = t/50$ using 4×4, 6×6, and 8×8 clusters. In the shaded region a PS-IC crossover was observed but the actual boundary position is difficult to find; (c) corresponds to results in the $D = \infty$ limit at a fixed coupling $J_H/W = 4.0$ and as a function of T and $\langle n \rangle$ (W is defined in the text). The "PS (AF-PM)" region denotes PS between undoped AF and hole-rich PM regions.

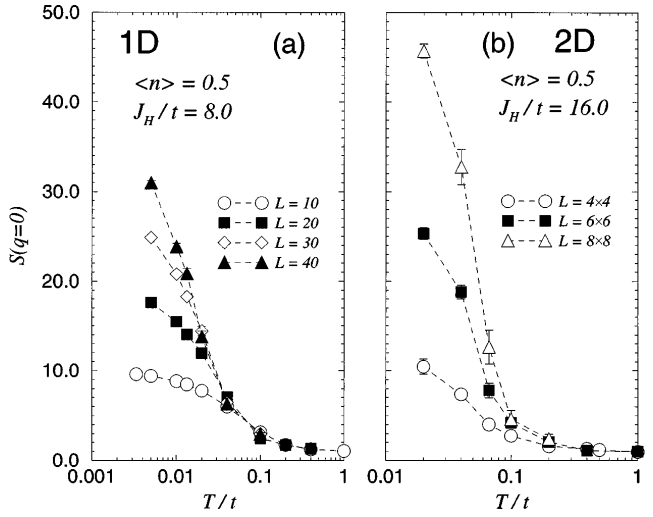

FIG. 2. Spin-spin correlations of the classical spins at zero momentum $S(\mathbf{q} = 0)$ vs temperature T (in units of t). MC results for several lattice sizes are shown on (a) chains and (b) 2D clusters. The density and coupling are shown. In (a) closed shell BC are used, i.e., periodic BC for $L = 10$ and 30 and antiperiodic BC for $L = 20$ and 40. In (b) open BC are used.

in the classical limit was obtained. PS for $S = 3/2$ (and $S = 1/2$) is between hole undoped AF and hole-rich nonfully saturated FM regions. In Fig. 1(c) results in $D = \infty$ are shown at $J_H/W = 4$, where W is the half-width of the e_g density of states $D(\epsilon) = (2/\pi W)\sqrt{1 - (\epsilon/W)^2}$. In agreement with the predictions for $D = 1$ and 2, at low temperatures PS between undoped AF and hole-rich FM regions was observed. For $\langle n \rangle < 0.88$ and $T/W \ll 1$ the ground state becomes FM. The quantitative similarities between the results obtained for $D = 1$, 2, and ∞ led us to believe that the conclusions of this paper are also valid for 3D manganite systems.

The boundaries of the FM region of the phase diagram were found evaluating the spin-spin correlation between the classical spins defined as $S(\mathbf{q}) = (1/L) \times \sum_{j,m} e^{i(j-m)\cdot\mathbf{q}} \langle \mathbf{S}_j \cdot \mathbf{S}_m \rangle$. Figure 2 shows $S(\mathbf{q})$ at zero momentum vs T/t for typical examples in 1D and 2D. The rapid increase of the spin correlations as T is reduced and as the lattice size grows clearly points towards the existence of ferromagnetism in the system [15]. Repeating this procedure for a variety of couplings and densities, the robust region of FM shown in Fig. 1 was determined, in qualitative agreement with previous studies [12,13].

In the small J_H/t region IC correlations were observed monitoring $S(\mathbf{q})$ [16]. Both in 1D and 2D there is one dominant peak which moves away from the AF location at $\langle n \rangle = 1$ towards zero momentum as $\langle n \rangle$ decreases. In the 2D clusters the peak moves from (π, π) towards $(\pi, 0)$ and $(0, \pi)$, rather than along the main diagonal [17]. Note that our computational study predicts IC correlations only in the small and intermediate J_H/t regime.

The main result of the paper is contained in Fig. 3 where the computational evidence for the existence of phase separation in dimensions 1, 2, and ∞ is given [18]. The presence of a discontinuity in $\langle n \rangle$ vs μ shows that some electronic densities cannot be stabilized. If the system is nominally prepared with such density it will spontaneously separate into two regions with the densities corresponding to the extremes of the discontinuities of Fig. 3. By analyzing these extremes the properties of the two domains can be studied. One region is undoped ($\langle n \rangle = 1$) with strong AF correlations, while the other contains all the holes, and the spin-spin correlations between the classical spins are FM [19]. [See the inset of Fig. 3(a). The results are similar in $D = 2$ and infinite.] This is natural since holes optimize their kinetic energy in a FM background. On the other hand, at $\langle n \rangle = 1$ the DE mechanism is not operative: If the electrons fully align their spins they cannot move in the conduction band due to the Pauli principle. Then, energetically an AF pattern is formed (the same occurs for $S = 3/2$ and $1/2$ localized

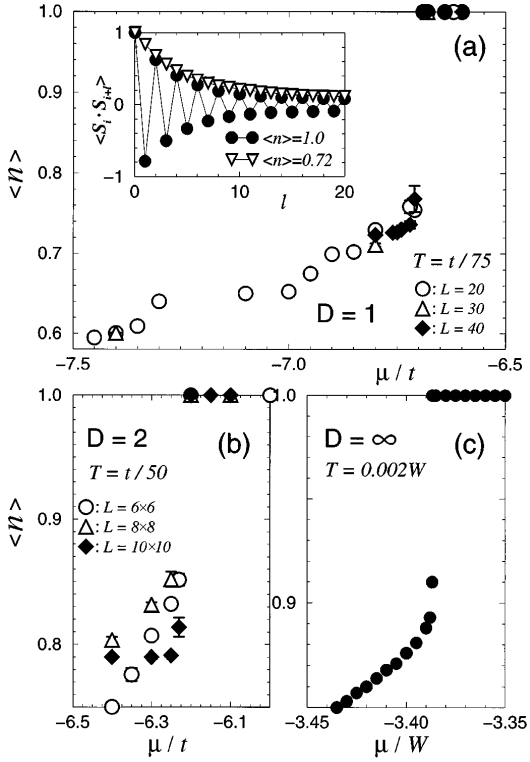

FIG. 3. Electronic density $\langle n \rangle$ vs chemical potential μ for (a) $D = 1$, (b) $D = 2$, and (c) $D = \infty$ clusters. Temperatures are indicated. The coupling is $J_H/t = 8.0$ in (a) and (b) and $J_H/W = 4.0$ in (c). PBC were used both in $D = 1$ and 2. The discontinuities shown in the figures are indicative of PS. In (a) the inset contains the spin-spin correlation in real space at densities 1.0 and 0.72 showing that indeed PS occurs between AF and FM regions.

spins). As J_H grows, the jump in Fig. 3 is reduced and it tends to disappear in the $J_H = \infty$ limit [20].

Experimentally, PS may be detectable using neutron diffraction techniques if the two coexisting phases have different lattice parameters as in $La_2CuO_{4+\delta}$ [21,22]. Note also that in the PS regime $S(\mathbf{q})$ presents a two peak structure, one located at the AF position and the other at zero momentum. Since this also occurs in a canted ferromagnetic state, care must be taken in the analysis of the experimental data. In particular, recent experimental results [23] are in qualitative agreement with Fig. 1(c) since a reentrant structural phase transition was observed accompanied by "canted ferromagnetism" below $T_c^{\rm FM}$, at $0.10 < x < 0.17$ in $La_{1-x}Sr_xMnO_3$ [24].

Another alternative is that Coulombic forces and low Sr mobility prevent the macroscopic accumulation of charge intrinsic of a PS regime. Thus, extended hole-rich domains in the form of stripes (as in cuprates [11]), or some other arrangement, could be formed. Although these details certainly deserve further work, the results in this paper are enough to show that tendencies similar to those found in models for the 2D cuprates, notably the t-J model, may also be operative in manganites. The main difference is that instead of separation between hole-poor AF and hole-rich superconducting regions, as in $La_2CuO_{4+\delta}$, here the observed PS is between hole-undoped AF and hole-rich *ferromagnetic* regimes. Tendencies to pairing in Cu oxides are replaced by tendencies to form ferromagnetic ground states in Mn oxides [13].

Although the phase diagrams of Fig. 1 have PS close to half-filling, actually this phenomenon also occurs at $\langle n \rangle \sim 0$ if an extra direct AF exchange interaction between the localized spins is included. This coupling may be originated in a small hopping amplitude for the t_{2g} electrons. At $\langle n \rangle = 0$ model Eq. (1) supplemented by a Heisenberg coupling J'/t among the localized spins will certainly produce an AF phase, as in experiments, which upon electron doping will induce a competition between AF (with no e_g electrons) and FM electron-rich regions, similarly as for $\langle n \rangle = 1$ but replacing holes by electrons. Previous studies in 1D support these claims [13]. Thus, PS or charge ordering could exist in manganites both at large and small fermionic densities.

For completeness, upper bounds on the 3D critical temperature $T_c^{\rm FM}$ are also provided. Using MC simulations in principle it is possible to calculate $T_c^{\rm FM}$ accurately. However, the algorithm used here prevented us from studying clusters larger than 6^3 even at $J_H = \infty$. In spite of this limitation, monitoring the spin-spin correlations in real space allows us to judge at what temperature T^* the correlation length reaches the boundary of the 6^3 cluster. Since the bulk $T_c^{\rm FM}$ is smaller than T^*, this give us upper bounds for the critical temperature. Figure 4(a) shows the spin-spin correlations at several temperatures in the $J_H = \infty$ limit and at $\langle n \rangle = 0.5$. When $T \sim 0.1t$ robust correlations reach the boundary, while for $T \geq 0.12t$ the correlation is short ranged. Thus, at this density we estimate that $T_c^{\rm FM} < 0.12t$. Results for several densities in this limit are shown in Fig. 4(b). For realistic densities, such as $\langle n \rangle \sim 0.7$, our results are about a factor of 1.7 smaller than predicted by high temperature expansions for $S = 1/2$ localized spins [25]. Nevertheless, the order of magnitude of both calculations is similar. Monitoring the rapid growth of the zero momentum spin correlations [inset of Fig. 4(a)] provides similar bounds. $T_c^{\rm FM}$ is the highest at $\langle n \rangle = 0.5$, if $J_H = \infty$. Since results for the e_g electrons bandwidth range from $BW \sim 1$ eV [26] to $BW \sim 4$ eV [27], producing a hopping $t = BW/12$ between 0.08 and 0.33 eV, then our estimation for the critical temperature ranges roughly between $T_c^{\rm FM} \sim 100$ and 400 K. This is within the experimental range, in agreement with other results [12,25], and in disagreement with previous estimations [6]. Then, purely electronic models can account for $T_c^{\rm FM}$.

In summary, the main conclusion of the paper is that the phase separation occurs in realistic models for manganites. Then, experimentalists should consider this potential regime in the interpretation of their results since tendencies to phase separate could be as strong as those towards ferromagnetism in the real materials. It is hoped that the present paper will trigger discussion on how phase separation will experimentally reveal itself in manganites. The

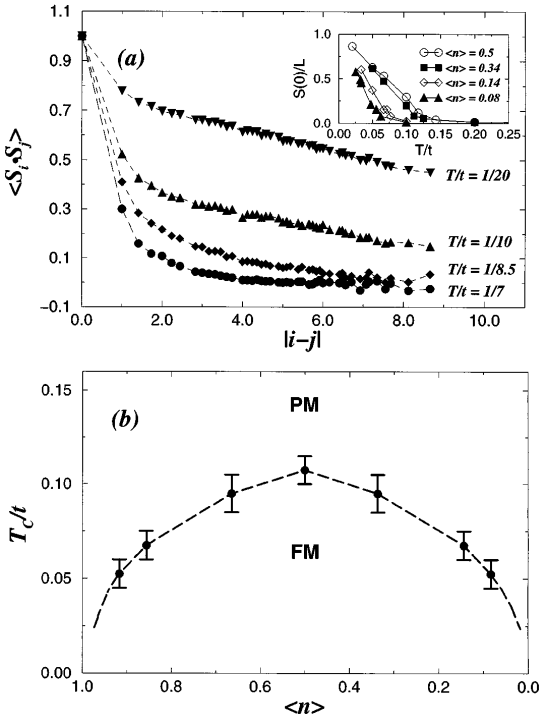

FIG. 4. (a) Real space MC spin-spin correlations among the classical spins at distance $|i - j|$, $\langle n \rangle = 0.5$, $J_H = \infty$, on a 6^3 cluster, and parametric with temperature T/t. The inset shows $S(\mathbf{q})$ at zero momentum and several densities vs T/t. (b) Bounds on the critical temperature as estimated from data as shown in (a) as a function of $\langle n \rangle$.

inclusion of long-range Coulombic interactions may stabilize complex charge ordered structures that could be observed using a variety of techniques. Neutron scattering experiments should detect these charge fluctuations above the critical temperature, as it occurs in the cuprates. From a more fundamental perspective, our results show that the presence of phase separation in electronic models for transition metal oxides is a more general phenomenon than previously anticipated.

S. Y. is supported by the Japanese Society for the Promotion of Science. A. L. M. acknowledges the financial support of the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil). A. M. and E. D. are supported by the NSF Grant No. DMR-9520776. We thank the NHMFL In-House Research Program No. DMR-9527035 for additional support.

[1] S. Jin *et al.,* Science **264**, 413 (1994).
[2] P. E. Schiffer, A. P. Ramirez, W. Bao, and S-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995); C. H. Chen and S-W. Cheong, Phys. Rev. Lett. **76**, 4042 (1996).
[3] Y. Moritomo *et al.,* Nature (London) **380**, 141 (1996).
[4] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).
[5] P. G. de Gennes, Phys. Rev. **118**, 141 (1960).
[6] A. J. Millis *et al.,* Phys. Rev. Lett. **74**, 5144 (1995); H. Röder *et al.,* Phys. Rev. Lett. **76**, 1356 (1996).
[7] E. Müller-Hartmann and E. Dagotto, Phys. Rev. B **54**, R6819 (1996).
[8] V. J. Emery, S. A. Kivelson, and H. Q. Lin, Phys. Rev. Lett. **64**, 475 (1990). Here PS between AF hole-poor and FM hole-rich regions was also mentioned in the t-J model although for unrealistic values of the couplings (in the FM Kondo model it is present in the realistic regime). We thank S. Kivelson for this comment. See also V. J. Emery and S. A. Kivelson, Physica (Amsterdam) **209C**, 597 (1993).
[9] E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994).
[10] J. M. Tranquada *et al.,* Nature (London) **375**, 561 (1995).
[11] U. Löw *et al.,* Phys. Rev. Lett. **72**, 1918 (1994); S. Haas *et al.,* Phys. Rev. B **51**, 5989 (1995).
[12] N. Furukawa, J. Phys. Soc. Jpn. **63**, 3214 (1994).
[13] J. Riera, K. Hallberg, and E. Dagotto, Phys. Rev. Lett. **79**, 713 (1997).
[14] Closed shell BC or open BC are needed to stabilize a ferromagnet. If other BC are used the spin correlations at short distances are still strongly FM (if working at couplings where ferromagnetism is stable), but not at large distances where they become negative. This well-known effect was observed before in K. Kubo, J. Phys. Soc. Jpn. **51**, 782 (1982); J. Zang *et al.,* J. Phys. Condens. Matter **9**, L157 (1997); T. A. Kaplan and S. D. Mahanti, *ibid.* **9**, L291 (1997); and in Ref. [13]. It does not present a problem in the analysis shown in this paper.
[15] In both 1D and 2D the Mermin-Wagner theorem forbids a nonzero T_c^{FM} in the model. However, the correlation lengths can be very large even at finite T/t.
[16] IC effects were predicted using a Hartree-Fock approximation [J. Inoue and S. Maekawa, Phys. Rev. Lett. **74**, 3407 (1995)] as an alternative to canted FM [5].
[17] M. Hamada and H. Shimahara, Phys. Rev. B **51**, 3027 (1995).
[18] Up to 10^6 sweeps were needed to obtain accurate results in Figs. 3(a) and 3(b), with an acceptance rate of 0.5.
[19] The FM correlations at the boundary with PS in Fig. 1 are weaker than at the center of the FM phase, probably caused by a small $T = 0$ order parameter.
[20] PS in manganites was also conjectured in Ref. [13] based on 1D studies of the "t-J" version of Eq. (1). See also E. L. Nagaev, Phys. Status Solidi (b) **186**, 9 (1994), and references therein.
[21] P. G. Radaelli *et al.,* Phys. Rev. B **49**, 6239 (1994).
[22] NMR and NQR spectra, as well as magnetic susceptibility measurements, can also be used to detect PS. Note that experimental studies of $Sr_{2-y}La_yMnO_4$ have reported evidence for electronic phase separation and charge ordering at small y. See W. Bao *et al.* (to be published).
[23] H. Kawano *et al.,* Phys. Rev. B **53**, R14 709 (1996); **53**, 2202 (1996).
[24] Also the polaron-ordered phase [Y. Yamada *et al.,* Phys. Rev. Lett. **77**, 904 (1996)] can be reanalyzed in terms of the present results since it is known that the AF phase in 3D manganites is orthorhombic while the FM is pseudocubic. The formation of a lattice superstructure may stabilize the magnetic tendency to phase separate.
[25] H. Röder *et al.,* Phys. Rev. B **56**, 5084 (1997).
[26] Y. Moritomo *et al.,* Phys. Rev. B **51**, 16 491 (1995).
[27] D. D. Sarma *et al.,* Phys. Rev. B **53**, 6873 (1996).