Orbital Degree of Freedom and Phase Separation in Ferromagnetic Manganites at Finite Temperatures

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The spin and orbital phase diagram for perovskite manganites are investigated as a function of temperature and hole concentration. The superexchange and double exchange interactions dominate the ferromagnetic phases in the low and high concentration regions of doped holes, respectively. The two interactions favor different orbital states each other. Between the phases, two interactions compete with each other and the phase separation appears in the wide range of temperature and hole concentration. The anisotropy of the orbital space causes discontinuous changes of the orbital state and promotes the phase separation. The relation between the phase separation and the stripe-and sheet-type charge segregation is discussed.

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1. INTRODUCTION

Doped perovskite manganites and their related compounds have attracted much attention, since they show not only the colossal magnetoresistance (CMR) but many interesting phenomena such as a wide variety of magnetic structure, charge ordering and structural phase transition. Although the ferromagnetic phase commonly appears in the manganites, the origin still remains to be clarified. Almost a half-century ago, the double exchange (DE) interaction was proposed to explain the close connection between the appearance of ferromagnetism and the metallic conductivity. In the scenario, the Hund coupling between carriers and localized spins is stressed. It has been recognized that the ferromagnetic metallic state in the highly doped region of La$_{1-x}$A$_x$MnO$_3$ ($x \sim 0.3$) with A being a divalent ion is understood based on this scenario, where the compounds show the wide band width.

On the contrary, the DE scenario is not applied to the lightly doped region ($x < 0.2$) where the CMR effect is observed. In the region, the degeneracy of $e_g$ orbitals in a Mn$^{3+}$ ion exists and affects the physical properties. The degeneracy is called the orbital degree of freedom. With taking into account the orbital degree together with the electron correlation, the additional ferromagnetic interaction, that is, the ferromagnetic superexchange (SE) interaction, is derived. This is associated with the alternate alignment of the orbital termed antiferro(AF)-type orbital ordering. The SE interaction dominates the ferromagnetic spin alignment observed in the ab-plane in LaMnO$_3$ and the quasi two-dimensional dispersion relation of the spin wave in it.

When holes are introduced into the insulating LaMnO$_3$, the successive transitions occur in magnetic and transport phase diagrams; with increasing $x$, it is observed in La$_{1-x}$Sr$_x$MnO$_3$ as almost two dimensional ferromagnetic (A-type AF) insulator $\rightarrow$ isotropic ferromagnetic insulator $\rightarrow$ ferromagnetic metal. The first order phase transition between two ferromagnetic states recently discovered in La$_{1-x}$Sr$_x$MnO$_3$ with $x \sim 0.12$ indicates that the orbital state also changes at the transition. In order to understand a dramatic change of electronic states in lightly doped region and its relation to CMR, it is indispensable to study the mutual relation between the two ferromagnetic interactions, i.e., DE and SE.

In this paper, we investigate the spin and orbital phase diagram as a function of temperature ($T$) and hole concentration ($x$). We focus on the competition and cooperation between the two ferromagnetic interactions SE and DE. We show that the SE and DE interactions dominate the ferromagnetic phases in the low and high concentration regions of doped holes, respectively, and favor the different orbital structures each other. Between the two phases, the phase separation (PS) appears in the wide range of $x$ and $T$. It is shown that the phase separation is promoted by the anisotropy in the orbital space. The spin and orbital phase diagram at $T = 0$ was obtained by the Hartree-Fock theory and interpreted in terms of the SE and DE interactions in Ref. [7]. The PS state between two ferromagnetic phases driven by the DE interaction and the Jahn-Teller distortion at $T = 0$ was discussed in Ref. [8]. In this paper, we obtain the PS state based on the model with strong correlation of electrons at finite $T$.

In Sect. II, the model Hamiltonian, where the electron correlation and the orbital degeneracy are taken into account, is introduced. In Sect. III, formulation to calculate the phase diagram at finite $T$ and $x$ is presented. Numerical results are shown in Sect. IV and the last section is devoted to summary and discussion.

II. MODEL

Let us consider the model Hamiltonian which describes the electronic structure in perovskite manganites. We set up the cubic lattice consisting of manganese ions. Two $e_g$ orbitals are introduced in each ion and $t_{2g}$ electrons are treated as a localized spin ($\vec{S}_{t_{2g}}$) with $S = 3/2$. Between $e_g$ electrons, three kinds of the Coulomb interaction, that
is, the intra-orbital Coulomb interaction ($U$), the inter-orbital one ($U'$) and the exchange interaction ($I$), are taken into account. There also exist the Hund coupling ($J_H$) between $e_g$ and $t_{2g}$ spins and the electron transfer $t'_{ij}$ between site $i$ with orbital $\gamma$ and site $j$ with $\gamma'$. Among these energies, the Coulomb interactions are the largest one. Therefore, by excluding the doubly occupied state at each site, we derive the effective Hamiltonian describing the low energy spin and orbital states:

$$\mathcal{H} = \mathcal{H}_t + \mathcal{H}_J + \mathcal{H}_H + \mathcal{H}_{AF}. \quad (1)$$

The first and second terms correspond to the so-called $t$- and $J$-terms in the $tJ$-model for $e_g$ electrons, respectively. These are given by

$$\mathcal{H}_t = \sum_{\langle ij \rangle \gamma \gamma' \sigma} t_{ij}^{\gamma \gamma'} \tilde{d}_{i \gamma \sigma} \tilde{d}_{j \gamma' \sigma} + H.c., \quad (2)$$

and

$$\mathcal{H}_J = -2J_1 \sum_{\langle ij \rangle} \left( \frac{3}{4} n_in_j + \tilde{S}_i \cdot \tilde{S}_j \right) \left( \frac{1}{4} - \tau^l_{ij} \right)$$

$$-2J_2 \sum_{\langle ij \rangle} \left( \frac{1}{4} n_in_j - \tilde{S}_i \cdot \tilde{S}_j \right) \left( \frac{3}{4} + \tau^l_{ij} + \tau^r_{ij} \right), \quad (3)$$

where

$$\tau^l_{ij} = \cos \left( \frac{2\pi}{3} n_i \right) T_{iz} - \sin \left( \frac{2\pi}{3} n_i \right) T_{ix}, \quad (4)$$

and $(n_x, n_y, n_z) = (1, 2, 3)$. $l$ denotes the direction of bond connecting $i$ and $j$ sites. $d_{i \gamma \sigma}$ is the annihilation operator of $e_g$ electron at site $i$ with spin $\sigma$ and orbital $\gamma$ with excluding double occupancy. $\tilde{S}_i$ is the spin operator of the $e_g$ electron and $\tilde{T}_i$ is the pseudo-spin operator for the orbital degree of freedom defined as $\tilde{T}_i = (1/2) \sum_{\gamma \gamma' \sigma} \tilde{d}_{i \gamma \sigma} \bar{d}_{i \gamma' \sigma}$. $J_1 = t_0^2/(U' - I)$ and $J_2 = J_1/(U' + I + 2J_H)$ where $t_0$ is the transfer intensity between $d_{3z^2 - r^2}$ orbitals in the $z$-direction, and the relation $U = U' + I$ is assumed. The orbital dependence of $t_{ij}^{\gamma \gamma'}$ is estimated from the Slater-Koster formulas. The third and fourth terms in Eq. (1) describe the Hund coupling between $e_g$ and $t_{2g}$ spins and the antiferromagnetic interaction between $t_{2g}$ spins, respectively, as expressed as

$$\mathcal{H}_H = -J_H \sum_i \tilde{S}_{t_{2g}i} \cdot \tilde{S}_i, \quad (5)$$

and

$$\mathcal{H}_{AF} = J_{AF} \sum_{\langle ij \rangle} \tilde{S}_{t_{2g}i} \cdot \tilde{S}_{t_{2g}j}. \quad (6)$$

The detailed derivation of the Hamiltonian is presented in Ref. [14]. Main features of the Hamiltonian are summarized as follows: 1) This is applicable to the doped manganites, as well as the undoped insulator. 2) Since $J_1 > J_2$, the ferromagnetic state associated with the AF-type orbital order is stabilized by $\mathcal{H}_J$. Therefore, two kinds of the ferromagnetic interaction, that is, SE and DE are included in the model. 3) As seen in $\mathcal{H}_J$, the orbital pseudo-spin space is strongly anisotropic unlike the spin space.

### III. Formulation

In order to calculate the spin and orbital states at finite temperatures and investigate the phase separation, we generalize the mean field theory proposed by de Gennes. Hereafter, the spin ($\tilde{S}$) and pseudo-spin ($\tilde{T}$) variables are denoted by $u$ in the unified fashion. In this theory, the spin and orbital pseudo-spin are treated as classical vectors as follows

$$(S_{i z}^+, S_{i z}^-, S_i^0) = \frac{1}{2} \left( \sin \theta_i^t \cos \phi_i^t, \sin \theta_i^t \sin \phi_i^t, \cos \theta_i^t \right), \quad (7)$$

and

$$(T_{i z}^+, T_{i z}^-, T_i^0) = \frac{1}{2} \left( \sin \theta_i^t, 0, \cos \theta_i^t \right), \quad (8)$$

where the motion of the pseudo-spin is assumed to be confined in the $xz$-plane. $\theta_i^t$ in Eq. (8) characterizes the orbital state at site $i$ as

$$|\theta_i^t| = \cos(\theta_i^t/2)|d_{3z^2 - r^2}| + \sin(\theta_i^t/2)|d_{x^2 - y^2}|. \quad (9)$$

$t_{2g}$ spins are assumed to be parallel to the $e_g$ one. The thermal distributions of the spin and pseudo-spin are described by the distribution function which is a function of the relative angle between $\bar{u}_i$ and the mean field $\bar{X}_i^u$,

$$w_i^u(\bar{u}_i) = \frac{1}{\nu^u} \exp(\bar{X}_i^u \cdot \bar{m}_i^u), \quad (10)$$

where $\bar{m}_i^u(= \bar{u}_i/|\bar{u}_i|)$ is termed the spin(pseudo-spin) magnetization and the normalization factor is defined by

$$\nu^s = \int_0^\pi d\theta \int_0^{2\pi} d\phi \exp(\lambda^s \cos \theta), \quad (11)$$

and

$$\nu^l = \int_0^{2\pi} d\theta \exp(\lambda^l \cos \theta). \quad (12)$$

The mean fields are assumed to be written as $\bar{X}_i^u = \lambda^u(\sin \Theta_i^u, 0, \cos \Theta_i^u)$. By utilizing the distribution functions defined in Eq. (10), the expectation values of operators $A_i(\tilde{S})$ and $B_i(\tilde{T})$ are obtained as

$$\langle A_i \rangle_s = \int_0^\pi d\theta^s \int_0^{2\pi} d\phi^s w_i^u(\tilde{S}_i) A(\tilde{S}), \quad (13)$$

and
\[ (B_i)_{\gamma} = \int_0^{2\pi} d\theta' w_i'(\tilde{T}_i) B(\tilde{T}) , \]
respectively. In this scheme, the free energy is represented by summation of the expectation values of the Hamiltonian and the entropy of spin and pseudo-spin as follows:

\[ \mathcal{F} = \langle \mathcal{H} \rangle - NT(S^z + S^t) . \]

\( N \) is the number of Mn ions and \( S^u \) is the entropy calculated by

\[ S^u = - \langle \ln \omega^u(\hat{a}) \rangle_u . \]

By minimizing \( \mathcal{F} \) with respect to \( \lambda_i^u \) and \( \Theta_i \), the mean field solutions are obtained. It is briefly noticed that the above formulation gives the unphysical states at very low temperatures \( T < T_{\text{neg}} \sim J_1(2)/10 \) where the entropy becomes negative. Therefore, we restrict our calculation in the region above \( T_{\text{neg}} \). However, at \( T = 0 \), the spin and orbital states are calculated without any trouble in the entropy with the assumption of the full polarizations of spin and pseudo-spin.

Next, we concentrate on the calculation of \( \langle \mathcal{H} \rangle \) in Eq. (13). As shown in Eq. (3), \( \mathcal{H}_f \) is represented by \( S \) and \( T \). By introducing the rotating frame in the spin(pseudo-spin) space, the \( z \)-component of the spin (pseudo-spin) in the frame is given by

\[ \tilde{u}_i^z = \cos \Theta_i^u u_i^z + \sin \Theta_i^u u_i^\xi , \]

which is parallel to the mean field \( \tilde{X}_i^u \). Thus, \( \langle \tilde{u}_i^z \rangle_u \) is adopted as the order parameter which has the relation, \( \langle \tilde{u}_i^z \rangle_u = \frac{1}{2} \langle \tilde{X}_i^u \rangle_u \). The spin part in \( \mathcal{H}_f \) is rewritten by using \( \langle \tilde{m}_i^{xz} \rangle_s \) and the relative angle in the spin space as \( \langle \tilde{m}_i^{xz} \rangle_s \cos (\Theta_i^s - \Theta_i^u) \). On the other hand, the orbital part includes the term \( \cos (\Theta_i^t + \Theta_i^\xi) \), which originates from the anisotropy in the orbital space. \( \mathcal{H}_{AX} \) is also rewritten by using \( \langle \tilde{m}_i^{xz} \rangle_s \) and \( \Theta_i^\xi \) under the relation of \( \langle \tilde{S} \rangle_\gamma = 4 \langle \tilde{S}_{12} \rangle_\gamma \). As for the transfer term \( \mathcal{H}_t \), we introduce the rotating frame and decompose the electron operator as \( \tilde{a}_{\gamma\sigma} = h_{i\gamma}^* z_{i\gamma} + z_{i\gamma}^* \tilde{a}_{i\gamma} \), where \( h_{i\gamma}^* \) is a spin-less and orbital-less fermion operator and \( z_{i\sigma}^\dagger \) and \( z_{i\sigma} \) are the elements of the unitary matrix \( U^{(u)}(\gamma) \) in the spin and pseudo-spin frames, respectively. These are defined by

\[ U^u = \left( \begin{array}{cc} z_{i\gamma}^\dagger & -z_{i\gamma}^u \\ z_{i\gamma}^* & z_{i\gamma}^u \end{array} \right) , \]

with \( z_{i\sigma}^u = \cos(\theta_i^u/2) e^{-i\phi_i^u/2} \) and \( z_{i\sigma}^\dagger = \sin(\theta_i^u/2) e^{i\phi_i^u/2} \) for spin, and \( z_{i\gamma}^\dagger = \cos(\theta_i^t/2) \) and \( z_{i\gamma} = \sin(\theta_i^t/2) \) for orbital. By using the form, \( \mathcal{H}_t \) is rewritten as

\[ \mathcal{H}_t = \sum_{ij} t_{ij}^x \epsilon_{ij}^x h_i^t h_j^t + H.c., \]

with \( t_{ij}^x = \sum_\sigma z_{i\sigma}^x z_{i\sigma}^\dagger \) and \( t_{ij}^x = \sum_{\gamma\gamma'} z_{i\gamma}^x z_{i\gamma'}^\dagger \). The former gives \( e^{i(\phi_i^u - \phi_j^u)/2} \cos \theta_i^u \cos \theta_j^u - e^{-i(\phi_i^u - \phi_j^u)/2} \sin \theta_i^u \sin \theta_j^u \) as expected from the double exchange interaction. By diagonalizing the energy in the momentum space, \( \mathcal{H}_t \) is given by

\[ \mathcal{H}_t = \sum_{\gamma} \epsilon_{\gamma}^t \mathcal{F}(\epsilon_{\gamma}^t) , \]

where \( I \) indicates the band of \( h_i^\gamma \) and \( N_i \) is the number of the bands. \( \epsilon_{\gamma}^t \) corresponds to the energy of the \( I \)-th band. As a result, the expectation value of \( \mathcal{H}_t \) per site is obtained by

\[ E_I = \left\langle \sum_{\gamma} \epsilon_{\gamma}^t \mathcal{F}(\epsilon_{\gamma}^t - \epsilon_F) \right\rangle , \]

which is a function of the spin and pseudo-spin angles at each site, \( \{ \Theta_i^t \} \) and \( \{ \Theta_i^u \} \), and the amplitudes of the mean fields, \( \lambda^t \) and \( \lambda^u \). \( \epsilon_F \) in Eq. (23) is the fermi energy of \( h_i^\gamma \) determined in the equation,

\[ x = \sum_{\gamma} \epsilon_{\gamma}^t \mathcal{F}(\epsilon_{\gamma}^t - \epsilon_F) , \]

where \( \mathcal{F}(\epsilon) \) is the fermi distribution function.

IV. NUMERICAL RESULTS

A. phase diagram at \( T = 0 \)

In this subsection, we show the numerical results at \( T = 0 \). For examining both spin and orbital orderings, two kinds of sublattice are introduced. We assume ferromagnetic (F)-type and three kinds of antiferro (AF)-type spin (pseudo-spin) orderings, which are layer (A)-type, rod (C)-type and NaCl (G)-type.

In Fig. 1(a), the ground state energy \( E_{GS}(x) \) is shown as a function of hole concentration \( x \) for several values of \( J_{AF}/t_0 \). Double- or multi-minima appear in the \( E_{GS}(x) \) curve depending on the value of \( J_{AF}/t_0 \). Therefore, the homogenous phase is not stable against the phase separation. This feature is remarkable in the region of \( 0.1 < x < 0.4 \). In Fig. 1(b), \( E_{GS}(x) \) is decomposed into \( \langle \mathcal{H}_i \rangle \) and \( \langle \mathcal{H}_t \rangle \) for \( J_{AF}/t_0 = 0 \). By drawing a tangent line in the \( E_{GS}(x) \) curve as shown in Fig. 1(a), the phase separation is obtained. By using the so-called Maxwell construction, the phase diagram at \( T = 0 \) is obtained in the plane of \( J_{AF} \) and \( x \) (Fig. 2). The parameter values are chosen to be \( J_1/t_0 = 0.25 \) and \( J_2/t_0 = 0.0625 \). \( J_{AF}/t_0 \) for manganites is estimated from the Néel temperature in CaMnO_{3} to be 0.001 ~ 0.01. Let us consider the case of \( J_{AF}/t_0 = 0.004 \). With doping of holes, the magnetic structure is changed as A-AF \( \rightarrow \) PS(A-AF/F_{1}) \( \rightarrow \) F_{1} \( \rightarrow \) PS(F_{1}/F_{2}) \( \rightarrow \) F_{2}, where PS(A/B) implies the phase separation between A and B phases. The canted
spin structure does not appear. $F_1$ and $F_2$ are the two kinds of ferromagnetic phase discussed below in more detail. Between $F_1$ and $F_2$ phases, the PS state appears and dominates the large region of the phase diagram. For example, at $x = 0.2$, the $F_1$ and $F_2$ phases coexist with the different volume fractions of 60% and 40%, respectively. We also find the PS state between $A$-AF and $F_1$ phases in the region of $0.0 < x < 0.03$.

Now we focus on two kinds of ferromagnetic phase and the PS state between them. The $F_1$ and $F_2$ phases originate from the SE interaction between $e_g$ orbitals and the DE one, respectively. The interactions have different types of orbital ordering as shown in Fig. 2. These are the C-type with $(\theta_A/\theta_B) = (\pi/2, 3\pi/2)$ and the A-type with $(\theta_A/\theta_B) = (\pi/6, -\pi/6)$, respectively, where $\theta_A(B)$ is the angle in the orbital space in the $A(B)$ sublattice. It is known that the AF-type orbital ordering obtained in the $F_1$ phase is favorable to the ferromagnetic SE interaction through the coupling between spin and orbital degrees in $H_{J\theta}$. On the other hand, the $F$-type orbital ordering promotes the DE interaction by increasing the gain of the kinetic energy. To show the relation between the orbital ordering and the kinetic energy, we present the density of state (DOS) of the spin-less and orbital-less fermions in the $F_1$ and $F_2$ phases in Fig. 3(a) and (b), respectively. It is clearly shown that the band width in the $F_2$ phase is larger than that in the $F_1$ phase. In addition, DOS in the $F_2$ phase has a broad peak around $-2 < \omega/t_0 < -0.8$ which results from the quasi-one dimensional orbital ordering. Because of the structure in

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**FIG. 1.** The ground state energy ($E_{GS}$) as a function of hole concentration ($x$). (a): $J_{AF}/t_0$ is chosen to be $0.004$ and $0.01$. The broken lines and the filled triangle show the tangent lines of the $F_{1,2} = 0$ curve and the point.

**FIG. 2.** The phase diagram at $T = 0$ in the plane of antiferromagnetic interaction $J_{AF}$ and hole concentration $x$. $F_1$ and $F_2$ are the ferromagnetic phases with different types of orbital ordering. $PS(F_1/F_2)$ is the phase separated state between the $F_1$ and $F_2$ phases. Types of orbital ordering in the two phases are schematically presented. In the dotted region, there exist $PS(A-AF/F_1)$ and $PS(A-AF/C-AF)$. The parameter values are chosen to be $J_1/t_0 = 0.25$ and $J_2/t_0 = 0.0625$.

**FIG. 3.** The densities of state (DOS) for the spin-less and orbital-less fermions $h_\xi$ (a) in the $F_1$ phase and (b) in the $F_2$ phase. The shaded areas show the occupied state of $h_\xi$. 

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[Diagram of phase diagram and density of state (DOS) for spin-less and orbital-less fermions]
DOS, the kinetic energy further decreases in the F2 phase more than the F1 phase.

In order to investigate the stability of the PS state pearing between the F1 and F2 phases, the ground state energy is decomposed into the contributions from the interaction \( \langle H_J \rangle \) and the DE one \( \langle H_t \rangle \) (see Fig. 1). We find that with increasing \( x \), \( \langle H_J \rangle \) increases and \( \langle H_t \rangle \) decreases. Several kinks appear in the \( \langle H_J \rangle - x \) and \( \langle H_t \rangle - x \) curves, which imply the discontinuous change of the state with changing \( x \). The PS(F1/F2) state shown in Fig. 2 corresponds to the region, where the two ferromagnetic interactions compete with each other and the discontinuous changes appear in the \( \langle H_J \rangle - x \) and \( \langle H_t \rangle - x \) curves. In Fig. 4, we present the \( x \) dependence of the orbital state assuming the homogeneous phase. It is clearly shown that the discontinuous change of \( \langle H_J(t) \rangle - x \) curve is ascribed to that of the orbital state. In particular, in the phase-I and -II, the symmetry of the orbital is lower than that in the F1 and F2 phases and the stripe-type (quasi one dimensional) and sheet-type (two dimensional) charge disproportion is realized, respectively. These remarkable features originate from the anisotropy in the orbital pseudo-spin space. We also note that because of the anisotropy, the orbital state dose not change continuously from F1 to F2. It is summarized that the main origin of the PS state in the ferromagnetic state is 1) the existence of two kinds of ferromagnetic interaction which favor the different types of orbital state, and 2) the discontinuous change of orbital state due to the anisotropy in the orbital space unlike the spin case.

**B. phase diagram at finite \( T \)**

In this subsection, we show the numerical results at finite \( T \) and discuss how the PS state changes with \( T \). As the order parameter of spin, we assume the ferromagnetic ordering and focus on the F1 and F2 phases and the PS state between them. We consider the G- and F-type orbital orderings which are enough to discuss the orbital state in the ferromagnetic state of the present interest.

In Fig. 5, the phase diagram is presented at finite \( T \) where the homogeneous phase is assumed. Parameter values are chosen to be \( J_1/t_0 = 0.25, J_2/t_0 = 0.0625 \) and \( J_{AF}/t_0 = 0.004 \). The straight and dotted lines show the ferromagnetic Curie temperature \( T_C \) and the orbital ordered temperature \( T_{OO} \), respectively. The parameter values are chosen to be \( J_1/t_0 = 0.25, J_2/t_0 = 0.0625 \) and \( J_{AF}/t_0 = 0.004 \).

![FIG. 5. The phase diagram in the plane of temperature \( T \) and hole concentration \( x \). The homogeneous state is assumed. The straight and dotted lines show the ferromagnetic Curie temperature \( T_C \) and the orbital ordered temperature \( T_{OO} \), respectively. The parameter values are chosen to be \( J_1/t_0 = 0.25, J_2/t_0 = 0.0625 \) and \( J_{AF}/t_0 = 0.004 \).](image-url)
two different kinds of the PS state appear at the temperature. With further increasing temperature, several shallow minima appear in the $F_x$ curve. Finally, fine structure disappears and the homogeneous phase comes stable in the whole region of $x$. In Fig. 6(b), free energy is decomposed into the contributions from $\langle H_s \rangle / t_0$, $\langle H_t \rangle / t_0$, and $\langle h \rangle / t_0$ is chosen to be 0.04.

By applying the Maxwell construction to the free energy presented in Fig. 6(a), the PS states are obtained and presented in Fig. 7. The PS states dominate the large area in the $x$-$T$ plane. A variety of the PS states appears with several types of spin and orbital states. Each PS state is represented by the combination of spin and orbital states, such as PS(spin-P, orbital-G/spin-F, orbital-P) for PS-III and PS(spin-F, orbital-G/spin-F, orbital-F) = PS($F_1/F_2$) for PS-VII. Here, P indicates the paramagnetic (orbital) state. It is mentioned that the phase diagram in Fig. 7 has much analogy with that in eutectic alloys. For example, let us focus on the region below $T/t_0 = 0.05$. Here, the $F_1$ and $F_2$ phases and PS-VII correspond to the two kinds of homogeneous solid phases, termed A and B, and the PS state between them (PS(A/B)) in binary alloys, respectively. In the case of the binary alloys, the liquid(L)-phase becomes stable due to the entropy at high temperatures. Thus, with increasing temperature, the successive transition occurs as PS(A/B) $\rightarrow$ (PS(L/A(B))) $\rightarrow$ L. The states, L, PS(L/A) and PS(L/B), correspond to the (spin-F, orbital-P) phase, PS-V, and PS-VI in Fig. 7, respectively. By the analogy between two systems, the phase separated region. The spin and orbital states in each state is PS-I: PS(spin-P, orbital-G/spin-P, orbital-P), PS-II: PS(spin-P, orbital-P/spin-F, orbital-P), PS-III: PS(spin-P, orbital-G/spin-F, orbital-P), PS-IV: PS(spin-P, orbital-G/spin-F, orbital-G), PS-V: PS(spin-F, orbital-G/spin-F, orbital-P), PS-VI: PS(spin-F, orbital-P/spin-F, orbital-F), and PS-VII: PS(spin-F, orbital-G/spin-F, orbital-F) =($F_1/F_2$). The parameter values are the same as those in Fig. 5.

![Image](image_url)

**FIG. 6.** The free energy as a function of hole concentration $(x)$. (a): $T/t_0$ is chosen to be 0, 0.04, and 0.15. The broken lines and the filled triangles show the tangent lines of the $F_x$ curve and the points of contact between the two. (b): $j$ decomposed into the contributions from $TS$, $\langle H_s \rangle$ and $\langle h \rangle$ at $T/t_0 = 0.04$.

In Fig. 8, we present effects of the magnetic field ($B$) on the phase diagram. The magnitude of the applied magnetic field is chosen to be $g\mu_B B/t_0 = 0.02$ which corresponds to 50 Tesla for $t_0 = 0.3eV$ and $g = 2$. We find that the PS state shrinks in the magnetic field. The remarkable change is observed in PS-II and III where the spin-F and -P phases coexist. The magnetic field stabilizes the ferromagnetic phase so that the PS states are replaced by PS-V and the uniform ferromagnetic state. The region of PS-VII (PS($F_1/F_2$)) is also suppressed in the magnetic field. Because the magnitude of the magnetization in the phase $F_1$ is smaller than that in the $F_2$ phase, the magnetic field increases the magnetization and stabilizes the $F_1$ phase.

**V. SUMMARY AND DISCUSSION**

In this paper, we study the spin and orbital phase diagram for perovskite manganites at finite $T$ and $x$. In particular, we pay our attention to two kinds of ferromag-
The microscopic charge segregation and favor the AF- and F-
phases in the lower and higher phases, respectively. Between the phases, the two interactions compete with each other and the phases are unstable against the phase separation. The PS states at finite $T$ have much analogy with that in the binary alloys.

It is worth to compare PS(F$_1$/F$_2$) with PS(AF/F). As shown in Fig. 2 ($J_{AF}/t_0 = 0.004$), PS(F$_1$/F$_2$) appears in the region of higher $x$ than PS(A-AF/F). This originates from the following sequential change of the state with doping of holes as I:(spin-A, orbital-G) $\rightarrow$ II:(spin-F, orbital-G) $\rightarrow$ III:(spin-F, orbital-F). The orbital state changes at higher $x$ than the spin state. As a result, PS(A-AF/F) and PS(F$_1$/F$_2$) appear between I and II, and II and III, respectively. This is because 1) at $x = 0$, the ferromagnetic interaction between spins is weaker than the AF one between orbitals, as mentioned in Sect. IV B, and 2) at $x = 0$, the AF interaction along the $c$-axis is much weaker than the ferromagnetic one in the $ab$-plane. We also notice in Fig. 2 that PS(F$_1$/F$_2$) dominates a larger region in the phase diagram than PS(A-AF/F). This mainly results from the anisotropy in the orbital pseudo-spin space. As shown in Fig. 4, $\theta^{(B)}_{A/B}$ indicating the orbital state discontinuously changes with $x$ in the region of $0.06 < x < 0.41$. Continuous change from F$_1$ to F$_2$ is prevented by the anisotropy in the orbital space. This is highly in contrast to the spin case where the incommensurate and/or flux states associated with the continuous change of the spin angle become more stable than some PS states. The anisotropy in the orbital space also stabilizes the homogeneous state in the region of $x < 0.06$. On the other hand, PS(A-AF/F) appears by doping of infinitesimal holes. Furthermore, the microscopic charge segregation appearing in the phase-I and -II (Fig. 4) is also due to the orbital degree of freedom. Here, the stripe- or sheet-type charge disproportion is realized and the SE and DE interactions dominate different microscopic regions (bonds). These unique phases are ascribed to the dimensionality control of charge carriers through the orbital orderings. It is mentioned that when the orbital degree of freedom is taken into account, PS(AF/F) discussed in the double exchange model is suppressed. This is because A-AF is realized at $x = 0$ instead of G-AF and the ratio of the band width between A-AF and F is $W_{AF}/W_F=2/3$. This ratio is much larger than that between G-AF and F which is of the order of $O(t_0/J_H)$. Therefore, the PS region, where the compressibility ($\kappa = (\partial \mu/\partial x)^{-1}$) is negative, shrinks. The $(d_{3x^2-r^2}/d_{3y^2-r^2})$-type orbital ordering expected from the lattice distortion in LaMnO$_3$ further enhances $W_{AF}/W_F$, because the transfer intensity along the $c$-axis is reduced in the ordering.

It should be noticed that the following effects may suppress the phase separation discussed in the paper. In the present calculation, the order parameters for spin and orbital are restricted in a dice consisting of $2 \times 2 \times 2$ Mn ions. Other types of the ordering become candidates for the solution with the lower energy, especially, in the lightly doped region. However, the orbital ordering with the long periodicity is less important in comparison with that in the spin case. The orbital ordering associated with continuous change of the pseudo-spin is prohibited by the anisotropy, as discussed above. Neither the quantum fluctuation neglected in the mean field theory nor the long range Coulomb interaction favor the phase separation. When the effects are taken into account, the area of PS in the $x$-$T$ plane shrinks and certain regions will be replaced by the homogeneous phases. In this case, it is expected that the phases with the microscopic charge segregation, such as the phase-I and -II shown in Fig. 4, remain, instead of the macroscopic phase separation.

For observation of the PS(F$_1$/F$_2$) state proposed in this paper, the most direct probe is the resonant x-ray scattering which has recently been developed as a technique to observe the orbital ordering. Here, the detailed measurement at several orbital reflection points are required to confirm PS where different orbital orderings coexist. Observation of the inhomogeneous lattice distortion is also considered as one of the evidence of PS(F$_1$/F$_2$), although this is an indirect one. Several experimental results have reported an inhomogeneity in the lattice degree of freedom. In La$_{1-x}$Sr$_x$MnO$_3$, two kinds of Mn-O bond with different lengths are observed by the pair distribution function analyses. These values are almost independent of $x$, although the averaged orthohombicity decreases with $x$. Since two kinds of the bond are observed far below $T_c$, where the magnetization is almost saturated, PS(AF/F) is excluded and PS with different orbital orderings explain the experimental results. The more direct evidence of PS was reported by the synchrotron x-ray diffraction in La$_{0.88}$Srx$_{0.12}$MnO$_3$. Below 350K, some of the diffraction peaks split and the minor phase with 20% volume fraction appears. This
phase shows the larger orthohombic distortion than the major one in the region of $105 \text{K} < T < 350 \text{K}$. Thus, the experimental data are consistent with the existence of $\text{PS}(F_1/F_2)$ where the major and minor phases correspond to the $F_2$ and $F_1$ phases, respectively. In this compound, the first order phase transition from ferromagnetic insulator to ferromagnetic metal occurs at $T = 145 \text{K}$. Through the systematic experiments, it has been revealed that this magnetic transition is ascribed to the transition between the orbital ordering and disordering. The experimental results strongly suggest that the two different interactions, i.e., SE and DE, are concerned in the transition and unconventional experimental results are understood in terms of the interactions. It is desired to carry out further experimental and theoretical investigations to clarify roles of the PS state on the unconventional phenomena.

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