PHYSICAL REVIEW B **67**, 014412 (2003)

Nonlocal coherent potential approximation for the paramagnetic state of the degenerate double-exchange model

I. V. Solovyev*
Tokura Spin Superstructure Project, ERATO Japan Science and Technology Corporation,
c/o National Institute of Advanced Industrial Science and Technology,
Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

(Received 6 March 2002; revised manuscript received 3 September 2002; published 21 January 2003)

The coherent potential approximation (CPA) is applied to the problem of off-diagonal disorder caused by random spin orientations in the paramagnetic (PM) state of the double-exchange (DE) model. The CPA calculations are supplemented by the variational mean-field approach for the Curie temperature (T_C). Our formulation of CPA is essentially nonlocal and based on the perturbation theory expansion for the T matrix with respect to fluctuations of interatomic hopping parameters near the ''mean values'' specified by matrix elements of the self-energy for the effective medium, so that in the first order it becomes equivalent to the DE theory by de Gennes. The second-order effects, considered in the present work, are not negligible and lead to substantial reduction of T_C in the one-orbital case. Even more dramatic changes are expected for the degenerate DE model, where each site of the cubic lattice is represented by two e_g orbitals, which also specify the form of interatomic hoppings. Particularly, the existence of two Van Hove singularities in the spectrum of the degenerate model lead to the branching of CPA solutions, when Green's function and the self-energy become multivalued functions in certain regions of the complex plane. Different solutions can be classified by some nonlocal parameter of interatomic orbital polarization $\mathcal{O}_{\rm NL}$, and the multivalued behavior itself has many similarities with the phenomenon of metamagnetism with respect to $\mathcal{O}_{\rm NL}$. This changes the traditional concept of the DE physics dramatically. Particularly, we predict the transition to the two-phase state (with different values of the order parameter $\mathcal{O}_{\rm NL}$) in the PM region below a certain temperature T_P. It is followed by two consecutive magnetic transitions, which go separately in two different phases. Our scenario naturally explains the phase coexistence and the appearance of several magnetic transition points, which are frequently observed in perovskite manganites.

DOI: 10.1103/PhysRevB.67.014412 PACS number(s): 75.10.Lp, 75.20.−g, 74.81.−g, 75.47.Gk

I. INTRODUCTION

The nature of the paramagnetic (PM) state in perovskite manganese oxides (the manganites) is one of the fundamental questions, the answer to which is directly related to our understanding of the phenomenon of colossal magnetoresistance.

There is no doubt that any theoretical model for manganites should include (at least, as one of the main ingredients) the double-exchange (DE) physics, which enforces the atomic Hund's rule and penalizes kinetic hoppings of polarized e_g electrons to the neighboring site if the latter has the opposite direction of the localized t_{2g} spin.[1–3] The corresponding Hamiltonian is given, in the local coordinate frame specified by the directions $\mathbf{e_i}=(\cos\phi_{\mathbf{i}}\sin\theta_{\mathbf{i}},\sin\phi_{\mathbf{i}}\sin\theta_{\mathbf{i}},\cos\theta_{\mathbf{i}})$ of the spin magnetic moments, by[4]

$$\mathcal{H}_{\mathbf{ij}}=-\xi_{\mathbf{ij}}t_{\mathbf{ij}}, \tag{1}$$

where $t_{\mathbf{ij}}$ are the (bare) parameters of kinetic hoppings between e_g orbitals located at neighboring sites $\mathbf{i}$ and $\mathbf{j}$, and $\xi_{\mathbf{ij}}=\cos(\theta_{\mathbf{i}}/2)\cos(\theta_{\mathbf{j}}/2)+\sin(\theta_{\mathbf{i}}/2)\sin(\theta_{\mathbf{j}}/2)e^{-i(\phi_{\mathbf{i}}-\phi_{\mathbf{j}})}$ describes the modulations caused by deviations from the ferromagnetic (FM) spin alignment in the bond **i**-**j**. The Hamiltonian (1) can be viewed as the DE limit of the FM Kondo lattice model (KLM), assuming an infinite splitting between majority- and minority-spin states, and that all other interactions such as the electron-phonon coupling and the on-site Coulomb repulsion, which can lift the local degeneracy of the e_g orbitals, are small in comparison with the e_g bandwidth W ($W\approx 4$ eV, according to band structure calculations in the local-spin-density approximation).[5] The localized spins are treated classically, which seems to be a reasonable approximation for the 3/2 t_{2g} spins in manganites.[6,7]

According to the formulation of the DE model, the spin magnetic moments are always saturated, and in order to describe the PM states we need to address the problem of orientational spin disorder. Despite an apparent simplicity, this is a very serious problem, which was studied only in few theoretical approaches, based on rather severe (and presumably unsatisfactory) approximations.

The first one was proposed by de Gennes more than forty years ago.[3] In his theory, all $\xi_{\mathbf{ij}}$ are replaced by an averaged value $\overline{\xi}$, so that the spin disorder enters the model only as a renormalization of W. The effect is not particularly strong and the fully disordered PM state corresponds to $\overline{\xi}=\frac{2}{3}$. The same idea was exploited recently in a number of theories aiming to study the behavior of orbital degrees of freedom at elevated temperature,[8] but based on the same kind of simplifications for the spin disorder.

Another direction, which features more recent activity, is the single-site dynamical mean-field theory (DMFT) for the FM KLM.[9–12,60] If the localized spins are treated classically, this method is similar to the disordered local moment approach proposed by Gyorffy *et al.*,[13] and based on the coherent potential approximation (CPA) for the electronic structure of the disordered PM state.[14] A more conventional CPA-type formulation for the spin disorder in the FM KLM can be found in Refs. 7, 15, and 16.

Now it is almost generally accepted that both approaches are inadequate as they fail to explain not even all, but a certain number of observations in manganites of a principal character such as the absolute value and the doping dependence of the Curie temperature (T_C),[17] the insulating behavior above T_C,[18] and a rich magnetic phase diagram along the temperature axis, which typically show a number of magnetic transitions[19] and the phase coexistence[20–22] in certain temperature intervals. Therefore, it is clear that the theory must be revised.

There are two possible ways to proceed. One is to modernize the model itself by including additional ingredients such as the electron-phonon coupling,[23] Coulomb repulsion,[8,24,25] and chemical disorder.[16,26–28] Another possibility is to stick to the basic concept of the DE physics and try to formulate a more advanced approach for the spin disorder, which would go beyond the simple scaling theory by de Gennes[3] as well as the single-site approximation inherent to DMFT.[11,12]

Attention to the second direction was brought recently by Varma,[29] who emphasized that the orientational spin disorder enters the DE Hamiltonian (1) as an off-diagonal disorder of interatomic hopping parameters, which presents very challenging and not well investigated problem. In the present work we try to investigate some possibilities along this line by employing a nonlocal CPA approach.

What do we expect?

(1) It was realized very recently that many aspects of seemingly complicated low-temperature behavior of doped manganites can be understood from the viewpoint of DE physics, if the latter is combined with details of realistic electronic structure for the e_g states and takes into account strong dependence of this electronic structure on the magnetic structure.[5,30] At the present stage it is not clear to what extent the same scenario can be applied to the finite temperature regime and whether it can cover the physics of the disordered PM state. If it can, there should be something peculiar in the electronic structure of the PM state, which can be linked to the unique properties of perovskite manganites. The simplest way to address this question is to use the DE theory by de Gennes,[3] and to consider an approximate electronic structure for the PM state by scaling similar electronic structure for the FM state. The latter is shown in Fig. 1, using the results of the Slater-Koster parametrization for the e_g states in the cubic lattice.[31] The electronic structure is indeed very peculiar because of two Van Hove singularities at the $(\pi,\pi,0)$ and $(0,\pi,0)$ points of the Brillouin zone, which are responsible for two kinks of density of states at ± 1. The first singularity is expected to be near the Fermi level when the hole concentration is close to 0.3, i.e., in the most interesting regime from the viewpoint of colossal magnetoresistance.[32] If so, what are the possible roles of these singularities in the case of the spin disorder? Although the main details of the electronic structure will be broadened, it is still reasonable to expect some anomalies. Will they contribute to the properties of the PM state? If yes, in which form? Note that apart from the single-site approximation, most of recent DMFT calculations[10–12] employed a model semicircular (SC) density of states (DOS), and therefore could not address these questions.

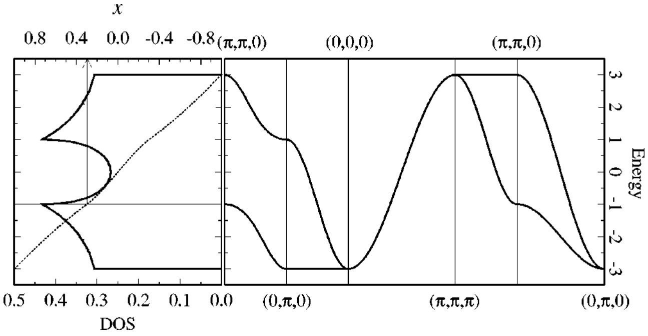

FIG. 1. Tight-binding density of states and dispersion of the e_g bands in the ferromagnetic state. The value of the $dd\sigma$ transfer integral is used as the energy unit. Dotted line shows positions of the Fermi level as a function of hole concentration $x = 1 - n$, where n is the integrated density of states. Note the existence of two Van Hove singularities at $(\pi,\pi,0)$ and $(0,\pi,0)$, responsible for the kinks of density of states at ± 1. The first singularity is located near the Fermi level when $x \simeq 0.3$ (shown by arrow).

(2) There are many anticipations that there is some hidden parameter, which controls the properties of perovskite manganites. A typical example is the picture of orbital disorder,[24,25] according to which the degeneracy of e_g orbitals is lifted by strong on-site Coulomb repulsion. It breaks the cubic symmetry of the crystal, at least locally, and produces a nonvanishing orbital polarization at each site of the system. The main conjecture in Ref. 24 is that this effect persists in the FM state of cubic manganites without forming the long-range ordering. In the present work we will show that by considering nonlocal effects in the degenerate DE model, one may have an alternative scenario, when there is certain degree of freedom which does control the properties of cubic manganites. However, contrary to the ordinary orbital polarization, this new order parameter is essentially nonlocal. It is attached to the bonds of the DE system and does not conflict with the cubic symmetry of the crystal.

(3) There are many debates about possible phase coexistence in perovskite manganites,[33,34] and according to some scenarios this effect plays an important role around T_C, being actually the main trigger behind phenomenon of colossal magnetoresistance.[27] The problem was intensively studied numerically, by employing the Monte Carlo simulations.[27,34] If this is indeed the case, what does it mean in the language of analytical solutions of the DE model (and its refinements)? Presumably, the only possibility to have simultaneously two (and more) solutions is to admit that the self-energy (and Green's function) can be a multivalued function in certain region of the complex plane. Such a behavior of nonlinear CPA equations was considered as one of the main troublemakers in the past,[35,36,59] but may have some physical explanation in the light of newly proposed ideas of phase coexistence.

The rest of the paper is organized as follows. In Sec. II we briefly review the variational mean-field approach. In Sec. III we describe general ideas of nonlocal CPA to the problem of orientational spin disorder in the DE model. In Sec. IV we consider CPA solutions for the PM phase of one-orbital DE model and evaluate T_C. We will argue that two seemingly different approaches to the problem of spin disorder in the DE model, one of which was proposed by de Gennes[3] and the other one is based on the DMFT,[10–12] have common basis and both can be regarded as CPA-type theories, but supplemented with different types of approximations. In Sec. V we consider a more realistic example of DE interactions between two e_g orbitals and argue that the physics of degenerate model is qualitatively different from the one-orbital case. Particularly, the CPA self-energy becomes a multivalued function in certain regions of the complex plane. This behavior is related with some hidden parameter of interatomic orbital polarization and hints at intrinsic inhomogeneity of the PM state. In Sec. VI we summarize the main results of our work, discuss possible connections with the experimental data as well as possible extensions of our model.

II. CALCULATION OF THERMAL AVERAGES

In order to proceed with the finite temperature description of the DE model we adopt the variational mean-field approach,[3,37] and compute the thermal (or orientational) averages of all quantities in terms of the single spin orientation distribution function, which depends only on the angle between the local spin and an effective molecular field $\boldsymbol{\lambda}$:

$$p_{\mathbf{i}}(\mathbf{e_i}) \propto \exp(\boldsymbol{\lambda}\cdot\mathbf{e}_i). \tag{2}$$

For the purposes of our work, which deals with the PM and FM states, the effective field can be chosen as $\boldsymbol{\lambda}=(0,0,\lambda)$.

The application of this procedure to the DE Hamiltonian requires several comments, because Eq. (1) is formulated in the local coordinate frame, whereas the form of the distribution function (2) corresponds to the global one.[38] Then, in order to compute the orientational average of the matrix element associated with an arbitrary chosen site $\mathbf{0}$, we specify the coordinate frame in Eq. (2) by $\mathbf{e_0}$, so that at each instant the local frame at the site $\mathbf{0}$ coincides with the global one. The averaging over all possible directions $\mathbf{e_0}$ in the molecular filed $\boldsymbol{\lambda}$ is performed as the second step.

Therefore, the distribution function at the site $\mathbf{0}$ is given by Eq. (2). The distribution functions at remaining sites, formulated in the local coordinates of the site $\mathbf{0}$ and taking into account the motion of $\mathbf{e_0}$ in the molecular field $\boldsymbol{\lambda}$, can be obtained by transforming $\mathbf{e_i}$ and $\boldsymbol{\lambda}$ to the local coordinate frame: $\mathbf{e_i}\to\mathbf{e_i}'=\hat{R}\mathbf{e_i}$ and $\boldsymbol{\lambda}\to\boldsymbol{\lambda}'=\hat{R}\boldsymbol{\lambda}$, where $\hat{R}\mathbf{e_0}=(0,0,1)$; and averaging $p_{\mathbf{i}}(\mathbf{e_i}')$ over all possible directions $\mathbf{e_0}$ with the weights $p_{\mathbf{0}}(\mathbf{e_0})$:

$$P_{\mathbf{i}}(\mathbf{e_i}',\lambda)=\frac{1}{\nu}\int d\boldsymbol{\Omega}_{\mathbf{0}}\exp(\boldsymbol{\lambda}'\cdot\mathbf{e_i}'+\boldsymbol{\lambda}\cdot\mathbf{e_0}), \tag{3}$$

where the normalization constant ν is given by the condition $\int d\boldsymbol{\Omega}_{\mathbf{i}}' P_{\mathbf{i}}(\mathbf{e_i}',\lambda)=1$. The form of Eq. (3) implies that the directions of magnetic moments are not correlated (that is in the spirit of the mean-field approach) and that the averaging over $\mathbf{e_0}$ can be performed independently for all sites of the system.

For the analysis the PM state and T_C, it is sufficient to consider the small-λ limit

$$P_{\mathbf{i}}(\mathbf{e_i}',\lambda)\simeq\frac{1}{4\pi}\left(1+\frac{1}{3}\cos\theta_{\mathbf{i}}'\lambda^2\right). \tag{4}$$

Then, the spin entropy is given by[3]

$$-TS(\lambda)\simeq\frac{k_BT}{6}\lambda^2 \tag{5}$$

and the free energy of the DE model can be found as[3,37]

$$\mathcal{F}(T,\lambda)=E_D(T,\lambda)-TS(\lambda), \tag{6}$$

where $E_D(T,\lambda)$ is the electron free energy (or the double-exchange energy)

$$E_D(T,\lambda)=-\int_{-\infty}^{+\infty}dz f_T(z-\mu)\overline{n}(z,\lambda), \tag{7}$$

calculated in terms of orientationally averaged integrated DOS $\overline{n}(z,\lambda)$, which comes from the solution of CPA equations for corresponding Green's function. $f_T(z-\mu)=\{\exp[(z-\mu)/k_BT]+1\}^{-1}$ is the Fermi-Dirac function with the chemical potential μ.

The best approximation for the molecular field λ is that which minimizes the free energy (6). Assuming that the transition to the FM state is continuous (of the second order),[39] T_C can be obtained from the following equation:

$$\left.\frac{\partial^2\mathcal{F}(T_C,\lambda)}{\partial\lambda^2}\right|_{\lambda=0}=0. \tag{8}$$

III. NONLOCAL CPA FOR THE DOUBLE EXCHANGE MODEL

In this section we discuss general aspects of the nonlocal CPA approach to the problem of orientational spin disorder in the DE model. We attempt to describe the disordered system in an average sense by introducing an effective energy-dependent Hamiltonian

$$\overline{\mathcal{H}}_{\mathbf{ij}}(z)=\Sigma_{\mathbf{ii}}(z)\,\delta_{\mathbf{ij}}-\Sigma_{\mathbf{ij}}(z)(1-\delta_{\mathbf{ij}}), \tag{9}$$

where $\Sigma_{\mathbf{ij}}$ is the nonlocal part of the self-energy, which is restricted by the nearest neighbors and $\Sigma_{\mathbf{ii}}$ is the local (site-diagonal) part. The nonlocal formulation of CPA is essential because in the low-temperature limit $\Sigma_{\mathbf{ij}}$ shall be replaced by the conventional parameters of kinetic hoppings $t_{\mathbf{ij}}$. The diagonal part $\Sigma_{\mathbf{ii}}$ is required in order to formulate a closed system of CPA equations.

The Hamiltonian (9) is requested to preserve the cubic symmetry of the system and be translationally invariant. Using these symmetry constraints, all matrix elements of the self-energy $\{\Sigma_{\mathbf{ii}},\Sigma_{\mathbf{ij}}\}$ can be expressed through $\{\Sigma_{\mathbf{00}},\Sigma_{\mathbf{01}}\}$ for one of the dimers (for example, **0-1** in Fig. 2). Then, Hamiltonian (9) can be Fourier transformed to the reciprocal space $\overline{\mathcal{H}}_{\mathbf{q}}(z)=\Sigma_{\mathbf{j}}e^{-i\mathbf{q}\cdot(\mathbf{R_i}-\mathbf{R_j})}\overline{\mathcal{H}}_{\mathbf{ij}}(z)$, and the first equation for the orientationally averaged Green function can be written as

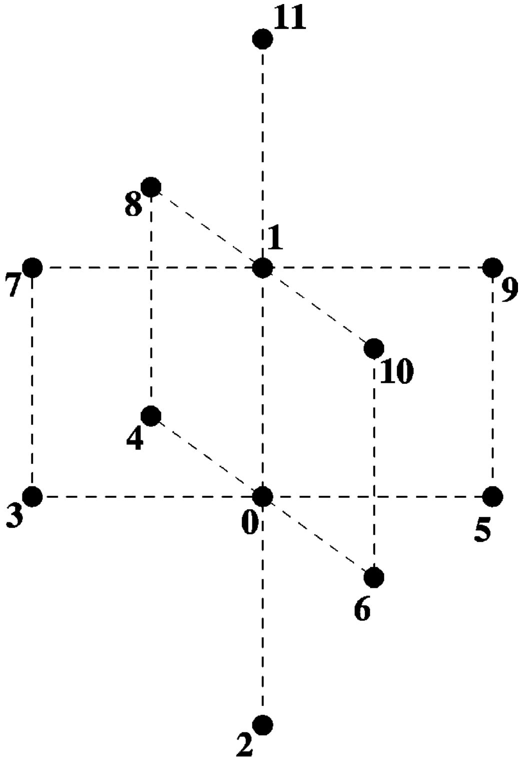

FIG. 2. Atomic sites which contribute to the matrix elements of orientationally averaged T matrix for the dimer **0**-**1** in the second-order perturbation theory expansion.

$$\overline{G}_{\mathbf{ij}}(z)=\frac{1}{\Omega_{\mathrm{BZ}}}\int d\mathbf{q}e^{i\mathbf{q}\cdot(\mathbf{R_i}-\mathbf{R_j})}[z-\overline{\mathcal{H}}_{\mathbf{q}}(z)]^{-1}, \tag{10}$$

where integration goes over the first Brillouin zone of the simple cubic lattice with the volume Ω_{BZ}.[40]

In order to formulate the CPA equations we consider only site-diagonal and nearest-neighbor elements of $\overline{G}_{\mathbf{ij}}$. Again, using the symmetry constraints, all matrix elements of $\overline{G}_{\mathbf{ij}}$ can be expressed through $\overline{G}_{\mathbf{00}}$ and $\overline{G}_{\mathbf{01}}$. In addition, there is a simple relation connecting $\overline{G}_{\mathbf{00}}$ and $\overline{G}_{\mathbf{01}}$ for given $\Sigma_{\mathbf{00}}$ and $\Sigma_{\mathbf{01}}$:

$$\overline{G}_{\mathbf{00}}(z)[z-\Sigma_{\mathbf{00}}(z)]+\sum_{\mathbf{i}}\overline{G}_{\mathbf{0i}}(z)\Sigma_{\mathbf{i0}}(z)=1, \tag{11}$$

which follows from the definition of the Green function (10) and the Hamiltonian (9).

In order to obtain the closed system of CPA equations, which connects $\{\Sigma_{\mathbf{00}},\Sigma_{\mathbf{01}}\}$ with $\{\overline{G}_{\mathbf{00}},\overline{G}_{\mathbf{01}}\}$, we construct the T matrix[13–15,41]

$$\hat{T}(z)=[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\{\hat{1}-\hat{\overline{G}}(z)[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\}^{-1}, \tag{12}$$

and require the average of scattering due to the fluctuations $\Delta\hat{\mathcal{H}}=\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}$ to vanish at every site and every bond of the system, i.e.,

$$\overline{T}_{\mathbf{00}}(z)=\overline{T}_{\mathbf{01}}(z)=0. \tag{13}$$

The hat symbols in Eq. (12) means that all the quantities are infinite matrices in the real space and the matrix multiplications imply also summation over the intermediate sites.[42] This causes an additional problem, because the nonlocal fluctuations $\Delta\hat{\mathcal{H}}$ tend to couple an infinite number of sites in Eq. (12). Therefore, we employ the perturbation theory expansion up to the second order with respect to $\Delta\hat{\mathcal{H}}$:

$$\hat{T}(z)\simeq[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]+[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\hat{\overline{G}}(z)[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]. \tag{14}$$

As we will show, the first term in this expansion corresponds to the approximation considered by de Gennes,[3] and the next term is the first correction to this approximation. In all subsequent discussions, the terminology "first" or "second order expansion" with respect to $\Delta\hat{\mathcal{H}}$ will mean the number of terms retained in Eq. (14) for the T matrix.

Since $t_{\mathbf{ij}}$ and $\Sigma_{\mathbf{ij}}$ are restricted by the nearest neighbors, and we retain only site-diagonal and nearest-neighbor elements of $\overline{G}_{\mathbf{ij}}$, in order to evaluate $\overline{T}_{\mathbf{00}}(z)$ and $\overline{T}_{\mathbf{01}}(z)$ in the approximation given by Eq. (14) we need to consider the interactions confined within the twelve-atom cluster which is shown in Fig. 2 (obviously, an additional term in the perturbation theory expansion for the T matrix would require a bigger cluster).

IV. ONE-ORBITAL DOUBLE EXCHANGE MODEL

A. Solution for the paramagnetic state

In the one-orbital case, the effective DE Hamiltonian takes the following form, in the reciprocal space

$$\overline{\mathcal{H}}_{\mathbf{q}}(z)=\Sigma_{\mathbf{00}}(z)-2(c_x+c_y+c_z)\Sigma_{\mathbf{01}}(z),$$

where $\Sigma_{\mathbf{00}}(z)$ and $\Sigma_{\mathbf{01}}(z)$ are C numbers, $c_\gamma=\cos q_\gamma$, and all energies throughout in this section are in units of the effective transfer integral $t_0=W/12$.

Matrix elements of the Green function $\overline{G}_{\mathbf{00}}(z)$ and $\overline{G}_{\mathbf{01}}(z)$ are obtained from Eq. (10). The self-consistent CPA equations are given by Eq. (13). The thermal averages $\overline{T}_{\mathbf{00}}(z)$ and $\overline{T}_{\mathbf{01}}(z)$ can be calculated in the local coordinate frame associated with the site **0**, where $\mathbf{e}'_{\mathbf{0}}=(0,0,1)$, and using distribution functions (4) for all remaining sites of the cluster shown in Fig. 2. This is a tedious, but rather straightforward procedure. Here we present only the final result (some details can be found in Ref. 43). After introducing the short notations for the self energies $\vec{\sigma}=\{\sigma_0,\sigma_1\}\equiv\{\Sigma_{\mathbf{00}},\Sigma_{\mathbf{01}}-\frac{2}{3}\}$, and for the Green function $\vec{g}=\{g_0,g_1\}\equiv\{\overline{G}_{\mathbf{00}},\overline{G}_{\mathbf{01}}\}$, the CPA equations $\overline{T}_{\mathbf{00}}(z)=0$ and $\overline{T}_{\mathbf{01}}(z)=0$ can be presented in the form (for $\alpha=0$ and 1, respectively):[44]

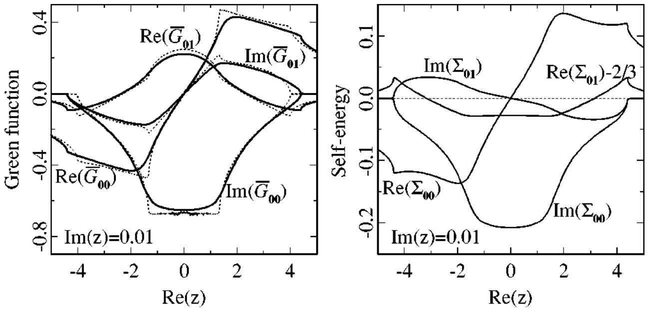

FIG. 3. Paramagnetic state of the one-orbital double exchange model: behavior of matrix elements of the Green function and the self-energy along the real axis. Dotted line shows the same matrix elements in the double exchange theory by de Gennes (the first order expansion for the T matrix).

$$\sigma_\alpha=\Phi_\alpha(\vec{\sigma},\vec{g})+\Psi_\alpha(\vec{\sigma},\vec{g})\lambda^2, \tag{15}$$

where

$$\Phi_0(\vec{\sigma},\vec{g})=\left(\sigma_0^2+6\sigma_1^2+\frac{1}{3}\right)g_0-12\sigma_0\sigma_1 g_1,$$

$$\Phi_1(\vec{\sigma},\vec{g})=2\sigma_0\sigma_1 g_0-\left(\sigma_0^2+15\sigma_1^2+2\sigma_1+\frac{13}{54}\right)g_1,$$

$$\Psi_0(\vec{\sigma},\vec{g})=\frac{8}{15}(\sigma_0 g_1-\sigma_1 g_0)-\frac{1}{45}g_0,$$

and

$$\Psi_1(\vec{\sigma},\vec{g})=\frac{2}{45}-\frac{4}{45}\sigma_0 g_0+\left(\frac{22}{15}\sigma_1-\frac{7}{48}\right)g_1.$$

These equations should be solved self-consistently in combination with the definition (10) for the Green function.

Results of these calculations for the PM state ($\lambda=0$) are shown in Fig. 3. In the one-orbital case there is only one CPA solution in each point of the complex energy plane. The integrated DOS lies in the interval $0\leqslant\overline{n}(\mu)\leqslant 1$ and takes all intermediate values as the function of chemical potential μ, meaning that our system is well defined for all physical values of the electronic density.

The nonlocal CPA formulation in the one-orbital case is formally equivalent to the local one, which can be obtained after scaling transformation of the Green function $\{2/3+\sigma_1(z)\}\overline{G}_{\mathbf{ij}}(z)=\overline{G}'_{\mathbf{ij}}(z)$, where $\overline{G}'_{\mathbf{ij}}(z)=[z-\sigma'_0(z)+\hat{t}]^{-1}_{\mathbf{ij}}$ and $\sigma'_0(z)=z-[z-\sigma_0(z)]/[2/3+\sigma_1(z)]$. Therefore, the quasiparticle electronic structure in this case is controlled by only one parameter $\sigma'_0(z)$. Since $\sigma_1(z)\leqslant 2/3$ and $\mathrm{Im}\,\sigma_0(z)\leqslant 0$, $\mathrm{Im}\,\sigma'_0(z)\leqslant 0$ and the obtained solution is causal in the upper half plane.[35,36] The electronic structure is metallic. The spin disorder alone is insufficient to cause the Anderson localization at realistic values of the electronic density, either.[26]

The first order expansion with respect to $\Delta\mathcal{H}$ (the DE theory by de Gennes,[3] thereafter all parameters in this limit will be denoted by tilde) yields $\tilde{\Phi}_0=\tilde{\Phi}_1=\tilde{\Psi}_0=0$ and $\tilde{\Psi}_1=2/45$. Corresponding matrix elements of the Green function are also shown in Fig. 3. Despite significant difference in the self energies, the matrix elements of the Green function obtained in the first and second order approach are surprisingly close, meaning that there is a good deal of cancellations of different contributions to $\vec{g}$.

However, it is not true for the Curie temperatures. While in the first order, T_C is solely determined by $\overline{G}_{\mathbf{00}}$, in the second order it explicitly depends on both $\overline{G}_{\mathbf{00}}$ and $\vec{\sigma}$, which make significant difference from the canonical scaling relation between T_C and the DE energy of the FM state.[3]

B. Curie temperature

T_C is obtained from Eq. (8). In order to evaluate the DE energy, we start with the PM solution ($\lambda=0$) and include all contributions in the first order of λ^2 as a perturbation. Employing variational properties of integrated DOS in CPA,[41,45] $\Delta\overline{n}(z,\lambda)=\overline{n}(z,\lambda)-\overline{n}(z,0)$ can be obtained using the Lloyd formula for the small changes of the self-energies $\Delta\sigma_\alpha(z)=\Psi_\alpha(z)\lambda^2$:

$$\Delta\overline{n}(z,\lambda)\simeq\frac{1}{\pi}\mathrm{Im}\{\Psi_0(z)g_0(z)-6\Psi_1(z)g_1(z)\}\lambda^2. \tag{16}$$

$g_1(z)$ can be further expressed through $g_0(z)$ using identity (11). Then, the change of the DE energy takes the form $\Delta E_D(T,\lambda)\simeq\mathcal{D}(T)\lambda^2$, where $\mathcal{D}(T)$ is given by

$$\mathcal{D}(T)=-\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{+\infty}dz f_T(z-\mu)\left\{\left(\Psi_0(z)+\frac{\Psi_1(z)[z-\sigma_0(z)]}{\sigma_1(z)+2/3}\right)g_0(z)-\frac{\Psi_1(z)}{\sigma_1(z)+2/3}\right\}. \tag{17}$$

Taking into account the entropy term, Eq. (5), we obtain

$$k_B T_C=-6\mathcal{D}(T_C). \tag{18}$$

In the first order with respect to $\Delta\hat{\mathcal{H}}$ we recover the well known relation between T_C and the DE energy of fully polarized FM state $E_D(\mathrm{FM})$:[3,46]

$$k_B\tilde{T}_C=-\frac{4}{15}E_D(\mathrm{FM}).$$

The second order corrections significantly reduce T_C [up to 20% at $\overline{n}=0.5$ (Fig. 4)], which is also lower in comparison with results of (local) DMFT calculations, suggesting importance of the off-diagonal disorder.[47] Very similar conclusion was obtained recently by Alonso *et al.*,[37] who used (the same) variational mean-field approach supplemented by the moments-method for the averaged DOS in the one-orbital DE model.

Using the value $W\approx 4$eV, T_C can be estimated as $T_C\leqslant 800$ K. The upper bound, corresponding to $\overline{n}=0.5$, ex-

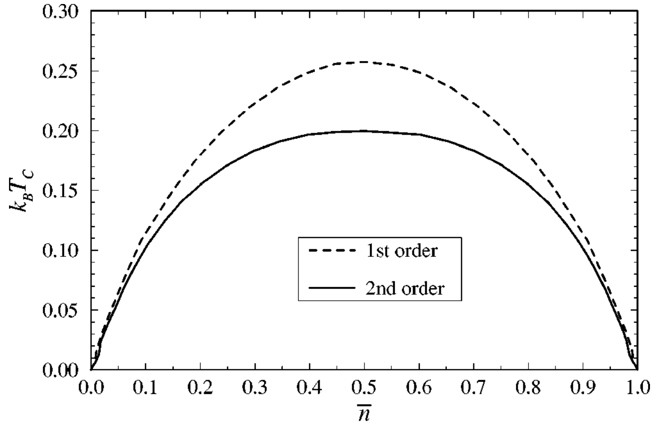

FIG. 4. Curie temperature of the one-orbital double exchange model, obtained using the first and second order expansion for the T matrix, as the function of averaged electronic density.

ceeds the experimental values by factor two. T_C can be further reduced by the antiferromagnetic (AFM) superexchange (SE) interactions between the localized spins[3,37,48,49] or taking into account the spatial spin correlations.[50]

V. DOUBLE EXCHANGE BETWEEN DEGENERATE e_g ORBITALS

A. General remarks

Let us consider more realistic example of the DE interactions between two e_g orbitals,[30] which have the following order: $|1\rangle \equiv |3z^2-r^2\rangle$ and $|2\rangle \equiv |x^2-y^2\rangle$. Then, all quantities such as the transfer integrals $t_{\mathbf{ij}}$, the averaged Green function $\overline{G}_{\mathbf{ij}}(z)$, and the self-energy $\Sigma_{\mathbf{ij}}(z)$ are the 2×2 matrices in the basis of these two orbitals.

Since the cubic symmetry is not destroyed by the spin disorder, the local part of the self energy is both diagonal and degenerate with respect to the orbital indices L and L':

$$\Sigma_{\mathbf{00}}^{LL'}(z)=\sigma_0(z)\,\delta_{LL'}.$$

Throughout in this section, all quantities will be in units of the transfer integral $dd\sigma = W/6 \approx 0.7$ eV.[31]

All matrix elements associated with the bond **0**-**1** (see Fig. 2) should obey the tetragonal C_{4v} symmetry. Since $3z^2-r^2$ and x^2-y^2 orbitals belong to different representations of the C_{4v} group (a_1 and b_1, respectively), one can write very generally

$$\Sigma_{\mathbf{01}}(z)=\begin{pmatrix} \Sigma_{\mathbf{01}}^{11}(z) & 0 \\ 0 & \Sigma_{\mathbf{01}}^{22}(z) \end{pmatrix} \equiv \begin{pmatrix} \sigma_1(z)+\dfrac{2}{3} & 0 \\ 0 & \sigma_2(z) \end{pmatrix}, \tag{19}$$

i.e., $\Sigma_{\mathbf{01}}(z)$ is a diagonal matrix, but not necessarily degenerate one. Corresponding matrix of bare $dd\sigma$ hoppings in the z direction has the form[31]

$$t_{\mathbf{01}}=\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{20}$$

The hoppings are allowed only between $3z^2-r^2$ orbitals, that reflects a hidden symmetry of the ordered FM state. The same property does not necessarily apply to the self-energy in the case of spin disorder. Therefore, we shall retain $\sigma_2(z)$, which is required in order to formulate a closed system of CPA equations. In some sense, $\sigma_2(z)$ can be viewed as an effective $dd\delta$ hopping,[31] induced by the spin disorder.

Matrix elements of $t_{\mathbf{ij}}$, and $\Sigma_{\mathbf{ij}}(z)$ in the xy plane can be obtained using the 2×2 rotation matrices for the e_g orbitals.[51] This yields the following Hamiltonian, in the reciprocal space:

$$\overline{\mathcal{H}}_{\mathbf{q}}=\Sigma_{\mathbf{00}}-\frac{1}{2}\begin{pmatrix} (3\Sigma_{\mathbf{01}}^{11}+\Sigma_{\mathbf{01}}^{22})(c_x+c_y)+4\Sigma_{\mathbf{01}}^{22}c_z & \sqrt{3}(\Sigma_{\mathbf{01}}^{11}-\Sigma_{\mathbf{01}}^{22})(c_y-c_x) \\ \sqrt{3}(\Sigma_{\mathbf{01}}^{11}-\Sigma_{\mathbf{01}}^{22})(c_y-c_x) & (\Sigma_{\mathbf{01}}^{11}+3\Sigma_{\mathbf{01}}^{22})(c_x+c_y)+4\Sigma_{\mathbf{01}}^{11}c_z \end{pmatrix}.$$

Then the orientationally averaged Green function is given by Eq. (10). Matrix elements of the Green function $\overline{G}_{\mathbf{00}}^{LL'}$ and $\overline{G}_{\mathbf{01}}^{LL'}$ obey the same symmetry properties as the self-energy.

Three CPA equation $\overline{T}_{\mathbf{00}}^{11}(z)=0$, $\overline{T}_{\mathbf{01}}^{11}(z)=0$, and $\overline{T}_{\mathbf{01}}^{22}(z)=0$ can be written in the compact form (15) for $\alpha=0$, 1, and 2, respectively, after introducing the notations $\vec{\sigma}=\{\sigma_0,\sigma_1,\sigma_2\}$ and $\vec{g}=\{g_0,g_1,g_2\}\equiv\{\overline{G}_{\mathbf{00}}^{11},\overline{G}_{\mathbf{01}}^{11},\overline{G}_{\mathbf{01}}^{22}\}$. Some details of these derivations and explicit expressions for $\Phi_\alpha(\vec{\sigma},\vec{g})$ and $\Psi_\alpha(\vec{\sigma},\vec{g})$ can be found in Ref. 43.

What is so special about the degenerate DE model, and why it can lead to qualitatively new behavior for the PM state? Here we would like to discuss the physical side of this problem and emphasize rather unique combination of two factors.

(1) The nonlocal part of the self-energy acquires an additional degree of freedom $\sigma_2(z)$ which may directly control details of quasiparticle electronic structure (including positions of the Van Hove singularities). This is qualitatively different from the one-orbital case, where the electronic structure is determined by only one local parameter $\sigma_0'(z)$. The new element of the self-energy can be formally linked to some nonlocal order parameter (an "interatomic orbital polarization"):

$$\mathcal{O}_{\mathrm{NL}}=-\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{+\infty} dz f_T(z-\mu)\{\overline{G}_{\mathbf{01}}^{11}(z)-\overline{G}_{\mathbf{01}}^{22}(z)\}, \tag{21}$$

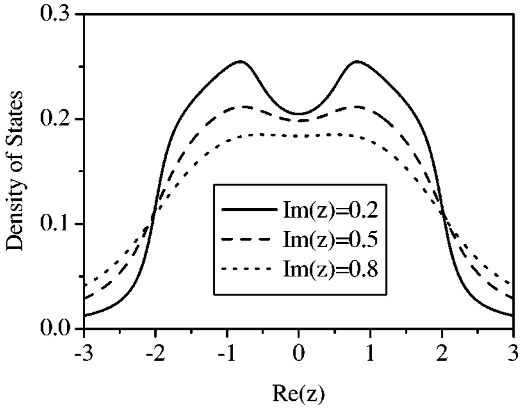

FIG. 5. Behavior of density of states in the complex plane, expected for the paramagnetic state in the double-exchange theory by de Gennes. Note two peaks, which are related with the existence of two Van Hove singularities on the real axis (Fig. 1). Far away from the real axis the peaks are smeared.

which is attached to the bonds of the DE system and does not destroy the local degeneracy of the e_g orbitals. Note that $\mathcal{O}_{\rm NL}=0$ if $t_{\mathbf{01}}$ is proportional to the unity matrix (a purely fictitious case of independent e_g orbitals) and $\mathcal{O}_{\rm NL}\neq 0$ in the case of anisotropic hopping parameters given by Eq. (20) for the FM state. Our conjecture is that $\mathcal{O}_{\rm NL}$ is further modified by the spin disorder. Note also that in all three cases, the local parameter of orbital polarization, defined by Eq. (21) with $\overline{G}_{\mathbf{01}}$ replaced by $\overline{G}_{\mathbf{00}}$, vanishes due to the cubic symmetry of the system.

(2) Because of the Van Hove singularities, the matrix elements of the Green function are nonmonotonous functions of both z and the matrix elements of the self-energy (Fig. 5). Since $\vec{g}$ enters the self-consistent CPA equations (15), they will be highly nonlinear and one can naturally expect several CPA solutions corresponding to different starting conditions for $\sigma_2(z)$. The mechanism has many similarities with the occurrence of metamagnetism in itinerant electron systems.[52] The only difference is that now $\mathcal{O}_{\rm NL}$ plays the same role as the spin magnetization for the conventional metamagnetism, and $\{\Sigma_{\mathbf{01}}^{11}-\Sigma_{\mathbf{01}}^{22}\}$ is a nonlocal analog of the magnetic field.

Indeed, let us start with a trial Green function $\vec{g}$ corresponding to the self-energy $\vec{\sigma}$. For simplicity we assume that our choice is close to the first order CPA solution for the PM state. Our goal is to investigate the behavior of CPA equations near the point $\mathrm{Re}(z)=-\frac{2}{3}$, corresponding to the position of the first Van Hove singularity on the real axis and leading to the peak of DOS (Fig. 5). Let us consider a small trial change of the self-energy $\delta\vec{\sigma}^{\rm in}$ near $\vec{\sigma}$, which leads to the change of the Green function $\delta\vec{g}=\partial\vec{g}/\partial\vec{\sigma}\;\delta\vec{\sigma}^{\rm in}$ in Eq. (10). Then, we would like to calculate the new change $\delta\vec{\sigma}^{\rm out}$, which satisfies the CPA equations (15). It is given by

$$\delta\vec{\sigma}^{\rm out}=\left(1-\frac{\partial\vec{\Phi}}{\partial\vec{\sigma}}\right)^{-1}\frac{\partial\vec{\Phi}}{\partial\vec{g}}\,\frac{\partial\vec{g}}{\partial\vec{\sigma}}\,\delta\vec{\sigma}^{\rm in}, \tag{22}$$

where we have introduced the short notation $\vec{\Phi}=\{\Phi_0,\Phi_1,\Phi_2\}$.

Suppose that our first choice for the self-energy is $\vec{\sigma}(z)=\vec{\sigma}^{(1)}(z)+\delta\vec{\sigma}^{\rm in_1}(z)$ and, for a given z, $\mathrm{Re}(z)$ is located on the left slope of DOS, i.e., $\mathrm{Re}(z)<\mathrm{Re}(z_{\rm VH})$, where $\mathrm{Re}(z_{\rm VH})=\mathrm{Re}\{\sigma_0(z)-\sigma_1(z)+3\sigma_2(z)-\frac{2}{3}\}$ is the position of the Van Hove singularity on the real axis. This solution will be stable if the maximum of DOS will be further shifted from the considered point z by $\delta\vec{\sigma}^{\rm out_1}(z)$, that is equivalent to the requirement $\mathrm{Re}(\delta z_{\rm VH}^{\rm out_1})>\mathrm{Re}(\delta z_{\rm VH}^{\rm in_1})$.

One can also try to find another solution by starting with $\vec{\sigma}(z)=\vec{\sigma}^{(2)}(z)+\delta\vec{\sigma}^{\rm in_2}(z)$, which places $\mathrm{Re}(z)$ on the right slope of DOS. This solution will be stable if $\mathrm{Re}(\delta z_{\rm VH}^{\rm out_2})<\mathrm{Re}(\delta z_{\rm VH}^{\rm in_2})$.

Is it possible that *both* solutions are stable? The quantitative answer is rather cumbersome. However, qualitatively it is clear that such situation is rather likely because the matrix elements of $\partial\vec{g}/\partial\vec{\sigma}$ will change sign near the point of Van Hove singularity, and according to Eq. (22), the matrices $\partial\vec{g}/\partial\vec{\sigma}|_{\vec{\sigma}=\vec{\sigma}^{(1)}}$ and $\partial\vec{g}/\partial\vec{\sigma}|_{\vec{\sigma}=\vec{\sigma}^{(2)}}$ will lead to two different estimates for $\delta\vec{\sigma}^{\rm out}$.

Far away from the real axis, the Van Hove singularities are smeared, and we should regain to the standard behavior when there is only one CPA solution for each z. Such a situation is expected when $\mathrm{Im}(z)\geqslant 0.8$ (Fig. 5). The qualitative analysis is supported by results of numerical CPA calculations, which will be discussed in the next section.

B. CPA solution for the paramagnetic phase

A typical example of the numerical solution of CPA equations is shown in Fig. 6. In these calculations we fix $\mathrm{Im}(z)$ and solve CPA equations by moving parallel to the real axis and in each point beginning the iterations with the self-consistent self-energy obtained for the previous value of $\mathrm{Re}(z)$. As expected, when $\mathrm{Im}(z)$ is large we obtain only one CPA solution for each z. This is the typical behavior for $\mathrm{Im}(z)\geqslant 0.75$. However, when we approach the real axis, the situation changes dramatically and for $\mathrm{Im}(z)=0.7$ we obtain two different solutions near the points of Van Hove singularities, depending on whether we move in the positive or negative direction of the real axis and resulting in the characteristic ''hysteresis loop'' shown in Fig. 6.

A better idea about topology of CPA solutions in the complex plane can be obtained from Fig. 7, where we plot $\mathrm{Re}(\Sigma_{\mathbf{01}}^{11}-\Sigma_{\mathbf{01}}^{22})$ calculated by using two different starting conditions in each z point. Depending on the location in the complex plane, the CPA equations are converged to either the same or two different solutions. The latter situation occurs within the shaded area. Note that this area is the result of numerical calculations. In principle, we do not exclude the possibility that our result may be incomplete and that with a better choice of the starting conditions this area can be enlarged.

Our analysis is limited by $\mathrm{Im}(z)\approx 0.5$. When we further approach the real axis the topology of CPA solutions becomes increasingly complicated. At the present stage we do

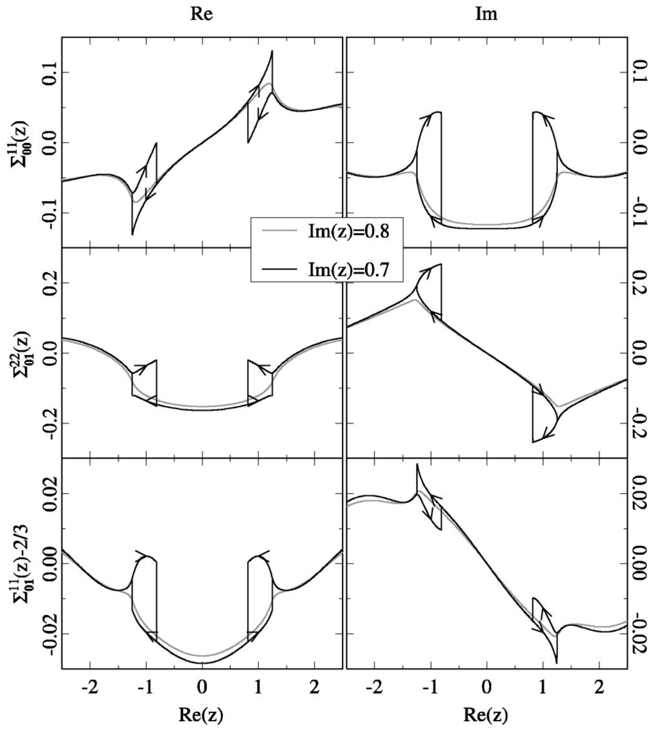

FIG. 6. Behavior of matrix elements of the self-energy in the paramagnetic state of degenerate double exchange. For $\mathrm{Im}(z) \geqslant 0.75$ there is only one CPA solution, while for $\mathrm{Im}(z) < 0.75$ one can obtain two self-consistent solutions in certain interval of $\mathrm{Re}(z)$ by starting the iterations with the self-energy obtained for the previous value of $\mathrm{Re}(z)$ and moving either in the positive or negative direction of the real axis (shown as a hysteresis).

not have a clear strategy of how to deal with this problem and how to interpret the behavior of our model near the real axis. Nevertheless, as it was already pointed out in the previous section, the multivalued behavior itself is quite physical as it is related with peculiarities of DOS of the degenerate DE model. Note that $\mathrm{Im}(z) \approx 0.5$ corresponds to the position of the first Matsubara pole for $T \approx 0.16/k_B \approx 1200$ K, which can be regarded as the lowest estimate for the temperature for which our analysis is strictly justified.

Below we discuss possible consequences of the existence of two different CPA solutions in the PM state. Mathematically, our analysis is based on the following observations.

(1) The existence of the branch point (B in Fig. 7), which forms two physical branches of CPA solutions in certain area of the complex plane. The requirement implies that there is a continuous path around the branch-point, which connects the points located on two different branches.

(2) On both branches, Green's function and the self-energy are analytic functions (perhaps except the branch-point itself and the branch edges). The requirement allows us to use standard theorems of contour integration in the complex plane.

Then, the physical interpretation of the multi-valued behavior becomes rather straightforward and two CPA solutions can be linked to different PM phases. The crucial factor which connects the topology of CPA solutions in the complex plane with the temperature behavior of the PM state is

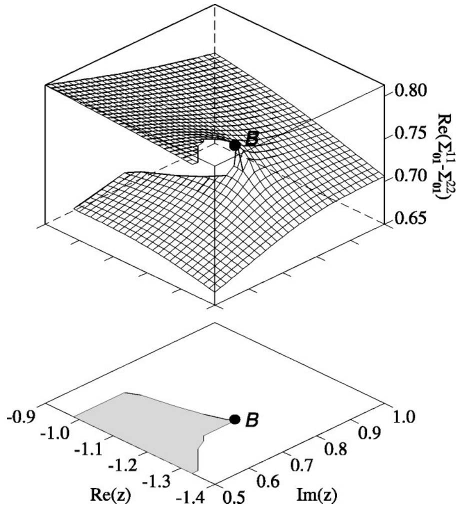

FIG. 7. Topology of the nonlocal part of the self-energy in the complex plane. The branch point is denoted by B. The projection shows an approximate position of the multivalued area of CPA solutions.

how many Matsubara energies fall into the multivalued area for the given temperature T and the chemical potential μ. If they do, the PM state will be represented by two phases existing at the same T and μ, and the position of the branch point itself can be related with the temperature, below which the PM state becomes intrinsically inhomogeneous. The situation has many things in common with the phenomenon of inhomogeneous phase separation, which was intensively discussed for manganites.[33,34] The new aspect in our case is that both phases can be paramagnetic. They are characterized by different densities and expected to have very different interatomic properties related with the ability of electrons to transfer between different sites. For example, taking into account very large difference of interatomic matrix elements of the self-energy for two CPA solutions (Figs. 6 and 7), it is natural to expect that two phases will have different conductivity and the optical properties.[15,53]

C. Energy integration and occurrence of two paramagnetic phases

In this section we discuss some aspects of the energy integration in the complex plane, related with the existence of two physical branches of CPA solutions. Let us consider the integral

$$X(\mu)=\int_{-\infty}^{+\infty} dz f_T(z-\mu) X(z), \tag{23}$$

where $X(\mu)$ is a physical quantity, which can be the density of e_g electrons, the double exchange energy or the change of either of them, and $X(z)$ has the same topology in the complex plane as the self-energy shown in Fig. 7. Then, the behavior of integral (23) will depend on the position of the chemical potential μ with respect to the multivalued area. Generally, we should consider three possibilities (see Fig. 8 for notations).

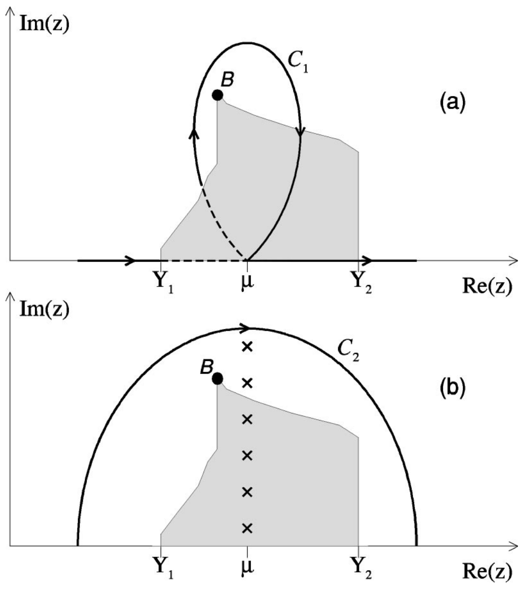

FIG. 8. Energy integration for the degenerate double-exchange model. (a) The integral along the real axis plus the discontinuity given by the contour integral C_1 around the branch point B. (b) An equivalent expression in terms of the contour integral C_2 passing round the multivalued area of the complex plane and residues calculated at Matsubara poles. The latter contributions are different for two different branches, that is equivalent to the discontinuity term in the scheme (a).

(1) $\mu < \Upsilon_1$. In this region there is only one CPA solution and $X(\mu)$ can be calculated using standard methods of energy integration in the complex plane (see, e.g., Ref. 54, and references therein).

(2) $\Upsilon_1 \leqslant \mu \leqslant \Upsilon_2$. Then, $X(\mu)$ can take two values for each value of the chemical potential μ: $X_1(\mu)$, if the integrand is solely confined within one physical branch and $X_2(\mu) = X_1(\mu) + \Delta X(\mu)$, if it is extended to the second branch. The discontinuity $\Delta X(\mu)$ is given by the contour integral C_1 around the branch point. Since $X(z)$ is an analytic function, the integral does not depend on the form of C_1. We would like to emphasize that we do not impose any restrictions on $X(\mu)$ and do not try to define it in as a single-valued fashion by introducing the branch cuts, which is largely arbitrary procedure.[35] Instead, we treat both branches on an equal footing, that inevitably leads to the multivalued behavior of $X(\mu)$, and we argue that this behavior can be interpreted on quite a physical basis. Integral (23) can be replaced by the contour integral C_2 passing round the multi-valued area and residues calculated at a limited number of Matsubara energies $z_n = \mu + i\pi k_B T(2n+1)$

$$X(\mu) = \int_{C_2} dz f_T(z-\mu) X(z) - 2\pi i k_B T \sum_{z_n} X(z_n), \quad (24)$$

so that in order to find X_1 and X_2, the residues should be calculated on the first and second branches, respectively.[55]

(3) $\mu > \Upsilon_2$. In this case the integration along the real axis shall be combined with the discontinuity ΔX term given by the contour integral C_1. The integration can be replaced by Eq. (24). In this region, all Matsubara poles fall on the single branch and $X(\mu)$ is the single-valued function.

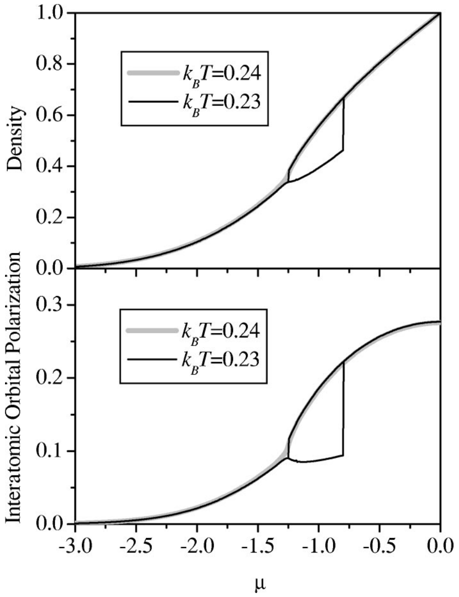

FIG. 9. Averaged electronic density ($\overline{n}$) and the parameter of interatomic orbital polarization ($\mathcal{O}_{\rm NL}$) as a function of chemical potential for the paramagnetic state of degenerate double exchange model. For $T \leqslant 0.23$, there are two different phases which are distinguished by $\overline{n}$ and $\mathcal{O}_{\rm NL}$.

As an illustration, we show in Fig. 9 the behavior of averaged electronic density as the function of μ. For $k_B T = 0.24$, corresponding to $\mathrm{Im}(z_0) \simeq 0.754$, which is slightly above the branch point, the first Matsubara pole falls beyond the multivalued area and $\overline{n}(\mu)$ shows a "normal" behavior when for each μ there is only one value of $\overline{n}(\mu)$. For smaller $k_B T$, $\overline{n}(\mu)$ can take two different values for the same μ, which means the existence of two different phases. Both phases are paramagnetic and can be distinguished by the parameter of inter-atomic orbital polarization, given by Eq. (21). The temperature $T_P \approx 0.23/k_B \approx 1800$ K below which the first Matsubara pole falls into the multivalued area of the complex plane can be regarded as the transition temperature to the two-phase state.

Finally, we would like to note that although $\overline{n}(\mu)$ for each of the phases exhibits a discontinuity at the boundary of the two-phase state, the total density, which is the superposition of the two solutions, is well defined in the whole integral $0 \leqslant \overline{n}(\mu) \leqslant 1$.

D. Two-phase state

In this section we briefly consider the problem of phase coexistence using a semiquantitative theory of noninteractive pseudoalloy. Namely, we assume that the free energy of the mixed PM state is given by

$$\mathcal{F}_{\rm mix}(y) = (1-y)E_D^{(1)} + yE_D^{(2)} - TS_{\rm mix}(y),$$

where $E_D^{(1)}$ and $E_D^{(2)}$ are the energies of two phases existing at the same T and μ (with lower and higher density, respectively), y is the "alloy concentration," and $S_{\rm mix}(y)$ is the configurational mixing entropy

$$-TS_{\rm mix}(y)=k_BT[y\ln y+(1-y)\ln(1-y)].$$

Then, the equilibrium concentration, which minimizes $\mathcal{F}_{\rm mix}(y)$ is given by

$$y=(e^{\Delta E_D/k_BT}+1)^{-1}.$$

The energy difference $\Delta E_D=E_D^{(2)}-E_D^{(1)}$ can be calculated using the definition (7). According to Eq. (24) we need to evauate the discontinuity of the integrated DOS

$$\Delta E_D=2\pi i k_BT\sum_{z_n}[\overline{n}^{(2)}(z_n)-\overline{n}^{(1)}(z_n)]$$

at a limited number of Matsubara energies, which fall into the multivalued area of the complex plane. Some details of these calculations can be found in the Appendix. It appears that just below the transition temperature to the two-phase state $k_BT_P\approx0.23$, ΔE_D is small (typically varies from 0 to -0.06, in units of the $dd\sigma$ transfer integral) and the main contribution to $\mathcal{F}_{\rm mix}(y)$ comes from the entropy term. Therefore, y is close to 0.5 and two PM phases coexist in almost equal percentage.

E. Curie temperature

The Curie temperature can be obtained from Eq. (18), where in the case of orbital degeneracy $\mathcal{D}(T)$ is given by[56]

$$\mathcal{D}(T)=-\frac{1}{\pi}{\rm Im}\int_{-\infty}^{+\infty}dz f_T(z-\mu)\{2\Psi_0(z)g_0(z)-6[\Psi_1(z)g_1(z)+\Psi_2(z)g_2(z)]\}. \tag{25}$$

Results of these calculations are shown in Fig. 10. For $\mu<-1$, the magnetic transition temperature appears to be lower than T_P. Corresponding density $\langle\overline{n}\rangle=(1-y)\overline{n}^{(1)}+y\overline{n}^{(2)}$, averaged over the spin orientations and the alloy concentrations can be estimated from Fig. 9. Using the value of equilibrium alloy concentration $y\approx0.5$, the regime $\mu<-1$ roughly corresponds to the densities range $\langle\overline{n}\rangle<0.5$. In this region, T_C should be calculated independently for two different phases. Not surprisingly that different phases are characterized by different T_C's. Therefore, we expect *two magnetic transition points*, and the behavior for $\mu<-1$ can be summarized as follows (see Fig. 10).

With the cooling down of the sample, the first transition (T_P) occurs within the PM state, which turns into the two-phase state. Both phases are paramagnetic and can be distinguished by $\overline{n}$ and a hidden parameter of interatomic orbital polarization $\mathcal{O}_{\rm NL}$. Further decreases of T gives rise to the FM transition in one of the phases, characterized by lower density (the hole-rich phase). In the interval $T_C^{(1)}<T<T_C^{(2)}$, the FM phase continues to coexist with the PM one, persisting in the hole-deficient part of the sample.[57] The difference $T_C^{(2)}-T_C^{(1)}$ depends on μ, and is expected to lie in the interval $0<T_C^{(2)}-T_C^{(1)}<650$ K, where the upper border was estimated using the value $dd\sigma\approx0.7$ eV. Finally, below $T_C^{(1)}$ the FM order is established in both phases. Both transitions to the FM states are continuous.

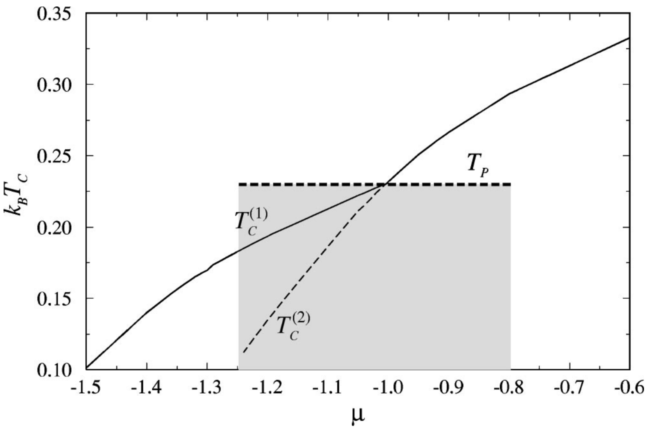

FIG. 10. Main transition temperatures for the degenerate double exchange model (in units of the $dd\sigma$ integral). T_P is the transition temperature to the two-phase paramagnetic state. The shaded area shows an approximate range of the chemical potentials (μ) when the paramagnetic state becomes intrinsically inhomogeneous. $T_C^{(1)}$ and $T_C^{(2)}$ are the Curie temperatures for two different phases (characterized by lower and higher densities of the e_g electrons, respectively).

Formally, the opposite scenario when the transition to the two-phase state occurs below T_C is also possible, and according to Fig. 10 may take place when $\mu\geqslant-1$ (corresponding to the densities range $\langle\overline{n}\rangle\geqslant0.5$). This would mean that the FM state at elevated temperatures could also become intrinsically inhomogeneous. We do not rule out such a possibility. However, the quantitative description of this situation is beyond the small-λ limit, considered in the present work.

VI. SUMMARY

We have considered a nonlocal CPA approach to the problem of orientational spin disorder in the double exchange model, which is based on the perturbation theory expansion for the T matrix with respect to fluctuations of kinetic hoppings near the mean values specified by matrix elements of the self-energy for the effective medium. In the first order it is equivalent to the DE theory by de Gennes.[3] Our main focus was on the corrections to this theory caused by the second-order effects.

In the one-orbital case, they led to substantial reduction of T_C, which was nevertheless largely overestimated in comparison with results of Monte Carlo calculations,[28] due to limitations inherent to the mean-field approach. Therefore, a sensible description of spatial spin correlations, beyond the mean-field approximation, presents a very important direction for the improvement of our method.

It appeared, however, that even on the mean-field level the situation is far from being fully understood, if considered in the combination with the effects of orbital degeneracy in the e_g band. Particularly, we have argued that the degenerate model should be characterized an additional order parameter of interatomic orbital polarization $\mathcal{O}_{\mathrm{NL}}$, which is essentially nonlocal and attached to the bonds of the DE system. Another important factor is the very peculiar form of density of the e_g states, which has two anomalies corresponding to the positions of the Van Hove singularities on the real axis. The "strange" electronic structure is responsible for an analog of the metamagnetism and leads to two different CPA solutions in certain regions of the complex plane. They correspond to different values of the order parameter $\mathcal{O}_{\mathrm{NL}}$ and the electronic density. Interestingly that both solutions can be paramagnetic in terms of conventional spin degrees of freedom. This changes the traditional concept of the DE physics dramatically. Particularly, we predict that the PM state becomes intrinsically inhomogeneous below certain temperature T_P, and then undergoes the FM transitions separately in two PM phases, which have different T_C's.

Unfortunately, there is no direct experimental evidence supporting the idea of mixed PM state below T_P, and it is not clear how this effect can be distinguished from those caused by extrinsic factors such as chemical and structural inhomogeneities and the grain boundaries.[58] On the other hand, the phase coexistence below T_C is rather common, and was observed in a number of experiments.[20–22] In addition, our result naturally explains appearance of several magnetic transition points in perovskite manganites.

Finally, we would like to discuss briefly possible extensions of our model.

(1) The present approach is based on the second order of perturbation theory expansion for the T matrix. The overall picture obtained for the degenerate model is qualitatively different from the DE theory by de Gennes. Since the effect is so dramatic, it naturally raises the question about the higher-order corrections. It seems to be a very important problem for the future analysis.

(2) The values of T_C obtained in the degenerate DE model are strongly overestimated. Presumably, the same is true for T_P, which is beyond the realistic range for known perovskite manganites. Therefore, the model should be corrected by including at least the AFM superexchange interactions between the localized spins (J^S).[49] This would also allow to consider the AFM structures, the appearance of which is expected for the densities $\langle \overline{n} \rangle \leqslant 0.5$, even in the simple DE model.[5,30] The main obstacle for such calculations is that the effect of J^S is not limited by the shift of T_C (i.e., $T_C \rightarrow T_C - 2|J^S|$ in the molecular field approximation). It will also affect the mesh of Matsubara poles in the right-hand side of Eq. (18) and will require a careful analysis of the topology of CPA solutions near the real axis. At the present stage we do not know how to deal with this problem.

(3) The topology of CPA solutions in the complex plane crucially depends on the details of electronic structure for the e_g states. Particularly, the exact position of these singularities, which are responsible for the anomalies of density of states, or even the fact of their existence in realistic compounds depend on many factors, such as the Mn$(3d)$-O$(2p)$ hybridization, the cation and structural disorder, the purity of sample. All of them may significantly modify conclusions of our work.

ACKNOWLEDGMENTS

I thank F. Aryasetiawan for discussions of energy integration in the complex plane in the case of two branches of physical solutions and Y. Tomioka for discussions of the experimental situation in manganites. The present work was started in the Joint Research Center of Atom Technology (JRCAT) where it was partly supported by NEDO.

APPENDIX: DISCONTINUITY OF INTEGRATED DENSITY OF STATES

In this appendix we discuss practical aspects of calculations of the discontinuity term $\overline{n^{(2)}}(z) - \overline{n^{(1)}}(z)$ caused by transitions between two different branches of CPA solutions in the PM state. According to Ducastelle,[41] $\overline{n}(z)$ is given by the following expression:

$$\overline{n}(z) = \frac{1}{\pi N} \mathrm{Im}\,\mathrm{Tr}\Big\{ \ln \hat{\overline{G}}(z) - \overline{\ln(\hat{1} - [\hat{\mathcal{H}} - \hat{\overline{\mathcal{H}}}(z)]\hat{\overline{G}}(z))} \Big\}, \tag{A1}$$

where Tr is the trace over site and orbital indices, N is the number of atomic sites, and the hat symbols stand for the matrices in the subspace of orbital and atomic coordinates.

Let us start with the first term. In the second order of $\hat{\overline{G}}^{(2)}(z) - \hat{\overline{G}}^{(1)}(z)$ we have

$$\mathrm{Tr}\{\ln \hat{\overline{G}}^{(2)}(z) - \ln \hat{\overline{G}}^{(1)}(z)\} \simeq 2\,\mathrm{Tr}\{[\hat{\overline{G}}^{(2)}(z) - \hat{\overline{G}}^{(1)}(z)] \times [\hat{\overline{G}}^{(2)}(z) + \hat{\overline{G}}^{(1)}(z)]^{-1}\},$$

which can be further transformed using the definition (10) for the Green function as

$$\mathrm{Tr}\{\ln \hat{\overline{G}}^{(2)}(z) - \ln \hat{\overline{G}}^{(1)}(z)\} \simeq 2\,\mathrm{Tr}\{[\hat{\overline{\mathcal{H}}}^{(2)}(z) - \hat{\overline{\mathcal{H}}}^{(1)}(z)] \times [2z - \hat{\overline{\mathcal{H}}}^{(1)}(z) - \hat{\overline{\mathcal{H}}}^{(2)}(z)]^{-1}\}.$$

The inverse matrix $\{\cdots\}^{-1}$ can be calculated in the same way as the Green function (10). Then, if $R_0(z)$ is the site-diagonal element of $\{\cdots\}^{-1}$, and $R_1(z)$ and $R_2(z)$ are the site-off-diagonal ones corresponding to the $3z^2 - r^2$ and $x^2 - y^2$ orbitals for the bond **0-1**, we can write

$$\frac{1}{N}\mathrm{Tr}\{\ln \hat{\overline{G}}^{(2)}(z) - \ln \hat{\overline{G}}^{(1)}(z)\} \simeq 4\Delta\sigma_0(z)R_0(z) - 12\{\Delta\sigma_1(z)R_1(z) + \Delta\sigma_2(z)R_2(z)\},$$

where $\Delta\sigma_\alpha(z) = \sigma_\alpha^{(2)}(z) - \sigma_\alpha^{(1)}(z)$.

Second term in Eq. (A1) (the so-called vortex correction) should be expanded up to the second order of $[\hat{\mathcal{H}} - \hat{\overline{\mathcal{H}}}(z)]$, in order to be consistent with the similar approximation (14) used for the T-matrix. Then, we have

$$\ln\{\hat{1}-[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\hat{\overline{G}}(z)\}\simeq-\Big\{[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]+\frac{1}{2}[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\hat{\overline{G}}(z)[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\Big\}\hat{\overline{G}}(z).$$

In order to calculate the thermal average, we note that

$$\overline{[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\hat{\overline{G}}(z)[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]}=-\overline{[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]},$$

which follows from the CPA equations (13) under the condition (14). Thus,

$$\overline{\ln\{1-[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]\widehat{\overline{G(z)}}\}}\simeq-\frac{1}{2}\overline{[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]G(z)},$$

and corresponding contribution to the integrated DOS is given by

$$\frac{1}{N}\mathrm{Tr}\,\overline{\ln\{\hat{1}-[\hat{\mathcal{H}}-\hat{\overline{\mathcal{H}}}(z)]G(z)\}}$$
$$\simeq\sigma_0(z)g_0(z)-3\{\sigma_1(z)g_1(z)+\sigma_2(z)g_2(z)\}.$$

---

*Electronic address: igor.solovyev@aist.go.jp

[1] C. Zener, Phys. Rev. **82**, 403 (1951).

[2] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[3] P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).

[4] E. Müller-Hartmann and E. Dagotto, Phys. Rev. B **54**, R6819 (1996).

[5] I. V. Solovyev and K. Terakura, in *Electronic Structure and Magnetism of Complex Materials*, edited by D. J. Singh (Springer-Verlag, Berlin, 2002).

[6] K. Kubo and N. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972).

[7] D. M. Edwards, A. C. M. Green, and K. Kubo, J. Phys.: Condens. Matter **11**, 2791 (1999); A. C. M. Green and D. M. Edwards, *ibid.* **11**, 10 511 (1999).

[8] R. Kilian and G. Khaliullin, Phys. Rev. B **60**, 13 458 (1999); S. Okamoto, S. Ishihara, and S. Maekawa, *ibid.* **61**, 451 (2000); M. S. Laad, L. Craco, and E. Müller-Hartmann, *ibid.* **63**, 214419 (2001).

[9] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).

[10] N. Furukawa, J. Phys. Soc. Jpn. **64**, 2754 (1995).

[11] N. Furukawa, in *Physics of Manganites*, edited by T. A. Kaplan and S. D. Mahanti (Kluwer/Plenum, New York, 1999).

[12] A. Chattopadhyay, A. J. Millis, and S. Das Sarma, Phys. Rev. B **61**, 10 738 (2000).

[13] B. L. Gyorffy, A. J. Pindor, J. B. Staunton, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. **15**, 1337 (1985).

[14] T. Oguchi, K. Terakura, and N. Hamada, J. Phys. F: Met. Phys. **13**, 145 (1983).

[15] P. E. de Brito and H. Shiba, Phys. Rev. B **57**, 1539 (1998).

[16] M. Auslander and E. Kogan, Phys. Rev. B **65**, 012408 (2001).

[17] Perhaps the absolute value of T_C is not a serious problem as it can be easily adjusted by adding a phenomenological antiferromagnetic superexchange interaction between the localized spins (Refs. 37,48). The situation with the doping dependence is more serious. The experimental T_C has a maximum around $x \approx 0.3$ (in $La_{1-x}Sr_xMnO_3$) (Ref. 18). The maximum does exist in the one-orbital DE model (at $x=0.5$) (Ref. 11). However, it is only an artifact of the one-orbital approach, whereas in a more realistic degenerate case T_C decreases as the function of x (Ref. 48).

[18] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14 103 (1995).

[19] Y. Tomioka and Y. Tokura, in *Colossal Magnetoresistive Oxides*, edited by Y. Tokura (Gordon and Breach Science Publishers, Tokyo, 2000).

[20] M. Uehara, S. Mori, C. H. Chen, and S.-W. Cheong, Nature (London) **399**, 560 (1999).

[21] M. Fäth, S. Freisem, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, Science **285**, 1540 (1999).

[22] J. W. Lynn, R. W. Erwin, J. A. Borchers, Q. Huang, A. Santoro, J-L. Peng, and Z. Y. Li, Phys. Rev. Lett. **76**, 4046 (1996); R. H. Heffner, J. E. Sonier, D. E. MacLaughlin, G. J. Nieuwenhuys, G. Ehlers, F. Mezei, S.-W. Cheong, J. S. Gardner, and H. Röder, *ibid.* **85**, 3285 (2000).

[23] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); A. J. Millis, Nature (London) **392**, 147 (1998).

[24] S. Ishihara, M. Yamanaka, and N. Nagaosa, Phys. Rev. B **56**, 686 (1997).

[25] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).

[26] Q. Li, J. Zang, A. R. Bishop, and C. M. Soukoulis, Phys. Rev. B **56**, 4541 (1997).

[27] A. Moreo, M. Mayr, A. Feiguin, S. Yunoki, and E. Dagotto, Phys. Rev. Lett. **84**, 5568 (2000).

[28] Y. Motome and N. Furukawa, J. Phys. Soc. Jpn. **69**, 3785 (2000); *ibid.* **70**, 3186 (2001).

[29] C. M. Varma, Phys. Rev. B **54**, 7328 (1996).

[30] J. van den Brink and D. Khomskii, Phys. Rev. Lett. **82**, 1016 (1999); I. V. Solovyev and K. Terakura, Phys. Rev. B **63**, 174425 (2001).

[31] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[32] M. O. Dzero, L. P. Gor'kov, and V. Z. Kresin, Solid State Commun. **112**, 707 (1999); Eur. Phys. J. B **14**, 459 (2000).

[33] E. L. Nagaev, Phys. Usp. **38**, 497 (1995); **39**, 781 (1996).

[34] E. Dagotto, S. Yunoki, A. L. Malvezzi, A. Moreo, J. Hu, S. Capponi, D. Poilblanc, and N. Furukawa, Phys. Rev. B **58**, 6414 (1998); A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1999).

[35] B. G. Nickel and W. H. Butler, Phys. Rev. Lett. **30**, 374 (1973).

[36] R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. **46**, 465 (1974).

[37] J. L. Alonso, L. A. Fernández, F. Guinea, V. Laliena, and V. Martín-Mayor, Phys. Rev. B **63**, 054411 (2001).

[38] Note that the attempt to average Eq. (1) with the distribution function (2) will yield an unphysical result, where the CPA self-energy depends linearly on λ. The linear term will then contrib-

ute to the free energy (6), that contradicts to the stationarity condition in the PM state.

[39] The PM-FM transition in the pure DE model is typically of the second order. However, an additional antiferromagnetic superexchange interaction between the localized spins can lead to the first-order transition: J. L. Alonso, L. A. Fernández, F. Guinea, V. Laliena, and V. Martín-Mayor, Phys. Rev. B **63**, 064416 (2001).

[40] All calculations have been performed using the mesh consisting of 374660 nonequivalent **q** points, which corresponds to the 258×258×258 divisions of the reciprocal lattice vectors.

[41] F. Ducastelle, J. Phys. C **8**, 3297 (1975).

[42] Note that the matrix multiplication in Eq. (12) is not restricted by a finite cluster (the dimer, in our case). This is the main difference from the so-called cluster CPA (Refs. 35,36, and 59). Our CPA scheme is compatible with the symmetry constraints, because all dimers are equivalent and equally contribute to the T matrix. This equivalence is artificially broken in the case of cluster CPA, which takes into account the contributions of only those sites which belong to a given cluster.

[43] I. V. Solovyev, cond-mat/0207544 (unpublished). Note that in the present paper we use reversed order of the e_g orbitals, which corresponds to the interchange of the orbital indices 1 and 2 in all formulas for the degenerate DM model.

[44] We retain both g_0 and g_1, but only for the sake of convenience, because formally g_1 can be expressed through g_0 using identity (11).

[45] P. Bruno, J. Kudrnovský, V. Drchal, and I. Turek, Phys. Rev. Lett. **76**, 4254 (1996).

[46] Note that the first order expansion with respect to $\Delta\hat{\mathcal{H}}$ corresponds to the following set of parameters in Eq. (17): $\widetilde{\sigma}_0=\widetilde{\sigma}_1=\widetilde{\Psi}_0=0$ and $\widetilde{\Psi}_1=2/45$. Then, after replacing $f_T(z-\mu)$ by $\Theta(z-\mu)=\lim_{T\to 0}f_T(z-\mu)$ one obtains $\widetilde{\mathcal{D}}=\frac{1}{15}\widetilde{E}_D(\mathrm{PM})$, where $\widetilde{E}_D(\mathrm{PM})$ is the energy of the PM state in the theory of de Gennes, which is related to the energy of fully polarized FM state as $\widetilde{E}_D(\mathrm{PM})=\frac{2}{3}E_D(\mathrm{FM})$.

[47] For example, for $\bar{n}=0.5$ and $\bar{n}=0.25$ we obtain $k_BT_C=0.20t_0$ and $0.17t_0$, respectively. Unfortunately, different authors reported very different estimates of T_C based on the DMFT. Using SC DOS, Furukawa alone reported two different values of k_BT_C at $\bar{n}=0.5$: 0.041 (Ref. 10) and 0.056 (Ref. 11), in units of half band width $\frac{1}{2}W$, which should correpond to $0.25t_0$ and $0.34t_0$ in our notations. Similar calculations for the one-orbital tight-binding model yielded $k_BT_C=0.0809\times(\frac{1}{2}W)\simeq 0.49t_0$ (Ref. 28). On the other hand, the values of parameters $(E_D/W, k_BT_C/E_D)=(0.106,0.21)$ and $(0.081,0.19)$ reported by Millis (Ref. 60) for $\bar{n}=0.5$ and $\bar{n}=0.25$, respectively, should correspond to $k_BT_C\simeq 0.27t_0$ and $0.18t_0$. Local CPA calculations for the SC DOS yield (in the case of classical t_2g spins) $k_BT_C=0.45\times(\frac{1}{2}W)\simeq 0.27t_0$ at $\bar{n}=0.5$ (Refs. 7 and 16). Anyway, all these values seems to be overestimated in comparison with results of nonlocal CPA calculations.

[48] M. O. Dzero, Solid State Commun. **117**, 589 (2001).

[49] The energy of the phenomenological SE interaction between nearest neighbors $\langle\mathbf{ij}\rangle$ is typically defined as $E_S=-\frac{1}{2}|J^S|\Sigma_{\langle\mathbf{ij}\rangle}\mathbf{e}_\mathbf{i}\cdot\mathbf{e}_\mathbf{j}$. For three-dimensional manganites, $|J^S|$ is of the order of 60–70 meV.[5]

[50] According to Monte Carlo calculations, k_BT_C is reduced till $0.12t_0\approx 460$ K at $\bar{n}=0.5$ (Ref. 28, and references therein).

[51] Transformations of the e_g orbitals in the cubic lattice can be described by the unitary matrices $\mathcal{U}=\left(\begin{smallmatrix}\cos\vartheta & \sin\vartheta\\ \sin\vartheta & -\cos\vartheta\end{smallmatrix}\right)$, where $\vartheta=-\pi/3$ and $\pi/3$ correspond to the 90° rotations around the x and y axes, respectively.

[52] E. P. Wohlfarth and P. Rhodes, Philos. Mag. **7**, 1817 (1962); M. Cyrot and M. Lavagna, J. Phys. (Paris) **40**, 763 (1979); M. Shimizu, *ibid.* **43**, 155 (1982).

[53] H. Shiba, R. Shiina, and A. Takahashi, J. Phys. Soc. Jpn. **66**, 941 (1997).

[54] K. Wildberger, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. B **52**, 11 502 (1995).

[55] In practical terms, we start iterations at z_0 with two different sets for the self-energy, which guarantee two different CPA solutions, and then at each consecutive pole z_n start with the self-consistent CPA solutions obtained for z_{n-1} (and so on until the merging of the two solutions).

[56] Equation (25) is obtained from the Lloyd formula for the integrated DOS and is the generalization of Eq. (16) for the two-orbital case, which includes also the trace over the orbital indices. The latter is responsible for the factor 2 in the first term and gives rise to two different contributions to the second term.

[57] Note that if the concentration of the FM phase is as large as $y\approx 0.5$, it is natural to expect that the system is above the percolation threshold. Then, the behavior in the interval $T_C^{(1)}<T<T_C^{(2)}$ should correpond to the proper FM order, rather than to the superferromagnetism (small FM islands in the PM matrix).

[58] Y. Tomioka (private communication).

[59] N. Hamada and H. Miwa, Prog. Theor. Phys. **59**, 1045 (1978).

[60] A. J. Millis, in *Colossal Magnetoresistive Oxides*, edited by Y. Tokura (Gordon and Breach Science Publishers, Tokyo, 2000).