Double Exchange Ferromagnetism in the Peierls Insulator State

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We study the effects of opening the band gap on the double exchange ferromagnetism. Applying the density-matrix renormalization group method and an analytical expansion from the dimer limit to the one-dimensional double exchange model, we demonstrate for a relevant region of the exchange coupling that, in the weak dimerization regime, the Peierls gap opens in the fully spin-polarized conduction band without affecting its ferromagnetism, whereas in the strong dimerization regime, the ferromagnetism is destroyed, and the Mott gap opens instead, leading the system to the antiferromagnetic quasi-long-range order. An insulator version of double exchange ferromagnetism is thus established.

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Magnetism and electronic transport properties of materials are closely related to each other; e.g., insulating transition-metal oxides are typically antiferromagnetic, and ferromagnetism usually goes hand in hand with metallicity [1]. Elucidation of the mechanisms of this relationship is one of the major issues in the field of physics of strong electron correlations. A well-known example is the double exchange ferromagnetism that occurs in mixed systems of localized spins and itinerant electrons interacting via the Hund's rule coupling, where the coherent motion of the itinerant electrons aligns the localized spins ferromagnetically to gain in kinetic energy of the itinerant electrons [2–4].

A question then arises as to what happens in this ferromagnetism if the coherent motion of electrons ceases due, e.g., to the opening of the band gap. This issue becomes a real question in ferromagnetic hollandite $K_2Cr_8O_{16}$ [5], where the double exchange mechanism induces the three-dimensional (3D) full spin polarization in the system [6], and then the metal-insulator transition follows in its fully spin-polarized quasi-one-dimensional (1D) conduction band by the Peierls mechanism [7,8], without affecting its 3D ferromagnetism. Thus, the uncommon ferromagnetic insulating (FI) state is realized in this material [7].

A naive answer to the above frequently asked question may then be that the ferromagnetism can survive if the band gap is small enough in comparison with the width of the conduction band, and therefore, the motion of conduction electrons, though not coherent, is not significantly suppressed. However, to the best of our knowledge, no quantitative theoretical studies have been done on the issue of whether this is actually the case.

In this Letter, we address this issue from the theoretical standpoint. We apply the numerical density-matrix renormalization group (DMRG) technique [9] and analytical expansion from the dimer limit to the 1D double exchange model that simulates the quasi-1D chain of $K_2Cr_8O_{16}$ and study the effects of opening of the band gap on the double exchange ferromagnetism. We calculate the total-spin quantum number and charge gap of the system and extract the ground-state phase diagram of the model.

We will thereby demonstrate for a relevant region of the exchange coupling that, in the weak dimerization regime, the Peierls gap opens in the fully spin-polarized conduction band without affecting its ferromagnetism, whereas in the strong dimerization regime, the ferromagnetism is destroyed, and the Mott gap opens instead due to the effective "on-dimer" Coulomb interaction, which leads the system to the antiferromagnetic quasi-long-range order. The metallicity itself is not, therefore, a necessary condition for the realization of the double exchange ferromagnetism, and thus, an "insulator version" of the double exchange ferromagnetism is established. This is a route to the realization of insulating ferromagnets, different from those discussed in doped $LaMnO_3$ where the orbital ordering plays an essential role [10–12].

Our model (see Fig. 1) contains the terms of Peierls dimerization and Hund's rule coupling and is defined by the Hamiltonian

$$\mathcal{H} = -\sum_{i=1,\sigma}^{L} t_{i,i+1}(c^{\dagger}_{i,\sigma}c_{i+1,\sigma} + \text{H.c.}) - J_H \sum_{i=1}^{L} \boldsymbol{s}_i \cdot \boldsymbol{S}_i$$
$$\boldsymbol{s}_i = \frac{1}{2}\sum_{\sigma,\sigma'} c^{\dagger}_{i,\sigma}\boldsymbol{\tau}_{\sigma,\sigma'}c_{i,\sigma'}, \tag{1}$$

where $c^{\dagger}_{i,\sigma}$ is the creation operator of an electron with spin $\sigma(=\uparrow,\downarrow)$ at site i, $\boldsymbol{s}_i$ is the spin operator of a conduction electron at site i, $\boldsymbol{\tau}$ is the vector of Pauli matrices, and $\boldsymbol{S}_i$ is the quantum spin operator (of spin $1/2$) of a localized electron at site i. The hopping parameter between the nearest-neighbor sites is defined as $t_{i,i+1} = [1 - (-1)^i\delta/2]t$ with the dimerization strength δ of $0 \le \delta < 2$; we, in particular, define $t_{\pm} = (1 \pm \delta/2)t$. J_H is the strength of the Hund's rule coupling. L is the number of sites in the system, where the site contains a conduction orbital and a

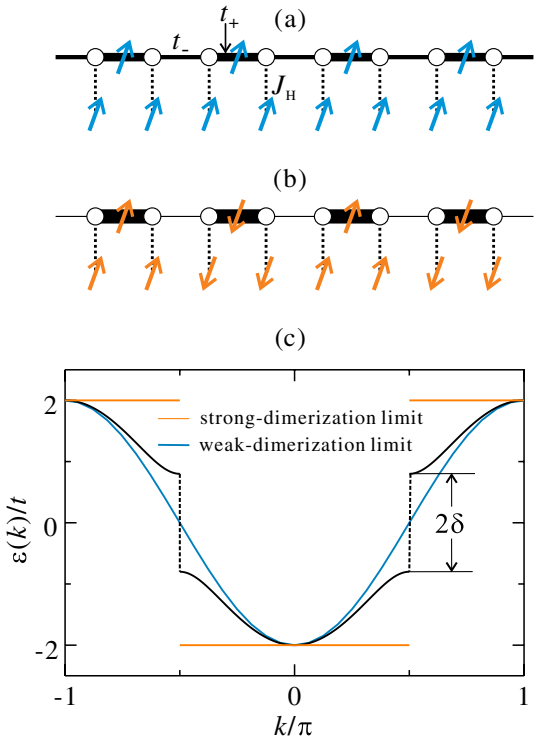

FIG. 1 (color online). Schematic representations of the double exchange model in (a) the weak dimerization regime and (b) strong dimerization regime. In (c), we illustrate the non-interacting band structure $\varepsilon(k)$ of our model with the lattice dimerization δ in the unfolded Brillouin zone.

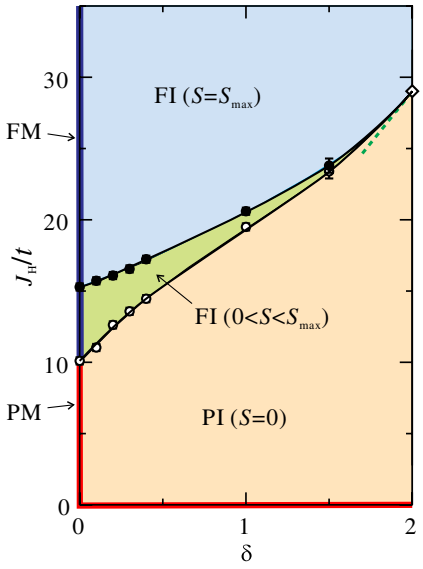

FIG. 2 (color online). Calculated ground-state phase diagram of the 1D double exchange model at quarter filling with the lattice dimerization δ. We find the FI (ferromagnetic insulating), PI (paramagnetic insulating), FM (ferromagnetic metallic), and PM (paramagnetic metallic) phases. The FI-PI phase boundary at $\delta \to 2$ is determined by the analytical expansion from the dimer limit and is shown by the open diamond and dashed line. The FM and PM phases at $\delta = 0$ or $J_H = 0$ are also indicated by the thick lines.

localized spin. We confine ourselves to the case at quarter filling of conduction electrons $n = N/L = 1/2$, where N is the number of conduction electrons in the system. We introduce δ as a controllable input parameter rather than the order parameter of the spontaneous lattice dimerization since our purpose is to study the effects of δ on the electronic states of the model.

We use the DMRG method to investigate the ground-state properties of the system Eq. (2), where the open-end boundary conditions are applied. We study the model with several lengths of $L = 8$–20, keeping $m = 1200$–3200 density-matrix eigenstates in the renormalization procedure; in this way, the largest truncation error, or the discarded weight, is on the order of 10^{-11}. Note that we have to keep relatively numerous density-matrix eigenstates to extract the true ground state from a number of nearly degenerate magnetic states, in particular, in the vicinity of the phase boundaries. The extrapolation to the thermodynamic limit $L \to \infty$ is made in the results presented unless otherwise indicated.

First, let us present the total-spin quantum number S of the system, which is calculated directly from the ground-state expectation value of $\boldsymbol{S}^2$ defined as $\langle \boldsymbol{S}^2 \rangle = S(S+1) = \sum_{ij}(\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_j \rangle + 2\langle \boldsymbol{s}_i \cdot \boldsymbol{S}_j \rangle + \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle)$. The results are given in Fig. 2 as a ground-state phase diagram. We find that there are three phases, $S = 0$, $0 < S < S_{\max}$, and $S = S_{\max}$, depending on the values of J_H and δ, where $S_{\max}$ denotes the full spin polarization. As expected, and in agreement with the previous calculations at $\delta = 0$ [13–16], the $S = S_{\max}$ phase appears when J_H is large, the $S = 0$ phase appears when J_H is small, and in between, the phase with the intermediate spin polarization also appears as in Ref. [15] at $\delta = 0$ [see also Fig. 3(a) below]. These phases are retained even when the dimerization δ is introduced. We note that the two critical values of J_H that separate the $S = S_{\max}$ and $S = 0$ phases increase with increasing δ and that the region with the intermediate spin polarization becomes narrower and vanishes at $\delta \to 2$ (see below).

Next, let us calculate the charge gap Δ defined as $\Delta = \lim_{L\to\infty}\Delta(L)$ with $\Delta(L) = \frac{1}{2}[E_0^{N+2}(L) + E_0^{N-2}(L) - 2E_0^N(L)]$, where $E_0^N(L)$ is the ground-state energy of the system of size L with N electrons. The gap Δ is defined with the prefactor $1/2$, so that the single-particle band gap is identical to Δ in the present case where pairing interactions are absent. The results are shown in Figs. 3(b)–3(d). We find that the charge gap opens in the entire parameter space except at the lines $\delta = 0$ and $J_H = 0$. The model at $J_H = 0$ is trivial, where the conduction electrons, decoupled completely from the localized spins, behave just as the non-interacting electrons, resulting in the paramagnetic metallic (PM) phase.

The model Eq. (1) at $\delta = 0$, on the other hand, is highly nontrivial, and much work has been done in recent years

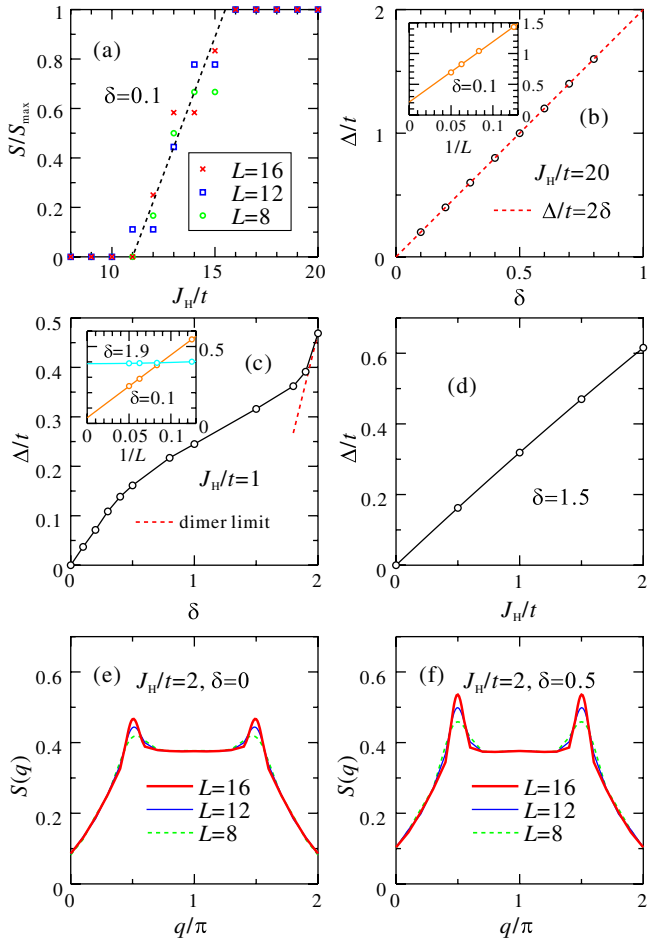

FIG. 3 (color online). (a) Calculated normalized total-spin quantum number $S/S_{\max}$ as a function of J_H/t. Also shown are the calculated results for the charge gap Δ: (b) δ dependence in the FI phase, (c) δ dependence in the PI phase (where the dotted line indicates the result of the strong-dimerization expansion), and (d) J_H/t dependence in the PI phase. Inset of (b) and (c) shows examples of the finite-size scaling of the gap. In (e) and (f), the calculated spin structure factors $S(q)$ in the PI phase without and with the lattice dimerization, respectively, are shown.

[13–16]: basically, the ferromagnetic metallic (FM) phase appears for the large J_H region, which changes into the PM phase when J_H becomes small. In addition, it has been claimed [15,17,18] that the region of phase separation, in particular, near half filling and the "spiral" phase with long-wavelength antiferromagnetic correlations appears at the FM-PM phase boundary. Although we have not detected any indications of the phase separation at least at quarter filling in our accurate DMRG calculations with very large m values, our results obtained are consistent with the results of previous work [13–16]: we find that either the FM phase (when J_H is large) or PM phase (when J_H is small) is realized, and in between there is the partially spin-polarized metallic phase [see Figs. 2 and 3(a)] that may correspond to the spiral phase predicted in Ref. [15].

Let us then introduce the lattice dimerization $\delta > 0$. The results are the following: in the $S = S_{\max}$ region, we find that the charge gap of $\Delta/t = 2\delta$ opens as shown in Fig. 3(b). This can simply be understood because in this region we have the noninteracting band of spinless fermions at half filling, and therefore, the lattice dimerization δ opens the band gap of the size $\Delta/t = 2\delta$. The FI phase is thus realized. Since the FM phase due to the double exchange mechanism is continuous to this FI phase, we may naturally refer to it as the insulator version of the double exchange ferromagnetism.

In the $S = 0$ region, we find that the gap actually opens as $\Delta \propto \delta$ in the weak dimerization limit as shown in Fig. 3(c). The size of the gap increases as the value of J_H increases as shown in Fig. 3(d). This phase with $\Delta > 0$ may then be denoted as the paramagnetic insulating (PI) phase. The Fourier transform of the spin-spin correlation function for the conduction electrons $S(q) = \frac{1}{L}\sum_{i,j} e^{iq(R_j - R_i)} \langle \boldsymbol{s}_i \cdot \boldsymbol{s}_j \rangle$ (as well as that for the localized electrons, see Fig. 2 of Ref. [15]) may characterize this phase. The calculated results are shown in Figs. 3(e) and 3(f), where we find that the antiferromagnetic spin correlation of the wave vector of $q = \pi/2$ is enhanced and that the lattice dimerization inducing the localization of conduction electrons further enhances this correlation. This result may therefore be interpreted as an enhancement by the lattice dimerization of the "island" state predicted in Ref. [15], where the high-spin ($S = 3/2$) clusters, formed by a conduction electron coupled ferromagnetically with the two neighboring localized spins, are arranged antiferromagnetically with the quasi-long-range order [15,19]. In higher spatial dimensions, this phase may well fall into the true long-range antiferromagnetic order, resulting in the antiferromagnetic insulating (AFI) phase. This situation resembles that of the "dimer-Mott" phase [20,21] in the dimerized Hubbard model at quarter filling, although in the latter the spins are of $S = 1/2$.

In the $0 < S < S_{\max}$ region, the charge gap also opens at $\delta > 0$, where its size increases rapidly with increasing J_H/t. We thus have the FI phase here as well, which may be the insulating spiral phase continuous to the metallic one predicted in Ref. [15].

Now, let us discuss the strong dimerization limit, where we start with the highly correlated clusters $\mathcal{C}_l$ ($l = 1, \cdots, L/2$) coupled weakly to each other through the hopping parameter t_- [see Fig. 1(b)]. Each of the clusters consists of the two conduction orbitals and two localized spins. In the ground state, the cluster contains one conduction electron (and two localized spins), and the internal three spins are fully polarized. The lowest energy of the single cluster is $e(1) = -J_H/4 - t_+$, where the conduction electron is in the bonding state of the two conduction orbitals. The eigenstates of the cluster with the 0 and 2 conduction electrons are also derived exactly, and the lowest energies are found to be $e(0) = 0$ and

$e(2) = -\sqrt{J_H^2 + 16t_+^2}/2$, respectively. In the strong-dimerization limit of the PI phase, we can therefore map our system Eq. (1) onto an effective single-band Hubbard model defined in terms of the bonding orbital on each dimer. The Hamiltonian may be written as

$$\mathcal{H}_{\rm eff} = t_{\rm eff} \sum_{i=1,\sigma}^{L/2} (b_{i,\sigma}^\dagger b_{i+1,\sigma} + \text{H.c.}) + U_{\rm eff} \sum_{i=1}^{L/2} n_{i,\uparrow}^b n_{i,\downarrow}^b \quad (2)$$

with the creation operator of an electron on the bonding orbital $b_i^\dagger = (c_{2i-1,\sigma}^\dagger + c_{2i,\sigma}^\dagger)/\sqrt{2}$ and $n_{i,\sigma}^b = b_{i,\sigma}^\dagger b_{i,\sigma}$. We obtain the effective hopping integral $t_{\rm eff} = t_-/2$ and effective "on-dimer" Coulomb interaction $U_{\rm eff} = e(2) + e(0) - 2e(1)$. In this mapping, the localized spins contribute only to $U_{\rm eff}$ and their degrees of freedom are not explicitly involved in the operator $b_{i,\sigma}^\dagger$. An analytical expression for the charge gap may thus be derived as

$$\begin{aligned}\Delta &= U_{\rm eff} - 2t_- \\ &= -\sqrt{J_H^2 + 4t^2(2+\delta)^2}/2 + 2t\delta + J_H/2, \end{aligned} \quad (3)$$

which is valid up to the first order of 2-δ. The result thus obtained is shown in Fig. 3(c) as a dotted line, where we find that the agreement with the DMRG result is very good. In the FI phase, on the other hand, the charge gap is always $\Delta/t = 2\delta$ in its entire region, independent of J_H. The two gaps are therefore discontinuous at the phase boundary.

Next, we derive the effective exchange interaction $J_{\rm eff}$ between conduction electrons on the neighboring clusters. We first take a direct product of the isolated clusters ($\prod_{l=1}^{L/2} \mathcal{C}_l$) to be the unperturbed ground state of the system. Then, taking into account all the processes up to the second order of the hopping t_-, we obtain the expression for $J_{\rm eff}$ as

$$\begin{aligned} J_{\rm eff} = t_-^2 \Bigg[&\frac{(J_H^2 + 8t_+^2)}{(J_H + 4t_+)(J_H^2 + 16t_+^2)} + \frac{1}{8(J_H + 2t_+)} \\ &+ \frac{\left(\sqrt{J_H^2 + 16t_+^2} + 4t_+\right)^2 (J_H + 4t_+)}{16 J_H t_+ (J_H^2 + 16t_+^2)} - \frac{3}{16t_+} \Bigg], \end{aligned} \quad (4)$$

where we should note that, if only the lowest intermediate state is taken into account in the second-order process, we obtain $J_{\rm eff} = 4t_-^2/U_{\rm eff}$, which is always positive (or antiferromagnetic). We thus find that, depending on the value of $J_{\rm eff}$ (either positive or negative), the ground state realized is either the PI phase or the FI phase. The critical value of J_H at $\delta \to 2$ is found to be $29.004t$, which determines the FI-PI phase boundary at $\delta \to 2$. The region of the intermediate spin state does not appear here. The result for the phase boundary obtained from Eq. (4) is shown as a dashed line in Fig. 2, where we find again that the agreement with our DMRG result is very good, reinforcing the validity of our phase diagram of Fig. 2.

In summary, we studied the effects of opening of the band gap on the double exchange ferromagnetism. We applied the DMRG technique and analytical expansion from the dimer limit to the 1D double exchange model at quarter filling with lattice dimerization and obtained the ground-state phase diagram. We found three phases: the FI phase with the Peierls gap and full spin polarization, the PI phase with the Mott gap and dominant antiferromagnetic spin correlations, and the FI phase with the partial spin polarization. The results for $J_H/t \gtrsim 15$ demonstrated that, in the weak dimerization regime, the Peierls gap opens in the fully spin-polarized conduction band without affecting its ferromagnetism. Therefore, the metallicity itself is not a necessary condition for the realization of the double exchange ferromagnetism. The concept of the insulator version of the double exchange ferromagnetism was thus established. In the strong dimerization regime, on the other hand, the ferromagnetism is destroyed at $J_H/t \lesssim 29$, and the Mott gap due to the effective on-dimer Coulomb interaction opens there with the antiferromagnetic quasi-long-range order in the system.

The uncommon FI state realized in $K_2Cr_8O_{16}$ [5,7] then means that this material is in the weak dimerization regime with the Peierls gap and full spin polarization. A recent experiment [22] suggests that, by applying high pressures of $\gtrsim 2$ GPa, the FM phase is suppressed very rapidly, while the metal-insulator transition remains almost unchanged, leading to the transition from the PM phase to the PI or AFI phase by lowering temperature. It may then be quite interesting to point out that, if the applied pressure decreases the value of J_H/t, this might correspond to the phase change in the quasi-1D chains from the FI to PI phase as in our phase diagram given in Fig. 2, where the intermediate spin state, or the spiral state of Ref. [15], may also be predicted to appear under high pressure. We hope that our work presented here will stimulate further searches for new phenomena and materials with intriguing magnetic and transport properties derived from the interplay between the double exchange and Peierls or Mott mechanisms.

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[1] D. I. Khomskii and G. A. Sawatzky, Solid State Commun. **102**, 87 (1997).
[2] C. Zener, Phys. Rev. **81**, 440 (1951); **82**, 403 (1951).
[3] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).
[4] P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).

[5] K. Hasegawa, M. Isobe, T. Yamauchi, H. Ueda, J. I. Yamaura, H. Gotou, T. Yagi, H. Sato, and Y. Ueda, Phys. Rev. Lett. **103**, 146403 (2009).
[6] M. Sakamaki, T. Konishi, and Y. Ohta, Phys. Rev. B **80**, 024416 (2009); **82**, 099903(E) (2010).
[7] T. Toriyama, A. Nakao, Y. Yamaki, H. Nakao, Y. Murakami, K. Hasegawa, M. Isobe, Y. Ueda, A. V. Ushakov, D. I. Khomskii, S. V. Streltsov, T. Konishi, and Y. Ohta, Phys. Rev. Lett. **107**, 266402 (2011).
[8] A. Nakao, Y. Yamaki, H. Nakao, Y. Murakami, K. Hasegawa, M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. **81**, 054710 (2012).
[9] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992); Phys. Rev. B **48**, 10345 (1993).
[10] H. Y. Hwang, S.-W. Cheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).
[11] T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **61**, R3776 (2000).
[12] J. Geck, P. Wochner, S. Kiele, R. Klingeler, A. Revcolevschi, M. v. Zimmermann, B. Büchner, and P. Reutler, New J. Phys. **6**, 152 (2004).
[13] J. Kienert and W. Nolting, Phys. Rev. B **73**, 224405 (2006).
[14] S. Henning and W. Nolting, Phys. Rev. B **79**, 064411 (2009).
[15] D. J. Garcia, K. Hallberg, B. Alascio, and M. Avignon, Phys. Rev. Lett. **93**, 177204 (2004).
[16] M. Gulácsi, Adv. Phys. **53**, 769 (2004).
[17] S. Yunoki, J. Hu, A. L. Malvezzi, A. Moreo, N. Furukawa, and E. Dagotto, Phys. Rev. Lett. **80**, 845 (1998).
[18] E. Dagotto, S. Yunoki, A. L. Malvezzi, A. Moreo, J. Hu, S. Capponi, D. Poilblanc, and N. Furukawa, Phys. Rev. B **58**, 6414 (1998).
[19] See, e.g., P. Fazekas, *Lecture Notes on Electron Correlation and Magnetism* (World Scientific, Singapore, 1999), p. 383.
[20] K. Penc and F. Mila, Phys. Rev. B **50**, 11429 (1994).
[21] H. Seo, J. Merino, H. Yoshioka, and M. Ogata, J. Phys. Soc. Jpn. **75**, 051009 (2006).
[22] T. Yamauchi, K. Hasegawa, H. Ueda, M. Isobe, and Y. Ueda (unpublished).