

## Electronic Hamiltonian for transition-metal oxide compounds

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An effective electronic Hamiltonian for transition-metal oxide compounds is presented. For Mn oxides, the Hamiltonian contains spin-2 ‘‘spins’’ and spin-3/2 ‘‘holes’’ as degrees of freedom. The model is constructed from the Kondo-lattice Hamiltonian for mobile  $e_g$  electrons and localized  $t_{2g}$  spins, in the limit of a large Hund’s coupling. The effective electron-bond-hopping amplitude fluctuates in sign as the total spin of the bond changes. In the large spin limit, the hopping amplitude for electrons aligned with the core ions is complex and a Berry phase is accumulated when these electrons move in loops. The model is compared with the standard double-exchange Hamiltonian. Both have ferromagnetic ground states at finite hole density and low temperatures, but their critical temperatures could be substantially different due to the frustration effects induced by the Berry phase. [S0163-1829(96)51634-6]

The discovery of giant magnetoresistance effects in ferromagnetic metallic oxides  $R_{1-x}X_x\text{MnO}_3$  (where  $R=\text{La,Pr,Nd}$ ;  $X=\text{Sr,Ca,Ba,Pb}$ ) has triggered renewed attention into these compounds.<sup>1</sup> A decrease in resistivity of four orders of magnitude has been observed in thin films of  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  at fields of  $\sim 8\text{ T}$ .<sup>2</sup> The phase diagram of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  is very rich with ferromagnetic (metal and insulator) phases, as well as regions where charge ordering is observed.<sup>3</sup> The magnetic and electronic properties of these manganese oxides are believed to arise, at least in part, from the strong coupling between correlated itinerant electrons and localized spins, both of  $3d$  character. The  $\text{Mn}^{3+}$  ions have three electrons in the  $t_{2g}$  state forming a local  $S=3/2$  spin, and one electron in the  $e_g$  state which hops between nearest-neighbor Mn ions, with double occupancy suppressed by Coulombic repulsion. The widely used Hamiltonian to describe manganese oxides is<sup>4</sup>

$$H = -t \sum_{\langle \mathbf{m}\mathbf{n} \rangle \sigma} (c_{\mathbf{m}\sigma}^\dagger c_{\mathbf{n}\sigma} + \text{H.c.}) - J_H \sum_{\mathbf{n}} \boldsymbol{\sigma}_{\mathbf{n}} \cdot \mathbf{S}_{\mathbf{n}}, \quad (1)$$

where the first term is the  $e_g$  electron transfer between nearest-neighbor Mn-ions at sites  $\mathbf{m}, \mathbf{n}$ , while the second term is the ferromagnetic Hund coupling between the  $S=3/2$  localized spin  $\mathbf{S}_{\mathbf{n}}$  and the mobile electron with spin  $\boldsymbol{\sigma}_{\mathbf{n}}$  ( $J_H > 0$ ). A Coulombic repulsion to suppress double occupancy in the itinerant band is implicit. The on-site Hund coupling energy is larger than the conduction bandwidth favoring the alignment of the itinerant and localized spins. For  $\text{Mn}^{3+}$ , the resulting spin is 2, while for  $\text{Mn}^{4+}$  (vacant  $e_g$  state) the spin is  $3/2$ .

Since the study of Hamiltonian Eq. (1) is a formidable task, simplifications have been introduced to analyze its properties. A familiar approach is the use of the double-exchange Hamiltonian,<sup>4-9</sup> where the  $e_g$  electrons move in the background of classical spins  $\mathbf{S}_{\mathbf{n}}^{\text{cl}}$  that approximate the  $S=3/2$  almost localized  $t_{2g}$  electrons. The conduction electron effective hopping between sites  $\mathbf{m}$  and  $\mathbf{n}$  used in previous

work is  $t_{\mathbf{mn}}^{\text{eff}} = t \sqrt{1 + (\mathbf{S}_{\mathbf{m}}^{\text{cl}} \cdot \mathbf{S}_{\mathbf{n}}^{\text{cl}}/S^2)}$ , where  $S$  is the magnitude of the classical spin.<sup>4,6</sup> Using this model, the ferromagnetic critical temperature,  $T_c$ , was recently estimated.<sup>9</sup> Since the result was much larger than experimentally observed, the need for nonelectronic interactions to describe Mn oxides was remarked.<sup>9,10</sup>

The purpose of this paper is to reexamine the large  $J_H$  limit of model Eq. (1). We derive an effective Hamiltonian for Mn oxides which is valid for the quantum mechanical case of  $S=2$   $\text{Mn}^{3+}$  ions. Actually, the Hamiltonian is discussed for an arbitrary spin  $S$ . The ideas followed in this paper are a generalization of the calculation recently presented for NiO compounds, where ‘‘holes’’ doped into a  $S=1$  background carry  $S=1/2$  and they move following non-trivial hopping processes.<sup>11</sup> At large  $S$ , the model described here contains a complex effective coupling for electrons whose spin is aligned with the core spins. These electrons acquire a phase when they move in closed loops, an effect not taken into account in previous literature for Mn oxides. Although the double-exchange model is not recovered at large  $S$ , the presence of a ferromagnetic phase at low temperatures is likely even in the revised model and most of the differences between double-exchange and the model will occur at finite temperatures.

In the limit  $J_H \rightarrow \infty$ , it is natural to restrict the Hilbert space corresponding to a given site to spin eigenstates with the maximum allowed spin  $S'$ , and projection  $m' = -S', \dots, S'$ , compatible with the number of electrons at that site. Thus, the ions are in a state either with  $S'=S$ , if the  $e_g$  level is occupied, or of  $S'=S-1/2$ , if there is no  $e_g$  electron. The corresponding degrees of freedom will be referred to as ‘‘spins’’ and ‘‘holes,’’ respectively. They are coupled by standard nearest-neighbor Heisenberg interactions, plus ‘‘hopping’’ terms for the movement of holes, respecting the large  $J_H$  approximation. The site states will be denoted by  $|S', m'\rangle_{\mathbf{n}}$ . For charge-transfer compounds, the absence of an  $e_g$  electron can be considered as caused by the

Zhang-Rice singlet formation between oxygen and  $d$  electrons.<sup>11</sup> Thus, our results are not restricted to Mott-Hubbard compounds but are valid for transition metals in general in arbitrary dimensions, and contain as a special case the well-known  $t$ - $J$  model widely used for cuprates.

The hopping amplitude  $t_{\mathbf{mn}}$  for nearest-neighbor sites  $\mathbf{m}$  and  $\mathbf{n}$  certainly depends on the values of the spin at both sites, as well as on their projections. Let us assume that at site  $\mathbf{m}$  we have a spin  $S'=S$ , while at site  $\mathbf{n}$  there is a  $S'=S-1/2$  hole. The eigenstates of the  $\mathbf{mn}$  bond can be labelled by the total bond spin,  $S_T$ , and its projection,  $M_T$ , and they admit an expansion in the basis compatible with  $J_H \rightarrow \infty$  as

$$\begin{aligned} & |\widetilde{S_T, M_T}\rangle_i \\ &= \sum_{mm'} |S, m\rangle_{\mathbf{m}} \left| S - \frac{1}{2}, m' \right\rangle_{\mathbf{n}} C \left( S, S - \frac{1}{2}, m, m', S_T, M_T \right), \end{aligned} \quad (2)$$

where  $C$  are Clebsch-Gordan (CG) coefficients, and  $m$  ( $m'$ ) runs from  $-S$  to  $+S$  [ $-(S-\frac{1}{2})$  to  $+(S-\frac{1}{2})$ ]. Let us consider Eq. (2) as the *initial* state, i.e., the one before the hopping occurs. The *final* state  $|\widetilde{S_T, M_T}\rangle_f$ , where the hole has moved from  $\mathbf{n}$  to  $\mathbf{m}$ , admits the same decomposition but with the site indices permuted. Since the hopping Hamiltonian  $H_t$  [first term in Eq. (1)] is a scalar, the matrix element necessary to evaluate the effective hopping amplitude is

$$t(S_T, M_T) = {}_f \langle \widetilde{S_T, M_T} | H_t | \widetilde{S_T, M_T} \rangle_i. \quad (3)$$

Using the Wigner-Eckart theorem and after long, but straightforward, CG algebra it can be shown that

$$t(S_T, M_T) = t \frac{S_T + 1/2}{2S} (-1)^{2S - S_T - 1/2}. \quad (4)$$

The amplitude of this hopping, i.e.  $|t(S_T, M_T)|$ , is in agreement with the well-known results used by Zener,<sup>5</sup> Anderson and Hasegawa,<sup>4</sup> and de Gennes<sup>6</sup> to introduce the double-exchange model. Actually, it can be easily shown that for any value of the spin the following operatorial equality holds:

$$\frac{S_T + 1/2}{2S} = \frac{1}{\sqrt{2}} \sqrt{1 + \frac{1}{2S} + \frac{\mathbf{S}_{\mathbf{m}} \cdot \mathbf{S}_{\mathbf{n}}}{S^2}}, \quad (5)$$

where  $\mathbf{S}_{\mathbf{m}}, \mathbf{S}_{\mathbf{n}}$  are spin operators that can act on a spin or a hole. However, note the presence of a nontrivial  $S_T$ -dependent sign in the effective hopping Eq. (4).<sup>12</sup> We will argue here that the presence of this sign is crucial for a proper quantum mechanical treatment of the large  $J_H$  limit of Eq. (1).

To better understand this nontrivial sign, consider, e.g., the special case of Eq. (1) where the localized degree of freedom has spin 1/2. Thus, at the link  $\mathbf{mn}$  used in Eqs. (2)–(4), and working at large  $J_H$ , the problem reduces to two electrons forming a spin  $S'=1$  in one site, interacting with one electron (i.e., a  $S'=1/2$  hole) at the other site. Let us verify Eq. (4) for some special cases using Eq. (1): (1) If  $S_T=3/2$  and  $M_T=3/2$ , moving the  $e_g$  electron across the  $\mathbf{mn}$  bond produces a matrix element 1, in agreement

with Eq. (4); (2) Suppose now that  $S_T=1/2$  and  $M_T=1/2$ . Using CG coefficients, the initial state before the hopping occurs can be written as  $|\widetilde{1/2, 1/2}\rangle_{i=(1/\sqrt{3})|1/2, 1/2\rangle_{\mathbf{m}}|1, 0\rangle_{\mathbf{n}} - (\sqrt{2/3})|1/2, -1/2\rangle_{\mathbf{m}}|1, 1\rangle_{\mathbf{n}}}$ , in the basis where at site  $\mathbf{m}$  there is a  $S=1/2$  hole and at  $\mathbf{n}$  a  $S=1$  spin. Applying explicitly the hopping Hamiltonian  $H_t$  we obtain  $H_t|\widetilde{1/2, 1/2}\rangle_i = -(t/2)|\widetilde{1/2, 1/2}\rangle_f - (t\sqrt{3}/2)|0, 0\rangle_{\mathbf{m}}|1/2, 1/2\rangle_{\mathbf{n}}$ . The last term is not favored by the strong Hund's coupling, and thus the matrix element relevant for the low energy effective Hamiltonian is simply  ${}_f \langle \widetilde{1/2, 1/2} | H_t | \widetilde{1/2, 1/2} \rangle_i = -t/2$ . The amplitude has the expected absolute value  $|t(S_T, M_T)|$  compatible with the double-exchange model. However, the matrix element is actually *negative*, compatible with our result Eq. (4). The negative sign originates in  $|\widetilde{1/2, 1/2}\rangle_i$ , where in order to make a total spin-1/2 combination out of individual spins 1/2 and 1, amplitudes of different signs are needed. While such effects are natural in quantum mechanical processes involving state overlaps, they are not included in the double-exchange model. These signs are important to properly reproduce the physics of model Eq. (1) at large  $J_H$  even close to a ferromagnetic configuration since just small deviations from a fully polarized link can involve a change in the sign of the hopping. If the sign is included, the hopping amplitude mean value vanishes at large spin  $S$ , while it is finite in the double exchange approximation.

While the  $S_T$  basis Eq. (2) is useful to find the hopping amplitudes, the effective Hamiltonian for the complete lattice has a more intuitive form in the basis of spin eigenstates at each site. Using Eq. (5) we can write an effective hopping Hamiltonian as a polynomial

$$H_{\text{eff}} = -t \sum_{\langle \mathbf{mn} \rangle} P_{\mathbf{mn}} Q_S(y), \quad (6)$$

where  $P_{\mathbf{mn}}$  is an operator that permutes the states at sites  $\mathbf{m}$  and  $\mathbf{n}$ ,  $y = \mathbf{S}_{\mathbf{m}} \cdot \mathbf{S}_{\mathbf{n}} / S(S-1/2)$ , and  $\mathbf{S}_{\mathbf{m}}, \mathbf{S}_{\mathbf{n}}$  acts either on the localized spin or the hole (actual spins  $S$  and  $S-1/2$ , respectively), as explained before.  $Q_S(y)$  is spin- $S$  dependent and it can be found iteratively starting from the lowest spin case using the relation

$$\begin{aligned} Q_S(y) &= -a_S Q_{S-1/2} [b_S (2 + (2S-1)y) / (2S+1)] \\ &+ [1 + a_S Q_{S-1/2}(b_S)] \\ &\times \prod_{l=1}^{2S-1} \frac{S[2S+1 + (2S-1)y] - l^2}{4S^2 - l^2}, \end{aligned} \quad (7)$$

where we used  $Q_{1/2}(y)=1$ ,  $a_S=(2S-1)/2S$ , and  $b_S=S(2S+1)/[(S-1)(2S-1)]$ . For  $S=1$ , this implies  $Q_1(y)=(1+y)/2$  which correctly reproduces the Hamiltonian recently derived for doped  $\text{Y}_2\text{BaNiO}_5$  compounds.<sup>11</sup> If only the absolute value of the matrix elements Eq. (3) would have been used, then  $Q_1(y)$  becomes instead  $(5+y)/6$ . This apparently small difference is nevertheless of much relevance: in the proper  $Q_{S=1}(y)$  polynomial, the hopping  $|1/2, -1/2\rangle_{\mathbf{m}}|1, 1\rangle_{\mathbf{n}} \rightarrow |1, 1\rangle_{\mathbf{m}}|1/2, -1/2\rangle_{\mathbf{n}}$  has zero amplitude, compatible with Hamiltonian Eq. (1), where the spin projection at each site can only change in units of 1/2, after one  $e_g$  electron moves. However, if the hopping amplitudes signs are neglected, such unphysical processes become incorrectly

allowed. Such hidden sum rules of the Kondo-lattice model are also illustrated when the effective Hamiltonian acts over an arbitrary link state. The result is

$$H_{\text{eff}}|S, m\rangle_{\mathbf{m}}|S-1/2, m'\rangle_{\mathbf{n}} \\ = -t[A(S, m, m')|S-1/2, m+1/2\rangle_{\mathbf{m}}|S, m'-1/2\rangle_{\mathbf{n}} \\ + B(S, m, m')|S-1/2, m-1/2\rangle_{\mathbf{m}}|S, m'+1/2\rangle_{\mathbf{n}}],$$

where  $A(S, m, m') = \sqrt{(S-m'+1/2)(S-m)}/2S$  and  $B(S, m, m') = \sqrt{(S+m'+1/2)(S+m)}/2S$ , clarifying the hopping processes that are allowed.

For the particular case of  $S=2$ , which would be applicable to  $R_{1-x}X_x\text{MnO}_3$ , the polynomial becomes

$$Q_{S=2}(y) = -1 - \frac{5}{4}y + \frac{7}{4}y^2 + \frac{3}{2}y^3. \quad (8)$$

Thus, we propose Eqs. (6) and (8) as the effective Hamiltonian for Mn-oxides in the large  $J_H$  limit.<sup>13</sup> It is the generalization to Mn oxides of the  $t$ - $J$  model for Cu oxides. Ours is a fully quantum mechanical model for spin 2  $\text{Mn}^{3+}$  that takes into account the proper signs of the effective hopping amplitudes. Unlike the double-exchange model, there are no classical spins in our effective model. However, note that for a small exchange  $J$  among the spins (in our approach there is always an implicit Heisenberg coupling between ions) and a small hole density, model Eq. (8) favors a ferromagnetic ground state to improve the hole kinetic energy, as the double-exchange model does. Recent many-body numerical results applied to the case of  $S=1$  in one dimension<sup>11</sup> have indeed detected a robust ferromagnetic state at zero temperature for a wide range of densities.<sup>14</sup>

To gain further intuition about the relevance of the signs in the effective hopping Eq. (4), we studied the Kondo-like Hamiltonian Eq. (1) for the special case where at large Hund coupling the localized spins are classical. Note that it is not well justified to apply this limit to manganites, since the neglected spin flip processes have amplitude  $1/\sqrt{2S}$  [see Eq. (5)] which is not small for  $S=2$ . Nevertheless, to establish a connection with the double-exchange model it is necessary to work at large  $S$ . In this limit, it is convenient to rotate the  $e_g$  electrons such that their spin quantization axis is parallel to the core spins.<sup>9</sup> Since the Hund's coupling is large, in the rotated basis only the "spin-up" component of the hopping matters, and the nontrivial effects of the core spins appear in the modulation of the hopping. In this limit the Hamiltonian becomes

$$H = - \sum_{\langle \mathbf{l}\mathbf{m} \rangle} (t_{\mathbf{l}\mathbf{m}} d_{\mathbf{l}}^\dagger d_{\mathbf{m}} + \text{H.c.}), \quad (9)$$

where  $d_{\mathbf{n}} = \cos(\theta_{\mathbf{n}}/2)c_{\mathbf{n}\uparrow} + i\sin(\theta_{\mathbf{n}}/2)\exp(i\phi_{\mathbf{n}})c_{\mathbf{n}\downarrow}$  are rotated electron operators with spin up, and the hopping amplitude is a complex number given by

$$t_{\mathbf{l}\mathbf{m}} = \cos\left(\frac{\theta_{\mathbf{l}}}{2}\right)\cos\left(\frac{\theta_{\mathbf{m}}}{2}\right) + \sin\left(\frac{\theta_{\mathbf{l}}}{2}\right)\sin\left(\frac{\theta_{\mathbf{m}}}{2}\right)\exp[i(\phi_{\mathbf{m}} - \phi_{\mathbf{l}})]. \quad (10)$$

When electrons move with this nontrivial hopping they effectively collect a phase. Alternatively, the problem can be

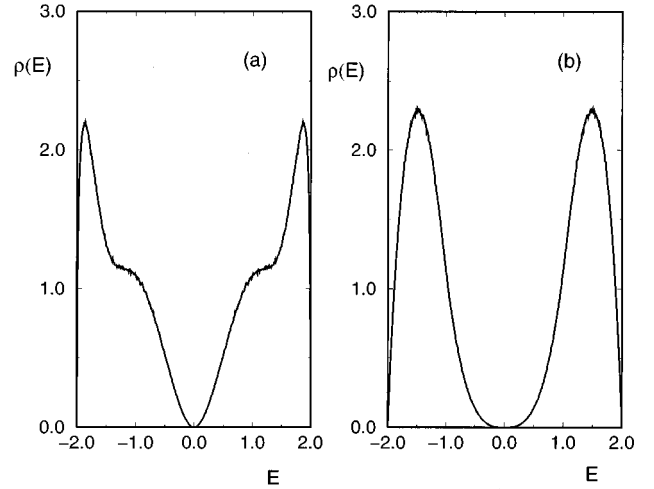


FIG. 1. Spectral density  $\rho(E)$  of nonvanishing energies vs energy  $E$  (in units of  $t$ ) in the large  $S$  limit of model Eq. (9) working on a  $2 \times 2$  plaquette with two electrons. The result is an average over two million core spin angle configurations: (a) using the proper hopping amplitude Eq. (10); (b) using  $|t_{\mathbf{l}\mathbf{m}}|$  (double exchange).

rephrased as that of electrons moving with hopping  $|t_{\mathbf{l}\mathbf{m}}|$  in the presence of a nonuniform gauge field  $e^{i\mathbf{A}_{\mathbf{l}\mathbf{m}}}$  which is the phase of the hopping.<sup>15</sup> This phase can have important interference consequences for closed loops. It is likely that the  $e_g$  electron mobility in Mn oxides will be reduced due to this quantum mechanical effect. Actually, the double-exchange model is recovered from Eqs. (9) and (10) only if the absolute value of  $t_{\mathbf{l}\mathbf{m}}$  is considered since the following identity holds:

$$|t_{\mathbf{l}\mathbf{m}}| = \sqrt{(1 + \cos(\theta_{\mathbf{l}})\cos(\theta_{\mathbf{m}}) + \sin(\theta_{\mathbf{l}})\sin(\theta_{\mathbf{m}})\cos(\phi_{\mathbf{m}} - \phi_{\mathbf{l}}))/2} \\ = \cos(\theta_{\mathbf{l}\mathbf{m}}/2),$$

where  $\theta_{\mathbf{l}\mathbf{m}}$  is the angle between the core spins at  $\mathbf{l}$  and  $\mathbf{m}$ .<sup>16</sup>

To illustrate the importance of keeping the complex nature of the hopping amplitude we have studied numerically Hamiltonian Eq. (9) with both  $t_{\mathbf{l}\mathbf{m}}$  and  $|t_{\mathbf{l}\mathbf{m}}|$  for the particular cases of 1 and 2 electrons moving on a  $2 \times 2$  plaquette (4 sites on a square). Here in principle we need eight angles to characterize a core spin configuration, but three of them correspond to a rigid rotation of the whole system. Then, to study this problem only five angles are needed. The four (six) eigenvalues of Eq. (9) corresponding to one (two) particles can be found exactly for an arbitrary set of angles, and we average over about two million randomly selected core spin configurations. Using this procedure we calculated the spectral density, i.e., the normalized probability distribution for the eigenvalues. The results are shown in Figs. 1(a) and 1(b). For the case where the proper hopping Eq. (10) is used, a large accumulation of weight appears at low energy [Fig. 1(a)] where the spectral density grows sublinearly. On the other hand, when only the absolute value of the hopping is used in Fig. 1(b), the spectral density grows only linearly. To the extent that the results for the square plaquette are qualitatively representative of the bulk limit and other dimensions, the low-energy accumulation of states could destabilize the ferromagnetic ground state at relatively low temperatures in model Eq. (9) with a complex hopping amplitude.<sup>17</sup> This is reasonable since the phase of the hop-

ping amplitude produces an effective random magnetic field, which could induce low-energy modes and even localization effects in the bulk<sup>18</sup> in the phase competing with ferromagnetism at  $T > T_c$ . Recent work in one-dimensional NiO models has indeed shown that the bandwidth of one hole at half filling is much reduced moving from a Cu background (spin 1/2) to a Ni background (spin 1).<sup>11</sup> In other words, while both model Eqs. (9) and (10) for classical core spins and model Eq. (8) for the  $S=2$  systems favor the presence of a ferromagnetic state in the ground state (zero temperature), they will likely differ with the double-exchange model in the value of  $T_c$ . Texture states of low energy may have such a large degeneracy that the ferromagnetic state could be rapidly destabilized with temperature.<sup>19</sup> Thus, contrary to Ref. 9 we believe that the Kondo-like model Eq. (1) may still describe basic aspects of the physics of the Mn oxides. This issue deserves further work.

Summarizing, we have derived a one band electronic model for the Mn oxides valid in the limit of a large Hund's

coupling. The model is the analog of the  $t$ - $J$  model used for Cu oxides and of a recently introduced model for NiO chains.<sup>11</sup> A generalization for arbitrary spin  $S$  is given. At large  $S$ , the electrons move effectively with a complex hopping amplitude. Our Hamiltonian differs in a fundamental way from the double-exchange model in that the electrons can now acquire nontrivial phases on closed loops, favoring interference, localization, and a small ferromagnetic  $T_c$ . We believe that future theoretical work for Mn oxides should use the proper complex hopping amplitude Eq. (9) rather than the double-exchange model, or, even better, use the finite  $S$  model Eqs. (6) and (8) proposed in this paper.

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<sup>12</sup>This sign is not contained in the Hamiltonian matrix (A6) in the Appendix of Ref. 4.

<sup>13</sup>The polynomial for spin 3/2 is  $Q_{S=3/2}(y) = -\frac{1}{2}$

+  $\frac{3}{4}y + \frac{3}{4}y^2$ . Expressions for  $S > 2$  can be easily obtained from the recursive formula Eq. (7).

<sup>14</sup>J. Riera and E. Dagotto (unpublished).

<sup>15</sup>In the context of the  $U=\infty$  Hubbard model in two dimensions, B. Douçot and R. Rammal, Phys. Rev. B **41**, 9617 (1990), have discussed effects somewhat similar to those found here but addressing the possible instability of the Nagaoka phase in one band models.

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<sup>17</sup>Note, however, that the spin waves are not effected by the Berry phase.

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<sup>19</sup>Recent neutron scattering data appear to support this scenario [J. Lynn *et al.* (unpublished).]