Ground State of the Double Exchange Model

Liang-Jian Zou\textsuperscript{a}, Qing-Qi Zheng\textsuperscript{a,b}, H. Q. Lin\textsuperscript{c}

\textsuperscript{a}Institute of Solid State Physics, Academia Sinica, P.O.Box 1129, Hefei 230031, China

\textsuperscript{b}State Key Lab of Magnetism, Institute of Physics, Academia Sinica, Beijing, China

\textsuperscript{c}Department of Physics, Chinese University of Hong Kong, Shatin, N.T. Hong Kong, China

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Abstract

We investigate the electronic correlation effect on the ground-state properties of the double exchange model for manganites by using a semiclassical approach and the slave-boson technique. It is shown that magnetic field has a similar effect on the canted angle between manganese spins as doping concentration does, and the canted angle exhibits weak dependence on the Coulomb interaction. The possibility of phase separation in the present model is also discussed. In the slave-boson saddle-point approximation in the ferromagnetic metallic regime, the dependence of the magnetization and the Curie temperature on the doping concentration exhibits maxima near 1/3 doping. These results agree with experimental data and suggest that the electronic correlation plays an important role for understanding the ground-state properties of manganites.

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It is essential to clarify the ground state and magnetic phase diagram for elucidating the microscopic mechanism of the colossal magnetoresistance (CMR) in lanthanum manganese. The ground state and the magnetic phase diagram of lanthanum manganese at low doping concentration in low temperature are still controversial, though some efforts [1-8] have been devoted to it. In 1950, Zener [5] proposed a double exchange (DE) model to explain the electrical conduction and the ferromagnetism (FM) of doped lanthanum manganese. Later Anderson and Hasegawa [6] derived the DE energy for a pair of Mn ions and showed that in such a system, the DE interaction tends to align the spins of Mn ions parallel and the DE energy is proportional to \( \cos(\theta_{ij}/2) \), not to \( \cos(\theta_{ij}) \) as in the Heisenberg model, here \( \theta_{ij} \) denotes the angle between spins \( S_i \) and \( S_j \). In 1960, De Gennes [7] generalized their results to the case with finite doping concentration. He assumed that the total DE energy is proportional to \( \cos(\theta_{ij}/2) \), and showed that the Mn spins in the case of finite doping are ferromagnetically ordered but canted by an angle \( \theta \) that depends on the carrier concentration before a critical concentration \( x_c \). Since then the concept of canted ferromagnet or antiferromagnet was accepted, but not confirmed definitively by early experiments [8]. In recent experiments some researchers declared that there exists canted structure [4,9], but negative results were also reported. Schiffer et al. [1] reported that at low doping (0 < \( x < 0.2 \)), La\(_{1-x}\)Ca\(_x\)MnO\(_3\) is ferromagnetically ordered, whereas Jonker and Van Santan’s early report [2] suggested an antiferromagnetic order. Martin et al. [4] showed that La\(_{1-x}\)Sr\(_x\)MnO\(_3\) is spin-canted for 0 < \( x < 0.1 \), and ferromagnetic ordered for 0.1 < \( x < 0.2 \). These reports on the low-temperature low-doping magnetic phase diagram do not agree with each other. Thus it is necessary to study the DE model in details to clarify the magnetic structure in low-doping regime.

Both the early and the recent experiments [1-4] have shown that in La\(_{1-x}\)R\(_x\)MnO\(_3\) (R=Ca, Sr), the magnetization and the Curie temperature exhibit maxima around \( x=1/3 \). Theoretically, these observations have not been explained satisfactory. Varma [10] estimated that the maximum of the Curie temperature appears at 1/2 doping, Xing and Shen [11] also showed that the zero-temperature magnetization reaches its maximum near 1/2
doping. Another interesting problem is how the magnetic field affects the magnetic structure, since the resistivity of doped lanthanum manganeses is changed by several orders of magnitude under the external magnetic field, such a huge change might be related to the variation of the magnetic structure modulated by magnetic field. Furthermore, the role of electronic correlation was taken into account lightly in previous studies [5-8], since in the primary DE model it only includes the Hund’s coupling between conduction electrons and the core spins but not the Coulomb interaction among conduction electrons. A clear picture of the ground state magnetic properties is needed in order to have a coherent understandings of these phenomena in manganites. In the present paper, we first derive the DE energy in the presence of the Coulomb interaction and the magnetic field, then discuss doping dependence of the mean-field ground state energy, the magnetization and the Curie temperature in ferromagnetic metallic regime in the strong correlation limit.

I. Diagonalization in Momentum Space.

The electronic states in doped lanthanum manganese have been depicted in many papers [5-8,12], in the presence of Coulomb interaction and magnetic field, the model Hamiltonian can be written as a summation of two parts: the double exchange interaction $H_{DE}$ and the superexchange interaction $H_m$

\[
H = H_{DE} + H_m
\]

\[
H_{DE} = \sum_{\langle ij \rangle \sigma} t_{ij} d^\dagger_{i\sigma} d_{j\sigma} + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}} - J_H \sum_{i\mu\nu} S_i \cdot d^\dagger_{i\mu} \sigma_{\mu\nu} d_{i\nu}
\]

\[
H_m = -g\mu_B B \sum_i S^z_i + \sum_{\langle ij \rangle} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j
\]

where the three d electrons of Mn ions are in the $t_{2g}$ state at site $R_i$ and they form a localized core spin $S_i$, $d^\dagger_{i\sigma}$ creates a mobile electron in the $e_g$ band at site $R_i$ with spin $\sigma$, $t_{ij}$ denotes effective hopping matrix element of the mobile electrons to its nearest neighbor, $U$ denotes the on-site Coulomb interaction among mobile electrons, and $J_H$ represents the Hund’s coupling between the local spins and the mobile electrons, $J_H \gg zt/S$ as required by the DE mechanism. In Eqs.(1) and (2), $\langle \cdots \rangle$ indicates that only the nearest neighbor
interaction is considered. In Eq.(2), \( g\mu_B \) represents the effective magnetic moment of local spin, \( B \) represents the external magnetic field, and the last term represents the superexchange interaction between Mn ions, \( A_{ij} \) denotes the superexchange interaction constant which is negative (-\( A' \)) for \( R_i \) and \( R_j \) on the \( ac \) plane and positive (\( A \)) for \( R_i \) and \( R_j \) on the \( b \)-axis. The Jahn-Teller effect and electron-phonon interaction are not included here.

To start, we assume \( S_i \) are classical spins in this section, which corresponds to the following substitution:

\[
S_i^z = S \cos(\theta), \quad S_i^\pm = S e^{\pm iQ \cdot R_i \sin(\theta)}
\]

here \( Q=(0,\pi/b,0) \), \( \theta \) is the canted angle and \( 2\theta \) the angle between two spins. For small doping \( \text{LaMnO}_3 \), the carrier is hole, translating the electron representation into hole representation, \( h^+ \) the model Hamiltonian can then be expressed in momentum space:

\[
H = \sum_k \left[ -g\mu_B B S \cos(\theta) - 4A' S^2 + 2AS^2 \cos(2\theta) \right] + \sum_{k\sigma} [(-\epsilon_k + U < n_\sigma > + \sigma J_H S) h_{k\sigma}^\dagger h_{k\sigma} + J_H S \sin(\theta)(h_{k+Q\uparrow}^\dagger h_{k\downarrow} + h_{k\downarrow}^\dagger h_{k+Q\uparrow})]
\]

where \( \epsilon_{k\sigma} = zt \gamma_k \) denotes dispersion of holes, \( \gamma_k = (1/3)(\cos k_x + \cos k_y + \cos k_z) \) is the structure factor. In this section the Coulomb interaction is treated by the Hatree-Fock approximation. Diagonalization of the hole part in Eq. (4) gives rise to two subbands:

\[
E_{k\sigma} = U < n_\sigma > \pm \sqrt{\epsilon_{k\sigma}^2 + (J_H S)^2 + 2J_H S \epsilon_{k\sigma} \cos(\theta)}
\]

A similar expression has been obtained by Dimashko et al. [13] to address the phase separation issue for high-temperature superconductivity in the limit of \( 2zt/J_H S >> 1 \) with \( U=0 \). Inoue et al. [14] also obtained similar expression in the DE limit and suggested that a spiral state may be more stable than the canted state in \( \text{La}_{1-x}\text{R}_x\text{MnO}_3 \), but they did not consider the effect of the Coulomb interaction on the ground state and the possibility of phase separation. Later we will show that the Coulomb correlation can not be neglected.

To explore the ground-state properties of lanthanum manganeses, we are only interested of the lower subband of (5). In the DE model, \( zt/J_H S \) is a small quantity and we can
expand $E_k$ to the linear term of $zt/J_H S$. At zero temperature, the ground-state energy of the system with uniform doping concentration $x$ is:

$$E_G = NS[-g\mu_B B\cos(\theta) - 4A'S + 2AS\cos(2\theta)] + \sum_{k\sigma}^{k_F} [U < n_{\sigma} > - J_H S - \epsilon_{k\sigma}\cos(\theta)] ,$$

(6)

where $N$ is the total number of core spins. The summation of the mean occupation over spin is the carrier concentration, i.e., $\sum_{k\sigma}^{k_F} < n_{k\sigma} > = x$, the Fermi wave vector is $k_F$.

Minimizing the total energy with respect to $\theta$ gives rise to the canting angle,

$$\cos(\theta) = \frac{g\mu_B BS + 2zt\alpha}{8AS^2} , \quad \alpha = \frac{2}{N} \sum_k^{k_F} \gamma(k) .$$

(7)

For small doping concentration, $x \ll 1$, $\alpha$ depends on doping concentration, we have

$$k_F^3 = 3\pi^2 x ,$$

$$\alpha = x[1 - (3\pi^2 x)^{2/3}/10] .$$

in a three-dimensional isotropic lattice system. This result is slightly different from that of [7], due to the lattice effect. In the absence of the external magnetic field ($B = 0$) for very small doping, $\alpha \approx x$, the critical hole density for the system evolving from canted antiferromagnet into ferromagnet is $x_c = 4AS^2/zt$, this result is similar to that of Ref [7]. Both the present result (in the limit $zt/J_H S << 1$) and that of [13] (in the limit $zt/J_H S >> 1$) have shown that the ground state is antiferromagnetic in the zero doping limit when there is no external magnetic field, so it is reasonable to expect that the ground state is always antiferromagnetic for all values of $zt/J_H S$ in pure lanthanum manganites.

Furthermore the present theory contains some more interesting results. First, the influence of the external magnetic field on the magnetic structure can be discussed for almost pure lanthanum manganites ($x \approx 0$), the effect of magnetic field is similar to that of doping, the cosine of canted angle linearly increases with magnetic field. At a certain critical value $B_c = 8AS/g\mu_B$, the external magnetic field exceeds the superexchange field, all spins tend to align paralleled, the ferromagnetic alignment of local spins are in favor of the motion of holes, so the system may exhibit large decrease in resistivity, however the critical field may be as high as hundreds of T, so it would not like that
the metal-insulator transition induced by the external magnetic field causes the CMR effect. Second, in the Hatree-Fock approximation and expanding $E_{k\sigma}$ (see (5)) to the second order of $(2zt/JH S)$, one can find that the canted angle weakly depends on the Coulomb interaction $U$, so the consideration of the Coulomb correlation in the mean-field approximation does not change canted angle significantly. This is only attribute to the fact that treatment of the electronic correlation in the Hatree-Fock approximation is rather rough.

One conclusion of the above discussion is that manganites with uniform hole concentration is spin canted at low doping. However, Schiffer et al.’s report [1] on a low-doping phase diagram suggests ferromagnetic ordering. This may have two possible reasons: the first is that the oxygen content in $La_{1-x}Ca_xMnO_{3+δ}$ is not exactly stoichiometric ($δ \neq 0$), so the ferromagnetic component arising from the DE interaction plays a role; the second is that phase separation might take place, holes aggregate into a ferromagnetic droplet, so the ferromagnetic ground-state emerges. In the following, we briefly discuss the possibility of phase separation in the DE model ($2zt/JH S << 1$), as contrast to the usual $s$-$f$ model ($2zt/JH S >> 1$). After the holes aggregate into droplets from the antiferromagnetic background, in the absence of external magnetic field, the energy densities $e(x)$ in the hole-rich phase at hole density $x$ is $e(x)$:

$$e(x) = S[-4A'S + 2AS cos(2\theta)] + \left[\frac{Ux^2}{2} - xJH S - 2ztαcos(\theta)\right], \quad (8)$$

and leaving the hole-free antiferromagnetic background with energy density $e(0)$, $e(0) = -2S^2[2A' + A]$, here magnetic field $B=0$. Let $n_h$ be the total number of hole, then the number of sites occupied by the hole-rich phase is $n_h/x$. $N$ is the number of sites of the whole system. Then the total energy of the two-phase state is:

$$E(x) = -2NS^2(2A' + A) - 2n_hJH S + n_h[\frac{4AS^2cos^2(\theta)}{x} + \frac{Ux}{2} - \frac{4ztαcos(\theta)}{x}] \quad (9)$$

For very low hole concentration, $α \approx x$, one has:

$$E(x) = \begin{cases} 
\text{const} + n_h\left(\frac{U}{2} - \frac{(zt)^2}{AS^2}\right)x & x < x_c \\
\text{const} + n_h\left(\frac{4AS^2}{x} + \frac{Ux}{2}\right) & x \geq x_c 
\end{cases} \quad (10)$$
One finds that the presence of a strong on-site Coulomb interaction may prevent phase separation, however, if $U$ is smaller than a critical value $U_c$, 

$$U_c = \frac{(2z\tau)^2}{4AS^2}$$  \hspace{1cm} (11)

the two-phase energy has a minimum at density

$$x = \left( \frac{8AS^2}{U} \right)^{1/2},$$

so the phase separation into ferromagnetic droplet takes place at sufficiently low density $x < x_0$. When $U > U_c$, the $E(x)$ dependence is monotonous $[E'(x); 0]$, so there is no phase separation at all. For typical parameters in $La_{1-x}Ca_xMnO_3$, $4AS^2 = 4.84meV$[15], and by the electronic structure calculation of the local density functional technique, we find that $2z\tau=0.5$ eV, therefore $x_0 \approx 0.007$, which is much smaller than the critical concentration $x_c(\approx 0.1)$. This may address the experimental observation in Ref. 1. Further experiment is expected.

II. A Mean-Field Solution.

In the $La_{1-x}R_xMnO_3$ system, there exists Mn$^{+3}$ and Mn$^{+4}$ ions. Due to strong Hund’s coupling and Coulomb interactions [16], the Mn$^{+2}$ ions are excluded, i.e., double occupancy in the $e_{2g}$ orbital is prohibited. The hopping integral $t$ is far less than the on-site Coulomb interaction and the Hund’s coupling, so it is reasonable to take $U$ as infinity to exclude the appearance of Mn$^{+2}$ in manganites, or the double occupation. In the limit of large Coulomb interaction, the constraint of no double occupancy at site $R_i$ can be enforced by introducing auxiliary fermions [17], $f_{i\sigma}$, and bosons, $b_{\sigma}$, where $f_{i\sigma}^\dagger$ creates a slave fermion with spin $\sigma$ when site $R_i$ is occupied, while $b_i^\dagger$ creates a boson (hole) at $R_i$ when it is unoccupied. Thus $d_{i\sigma} = f_{i\sigma}b_i^\dagger$ and the model Hamiltonian can be rewritten as:

$$H = \sum_{<ij>\sigma} t_{ij} f_{i\sigma}^\dagger f_{j\sigma} b_i b_j^\dagger - J_H \sum_{i\mu\nu} S_i \cdot \sigma_{i\mu\nu} f_{ij\sigma} f_{ij\nu} + \sum_{<ij>} A_{ij} S_i \cdot S_j + \sum_i \epsilon_d (\sum_{\sigma} f_{i\sigma}^\dagger f_{i\sigma} + b_i^\dagger b_i - 1)$$  \hspace{1cm} (12)

where $\epsilon_d$ is the energy shift of the d-electron with respect to the original energy level, the other parameters are the same as in Eq. (1).
In the static (or saddle-point) approximation, the boson field is replaced by its mean value and assumed to be independent of $R_i$, $< b_i^\dagger > = < b_i > = b^{1/2}$, and one can obtain the mean-field equations by taking derivatives with respect to $\epsilon_d$ and $b$:

\[
\sum_\sigma < f_{i\sigma}^\dagger f_{i\sigma} > = 1 - b \tag{13}
\]

\[
\epsilon_d = -2t \sum_\delta < f_{i\sigma}^\dagger f_{i+\delta\sigma} > \tag{14}
\]

Physically, $b$ gives rise to the mean carrier (hole) concentration on every site (see Eq.(13)). If the localization effect of the carriers is neglected, $b$ corresponds to the doping concentration, $x$. Since spin components are relevant to the carrier concentration and the spin-dependent energy should be included in the mean value of fermion propagator, the spin configuration and the carrier concentration must be determined self-consistently.

The mean values in Eqs.(13) and (14) can be obtained from the fermion propagators, $G_\sigma(ij;\omega)$:

\[
G_\sigma(ij;\omega) = \sum_k 1/\{w - \epsilon_d - 2ztb\gamma_k + \sigma J_H S^z_Q \} e^{k(R_i - R_j)} \tag{15}
\]

where $S^z_Q$ denotes the $z$-component of the spin with wave vector $Q$: $Q = 0$ corresponds to ferromagnetic order, $\pi$ to antiferromagnetic order, and values between 0 and $\pi$ to canted structures. Then the self-consistent equations at zero temperature are:

\[
1 - b = -\frac{1}{\pi N} \sum_{k\sigma} \int_{\epsilon_F}^{\epsilon_F^\prime} d\omega \text{Im} \frac{1}{\omega + i\eta - \epsilon_d - 2ztb\gamma_k + \sigma J_H S^z_Q} \tag{16}
\]

and:

\[
\epsilon_d = \frac{4zt}{\pi N} \sum_{k\sigma} \gamma(k) \int_{\epsilon_F}^{\epsilon_F^\prime} d\omega \text{Im} \frac{1}{\omega + i\eta - \epsilon_d + 2ztb\gamma_k + \sigma J_H S^z_Q}, \tag{17}
\]

where $\epsilon_F$ is the Fermi energy. Accordingly, we can obtain the mean value of $< S^z_Q >$, the energy shift $\epsilon_d$ and the ground state energy $E_g$ for doping concentration, $b(= x)$, at zero temperature.

In the present section we are interested in the ferromagnetic metallic regime of La$_{1-x}$Ca$_x$MnO$_3$ ($0.2 < x < 0.5$) system, where the $z$-component of the spin, $S^z$, is the same at all the sites and is independent of the wave vector $Q$. In the ferromagnetic metallic regime,
the carrier is completely spin-polarized due to the strong Hund’s coupling, the density of states of the fermion may take a simple form:

$$\rho(\epsilon) = \begin{cases} 
1/2bD & |\epsilon - \epsilon_d + J_H < S^z >| < bD \\
0 & |\epsilon - \epsilon_d + J_H < S^z >| > bD 
\end{cases}$$

where 2bD is the bandwidth of fermion, the solutions of the self-consistent mean-field equations give rise to the energy shift, \(\epsilon_d\),

$$\epsilon_d = Db(1 - b) = D(1 - n^f)n^f$$

and the local spin moment:

$$< S^z > = (-\epsilon_F + 2bD - 3b^2D)/J_H$$

at zero temperature. An interesting result is that there is an optimized doping for the local spin moment, or the magnetization. From Eq.(20), one finds that the local spin will have a maximum at \(b = 1/3\). Since the magnetization \(M\) is proportional to \(< S^z >\), and as mentioned above, \(b\) corresponds to the hole or doping concentration, so one could expect that the magnetization exhibits a maximum around the doping concentration of 1/3, which agrees with experimental observations in \(\text{La}_{1-x}\text{Ca}_x\text{MnO}\) system [2,3]. Furthermore, one could show by a simple analysis that the Curie temperature also reaches to its maximum around 1/3 doping, which is in agreement with experiments [1,4], and different from the theoretical results in Refs. 10,11.

In the preceding discussion, the electron localization character resulting from the disorder effect in doping is not taken into account, and if it is taken into account, we could expect that optimizing doping concentration for magnetization and Curie temperature may not be at \(x=1/3\) precisely. It could be a little larger than 1/3. Therefore the complete consideration of the electron correlation is important to understand the ground state properties of CMR materials.

To summarize, external magnetic field has similar effect on the canted angle of the manganese spins as the doping concentration, the phase separation may take place in
doped manganites. The mean-field magnetization and the Curie temperature reach max-
ima near 1/3 doping.

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