Ferromagnetism and Colossal Magnetoresistance from the Coexistence of Comparable Charge and Spin Density Orders

Georgios VARELOGIANNIS

Max-Planck-Institut für Physik Komplexer Systeme
Nöthnitzer Str. 38, 01187 Dresden, Germany

Abstract

We report a complete multicomponent mean-field-theory for the coexistence and competition of charge ordering (CO), antiferromagnetic (AFM) and ferromagnetic (FM) spin ordering in the presence of a uniform magnetic field. Doping the AFM or CO state always generates a ferromagnetic component. Itinerant FM, AFM and CO, necessarily coexist and compete in a particle-hole asymmetric system. Melting of large AFM-CO orders by small magnetic fields and the related phenomenon of Colossal Magnetoresistance (CMR) may arise whenever the CO and AFM order parameters have similar magnitude and momentum structure. Hole doping favors FM metallic states and CMR while electron doping favors AFM-CO states in agreement with the phase diagram of perovskite manganites.

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1varelogi@mpipks-dresden.mpg.de
The pervovskite manganites \((La, Pr)_{1-x}(Ca, Sr, Ba)_xMnO_3\), in the doping region \(x \approx 0.2 - 0.4\) exhibit a transition to a ferromagnetic (FM) ground state which is accompanied by a large drop of the resistivity \(\text{[1]}\). This transition can be tuned by the application of a magnetic field producing negative “Colossal Magnetoresistance” (CMR) \(\text{[2]}\). Despite the intense experimental and theoretical efforts, many fundamental issues are still under debate including the physical origin of the CMR phenomenon. Ferromagnetism in these materials is usually attributed to the double exchange mechanism \(\text{[3, 4]}\), in which the lattice degrees of freedom \(\text{[5, 6]}\) might also be involved. However, the CMR phenomenon could be more general since it has also been observed in pyrochlore manganites \(\text{[7]}\), where double exchange and Jahn-Teller effects on the transport can be safely excluded \(\text{[8, 9]}\).

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 \(\text{[10, 11, 12, 13, 14, 15, 16, 17]}\) reporting some additional puzzling facts. The coexistence of the AFM charge ordered (AFM-CO) state with FM metallic state has been established \(\text{[16, 13, 14, 15]}\). Apparently a small part of the carriers remains metallic in the AFM-CO regime, and has been reported that even in the hole doped regime the carriers are separated into a part that is metallic and a part that is still charge ordered \(\text{[16, 18, 19]}\). Microscopic theoretical models would also support a spatial separation of FM and AFM-CO phases \(\text{[20]}\). Even more puzzling is the fact that the AFM-CO state near the half-filling boundary can be melt by the application of magnetic fields of few Teslas despite the fact that the CO gap is very large \((\approx 0.5eV)\) and would correspond to several hundreds of Teslas \(\text{[16, 14, 10]}\). The melting of the AFM-CO state appears to progress through the increase of the number of carriers which are FM metallic \(\text{[16]}\).

The above experimental findings suggest that CO, AFM and FM coexist and compete...
and a general mean-field theory is therefore necessary in which all these order parameters are considered self-consistently on the same footing. Such theory is reported for the first time in this Letter and surprisingly, not only provides a natural understanding of the above puzzling behavior in the intermediate doping region of perovskite manganites but also provides unexpected fundamental insight in the underlying physics of CMR and itinerant FM. Other mean-field theories have considered the above orders but only one by one and therefore cannot account for their coexistence to which our original results are due.

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

\[ H = \sum_{\mathbf{k},\alpha} \xi_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}\alpha} + \sum_{\mathbf{k},\alpha,\beta} \delta_{\alpha\beta} W_k \left( c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}+\mathbf{Q}\beta} + HC \right) \]

\[ - \sum_{\mathbf{k},\alpha,\beta} (\sigma \cdot \mathbf{n})_{\alpha\beta} M_k \left( c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}+\mathbf{Q}\beta} + HC \right) \]

\[ - \sum_{\mathbf{k},\alpha,\beta} (\sigma \cdot \mathbf{n})_{\alpha\beta} \left( F_k + \mu_B H \right) \left( c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}\beta} + HC \right) \]

(1)

where \( \alpha, \beta \) are spin indices, \( W_k \), \( M_k \) and \( F_k \) are the CO, AFM and FM order parameters respectively, \( \mathbf{n} \) the polarizations of the AFM and FM orders considered here parallel without influence on the generality of the results, \( \xi_k \) the electronic dispersion and \( \mu_B H \) the Zeeman contribution of the applied magnetic field. The above hamiltonian accounts for the physics resulting from the coexistence of the AFM, CO and FM orders whatever the exact microscopic mechanism responsible for these orderings exactly as the BCS hamiltonian accounts for the physics related to the superconducting ordering irrespective of the exact pairing mechanism. The general conclusions of our study apply 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 [21]. We use an eight component spinor formalism with a basis defined by the following tensor products: \( \hat{\tau} = \hat{\sigma} \otimes (\hat{I} \otimes \hat{I}) \), \( \hat{\rho} = \hat{I} \otimes (\hat{\sigma} \otimes \hat{I}) \), \( \hat{\sigma} = \hat{I} \otimes (\hat{I} \otimes \hat{\sigma}) \), where \( \hat{\sigma} \) are the usual Pauli matrices and \( \hat{I} \) the identity matrix. We define \( 2\gamma_k = \xi_k - \xi_{k+\mathbf{Q}} \) and
2\delta_k = \xi_k + \xi_{k+Q}$. When \delta_k = 0 there is particle-hole symmetry or perfect nesting at the wavevector $Q$. With the above notations and considering all order parameters real we have obtained the one particle diagonal thermal Green’s function corresponding to our hamiltonian. It can be written as follows:

$$
\hat{G}_o(k, i\omega_n) = -[i\omega_n\hat{\tau}_2 + i\gamma_k\hat{\tau}_1\hat{\rho}_3 + \delta_k\hat{\tau}_2\hat{\rho}_3 + iW_k\hat{\tau}_3\hat{\rho}_3 + iM_k\hat{\tau}_3\hat{\rho}_3\hat{\sigma}_3 + (F_k + \mu_B H)\hat{\tau}_2\hat{\rho}_3\hat{\sigma}_3]
$$

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

$$
A(k, i\omega_n) = \omega_n^2 + \gamma_k^2 + \delta_k^2 + W_k^2 + M_k^2 + (F_k + \mu_B H)^2 
$$

$$
B(k, i\omega_n) = A^2(k, i\omega_n) - 4\gamma_k^2\delta_k^2 - 4[W_k\delta_k + M_k(F_k + \mu_B H)]^2 + 4[W_kM_k + \delta_k(F_k + \mu_B H)]^2 
- 4[M_k\delta_k + W_k(F_k + \mu_B H)]^2 - 4\gamma_k^2(F_k + \mu_B H)^2 
$$

$$
\Gamma(k, i\omega_n) = 4A(k, i\omega_n)[W_kM_k + \delta_k(F_k + \mu_B H)] - 8\gamma_k^2\delta_k(F_k + \mu_B H) 
- 8[W_k\delta_k + M_k(F_k + \mu_B H)][M_k\delta_k + W_k(F_k + \mu_B H)] 
$$

$$
D(k, i\omega_n) = \left[\omega_n^2 + E_{++}^2(k)\right]\left[\omega_n^2 + E_{+-}^2(k)\right]\left[\omega_n^2 + E_{-+}^2(k)\right]\left[\omega_n^2 + E_{--}^2(k)\right]^{-1} 
$$

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

$$
E_{++}(k) = \sqrt{\gamma_k^2 + (W_k \pm M_k)^2 + \delta_k \pm (F_k + \mu_B H)} 
$$

$$
E_{--}(k) = \sqrt{\gamma_k^2 + (W_k \pm M_k)^2 - \delta_k \pm (F_k + \mu_B H)} 
$$

The order parameters $W_k$, $M_k$ and $F_k$ obey self-consistency relations (e.g. $W_k = T \sum_{k'} \sum_n V_{kk'} C_{1/8} T r \left\{ \hat{\tau}_1\hat{\rho}_3\hat{G}_o(k', i\omega_n) \right\}$ etc.). The requirement of self-consistency leads to a
system of coupled equations which are reported here because they are necessary for the following discussion

\[ W_k = - \sum_{k'} \sum_n V_{kk'}^{CO} \left\{ W_{k'} f(k', i\omega_n) + M_{k'} g(k', i\omega_n) \right\} \]

\[ - (F_{k'} + \mu_B H) h(k', i\omega_n) - \delta_{k'} u(k', i\omega_n) \right\} D(k', i\omega_n) \] (9)

\[ M_k = - \sum_{k'} \sum_n V_{kk'}^{AFM} \left\{ M_{k'} f(k', i\omega_n) + W_{k'} g(k', i\omega_n) \right\} \]

\[ - (F_{k'} + \mu_B H) u(k', i\omega_n) - \delta_{k'} h(k', i\omega_n) \right\} D(k', i\omega_n) \] (10)

\[ F_k = - \sum_{k'} \sum_n V_{kk'}^{FM} \left\{ (F_{k'} + \mu_B H) f(k', i\omega_n) + \delta_{k'} g(k', i\omega_n) - y(k', i\omega_n) \right\} \]

\[ - W_{k'} h(k', i\omega_n) - M_{k'} u(k', i\omega_n) \right\} D(k', i\omega_n) \] (11)

where

\[ f(k, i\omega_n) = A(k, i\omega_n) B(k, i\omega_n) - 2[W_k M_k + \delta_k (F_k + \mu_B H)] \] (12)

\[ g(k, i\omega_n) = 2[W_k M_k + \delta_k (F_k + \mu_B H)] B(k, i\omega_n) - A(k, i\omega_n) \Gamma(k, i\omega_n) \] (13)

\[ h(k, i\omega_n) = 2[M_k \delta_k + W_k (F_k + \mu_B H)] B(k, i\omega_n) - 2[W_k \delta_k + M_k (F_k + \mu_B H)] \Gamma(k, i\omega_n) \] (14)

\[ u(k, i\omega_n) = 2[W_k \delta_k + M_k (F_k + \mu_B H)] B(k, i\omega_n) - 2[M_k \delta_k + W_k (F_k + \mu_B H)] \Gamma(k, i\omega_n) \] (15)

\[ y(k, i\omega_n) = 2\gamma_k^2 \left[ (F_k + \mu_B H) B(k, i\omega_n) - \delta_k \Gamma(k, i\omega_n) \right] \] (16)

We look upon the system of coupled equations (9-11) as equivalent to the BCS gap equation in superconductivity. The kernels \( V_{kk'} \) in the different CO, AFM or FM channels are input parameters, like the pairing potential is in BCS theory. 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 equations (9-11) for each \( \mathbf{Q} \) in the Brillouin zone. The solution that minimizes the free energy characterized by a wave vector \( \mathbf{Q} \) 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 is shown to be unavoidable.

Implementing the above procedure for a real system like manganites is a complex computational task and requires a specific model assumption and perhaps related simplifications which are outside of the scope of this Letter. Furthermore, for a detailed comparison with the experiments in manganites additional elements like for example orbital ordering may also be necessary to involve. We focus in this Letter on stronger qualitative arguments which are valid whenever itinerant FM, AFM and CO coexist whatever the exact microscopic physics is and are therefore valid for manganites as well. With these arguments we explain only a part of the physics of manganites which results directly from the competition of the above symmetry breakings. However, this part contains some of the most fascinating puzzles in manganites including the CMR phenomenon.

We first note in (5) that particle-hole symmetry (i.e. \( \delta_k = 0 \)) implies \( \Gamma_k \propto W_k M_k \). With this one can show that if \( \delta_k = 0 \) then \( W_k = 0 \) is a trivial solution of (9), \( M_k = 0 \) a trivial solution of (10) and \( F_k = 0 \) a trivial solution of (11). Therefore any combination of the above orders is possible. Particle-hole asymmetry induced by \( \delta_k \neq 0 \) implies unexpected constraints. In fact, let us start by considering \( F_k = 0 = \mu_B H \). In both particle-hole symmetric (\( \delta_k = 0 \)) and particle-hole asymmetric (\( \delta_k \neq 0 \)) cases, the trivial solutions \( W_k = 0 \) 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 \( \delta_k = 0 \) the trivial solutions \( W_k = 0 \) and \( M_k = 0 \) are still true independently so that we may still have CO or AFM alone at perfect nesting. However, when we dope the system having \( \delta_k \neq 0 \), the trivial solutions \( W_k = 0 \) and \( M_k = 0 \) are no more true independently. We must either have both \( W_k, M_k = 0 \) or both \( W_k, M_k \neq 0 \) provided that none of \( V_{kk'}^{CO} \) and \( V_{kk'}^{AFM} \) 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 \( W_k \neq 0 \) and \( M_k \neq 0 \) and there is no particle-hole
symmetry \((\delta_k \neq 0)\), then \(F_k = 0\) 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. This may improve our understanding of FM in a variety of materials ranging from transition metal compounds like \(MnSi\) \(^{22}\) to borocarbides like \(TbNi_2B_2C\) \(^{38}\) or organic materials like the doped fullerenes \(TDAE - C_{60}\) (TDAE=tetrakis dimethyl amino ethylene) \(^{24}\) where signs of coexistence and/or 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 lightly doped hexaborides \(^{25}\). We therefore stress the remarkable perspective that doped hexaborides and manganites may have some similar underlying physics.

We focus now on the behavior of the perovskite manganites. In \(La_{1-x}Ca_xMnO_3\) for example particle-hole symmetry \((\delta_k = 0)\) 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, the carriers from the AFM-CO state will be liberated and the resistivity will drop. The AFM-CO state will be melt when one of our quasiparticle poles given in Eqs. (7) and (8) will go to zero, in analogy with the estimate of the critical in-plane fields for the melting of superconductivity in films \(^{21}\). When \(W_k \approx M_k\), 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 producing quasiparticle poles with \(W_k + M_k\) and \(W_k - M_k\) the later being the relevant since these are likely to become zero. We therefore consider the \(W_k - M_k\) terms in (7) and (8), namely \(E_{+-}(k)\) and \(E_{-+}(k)\). We distinguish here two cases: Hole doping corresponding to \(\delta_k < 0\) and electron doping for \(\delta_k > 0\). In the case of hole doping, in \(E_{+-}(k) = \sqrt{\gamma^2_k + (W_k - M_k)^2 + \delta_k - F_k - \mu_B H}\), the doping \(\delta_k\), the FM order \(F_k\) and the magnetic field \(\mu_B H\) all have the same negative sign and cooperatively compete with the AFM-CO order making probable the softening of the \(E_{+-}(k)\) branch and therefore the melting of the AFM-CO order. On the other hand, in the case of electron doping \((\delta_k > 0)\), in both relevant quasiparticle branches \(E_{+-}(k)\) and \(E_{-+}(k)\), \(\delta_k\) will necessarily have its sign opposite to \(F_k\) and \(\mu_B H\). Therefore electron doping does not cooperate with FM against the AFM-CO state but instead electron doping.
contributes to prevent the melting of the AFM-CO order. This explains the systematic difference between electron-doped and hole-doped perovskite manganites.

Similarly, we can account for some basic aspects of the recent experimental picture of perovskite manganites drawn by Roy, Mitchell, Ramirez and Schiffer \[16\]. Near half filling AFM-CO states and FM coexist since even a small non-zero value of $\delta_k$ 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 \[3\]) indicating that indeed $W_k$ and $M_k$ have similar magnitude and $E_{+-}$ may easily soften. When we go with doping from the hole doped regime to the slightly electron doped regime, the critical field for the melting of the AFM-CO order increases because electron doping acts against the melting. A marginal FM component exists even in the electron doped insulating state and the melting of the AFM-CO state indeed proceeds through an increase of the number of free carriers.

The CMR phenomenon can be understood considering the relevant pole $E_{+-}(k)$. 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 $E_{+-}(k)$ softens 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 picture CMR is due to the increase of the number of carriers and not to a decrease in the scattering in agreement with the experiments \[16\]. The occurrence of CMR in both perovskite and pyrochlore manganites demonstrates that CMR is not particular to a specific microscopic mechanism, which corroborates the above derived picture.

In summary, based on symmetry arguments associated with the coexistence and competition of CO, AFM and FM orders we explain the particle-hole asymmetry in the phase diagram of perovskite manganites and associate the melting of the AFM-CO order and CMR to the similarity of CO and AFM order parameters. Because of its generic (i.e. ma-
terial independent) character our analysis may help the search for new magnetoresistive materials. Our arguments should be valid whenever these orders have some itinerant character. Therefore itinerant FM should normally be analyzed in the context of coexistence and competition with AFM and CO orders as above. This may improve our understanding of itinerant FM in many different materials, and that of various related problems like for example the melting of the spiral phases in $MnSi$ \cite{22} or the metamagnetic transitions in $Y(Co_{1-x}Al_x)_2$ compounds \cite{27}.

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