New Type of Charge and Magnetic Order in the Ferromagnetic Kondo Lattice

D. J. García,[1] K. Hallberg,[1] C. D. Batista,[1] M. Avignon,[2] and B. Alascio[1]

[1]*Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 S.C. de Bariloche, Argentina*
[2]*Laboratoire d' Etudes des Propriétés Electroniques des Solides (LEPES), Centre National de la Recherche Scientifique (CNRS), BP 166, 38042 Grenoble Cedex 9, France*

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We study numerically the one dimensional ferromagnetic Kondo lattice, a model widely used to describe nickel and manganese perovskites. By including a nearest-neighbor Coulomb interaction (V) and a superexchange interaction between the localized moments (K), we obtain the phase diagram in parameter space for several dopings at $T = 0$. Because of the competition between double and superexchange, we find a region where the formation of magnetic polarons induces a charge-ordered state which survives also for $V = 0$. This mechanism should be taken into account in theories of charge ordering involving spin degrees of freedom.

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In recent years there has been great interest in the nontrivial interplay between charge, spin, and lattice degrees of freedom in strongly correlated electron systems, especially in perovskite transition-metal oxides. One of the most striking phenomena is the simultaneous appearance of charge and spin superstructures. For example, neutron scattering [1] and electron diffraction [2] experiments in $La_{2-x}Sr_xNiO_4$ showed the presence of charge/lattice and spin modulations with doping-dependent wave vector. Stripe formation together with incommensurate spin fluctuations in high-T_c superconductors can also be regarded as a manifestation of similar phenomena [3]. The charge and spin ordering found in many of the doped manganese perovskites also fall in the same category. Experiments have revealed CO in $Nd_{0.5}Sr_{0.5}MnO_3$ [4] and similar compounds, such as $Pr_{0.5}Ca_{0.5}MnO_3$ [5–8]. More recent interest has focused on electron doped charge-ordered manganites [9–11]. CO has also been found for other dopings as in $Bi_{1-x}Ca_xMnO_3$ [9] and in $La_{1-x}Ca_xMnO_3$ (doped with Pr) [11] for $x \geq 1/2$.

Although there have been several attempts to explain the CO phase theoretically in the $x = 1/2$ case by considering two Mn orbitals [12,13] with and without intersite Coulomb interaction V, and adding strong on-site Coulomb interactions [12], there remains, to the best of our knowledge, no explanation for the existence of CO in the electron-doped region ($x > 1/2$) [9,10]. Numerical studies [14] have included the effect of V and obtained a very rich phase diagram, finding phase separated (for either extreme dopings) and CO ($x \simeq 1/2$) regimes. In Ref. [15] the $x = 1/2$ two-orbital case is also studied using Monte Carlo techniques, and the CO phase is stabilized by Jahn-Teller phonons. As mentioned in this work, the z-axis stacking of charge and existence of bistripes at $x > 1/2$ [10], both penalized by a large Coulomb interaction, indicate that V is smaller than expected and is not enough to understand the CO state.

Unlike CO in nonmagnetic materials where the Peierls instability or large intersite Coulomb interactions are required, we will show here that in these magnetic materials charge density waves can result from the formation of magnetic superstructures arising from the presence of competing interactions. By changing the carrier concentration or the relationship between the competing interactions, this new mechanism gives rise to a very rich family of inhomogeneous spin and charge structures.

In order to illustrate this new mechanism we will study here a simplified model where the competing forces are personified by the double and superexchange (SE) interactions. The first model that considered this competition was studied by de Gennes [16]. The most intriguing question is what happens at an intermediate regime, where the competing interactions are energetically similar. de Gennes proposed canting of two interpenetrating lattices as the compromise solution of this competition. This concept was also used subsequently in recent analytical approaches [17,18]. Phase separation has also been considered as a possible solution to this competition [19]. As will be shown below, we find spin phases which cannot be described in terms of two interpenetrating sublattices nor do they correspond to phase separation.

As a result of the competition between the double exchange (DE) and the SE between local spins, we find what can be described as an ordered phase of ferromagnetic (FM) islands in which carriers are localized. The formation of this spin superstructure opens a gap at the Fermi level of the metallic fully saturated FM phase. Because of this, these phases are insulating, but a magnetic field can induce a transition to a FM metallic phase. In this way, we show that an inhomogeneous ground state can be obtained from a Hamiltonian with two competitive short ranged interactions.

The model we will consider consists of a one dimensional lattice of Mn ions formed by a localized t_{2g}^3 configuration that can be viewed as an $S = 3/2$ spin. On this lattice, $(1 - x)$ itinerant e_g electrons are distributed and coupled ferromagnetically to the localized spins due to Hund's rule. We will use here a widely accepted

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Hamiltonian [20–22] to describe this system [sometimes called the ferromagnetic Kondo lattice model (FKLM)]:

$$H = -t\sum_i (c^\dagger_{i\sigma}c_{i+1\sigma} + \text{H.c.}) + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_i n_i n_{i+1} + J_h\sum_i \mathbf{S}_i\boldsymbol{\sigma}_i + K\sum_i \mathbf{S}_i\mathbf{S}_{i+1}\,. \quad (1)$$

Here the first term represents the e_g-electron transfer between nearest-neighbor Mn ions at sites i and $i+1$, the second and third terms are the on-site and intersite Coulomb repulsions between these orbitals, and J_h is the Hund's rule coupling between localized $\mathbf{S}_i$ and itinerant $\boldsymbol{\sigma}_i$ spins. This last term, together with the transfer term, gives rise to the DE, favoring FM ordering of the local spins. K is the AF interaction between local spins and is due to the SE of the t_{2g}^3 electrons. It stabilizes the antiferromagnetic (AF) phase for $x = 1$ and competes with the DE term for intermediate fillings. In order to simplify the calculations, the localized spins are taken as $1/2$ instead of $3/2$ (without loss of generality) and we reduce the model to one dimension (1D). However, it is known that the basic features of the phase diagram in 3D problems appear in two and one dimensions as well [21].

Experiments indicate that $J_h \gg t$; hence we will fix the values $J_h/t = 20$. We will also take $U/t = 10$, so that the only free parameters are V/t and K/t. For this large value of J_h/t, U is irrelevant since double occupancy is suppressed by J_h. We consider here the case of one nondegenerated e_g orbital. The ground state of this model has also been calculated by other authors [14] using the finite-system density-matrix renormalization group [23,24]. Here we have taken special care in the growing of blocks in order not to frustrate the system in the cases when charge and spin order are expected [25]. With this consideration, and taking open systems, very accurate results were obtained with a discarded weight lower than 10^{-4} for the largest systems presented here ($L = 30$). Calculations on smaller systems with closed boundary conditions led to similar results.

Let us consider first the case $x = 1/2$ and $V = 0$, in order to isolate the two competing interactions K and t. For any finite concentration there is a fully polarized FM phase below some critical value of K/t, and an AF phase for sufficiently large K/t. This can be seen in Fig. 1 for $x = 1/2$. In the intermediate regime ($0.2 < K/t < 0.4$) we get a phase with clear peaks in the spin structure factor $S(q)$ at $q = \pm\pi/2$ (see Fig. 1a). The (nearly) logarithmic increase of the spin structure factors with system size L in Fig. 1c is indicative of a power-law decay (with exponent one) in the real space spin-spin correlation functions; however, other exponents are also possible and indistinguishable for the small systems considered. In any case the correlations are quasilong-ranged. This power-law decay is a consequence of the fact that no long-range order can be sustained in a one dimensional model with SU(2)

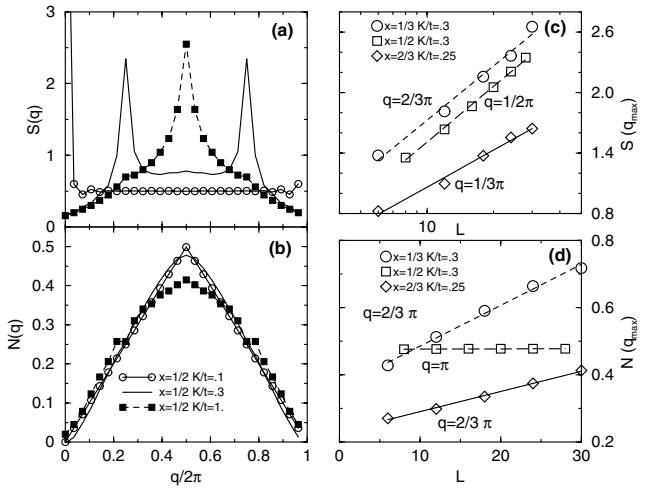

FIG. 1. Spin (a) and charge (b) structure factors for $x = 1/2$, $L = 28$, and $V = 0$. Size dependence of the peaks of the spin (c) and charge (d) structure factors ($V = 0$).

symmetry. This structure has been obtained with quantum Monte Carlo using classical spins and interpreted as a spiral state with pitch $q = \pi/2$ [22]. Instead, our results on the real space spin-spin correlation function show FM pairs coupled antiferromagnetically: ↑↑↓↓↑↑↓↓ .... Our classical Monte Carlo calculations [26] confirm this picture.

Now if we look at the charge distribution, we find that even though there is no CO in any of these phases, the charge-charge correlation functions $N(q)$ shown in Fig. 1b are qualitatively different. While the FM case ($K/t = 0.1$) corresponds to a spinless metallic phase at filling $x = 1/2$, the charge structure factor $N(q)$ for the AF case ($K/t = 1$) presents a broader momentum distribution. Concerning the $q = \pi/2$ spin phase, it can be seen from Figs. 1b and 1d that there is no CO for this phase, even when the charge-charge correlation function is quite different compared to the FM case. This change can be understood if we consider that the charges are "localized" in bonds due to the spin structure ↑↑↓↓↑↑↓↓ ..., which would give an insulating character to this phase (preliminary calculations of the Drude weight seem to confirm this view [27]). Each charge induces a FM island of two spins and tends to be localized in the bond in order to gain kinetic energy. The shape of $N(q)$ is closer to $(1 - \cos q)/4$ as a consequence of the enhancement of the charge correlations within an island. From this point of view it is easy to understand the absence of charge ordering, because both sites are completely equivalent in each island. However, this would not be the case if the tendency to form FM islands surrounding each charge were preserved for lower electron concentrations. If we consider, for example, $x = 2/3$ the expected spin phase for a particular parameter range may be represented schematically as ↑↑↑↓↓↑↑↑↓↓↓ ..., where the spins cluster in the form of magnetic polarons [28]. In this case, the centers of each island are not equivalent to the borders, and the charge will tend to accumulate in the

middle of the polarons. For this reason we expect to get CO together with a spin density wave for electron concentrations lower than 0.5. This scheme is confirmed by Fig. 2, where we show the charge and spin structure factors calculated for $x = 2/3$ and $K/t = 0.25$. $S(q)$ clearly shows a peak at $q = \pi/3$, while $N(q)$ has a pronounced peak at $q = 2\pi/3$. Figures 1c and 1d show that the intensity of these peaks scale approximately logarithmically with L for $S(q = \pi/3)$ and linearly for $N(q = 2\pi/3)$ which is a clear evidence of long-range CO and power-law decay of the spin correlation functions. The same calculations for $x = 1/5, 1/4$ show spin and charge correlation functions consistent with the formation of five- and four-sites spin islands containing one electron each. These structures could be regarded as a crystallization of the magnetic polarons described in Ref. [28] for the dilute limit. It is interesting to note that CO is induced by spin ordering and vice versa, demonstrating that the formation of these superstructures is a consequence of the interplay between charge and spin degrees of freedom.

In the case $x = 1/3$, it is evident from Figs. 1 and 2 that there is also a spin and charge-ordered state for this concentration. Both $N(q)$ and $S(q)$ now have peaks at $q = 2\pi/3$. This result can be understood clearly with the following image for the magnetic structure: ⇑⇑⇓⇑⇑⇓ ..., while the charge is distributed with one electron in each pair of up spin sites, and one in each down spin site. It is important to note that the formation of the spin structures obtained when the competitive interactions are of the same order, always open a gap at Fermi level of the metallic fully saturated FM phase which appears for any x when $t \gg K$.

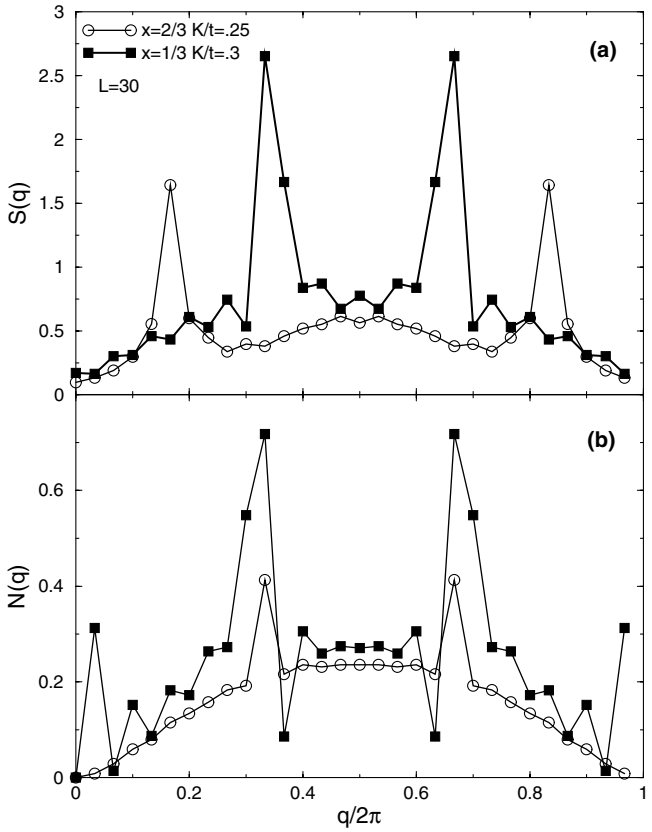

FIG. 2. Spin (a) and charge (b) structure factors for $x = 1/3, 2/3$, $L = 30$, and $V = 0$. The peak at small q in $N(q)$ for the $x = 1/3$ case is due to a kink in the center of the open chain.

The validity of the picture described above can be tested using a classical approach. We calculate the contributions of DE and SE to the energy of the different possible phases for each value of the concentration, assuming that the hopping vanishes at the AF bonds. In the case $x = 1/2$ we obtain $-2t/\pi + K/4$ for the FM phase, $-t/2$ for the $q = \pi/2$ ⇑⇑⇓⇓⇑⇑⇓⇓ ... phase, and $-K/4$ for the AF phase. The sequence of stable spin phases when increasing K/t, FM $\rightarrow$ $\pi/2$ $\rightarrow$ AF is obtained in agreement with the numerical results (see Fig. 3a). Here it is clearly seen how the FM state weakens for a larger SE parameter (K), giving rise to more complicated structures for intermediate values of the parameters and finally approaching an AF state for large K. In this classical picture a canted AF phase has a slightly lower energy than the pure AF phase, but the $\pi/2$ phase remains stable over a certain region in K/t. The same procedure leads to similar conclusions at $x = 1/3$ and $2/3$.

It is also of interest to consider the effect of an intersite Coulomb interaction V at $x = 1/2$, because at this concentration it is most effective in inducing CO. All phases exhibit CO above a critical value of V/t. In Fig. 3b we sketch the phase diagram in V and K. Our calculations for different values of K/t indicate a first-order transition from the metallic fully polarized FM (M-FM) phase to the insulating phase with $q = \pi/2$ spin order (I-$\pi/2$). At larger K/t the $\pi/2$ spin phase evolves into the AF phase.

The Coulomb repulsion V inhibits the double-exchange mechanism by reducing the mobility of the carriers. This reduces the phase space for the FM order. As K increases, the critical value of V for charge ordering diminishes from the spinless value $2t$ valid for the saturated FM regime. For $V \gg t$ we obtain the ferrimagnetic CO (CO-FIM) phase ⇑⇓⇑⇓⇑⇓ ... of alternating $S = 1$ (⇑) and $S = 1/2$ (⇓) total spin.

A great variety of experiments have found the presence of charge and spin ordering in manganites. The extraordinary colossal magnetoresistance effect for $La_{0.5}Ca_{0.5}MnO_3$ involves the abrupt destabilization of a CO-AF state by a magnetic field [29]. Insulating charge-ordered and metallic FM regions coexist in $(La_{0.5}Nd_{0.5})_{2/3}Ca_{1/3}MnO_3$ [30] and $Pr_{0.7}Ca_{0.3}MnO_3$ [31,32]. Both phenomena indicate that the CO phase is very close in energy to the FM state. These observations are consistent with a picture where spin and CO are driven by the strong interplay between charge and spin degrees of freedom. For these reasons, the phenomenon presented here could be the underlying physical mechanism for the stabilization of spin and charge structures in manganites. Our model calculations fail to include several effects that may play important roles in real systems like

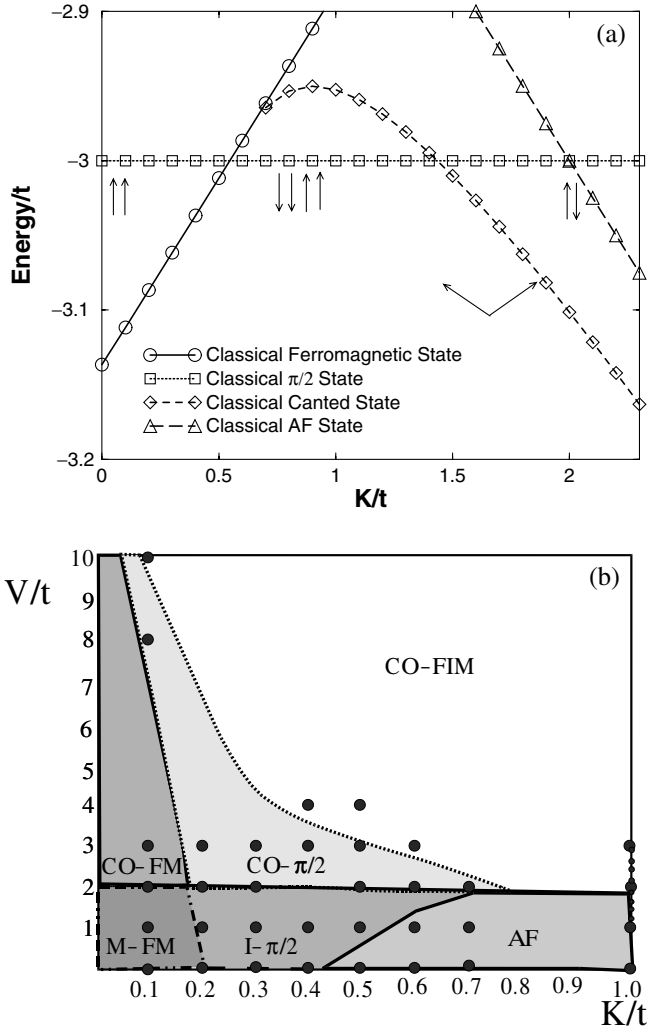

FIG. 3. (a) Classical energies as functions of K/t for $x = 1/2$. (b) Phase diagram K/t vs V/t for $x = 1/2$. The circles indicate the points where calculations have been performed. The phases are defined in the text.

Jahn-Teller distortions and orbital degeneracy. However, it is important to take into account that charge ordering can be induced simply as a result of the competition between DE and SE as shown here and that this mechanism should be included as an important ingredient for more general models.

We have presented numerical evidence of the existence of a new type of simultaneous charge and spin ordering in the FKLM. This mechanism, induced by the competition between DE and SE, is based on the interplay between charge and spin degrees of freedom. As we have shown in a previous work [28], in the dilute limit each carrier polarizes its neighborhood forming FM polarons. The size of these polarons is governed by the ratio K/t. We could interpret our results as an indication that, if this size is similar to the mean separation between carriers, then SE tends to order these islands in the form of a polaron lattice separating them by AF interfaces. We find that in this intermediate regime, the charge and spin structure factors peak at $2k_F$ and k_F, respectively, where $k_F = (1 - x)\pi$ is the Fermi momentum of spinless carriers. Similar results in the classical regime were found in Ref. [33].

We have found that, in an important range of parameter values, the competition between double and SE does not give rise to the canted states as conjectured by de Gennes in any of the classical or quantum limits. Instead, new phases exist in which microscopic FM islands appear, separated by AF links. An extension of this type of magnetic structures may appear in more than one dimension [26].

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[1] S. Hayden *et al.,* Phys. Rev. Lett. **68**, 1061 (1992).
[2] C. Chen *et al.,* Phys. Rev. Lett. **71**, 2461 (1993).
[3] J. M. Tranquada *et al.,* Nature (London) **375**, 561 (1995).
[4] H. Kawano *et al.,* Phys. Rev. Lett. **78**, 4253 (1997).
[5] Y. Tomioka *et al.,* Phys. Rev. B **53**, R1689 (1996).
[6] J. Li *et al.,* Phys. Rev. B **57**, R3205 (1998).
[7] Y. Moritomo *et al.,* Phys. Rev. B **56**, 14 879 (1997).
[8] C. Chen *et al.,* Phys. Rev. Lett. **76**, 4042 (1996).
[9] H. Liu *et al.,* Phys. Rev. Lett. **81**, 4684 (1998); W. Bao *et al.,* Phys. Rev. Lett. **78**, 543 (1997).
[10] S. Mori *et al.,* Nature (London) **392**, 473 (1998).
[11] M. Uehara *et al.,* Nature (London) **399**, 560 (1999); Z. Jirac *et al.,* J. Magn. Magn. Mater. **53**, 153 (1985).
[12] J. Van den Brink *et al.,* e-print cond-mat/9910253.
[13] T. Mizokawa *et al.,* Phys. Rev. B **56**, R493 (1997).
[14] A. Malvezzi *et al.,* Phys. Rev. B **59**, 7033 (1999).
[15] S. Yunoki, A. Moreo, and E. Dagotto, Phys. Rev. Lett. **81**, 5612 (1998).
[16] P-G. de Gennes, Phys. Rev. **118**, 141 (1960).
[17] H. Aliaga *et al.,* Solid State Commun. **110**, 525 (1999).
[18] D. P. Arovas and F. Guinea, Phys. Rev. B **58**, 9150 (1998).
[19] A. Moreo *et al.,* Science **283**, 2034 (1999).
[20] See, for example, J. Riera, K. Hallberg, and E. Dagotto, Phys. Rev. Lett. **79**, 713 (1997).
[21] S. Yunoki *et al.,* Phys. Rev. Lett. **80**, 845 (1998).
[22] S. Yunoki and A. Moreo, Phys. Rev. B **58**, 6403 (1998).
[23] S. White, Phys. Rev. Lett. **69**, 2863 (1992).
[24] *Density Matrix Renormalization,* Lectures Notes in Physics, edited by I. Peschel *et al.* (Springer-Verlag, Berlin, 1999).
[25] D. García *et al.* (to be published).
[26] H. Aliaga *et al.* (to be published).
[27] S. Capponi and D. Poilblanc (private communication).
[28] C. D. Batista *et al.,* Phys. Rev. B **58**, R14 689 (1998).
[29] Y. Tomioka *et al.,* J. Phys. Soc. Jpn. **64**, 3626 (1995); Phys. Rev. B **53**, R1689 (1996); H. Yoshizawa *et al.,* Phys. Rev. B **52**, R13 145 (1995).
[30] M. R. Ibarra *et al.,* Phys. Rev. B **57**, 7446 (1998).
[31] D. E. Cox *et al.,* Phys. Rev. B **57**, 3305 (1998).
[32] V. Kiryukhin *et al.,* Nature (London) **386**, 813 (1997).
[33] W. Koshibae *et al.,* Phys. Rev. Lett. **82**, 2119 (1999).