Bond Orders in a Frustrated Itinerant System on a Kagome Lattice

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Abstract. Extended double-exchange model on a Kagomé lattice is investigated numerically. We introduce a new Monte Carlo algorithm to perform finite-temperature calculation in the strong coupling limit. Carrier-induced hexamer formation, where electron hoppings are made along hexagonal bond clusters, is found at certain ranges of carrier densities. As a mechanism, we discuss the order-by-disorder phenomena that the macroscopic degeneracy of the geometrically frustrated spin system is lifted by the kinetic energy of itinerant electrons.

1. Introduction
Systems with macroscopic degeneracies are expected to exhibit various thermodynamical anomalies through residual perturbative interactions, which may lead to exotic phenomena. One of such example is the extended double-exchange model defined on a pyrochlore lattice [1, 2, 3]. The model has been introduced to investigate ferromagnetic to spin-glass transitions and metal-insulator transitions in Mo pyrochlore oxides $R_2\text{Mo}_2\text{O}_7$ [4, 5], where such phase transitions are driven by interplay between magnetism and transports in these strongly correlated electron systems.

More precisely, the model is given by

$$\mathcal{H} = \mathcal{H}_{\text{AF}} + \mathcal{H}_{\text{DE}},$$

where the first term gives the antiferromagnetic interaction between localized spins, while the second term gives the ferromagnetic double-exchange interaction [6]. In $\mathcal{H}_{\text{DE}}$, itinerant electrons are strongly coupled to localized spins. Thus the system is essentially in the strong coupling regime, and the magnetism and transports colossally affects each other.

Although many interesting properties are observed through numerical calculations, the system size is limited by numerical complexities of the system. In this paper, we introduce a two-dimensional analogue of the model to simplify the situation. Furthermore, when we take both strong coupling and Ising limits, it is shown that the numerical complexities is much reduced by introducing a new algorithm for Monte Carlo calculations. This enables us to perform finite temperature calculations for larger-sized systems in detail. Through such calculations, we show some thermodynamical properties of the model, including the carrier-induced bond orders.
2. Model

We introduce the extended double-exchange model on a Kagomé lattice in Eq. (1), where frustrated spin system are interacting with itinerant electrons, in detail. In the present study, the first term represents an antiferromagnetic Ising model defined on a Kagomé lattice,

\[ H_{AF} = J \sum_{<i,j>} S_i S_j, \]

where \( J > 0 \) and \( S_i = \pm 1 \). Summation is taken over nearest neighbor bonds. This model is one of the most canonical geometrically frustrated systems, and its ground state has macroscopic degeneracies. The ground state has no magnetic orders, but satisfies the so-called ice-rule. The ice-rule on a Kagomé lattice is that in all unit cell triangles, three spins take the configuration of either “2 up 1 down” or “1 up 2 down”.

The second term of the Hamiltonian (1) gives a double-exchange model [6] where conduction electrons interact with localized spin through Hund’s rule coupling as

\[ \text{HDE} = -t \sum_{<i,j>,\sigma} \left( c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.} \right) - J_H \sum_i \sigma_i^z S_i - \mu \sum_{i,\sigma} c_{i,\sigma}^\dagger c_{i,\sigma}. \]

Here \( c_{i,\sigma}^\dagger \) (\( c_{j,\sigma} \)) represents creation (annihilation) operator for conduction electrons, while \( \sigma_i^z = c_{i,\uparrow}^\dagger c_{i,\downarrow} - c_{i,\downarrow}^\dagger c_{i,\uparrow} \) is the z-component of the spin of the conduction electron at \( i \)-th site. Electron hopping integrals are expressed by \( t \), while \( J_H \) is the Hund’s coupling between local spins and conduction electrons. Chemical potential is given by \( \mu \). Note that, since the localized spins are Ising spins, we have only z-component of the Hund’s rule coupling.

We now restrict ourselves to the case of strong Hund’s rule coupling limit \( J_H/t \to \infty \). Then, we may energetically project out the states where directions of \( S_i \) and \( \sigma_i^z \) are antiparallel to each other [7]. Therefore, in the present case of Ising spins, electron hoppings are allowed only within ferromagnetic clusters, i.e., sites connected by bonds with ferromagnetic spin configurations. This is sometimes referred to as the “go/no go” rule. In order to gain of kinetic energies, ferromagnetic configuration of local spins are favored.

The effective Hamiltonian can be described as

\[ \mathcal{H}'_{DE} = \sum_{\text{Cluster}} \left\{ -t \sum_{<i_n,j_n>} \left( \tilde{c}_{i_n}^\dagger \tilde{c}_{j_n} + \text{h.c.} \right) \right\} - \mu \sum_i \tilde{c}_i^\dagger \tilde{c}_i. \]

Here, the first summation is taken with respect to ferromagnetic clusters. The second summation is taken over neighboring sites on \( n \)-th ferromagnetic clusters. Here, \( \tilde{c}_{i_n}^\dagger \) (\( \tilde{c}_{j_n} \)) represents creation (annihilation) operator for electrons with spins parallel to local \( S_i \). Although the Hamiltonian (4) may effectively be regarded as a spinless model, local spin quantization axes depend on \( S_i \) and are different from site to site.

In this model (1), the double-exchange ferromagnetic interactions compete with the antiferromagnetic exchange interactions \( J \). As \( J \) is increased, ferromagnetic metal phase become unstable. However, due to frustrated behavior of the system, the transition toward antiferromagnetism is also suppressed. Then, it is expected that various instabilities in spin as well as charge sectors may occur, as in the case of the pyrochlore systems where magnetic phase competitions accompany metal-insulator as well as metal-metal transitions [3].

Let us also note that the range of ferromagnetic interactions are not limited to nearest neighbors, due to the extended nature of the wave functions for itinerant electrons which can gain kinetic energy within the ferromagnetic clusters. Then, when the long-range part of the double-exchange interactions are introduce perturbatively to the frustrated antiferromagnetic systems with nearest neighbor interactions, they may act as residual interactions to lift macroscopic degeneracies and stabilize exotic phases.
3. New Monte Carlo Algorithm

In the Monte Carlo calculation of the model, the Boltzmann weight of each spin configuration is calculated by a sum of the kinetic energy part and the Ising spin exchange part. While the latter is easily obtained, the calculation of the former part needs quantum mechanical evaluation of the electronic Hamiltonian. In most cases, matrix diagonalization is performed for each Monte Carlo updates. The numerical complexity increases as $O(N^4)$, where $N$ is the system size. Moreover, in frustrated systems in general, typical temperature scale to observe interesting phenomena is much smaller and the typical relaxation time scale for thermal equilibrium is longer, compared to systems without frustrations. These give us further difficulties for detailed investigation of the system.

Here, in some limited parameter spaces, we show that the numerical complexity is much reduced by introducing a new algorithm. We restrict ourselves to the strong exchange coupling region $J \gg t$. At low temperatures, we may only consider the macroscopically degenerate ground state of $H_{AF}$, which have spin configurations obeying the ice-rule. In this case, double-exchange hopping is allowed only on one out of three bonds on a unit triangle which has a ferromagnetic spin configuration, since “2 up 1 down” or “1 up 2 down” rule is satisfied in the ground state (See Fig. 1). Between neighboring unit triangles, such bonds may be connected to form longer chain of bonds. However, they do not branch off into multiple chains, since multiple ferromagnetic bonds on a unit triangle are prohibited by the ice-rule. Then, such ferromagnetic bonds form simple one-dimensional clusters of spins; clusters are classified as “open chains” when they have open ends, while the closed ones are referred to as “rings”. Electronic Hamiltonian can analytically be solved for each finite-sized chain/ring; electronic eigenstates depends only on the size and the boundary of the cluster but not on its shape. Total electronic energies can be calculated by counting the length of each open chains/rings, without matrix diagonalization. Labeling of the connected clusters are made using the Hoshen-Kopelman algorithm for percolation systems [8].

As a conclusion, Boltzmann weights for a given spin configuration can easily be calculated by this method, if the system is in the strongly correlated limit $(J, J_H \gg t, T)$ where antiparallel-spin electrons are completely projected out and the configurations of local spins are within the manifold of macroscopically degenerate ground state. The numerical complexity scales as $O(N)$ to $O(N\sqrt{N})$, depending on the average length of the one-dimensional clusters. This allows us to perform calculations on larger-sized systems. In typical cases, maximum of the system size using the matrix diagonalization method is limited to $N \sim 10^2$ sites, while the new algorithm easily allows us to calculate systems with $N \sim 10^3$ sites.

Figure 1. Ferromagnetic bonds at the ground state of the antiferromagnetic Ising model on a Kagomé lattice. Filled (open) circles represent sites with up (down) spins. Thick (red) lines express bonds with ferromagnetic spin configurations. For the case of the bond $[a]$, both ends of are connected to other bonds, while for bond $[b]$ one of the end is terminated. Note that electrons are allowed to hop only along the thick bonds.
4. Results
Here we show our results. We have performed Monte Carlo calculation using the replica exchange method [9], typically in the range $T/t = 0.010, 0.015, 0.020, 0.025$ and $0.030$. We have run 100,000 steps of Monte Carlo measurements after 100,000 steps for thermalizations. In this paper, we focus on the low carrier concentration region $\mu/t = -1.85$. In this region, the carrier concentration is stabilized at $\rho \sim 0.1$. In Fig. 2, we show the spin correlation function at $T/t = 0.01$. We see typical peak features in our model. Since the largest part of the Hamiltonian, $\mathcal{H}_{AF}$, should show spin liquid state without sharp peaks in spin correlations, these features are due to the gain of kinetic energies for itinerant electrons, creating possible order-by-disorder phenomena.

![Figure 2. Spin correlation function at $T/t = 0.01$ and $\mu/t = -1.85$.](image)

Let us discuss what types of ordering may stabilize the system. Since open chains have larger kinetic energies than rings of identical sizes, we should consider some ways to tile the lattice with rings of ferromagnetic clusters in periodic manners under the constraint of the ice-rule. Simplest candidates are (a) stripe order and (b) hexamer order, as depicted in Fig. 3. In the former case, one-dimensional stripes extend toward the boundaries of the system and form a semi-macroscopic sized rings. Contrarily, the latter case has rings with the minimum size allowed in this system (length=6). (Note that trimers on unit triangles are prohibited by the ice-rule.) Through comparison with the numerical data, the position and the structure factor of the spin correlation function is consistent with the assumption of the hexamer formation.

![Figure 3. Possible bond orders without open boundary clusters under the restriction of ice-rule. These patterns are repeated periodically throughout the lattice. Thick bonds represent ferromagnetic bonds which are electron hopping paths. (a) Stripe order. (b) Hexamer order.](image)
The mechanism for hexamer order can be understood as follows. Let us first consider the density of states (DOS) of the stripe-ordered state in the thermodynamic limit. The order is constructed by one-dimensional hopping paths with parallel spins, and isolated sites with antiparallel spins. Then, they make a one-dimensional electronic DOS at $|\varepsilon| \leq 2t$ by stripes, plus a delta-functional DOS at the band center due to localized states, as shown in Fig. 4. In the low carrier concentration region, electrons fill the bottom of the DOS which has a square-root singularity $D(\varepsilon) \sim 1/\sqrt{4t^2 - \varepsilon^2}$.

On the other hand, in a thermodynamic limit of a ring-multimer order at the ground state, each ring consists of a finite-sized one-dimensional clusters with a periodic boundary condition so that DOS is discretized. Each multimer has the minimum energy eigenvalue of $\varepsilon = -2t$ irrespective of its size. Then, in the low carrier concentration region at $\mu \sim -2t$, the bottom part of the DOS, $D(\varepsilon) \sim \delta(\varepsilon + 2t)$, is occupied. Therefore, at low but finite carrier densities, electronic energies are pinned at $\varepsilon = -2t$ until the lowest level is completely occupied, whereas in the stripe ordered state the energies gradually increase as carrier is doped. Thus, multimer orders are more stabilized due to the gain of electronic energies in these regions, compared to the stripe orders.

Among possible ring-multimer orders within the ice-rule, hexamers are the smallest in the size so that they can tile the entire Kagome-lattice with a maximum number of rings. Then the number of the bottom energy levels with $\varepsilon = -2t$ is maximum. (Equivalently, the prefactor of the delta-functional DOS is maximum). Thus hexamers are mostly favored in the low carrier concentration regions, due to the energetics of the system. The DOS is also show in Fig. 4.

In the hexamer ordered state, prefactors of the delta-functional DOS are given by $N/9$ and $2N/9$ for $\varepsilon = \pm 2t$ and $\pm t$, respectively, since the number of hexamers $N_h$ is given by $N_h = N/9$. The delta-functional DOS at $\varepsilon = 0$ has the prefactor $N/3$ which the number of isolating sites. Note that a complete occupation of the lowest energy levels of hexamers occurs at $\rho = 1/9$. Our numerical data for carrier concentration are also consistent with the hexamer formation.

![Figure 4. Electronic density of states for the stripe order and the hexamer order.](image)

5. Summary

We have performed Monte-Carlo simulation for extended double-exchange model on a frustrated Kagomé lattice. A new algorithm has been introduced. In the strong coupling region, we have found the carrier induced bond orders. Thus, formation of the one-dimensional clusters not
merely provides us a method for calculation but is an essential nature for this spin-charge coupled model. Such formation of bond orders may be regarded as the order by disorder process to lift the macroscopic degeneracies. In the present investigations, we have showed the presence of characteristic hexamer ordered state in the strong coupling and low carrier concentration region at low temperatures, but alternative bond ordering may appear in different parameter regions. Details will be reported elsewhere.

It is worthwhile to mention that the shape and the size of the rings in this bond ordering are determined by the geometry of the lattice. This is in sharp contrast with the weak-coupling electron systems where spin/bond orders are determined by the Fermiology, i.e., size and shape of the Fermi surfaces. This may be considered as a sign of the strongly-correlatedness of the system.

Let us finally note that such cluster ordering is not a unique feature in this model but can be seen ubiquitously as one of the mechanisms to release the residual entropies in low temperatures. Experimentally, various transition metal oxides with frustrated interaction exhibit spontaneous cluster formations, including trimers in LiVO₂ [10], hexamers in ZnCr₂O₄ [11], heptamers in AlV₃O₄ [12, 13], and octamers in CuIr₂S₄ [14, 15]. Cluster formations are also in geometrically frustrated double exchange systems defined on a Kagomé lattice with uniaxial anisotropies [16]. In this case, formation of 12-site clusters or dodecamers has been found at low temperatures. The mechanism of such dodecamer formation is similar to the present case. Namely, the macroscopic degeneracy of the frustrated system is lifted by residual double-exchange interactions. However, the way the residual entropy is released is different. We expect that there should be many other candidates which exhibit more exotic orderings and transport anomalies accompanied by them.

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