Ferromagnetism and Colossal Magnetoresistance from Phase Competition

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We report a multicomponent theory for the coexistence of charge ordering (CO), and antiferromagnetic (AFM) and ferromagnetic (FM) spin ordering. This kind of state is invoked for manganites by Moreo *et al.,* Science **283**, 2034 (1999) and observed in recent experiments. We show that doping an AFM or CO state always generates a FM component. FM, AFM, and CO necessarily coexist in a particlehole asymmetric system. Melting of large AFM-CO orders by small magnetic fields and colossal magnetoresistance (CMR) arise whenever the CO and AFM order parameters have *similar magnitude and momentum structure*. Hole doping favors FM metallic states while electron doping favors AFM-CO states, as in CMR manganites.

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The perovskite manganites $(La, Pr)_{1-x} (Ca, Sr, Ba)_x$ -MnO₃, in the doping region $x \approx 0.2{\text -}0.4$ exhibit a transition to a ferromagnetic (FM) ground state which is accompanied by a large drop of the resistivity. This transition can be tuned by a magnetic field producing negative "colossal magnetoresistance" (CMR) [1]. Ferromagnetism in these materials is usually attributed to the double exchange mechanism [2,3], in which the lattice degrees of freedom [4,5] might also be involved. However, the CMR phenomenon could be more general since it has also been observed in pyrochlore manganites [6], where double exchange and Jahn-Teller effects on the transport can be safely excluded [7,8]. It has been suggested that CMR is a dynamic phenomenon and it was studied in the context of dynamic mean-field theories [9]. In general, polaronic models enter a similar line of ideas [10]. More recently, Moreo *et al.* [11] have proposed a phase separation (PS) scenario suggesting that instead the space (momentum) degrees of freedom play the crucial role. In both approaches, a proper explanation of CMR is still lacking.

One of the most puzzling aspects of perovskite manganites is that the hole doped $(x < 0.5)$ and the electron doped $(x > 0.5)$ compounds behave very differently. In the intermediate doping region $x \approx 0.5$ there is a kind of boundary between the hole doped regime, where the metallic ferromagnetic phases and CMR take place, and the electron doped regime where essentially there are phases of coexisting charge and spin ordering. Understanding the physics in this intermediate region $x \approx 0.5 \pm \varepsilon$ appears crucial, and much of the recent experimental activity has focused on it [12–19] reporting some additional puzzling facts. Apparently a small part of the carriers remains metallic in the antiferromagnetic-charge ordering (AFM-CO) regime, and even in the hole doped regime the carriers are separated into a part that is metallic and a part that is still charge ordered [18,20–22]. More puzzling is the fact that the insulating AFM-CO state near the half-filling boundary can be melt by a magnetic field of a few teslas despite the fact that the CO gap is very large (≈ 0.5 eV) and would correspond to several hundreds of teslas [12,13,18].

Numerical calculations on realistic microscopic models for manganites have reported a generic tendency for PS [23] which by including extended Coulomb interactions [24] and disorder [25] turns into charge inhomogeneous states similar to the experimental ones. These results motivated the PS scenario of Moreo *et al.* [11]. Here we develop a momentum space approach that may lead to the same mixed-phase ideas of Moreo *et al.* but from a different and more general perspective. We report for the first time a general multicomponent mean-field theory in which the AFM, CO, and FM order parameters are considered self-consistently on the same footing. Other mean-field theories have considered the above orders but only one by one and therefore cannot account for their coexistence to which our novel results are due. Our approach provides a natural understanding of the puzzling behavior in the intermediate doping region of perovskite manganites and helps in understanding the underlying physics of CMR and itinerant FM.

We propose a general mean-field Hamiltonian describing the coexistence of CO, AFM, and FM orders in the presence of a uniform magnetic field.

$$
H = \sum_{\mathbf{k},\alpha} \xi_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha}^{\dagger} c_{\mathbf{k}\alpha} - \sum_{\mathbf{k},\alpha,\beta} \delta_{\alpha\beta} W_{\mathbf{k}} (c_{\mathbf{k}\alpha}^{\dagger} c_{\mathbf{k}+\mathbf{Q}\beta} + \text{H.c.})
$$

$$
- \sum_{\mathbf{k},\alpha,\beta} (\boldsymbol{\sigma} \cdot \mathbf{n})_{\alpha\beta} M_{\mathbf{k}} (c_{\mathbf{k}\alpha}^{\dagger} c_{\mathbf{k}+\mathbf{Q}\beta} + \text{H.c.})
$$

$$
- \sum_{\mathbf{k},\alpha,\beta} (\boldsymbol{\sigma} \cdot \mathbf{n})_{\alpha\beta} (F_{\mathbf{k}} + \mu_B H) (c_{\mathbf{k}\alpha}^{\dagger} c_{\mathbf{k}\beta} + \text{H.c.}),
$$

(1)

where α , β are spin indices, W_k , M_k , and F_k are the CO, AFM, and FM order parameters, respectively, **n** are the polarizations of the AFM and FM orders considered here parallel without influence on the generality of the results, \overline{a}

 ξ_k is the electronic dispersion, and $\mu_B H$ is the Zeeman contribution of the applied magnetic field. This Hamiltonian is derived in analogy with other mean-field Hamiltonians such as the BCS mean-field Hamiltonian for the superconducting ordering. The above Hamiltonian accounts for the physics resulting from the coexistence of the AFM, CO, and FM orders irrespective of the exact microscopic mechanism responsible for these orderings, similarly as the BCS Hamiltonian accounts for the physics related to the superconducting ordering irrespective of the exact pairing mechanism. Our approach applies to *any itinerant system in which the above orders are present* and therefore to manganites as well.

To study all order phenomena on the same footing, we must work in a multicomponent spinor space [26]. We use an eight component spinor formalism with a basis defined by the following tensor products: $\hat{\tau} = \hat{\sigma} \otimes (I \otimes I),$ $\hat{\rho} = I \otimes (\hat{\sigma} \otimes I)$, and $\hat{\sigma} = I \otimes (I \otimes \hat{\sigma})$, where $\hat{\sigma}$ are the usual Pauli matrices and \hat{I} the identity matrix. We define $2\gamma_k = \xi_k - \xi_{k+0}$ and $2\delta_k = \xi_k + \xi_{k+0}$. When $\delta_{\mathbf{k}} = 0$ there is particle-hole symmetry or perfect nesting at the wave vector **Q**. With the above notations and considering all order parameters real we have obtained the one particle thermal Green's function corresponding to our Hamiltonian. It can be written as follows:

$$
\hat{G}_{\mathbf{k},n} = -[i\omega_n \hat{\tau}_2 + i\gamma_\mathbf{k} \hat{\tau}_1 \hat{\rho}_3 + \delta_\mathbf{k} \hat{\tau}_2 \hat{\rho}_3 + iW_\mathbf{k} \hat{\tau}_3 \hat{\rho}_3 + iM_\mathbf{k} \hat{\tau}_3 \hat{\rho}_3 \hat{\sigma}_3 + (F_\mathbf{k} + \mu_B H) \hat{\tau}_2 \hat{\rho}_3 \hat{\sigma}_3] \times \{A_{\mathbf{k},n} \hat{\tau}_2 + i2\gamma_\mathbf{k} \delta_\mathbf{k} \hat{\tau}_1 + i[2W_\mathbf{k} \delta_\mathbf{k} + 2M_\mathbf{k} (F_\mathbf{k} + \mu_B H)] \hat{\tau}_3 + [2W_\mathbf{k} M_\mathbf{k} + 2(F_\mathbf{k} + \mu_B H) \delta_\mathbf{k}] \hat{\tau}_2 \hat{\sigma}_3 + i[2M_\mathbf{k} \delta_\mathbf{k} + 2W_\mathbf{k} (F_\mathbf{k} + \mu_B H)] \hat{\tau}_3 \hat{\sigma}_3 + i2\gamma_\mathbf{k} (F_\mathbf{k} + \mu_B H) \hat{\tau}_1 \hat{\sigma}_3 \} [B_{\mathbf{k},n} - \Gamma_{\mathbf{k},n} \hat{\sigma}_3] D_{\mathbf{k},n}, \tag{2}
$$

where $\omega_n = (2n + 1)\pi T$ are the Matsubara frequencies for fermions. To condense the formal expressions, the following functionals have been defined:

$$
A_{\mathbf{k},n} = \omega_n^2 + \gamma_\mathbf{k}^2 + \delta_\mathbf{k}^2 + W_\mathbf{k}^2 + M_\mathbf{k}^2 + (F_\mathbf{k} + \mu_B H)^2,
$$
\n(3)

$$
B_{\mathbf{k},n} = A_{\mathbf{k},n}^2 - 4\gamma_{\mathbf{k}}^2 \delta_{\mathbf{k}}^2 - 4[W_{\mathbf{k}} \delta_{\mathbf{k}} + M_{\mathbf{k}} (F_{\mathbf{k}} + \mu_B H)]^2
$$

+ 4[W_{\mathbf{k}} M_{\mathbf{k}} + \delta_{\mathbf{k}} (F_{\mathbf{k}} + \mu_B H)]^2
- 4[M_{\mathbf{k}} \delta_{\mathbf{k}} + W_{\mathbf{k}} (F_{\mathbf{k}} + \mu_B H)]^2
- 4\gamma_{\mathbf{k}}^2 (F_{\mathbf{k}} + \mu_B H)^2, \tag{4}

$$
\Gamma_{\mathbf{k},n} = 4A_{\mathbf{k},n}[W_{\mathbf{k}}M_{\mathbf{k}} + \delta_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)]
$$

\n
$$
- 8\gamma_{\mathbf{k}}^2 \delta_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)
$$

\n
$$
- 8[W_{\mathbf{k}}\delta_{\mathbf{k}} + M_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)]
$$

\n
$$
\times [M_{\mathbf{k}}\delta_{\mathbf{k}} + W_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)], \qquad (5)
$$

$$
D_{\mathbf{k},n} = \{ [\omega_n^2 + E_{++}^2(\mathbf{k})] [\omega_n^2 + E_{+-}^2(\mathbf{k})] \times [\omega_n^2 + E_{-+}^2(\mathbf{k})] [\omega_n^2 + E_{--}^2(\mathbf{k})] \}^{-1}.
$$
 (6)

We obtain four different quasiparticle branches $E_{\pm\pm}(\mathbf{k})$ defined as follows:

$$
E_{+\pm}(\mathbf{k}) = \sqrt{\gamma_{\mathbf{k}}^2 + (W_{\mathbf{k}} \pm M_{\mathbf{k}})^2} + [\delta_{\mathbf{k}} \pm (F_{\mathbf{k}} + \mu_B H)], \tag{7}
$$

$$
E_{-\pm}(\mathbf{k}) = \sqrt{\gamma_{\mathbf{k}}^2 + (W_{\mathbf{k}} \pm M_{\mathbf{k}})^2}
$$

– [$\delta_{\mathbf{k}} \pm (F_{\mathbf{k}} + \mu_B H)$]. (8)

 $W_{\mathbf{k}}$, $M_{\mathbf{k}}$, and $F_{\mathbf{k}}$ obey self-consistency relations (e.g., $W_{\mathbf{k}} = T \sum_{\mathbf{k}}^{N}$ $\sum_{n} V_{\mathbf{k}\mathbf{k}'}^{CO} \frac{1}{8} \text{Tr} \{ \hat{\tau}_1 \hat{\rho}_3 \hat{G}_{\mathbf{k}',n} \}$, etc.). The requirement of self-consistency leads to a system of coupled equations:

$$
W_{\mathbf{k}} = -T \sum_{\mathbf{k}'} \sum_{n} V_{\mathbf{k}\mathbf{k}'}^{\text{CO}} \n\times \{W_{\mathbf{k}'} f_{\mathbf{k}',n} + M_{\mathbf{k}'} g_{\mathbf{k}',n} - (F_{\mathbf{k}'} + \mu_B H) h_{\mathbf{k}',n} \n- \delta_{\mathbf{k}'} u_{\mathbf{k}',n} \} D_{\mathbf{k}',n},
$$
\n(9)

$$
M_{\mathbf{k}} = -T \sum_{\mathbf{k}'} \sum_{n} V_{\mathbf{k}\mathbf{k}'}^{\text{AFM}} \times \{ M_{\mathbf{k}'} f_{\mathbf{k}',n} + W_{\mathbf{k}'} g_{\mathbf{k}',n} - (F_{\mathbf{k}'} + \mu_B H) u_{\mathbf{k}',n} - \delta_{\mathbf{k}'} h_{\mathbf{k}',n} \} D_{\mathbf{k}',n},
$$
\n(10)

$$
F_{\mathbf{k}} = -T \sum_{\mathbf{k}'} \sum_{n} V_{\mathbf{k}\mathbf{k}'}^{\text{FM}} \times \{ (F_{\mathbf{k}'} + \mu_B H) f_{\mathbf{k}',n} + \delta_{\mathbf{k}'} g_{\mathbf{k}',n} - y_{\mathbf{k}',n} - W_{\mathbf{k}'} h_{\mathbf{k}',n} - M_{\mathbf{k}'} u_{\mathbf{k}',n} \} D_{\mathbf{k}',n},
$$
\n(11)

where

$$
f_{\mathbf{k},n} = A_{\mathbf{k},n} B_{\mathbf{k},n} - 2[W_{\mathbf{k}} M_{\mathbf{k}} + \delta_{\mathbf{k}} (F_{\mathbf{k}} + \mu_B H)], \quad (12)
$$

$$
g_{\mathbf{k},n} = 2[W_{\mathbf{k}}M_{\mathbf{k}} + \delta_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)]B_{\mathbf{k},n} - A_{\mathbf{k},n}\Gamma_{\mathbf{k},n},
$$
\n(13)

$$
h_{\mathbf{k},n} = 2[M_{\mathbf{k}}\delta_{\mathbf{k}} + W_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)]B_{\mathbf{k},n}
$$

- 2[W_k\delta_k + M_k(F_k + \mu_BH)]\Gamma_{k,n}, (14)

$$
u_{\mathbf{k},n} = 2[W_{\mathbf{k}}\delta_{\mathbf{k}} + M_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)]B_{\mathbf{k},n}
$$

- 2[M_{\mathbf{k}}\delta_{\mathbf{k}} + W_{\mathbf{k}}(F_{\mathbf{k}} + \mu_B H)]\Gamma_{\mathbf{k},n}, (15)

$$
y_{\mathbf{k},n} = 2\gamma_{\mathbf{k}}^2[(F_{\mathbf{k}} + \mu_B H)B_{\mathbf{k},n} - \delta_{\mathbf{k}}\Gamma_{\mathbf{k},n}].
$$
 (16)

We look upon the system of coupled equations (9) – (11) as similar to the BCS gap equation in superconductivity. The kernels V_{kk} in the different CO, AFM, or FM channels are input parameters, as the pairing potential is in BCS theory. Inhomogeneous states as in manganites imply momentum dependent order parameters and kernels. The FM and AFM-CO orders that will result from Eqs. (9) – (11) will in general occupy different regions in momentum (real) space. This is illustrated with a simplified example

in Fig. 1 where it is reported the solution on a square two dimensional tight binding system with nearest neighbors (NN) and next nearest neighbors (NNN) hopping terms (corresponding, respectively, to γ_k and δ_k). The FM component develops near $(0, \pi)$ and symmetry related areas where the NNN term creates deviation from nesting destabilizing the AFM component [here $\mathbf{Q} = (\pi, \pi)$]. In real space, this kind of solution is similar to charge inhomogeneous solutions obtained by Moreo *et al.* (see Fig. 2B in [11]) on microscopic models with extended Coulomb terms and is unrelated to the spin canted state which is homogeneous and has the FM and AFM polarizations orthogonal unlike in the present formalism. To explain the coexistence of giant clusters and obtain a realistic fit of recent experiments [20,21], Moreo *et al.* have shown that the inclusion of disorder may be necessary [25]. Disorder is not explicitly included in our formalism, however the arguments that follow are valid whatever the momentum (space) structure of the order parameters and therefore should normally be valid in the presence of disorder as well.

A solvable microscopic model could in principle provide the various kernels $V_{kk'}$ for a given material system. Then we should solve a system of Eqs. (9) – (11) for each **Q** in the Brillouin zone. The solution that minimizes the free energy characterized by a wave vector **Q** and a set of order parameters W_k , M_k , and F_k will be the ground state of the system to be compared with the experiments. It results from the following analysis that this is the correct procedure for the study of the above orders in *any itinerant particle-hole asymmetric system* because in such systems the coexistence and competition of these orders are in practice shown to be unavoidable. In this Letter we focus on qualitative arguments which are generally valid irrespective of the microscopic model.

We first note that if $\delta_{\mathbf{k}} = 0$, then $W_{\mathbf{k}} = 0$ is a trivial solution of (9), $M_k = 0$ a trivial solution of (10), and

FIG. 1. Example of inhomogeneous state in our approach. The FM (black) and AFM (grey) order parameters over the first Brillouin zone of a 2D square tight binding system with NN and NNN hopping terms. For simplicity Eq. (9) has been ignored and a choice of potentials with maxima at (π, π) and $(0, \pi)$ is made.

 $F_k = 0$ a trivial solution of (11). Therefore, any combination of the above orders is possible. Particle-hole asymmetry induced by $\delta_{\mathbf{k}} \neq 0$ implies unexpected constraints. In fact, let us start by considering $F_k = 0 = \mu_B H$. In both particle-hole symmetric ($\delta_{\bf k} = 0$) and particle-hole asymmetric ($\delta_{\bf k} \neq 0$) cases, the trivial solutions $W_{\bf k} = 0$ and $M_k = 0$ are independently valid in (9) and (10), respectively. The situation is already different if we apply a uniform magnetic field ($\mu_B H \neq 0$). For $\delta_{\mathbf{k}} = 0$ the trivial solutions $W_{\mathbf{k}} = 0$ and $M_{\mathbf{k}} = 0$ are still true independently so that we may still have CO or AFM alone at perfect nesting. However, when we dope the system having $\delta_{\bf k} \neq 0$, the trivial solutions $W_{\bf k} = 0$ and $M_{\bf k} = 0$ are *no longer true independently*. We must either have both W_{k} , $M_{k} = 0$ or both W_{k} , $M_{k} \neq 0$, provided that none of $V_{kk'}^{\text{CO}}$ and $V_{kk'}^{\text{AFM}}$ is identically zero which is the most natural case for a real material system. Applying a uniform magnetic field in a doped CO or AFM system we *arrive at the coexistence of commensurate charge and spin density orders*.

Let us now take into account the possibility for FM ordering by considering also Eq. (11). A similar analysis can show that if $W_k \neq 0$ or $M_k \neq 0$ and there is no particle-hole symmetry ($\delta_{\bf k} \neq 0$), then $F_{\bf k} = 0$ is *not* a trivial solution of (10). Therefore W_k , M_k , and F_k *necessarily coexist* in a particle-hole asymmetric system. By doping the CO or AFM system we necessarily *generate a ferromagnetic component*. Given the generic validity of our mean-field approach, this result may improve our understanding of FM in a variety of materials like MnSi [27], TbNi₂B₂C [28], or some doped fullerenes TDAE-C₆₀ [29] where signs of coexistence and competition of FM with AFM-CO orders are evident. Note that this result can be viewed as a formal generalization of the "excitonic" FM picture, invoked recently for some lightly doped hexaborides [30].

We focus now on the behavior of perovskite manganites. In La_{1-x}Ca_xMnO₃, particle-hole symmetry ($\delta_{\bf k} = 0$) corresponds to $x = 0.5$. The metallic FM state is in competition with the insulating AFM-CO state. They both occupy a portion of the carriers at finite doping. If the AFM-CO state is melt, its portion of carriers is liberated and the resistivity drops. The AFM-CO state will melt when one of the quasiparticle poles given in Eqs. (7) and (8) will go to zero (will soften), in analogy with the estimate of the critical in-plane fields for the melting of superconductivity in films [31]. When $W_{\mathbf{k}} \approx M_{\mathbf{k}}$, small magnetic fields are sufficient to melt the AFM-CO state even if W_k and M_k are very large. In fact, CO and AFM interfere to produce quasiparticle poles with $W_{\bf k} + M_{\bf k}$ and $W_{\bf k} - M_{\bf k}$, the latter being the relevant ones since these are likely to become zero. We therefore consider the $W_{\mathbf{k}} - M_{\mathbf{k}}$ terms in (7) and (8), namely, $E_{+-}(\mathbf{k})$ and $E_{--}(\mathbf{k})$. We distinguish here two cases: In the case of hole doping $(\delta_k < 0)$, in $E_{+-}(\mathbf{k}) =$ $\gamma_{\mathbf{k}}^2 + (W_{\mathbf{k}} - M_{\mathbf{k}})^2 + \delta_{\mathbf{k}} - F_{\mathbf{k}} - \mu_B H$, the doping $\delta_{\mathbf{k}}$, the FM order $F_{\mathbf{k}}$, and the magnetic field $\mu_B H$ all

have a negative sign and cooperatively compete with the AFM-CO order, making probable the softening of the $E_{+-}(\mathbf{k})$ branch and therefore the melting of the AFM-CO order. On the other hand, in the case of electron doping ($\delta_{\bf k} > 0$), in both relevant quasiparticle branches $E_{+-}(\mathbf{k})$ and $E_{--}(\mathbf{k})$, $\delta_{\mathbf{k}}$ has *its sign opposite to that of* F_k and $\mu_B H$. Electron doping does not cooperate with FM against the AFM-CO state but instead *electron doping contributes to preventing the melting of the AFM-CO order*. This explains the systematic difference between electron doped and hole doped perovskite manganites.

Near half filling, AFM-CO states and FM coexist since even a small nonzero value of $\delta_{\bf k}$ generates a FM component. Near half filling ($x \approx 0.5$) the dominating AFM-CO state can be melt by a small magnetic field because *the critical temperatures of CO and AFM ordering coincide in the phase diagram of perovskite manganites* (see, for example, Fig. 2 in [5] or Fig. 5 in [11]) indicating that indeed W_k and M_k have similar magnitude. Since they also have the same momentum structure (they occupy the same regions in real space) the $E_{+-}(\mathbf{k})$ pole can easily go to zero by a small magnetic field melting the AFM-CO state. When we dope slightly with electrons, the critical field for the melting of AFM-CO increases [18] because electron doping acts against the melting.

The CMR phenomenon can be understood in part by considering the relevant pole $E_{+-}(\mathbf{k})$. At high hole doping, the FM order parameter F_k can be sufficiently large so that, as it develops by lowering the temperature, at $T = T_C$, the pole $E_{+-}(\mathbf{k})$ softens (goes to zero) and the AFM-CO order is melt, liberating its portion of carriers and leading to the large enhancement of the conductivity. The application of a magnetic field enhances the FM order parameter from F_k to $F_k + \mu_B H$ and correspondingly the melting critical temperature from T_C to $T_C + \delta T_C$, producing negative CMR in the temperature range $T_C < T < T_C + \delta T_C$. In the above mechanism, CMR is due to the *increase of the number of carriers* due to a transfer from the AFM-CO state to the coexisting FM state and *not to a decrease in the scattering*.

In conclusion, general symmetry arguments associated with the coexistence of CO, AFM, and FM orders explain the particle-hole asymmetry in the phase diagram of perovskite manganites and associate the melting of the AFM-CO order and CMR with the similarity in magnitude and momentum structure of CO and AFM order parameters. Itinerant FM should normally be analyzed in the context of coexistence and competition with AFM and CO orders as illustrated above.

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