Spin-fluctuations in the quarter-filled Hubbard ring: significance to LiV$_2$O$_4$

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Using the quantum Monte Carlo method, we investigate the spin dynamics of itinerant electrons in the one-dimensional Hubbard system. Based on the model calculation, we have studied the spin-fluctuations in the quarter-filled metallic Hubbard ring, which is aimed at the vanadium ring or chain defined along corner-sharing tetrahedra of LiV$_2$O$_4$, and found the dramatic changes of magnetic responses and spin-fluctuation characteristics with the temperature. Such results can explain the central findings in the recent neutron scattering experiment for LiV$_2$O$_4$.

LiV$_2$O$_4$ is a transition metal oxide with a cubic spinel (or pyrochlore) structure showing many essential features of the heavy-fermion system like Ce compounds. Its specific heat coefficient is the largest one observed among other 3$d$ metallic systems, $\gamma \sim 420$ mJ/mol K$^{-2}$. It has become an important issue to clarify the physical origin of a high density of low-energy fermionic excitations without localized f-levels. There's also a great interest in the unusual magnetic properties of LiV$_2$O$_4$ due to the itinerant frustrated nature. Another metallic system, Y(Sc)Mn$_2$, has also been focused on as a frustrated spin liquid belonging to a similar class to LiV$_2$O$_4$. Y(Sc)Mn$_2$ exhibits many similarities; it is the geometrically frustrated magnet with no long range order, nearly antiferromagnetic itinerant system, and most interestingly the heavy fermion system.

Three classes of theoretical mechanisms are most frequently referred to understand the heavy-fermion properties in LiV$_2$O$_4$. One is the spin-fluctuations in the three-dimensional frustrated lattice as in the study of Y(Sc)Mn$_2$. Due to the magnetic frustrations, the spin cannot order down to low temperatures, resulting in the large fermionic entropy. The other is the well-known Kondo effect. From the band structure calculations, it is shown that 3$d$ $t_{2g}$ bands of V are crossing the Fermi level and, by the trigonal crystal field, split to a bit narrow-band half-filled $A_{1g}$ singlet and a bit wide-band quarter-filled $E_g$ doublet. These results lead to the mapping of the electronic structure into the Kondo lattice model. The third candidate is the mechanism based on the one-dimensional electronic structure, where it is expected that the correlation effect is much enhanced, giving the large specific-heat coefficient. Fulde et al. have suggested that the large $\gamma$ coefficient results from excitations of Heisenberg spin 1/2 chains and rings, which are by the direct consequence of the frustration of corner-sharing tetrahedra of the vanadium lattice. Their idea on the formation of spin chain or ring in LiV$_2$O$_4$ dates back to the study on Yb$_3$As$_3$, where, due to a charge ordering of Yb ions, the electronic structure could be interpreted as well-decoupled (at least magnetically) one-dimensional chains.

In the last decades, the spin-fluctuation has been found to play fundamental roles in many of strongly correlated electron systems, especially in the high $T_c$ superconductors. The combined system of the strong electron correlation and the spin itineracy, where there is no magnetic long range order, leads to intriguing spin-fluctuations. Recent two inelastic neutron scattering experiments have delivered seminal informations on the spin dynamics in LiV$_2$O$_4$; (i) they have reported the dramatic crossover from a ferromagnetic (FM) to an antiferromagnetic (AFM) spin-fluctuation with the temperature $T$ lowered. Especially, Lee et al. have explicitly pointed out the AFM spin-fluctuation would be centered around $Q_s = 0.64A^{-1} = 0.59\pi/a$ ($a$ is the V-V distance), (ii) they have found the residual relaxation rate for $T \rightarrow 0$ and its monotonous increase at $Q_s$ with raising temperature, but the increasing behavior was reported differently from each other, i.e. Krimmel et al. have reported the square-root temperature behavior, whereas Lee et al. the linear behavior, and (iii) Krimmel et al. have also provided the momentum-transfer-dependence of the relaxation rate to elucidate the change of spin-fluctuation characteristics.

In this paper, we bring focus on the spin dynamics of LiV$_2$O$_4$ grounded on the one-dimensional mechanism. It is actually clear that the Heisenberg spin 1/2 chain by itself cannot explain the observed experiments because the low energy excitation of the system should be well-dispersive gapless magnon. Instead, the quarter-filled Hubbard ring is taken as the starting point, which gives the itinerancy to Fulde’s spins, toward an understanding of characteristic spin-fluctuations observed in LiV$_2$O$_4$. Fujimoto has studied the network of quarter-filled Hubbard chains accounting for the hybridization between chains along the similar line to the Fulde’s spin chain or ring. In the study, he has obtained quite a comparable size of $\gamma$ to the experimental value and introduced another energy scale $T^*$ giving the dimensional crossover; below $T^*$, three-dimensional Fermi-liquid state with the heavy mass is realized, but above $T^*$, one-dimensional characters dominate. He has also pointed out that Urano et al.’s transport data can be consistent with this picture and a characteristic low temperature scale ($\sim 20$ K) observed would correspond to $T^*$. In the present investigation, therefore, we do not consider the very low temperature region of $T \ll T^*$.

In an actual situation of LiV$_2$O$_4$, the one-dimensional ring (chain) is constructed on the corner-sharing tetrahedra of the vanadium network, which has been visualized in Refs. 8, 13. The Hubbard model is defined on the
one-dimensional lattice;

\[ \mathcal{H} = -t \sum_i \sum_{\delta = \pm 1} \sum_\sigma (c_{i\sigma}^\dagger c_{i+\delta\sigma} + \text{H.c.}) - \mu \sum_i (n_{i\uparrow} + n_{i\downarrow}) + U \sum_i n_{i\uparrow} n_{i\downarrow}, \]  

(1)

where \( c_{i\sigma}^\dagger \) and \( c_{i\sigma} \) are the creation and annihilation operators for electrons with spin \( \sigma \) at lattice \( i \) and \( n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \).

\( t \) is the hopping parameter, \( \mu \) the chemical potential, and \( U \) the on-site Coulomb correlation. The first and the last sites are connected by imposing the periodic boundary condition, i.e. it gives the "ring" geometry.

Among many versions of quantum Monte Carlo (QMC) methods, it is the path integral theory of QMC that is better proper for a description of the itinerant electron systems \([1, 13, 14]\). The path integral QMC for the correlated electron system cooperates the Hubbard-Stratonovich transformation and integrates out the electron field. Most of all the QMC methods are based on the Trotter decomposition \( e^{-\beta (\mathcal{H} + V)} \approx (e^{-\Delta \tau K} e^{-\Delta \tau V})^L \) with \( \beta = 1/T = \Delta \tau L \) where \( K \) should be the one-electron terms and \( V \) the electron-electron correlation term. The collective spin excitations probed by the inelastic neutron scattering are described in the time-dependent spin-spin correlation function \( S(q, \tau) \)

\[ S(q, \tau) = \frac{1}{N} \sum_{ij} e^{i q (R_i - R_j)} \langle [n_{i\uparrow}(\tau) - n_{i\downarrow}(\tau)][n_{j\uparrow} - n_{j\downarrow}] \rangle, \]

(2)

which is corresponding to the thermodynamic two-particle Green’s function in the imaginary time. Through the analytic continuation from \( S(q, \tau) \) under a condition \( S(q, \omega) \geq 0 \), we obtain the experimentally observable spectral function \( S(q, \omega) \) satisfying

\[ S(q, \tau) = -\int d\omega \frac{e^{-\omega \tau}}{2\pi i} e^{-\omega q} S(q, \omega). \]

(3)

For a numerical simulation in the study, the 24-site Hubbard ring with \( U/t = 4 \) is considered. We follow the basic approach for the grand canonical ensemble. For the quarter-filled occupation, the ensembles such that it can give \( 1/N \sum (n_{i\uparrow} + n_{i\downarrow}) = 0.5 \) should be sampled by adjusting the value of \( \mu \). The Trotter decomposition is done such that \( \Delta \tau = 0.1 \) (only for a case of \( 1/T = 1.5 \), \( \Delta \tau = 0.05 \)). We have taken the averages of the dynamical correlation functions over \( 10^4 \) updates of all the Hubbard-Stratonovich bosons on the lattice. Further, to keep the numerical stability, we have used the matrix factorization technique \([13]\). All the energy quantities are measured in a unit of \( t \) and all the momentum quantities in \( \pi/a \).

FIG. 1: (a)-(e) Dynamical spin-spin correlation function in the quarter-filled Hubbard ring as a function of \( q \) in the quasi-elastic mode \((\omega = 0)\) at several temperatures, i.e. \( S(q, \omega = 0) \). (f) Ratio of \( S(q = 1/2, \omega = 0) \) and \( S(q = 0, \omega = 0) \).

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It is shown in the figure that $\chi_q$ for $q = 1/2$ nicely follows the AFM Curie-Weiss susceptibility, $\propto 1/(T + \theta)$. Such Curie-Weiss behavior has been already observed in the experiment\cite{14}, where $\theta$ for the best fitting was estimated as 7.5 K. Our calculation gives the similar value, $\theta \sim 0.11 \sim 13.2$ K. Let us note it means that the quarter-filled one-dimensional Hubbard model could allow a formation of magnetic moments like Kondo lattice model in the high temperature\cite{20}, where the localized level manifests the Curie-Weiss susceptibility. Unstable magnetic moments produce the AFM short-range order centered around $\pi/(2a)$ (i.e. $q = 1/2$), where $2a$ is the distance between neighboring moments. It is consistent with the temperature behavior of the magnetic relaxation rate $\Gamma_q$ at $q = 1/2$ in Fig.2. Fig.2 also shows the crossover of magnetic characters from FM to AFM around $T \sim 0.25 \sim 30$ K, consistent with Fig.1(f).

Another important quantity is the magnetic relaxation rate $\Gamma_q$ usually defined by the simple ansatz for the dynamic susceptibility

$$S(q, \omega) = \frac{1}{1 - e^{-\omega/T}} \omega \Gamma_q \chi_q \omega^2 + \Gamma_q^2.$$

In the study, $\Gamma_q$ is evaluated by taking $\omega \rightarrow 0$ in Eq.(5),

$$S(q, 0) = \frac{T \chi_q}{\Gamma_q},$$

where $S(q, 0)$ and $\chi_q$ are already given in Figs.3 and 2, respectively. But it should be noted that, because the unit of $S(q, 0)$ is arbitrary, $\Gamma_q$ would be obtained only up to a constant. That is, we note the true relaxation rate should be $\eta \Gamma_q$ ($\eta$ is a nonzero constant). The results of $\Gamma_q$ are provided in Fig.3. The upper panel of Fig.3 shows that the spin magnetic relaxation rate $\Gamma_q$ at $q = 1/2$ increases linearly with temperature for a rather wide temperature range to $\sim 0.7 \sim 80$ K. The linear increasing behavior for such a wide $T$ range (to $\sim 80$ K) has been ascertained in the experiment by Lee et al.\cite{10}, where its increasing rate is found 0.46. Linear $T$ behavior is actually unusual in the $f$-electron heavy fermion system. It is however a bit common in frustrated metal oxides, normally related with unstable local moments. In the Kondo system, one most usually has $\Gamma_q \sim \Gamma_q^0 + bT^{1/2}$, where $\Gamma_q^0 \sim T_K$ (Kondo temperature)\cite{20}. Earlier, through mapping into the Kondo model, Anisimov et al.\cite{6} have estimated $T_K \sim 550$ K for the single-site case, but argued that another characteristic energy scale $T_{coh}$ ($\sim 25-40$ K, comparable to $\Gamma_q^0$) would replace $T_K$ in the dense Kondo lattice. The increasing rate of the present result shown in Fig.3 is estimated as 0.32 and $\Gamma_q^0$ at $T = 0$ is obtained about 0.1 meV. Comparing the increasing rates, we find an unknown constant $\eta$ should be about 1.44 and the residual relaxation rate $\Gamma_q^0$ be 0.14 meV. This value is smaller than experimental findings, i.e. Krimmel et al.\cite{6} have reported 0.5 meV and Lee et al.\cite{16} 1.4 meV. The lower panel of Fig.3 gives the $q$ dependence of $\Gamma_q$, whose dependences also agree with an observation of the experiment. For $1/T = 1.5$ (high temperature), $\Gamma_q$ shows a linear $q$ dependence, which is actually expected in the spin-fluctuation theories of weak FM metals\cite{22}. Therefore, the behavior of linear $q$ dependence is consistent with our argument that the system should be a metal with weak FM spin-fluctuations at high temperatures ($\sim 0.25$), being associated with Figs.3 and 2. On the other hand, $\Gamma_q$ at the low temperature ($1/T = 10$) is almost constant for small $q$’s ($q \leq 1/2$), but rapidly increases for high $q$’s ($q > 1/2$). The constant $\Gamma_q$ with $q$ at low $T$ (not anticipated by the simple Fermi-liquid theory) was found in the experiment, but a rapid increase for high $q$’s was not, which instead may be attributed to an-
other subtle feature of one-dimensional Hubbard model. Recently, it has been found that the nonlinear coupling between spin and charge in the one-dimensional Hubbard model would lead to coupled collective excitations other than spin-fluctuations (or magnons) in \( S(q,\omega) \) especially for high \( q's \). Those may serve as additional decaying channels for spin fluctuations. It is noted that such enhanced \( \Gamma_q \) is directly connected with the diminution of \( S(q,0) \) at low \( T \) for \( q > 1/2 \) in Fig.1.

In summary, we have discussed the recent inelastic neutron scattering experiments for LiV\(_2\)O\(_4\) based on the QMC study of spin-fluctuations in the quarter-filled Hubbard ring. In the study, neutron scattering cross sections, static spin susceptibilities, and spin relaxation rates have been evaluated with temperatures and momentum transfers. They are found quite consistent with the experiment qualitatively, or semi-quantitatively. Particularly, it is appealing that the AFM short-range correlation develops due to a formation of unstable magnetic moments as \( T \) decreases in the quarter-filled Hubbard ring, which explains the AFM spin-fluctuation around \( Q_c = 0.59 \) observed in LiV\(_2\)O\(_4\). Our finding that a single quarter-filled Hubbard ring can explain the neutron scattering experiment could be consistent with a case of decoupled chains in Yb\(_4\)As\(_3\) unless we think of the very low temperature regime. However, it is a difference that the one-dimensional electronic structure is expected from the geometrical frustration in LiV\(_2\)O\(_4\). We would like to remark that at least a few experimental findings cannot be explained by the Kondo lattice model, but by the one-dimensional quarter-filled metallic model; (i) features of nearly-FM metal at high temperatures, (ii) the linear \( T \) dependence of \( \Gamma_q \) for a wide \( T \) range, and (iii) the constant \( \Gamma_q \) with \( q \) at low temperatures (actually decreasing behaviors in CeCu\(_6\)\(_{2+}\)). Further, the recent nuclear magnetic resonance (NMR) study for LiV\(_2\)O\(_4\) under high pressure has reported an opposite behavior of \( T_1 \) (spin-lattice relaxation time) to that of Ce compounds. It is also worth stressing that magnetic responses (such as \( T \) dependence of \( \chi \)) of LiV\(_2\)O\(_4\) differ qualitatively from Y(Sc)Mn\(_2\). Therefore, the present results can be one of evidences along with other studies that LiV\(_2\)O\(_4\) comprises one-dimensional chains or rings and behaves like the one-dimensional system. Finally, it should be noted that the conclusion casts another important problem to us. It is well known that, in one-dimensional metallic system, some extreme realization of correlation effects like the spin-charge separation occurs, which has been actually observed in SrCuO\(_3\) by the photoemission spectroscopy. Thus it must be fascinating to search for the spin-charge separation in LiV\(_2\)O\(_4\) by the photoemission spectroscopy.

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