Ground state of the double-exchange model

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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. [S0163-1829(97)02146-2]

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 θ_{ij} denotes the angle between spins $\mathbf{S}_i$ and $\mathbf{S}_j$. 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 θ 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 a negative result was also reported. Schiffer *et al.*[1] reported that at low doping ($0<x<0.2$), $La_{1-x}Ca_xMnO_3$ is ferromagnetically ordered, whileas Jonker and Van Santan's early report[2] suggested an antiferromagnetic order. Martin *et al.*[4] showed that $La_{1-x}Sr_xMnO_3$ 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 the low-doping regime.

Both the early and the recent experiments[1–4] have shown that in $La_{1-x}R_xMnO_3$ (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 magnitute 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 the doping dependence of the mean-field ground-state energy, the magnetization, and the Curie temperature in the 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:

$$H = H_{\mathrm{DE}} + H_m ,$$

$$H_{\mathrm{DE}} = \sum_{\langle ij\rangle\sigma} (t_{ij} d^{\dagger}_{i\sigma} d_{j\sigma} + \mathrm{H.c.}) + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}} - J_H \sum_{i\mu\nu} \mathbf{S}_i \cdot d^{\dagger}_{i\mu} \boldsymbol{\sigma}_{\mu\nu} d_{i\nu}, \quad (1)$$

$$H_m = -g\mu_B B \sum_i S^z_i + \sum_{\langle ij\rangle} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j , \quad (2)$$

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 $\mathbf{S}_i$, $d^{\dagger}_{i\sigma}$ creates a mobile electron in the e_{2g} band at site R_i with spin σ, 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, the last term represents the superexchange interaction between Mn ions, and A_{ij} denotes the superexchange interaction constant which is negative $(-A')$ for $\mathbf{R}_i$ and $\mathbf{R}_j$ on the ac plane and positive (A) for $\mathbf{R}_i$ and $\mathbf{R}_j$ on the b axis. The Jahn-Teller effect and electron-phonon interaction are not included here.

To start, we assume $\mathbf{S}_i$ are classical spins in this section, which corresponds to the following substitution:

$$S^z_i = S\cos(\theta), \quad S^{\pm}_i = S e^{\pm i\mathbf{Q}\cdot\mathbf{R}_i} \sin(\theta) \quad (3)$$

Here $\mathbf{Q} = (0, \pi/b, 0)$, θ is the canted angle and 2θ the angle between two spins. For small doping $LaMnO_3$, the carrier is a hole, translating the electron representation into the hole representation. The model Hamiltonian can then be expressed in momentum space:

$$H = \sum_k [-g\mu_B BS\cos(\theta) - 4A'S^2 + 2AS^2\cos(2\theta)] + \sum_{k\sigma} [(-\epsilon_k + U\langle n_{\bar{\sigma}}\rangle + \sigma J_H S) h^{\dagger}_{k\sigma} h_{k\sigma} + J_H S \sin(\theta)(h^{\dagger}_{k+Q\uparrow} h_{k\downarrow} + h^{\dagger}_{k\downarrow} h_{k+Q\uparrow})], \quad (4)$$

where $\epsilon_{k\sigma} = 2zt\gamma_k$ denotes the dispersion of holes and γ_k is the structure factor. In this section the Coulomb interaction is treated by the Hatree-Fock approximation. Diagonalization of the hole part in Eq. (5) gives rise to two subbands:

$$E_{k\sigma} = U\langle n_{\bar{\sigma}}\rangle \pm \sqrt{\epsilon^2_{k\sigma} + (J_H S)^2 + 2J_H S \epsilon_{k\sigma}\cos(\theta)}. \quad (5)$$

A similar expression has been obtained by Dimashko *et al.*[13] to address the phase separation issue for high-temperature superconductivity in the limit $2zt/J_H S \gg 1$ with $U = 0$. Inoue *et al.*[14] also obtained the similar expression in the DE limit and suggested that a spiral state may be more stable than the canted state in $La_{1-x}R_xMnO_3$, but they did not consider the effect of the Coulomb interaction on the ground state. 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 Eq. (5). In the DE model, $2zt/J_H S$ 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 x is

$$E_G = NS[-g\mu_B B\cos(\theta) - 4A'S + 2AS\cos(2\theta)] + \sum_{k\sigma}^{k_F} [U\langle n_{\bar{\sigma}}\rangle - J_H S - \epsilon_{k\sigma}\cos(\theta)]. \quad (6)$$

The summation of the mean occupation over spin is the carrier concentration, i.e., $\Sigma_\sigma \langle n_\sigma\rangle = x$, the Fermi wave vector is K_F.

Minimizing the total energy with respect to θ gives rise to the angle.

$$\cos(\theta) = \frac{g\mu_B BS + 2zt\alpha}{8AS^2}, \quad \alpha = \frac{1}{N}\sum_k^{k_F} \gamma(k), \quad (7)$$

where N is the total number of the spins. For small doping concentration, α depends on doping concentration x:

$$\alpha = x[1 - (3\pi^2 x)^{2/3}/20].$$

in a three-dimensional isotropic lattice system. This result is slight different from that of Ref. 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 $x_c = zt/(4J_H S^2)$; this result is similar to that in Ref. 7. Both the present result (in the limit $2zt/J_H S \ll 1$) and that in Ref. 11 (in the limit $2zt/J_H S \gg 1$) have shown that the ground state is antiferromagnetic in the absence of doping and magnetic field, so it is reasonable to expect that the ground state is always antiferromagnetic for all values of $2zt/J_H S$ in pure lanthanum manganites.

Furthermore, the present theory contains some interesting results. First, the influence of the external magnetic field on the magnetic structure can be discussed for pure lanthanum manganites $(x = 0)$. The effect of the magnetic field is similar to that of doping. The cosine of the canted angle linearly increases with the magnetic field. At a certain critical field $B_c = 8AS/g\mu_B$, the external magnetic field exceeds the superexchange field, all the spins tend to align paralleled, the ferromagnetic alignment of local spins are in favor of the motion of holes, 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 magnetic field causes the CMR effect. Second, in the Hatree-Fock approximation and expanding $\langle n_\sigma\rangle$ to the second order of $(2zt/J_H S)$, 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 the canted angle significantly. This is attributed to the fact that the 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. It may have two possible reasons. The first is that the oxygen content in $La_{1-x}Ca_xMnO_{3+\delta}$ is not exactly stoichiometric ($\delta \neq 0$), so the ferromagnetic component arising from the DE interaction plays a role. The second is that phase separation might take place, the holes aggregate into a ferromagnetic droplet, so the ferromagnetic ground-state emerges. In the following, we briefly discuss the possibility of the phase separation in the DE model ($2zt/J_HS \ll 1$), as contrast to the usual s-f model ($2zt/J_HS \gg 1$). After the holes aggregate into droplets from the antiferromagnetic background, the energy densities in the hole-rich phase at hole density x is $e(x)$:

$$e(x)=S[-4A'S+2AS\cos(2\theta)] + \left[\frac{Ux^2}{2}-xJ_HS-2zt\alpha\cos(\theta)\right] \tag{8}$$

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 droplet is n_h/x, N is the number of sites of the whole system, then the total energy of the two-phase state is

$$E(x)=-2NS^2(2A'+A)-2n_hJ_HS + n_h\left[\frac{4AS^2\cos^2(\theta)}{x}+\frac{Ux}{2}-4zt\alpha\cos(\theta)\right]. \tag{9}$$

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

$$E(x)=\begin{cases} \text{const}+n_h\left(\dfrac{U}{2}-\dfrac{(zt)^2}{AS^2}\right)x, & x<x_c, \\ \text{const}+n_h\left(\dfrac{4AS^2}{x}+\dfrac{Ux}{2}\right), & x\geqslant x_c. \end{cases} \tag{10}$$

One finds that the presence of the strong on-site Coulomb interaction may prevent the phase separation, however, if U is smaller than a critical value U_c,

$$U_c=\frac{(2zt)^2}{AS^2} \tag{11}$$

the two-phase energy has a minimum at density

$$x_0=(8AS^2/U)^{1/2}.$$

So the phase separation into ferromagnet droplets 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 $La_{1-x}Ca_xMnO_3$, $4AS^2=4.84$ meV,[15] and by the electronic structure calculation of the local density functional technique, we find that $2zt=0.5$ 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 the 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_σ, where $f^\dagger_{i\sigma}$ creates a slave fermion with spin σ when site R_i is occupied, while $b^\dagger_i$ creates a boson (hole) at R_i when it is unoccupied. Thus $d_{i\sigma}=f_{i\sigma}b^\dagger_i$ and the model Hamiltonian can be rewritten as

$$H=\sum_{\langle ij\rangle\sigma}(t_{ij}f^\dagger_{i\sigma}f_{j\sigma}b_ib^\dagger_j+\text{H.c.})-J_H\sum_{i\mu\nu}\mathbf{S}_i\cdot f^\dagger_{i\mu}\boldsymbol{\sigma}_{\mu\nu}f_{i\nu} + \sum_{\langle ij\rangle}A_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+\sum_i\epsilon_d\left(\sum_\sigma f^\dagger_{i\sigma}f_{i\sigma}+b^\dagger_ib_i-1\right), \tag{12}$$

where ϵ_d is the energy shift of the d electron with respect to the original energy level and 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, $\langle b^\dagger_i\rangle=\langle b_i\rangle=b^{1/2}$ and one can obtain the mean-field equations by taking derivatives with respect to ϵ_d and b:

$$\sum_\sigma\langle f^\dagger_{i\sigma}f_{i\sigma}\rangle=1-b, \tag{13}$$

$$\epsilon_d=-2t\sum_\delta\langle f^\dagger_{i\sigma}f_{i+\delta\sigma}\rangle. \tag{14}$$

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 $G_\sigma(ij;\omega)$:

$$G_\sigma(ij;\omega)=\sum_k 1/[w-\epsilon_d-2ztb\gamma_k+\sigma J_HS^z_Q]e^{\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}, \tag{15}$$

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

$$1-b=-\frac{1}{\pi N}\sum_{k\sigma}\int^{\epsilon_F}d\omega\,\mathrm{Im}\frac{1}{\omega+i\eta-\epsilon_d-2ztb\gamma_k+\sigma J_H S_Q^z} \tag{16}$$

and

$$\epsilon_d=\frac{4zt}{\pi N}\sum_{k\sigma}\gamma(k)\int^{\epsilon_F}d\omega\,\mathrm{Im}\frac{1}{\omega+i\eta-\epsilon_d+2ztb\gamma_k+\sigma J_H S_Q^z}, \tag{17}$$

where ϵ_F is the Fermi energy. Accordingly, we can obtain the mean value of $\langle S_Q^z\rangle$, the energy shift ϵ_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 the $La_{1-x}Ca_xMnO_3$ $(0.2<x<0.5)$ system, where the z component of the spin S^z is the same at all the sites and is independent of the wave vector $\mathbf{Q}$. In the ferromagnetic metallic regime, the carrier is completely spin polarized due to the strong Hund's coupling and the density of states of the fermion may take a simple form:

$$\rho(\epsilon)=\begin{cases}1/2bD & |\epsilon-\epsilon_d+J_H\langle S^z\rangle|<bD,\\ 0 & |\epsilon-\epsilon_d+J_H\langle S^z\rangle|>bD,\end{cases} \tag{18}$$

where $2bD$ is the bandwidth of fermion, and the solutions of the self-consistent mean-field equations give rise to the energy shift ϵ_d,

$$\epsilon_d=Db(1-b)=D(1-n^f)n^f, \tag{19}$$

and the local spin moment

$$\langle S^z\rangle=(-\epsilon_F+2bD-3b^2D)/J_H \tag{20}$$

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 $\langle S^z\rangle$, and as mentioned above, b corresponds to the hole or doping concentration, one could expect that the magnetization exhibits a maximum around the doping concentration of 1/3, which agrees with experimental observations in the $La_{1-x}Ca_xMnO$ 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 $x=1/3$. 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, the external magnetic field has a similar effect on the canted angle of the manganese spins as the doping concentration and the phase separation may take place in doped manganites. The mean-field magnetization and the Curie temperature reach maxima near 1/3 doping.

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