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2004 J. Phys.: Condens. Matter 16 S621

(http://iopscience.iop.org/0953-8984/16/11/008)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S621–S627 PII: S0953-8984(04)74127-2

Electronic states and magnetic excitations in LiV_2O_4: exact diagonalization study

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Received 7 January 2004
Published 4 March 2004
Online at stacks.iop.org/JPhysCM/16/S621 (DOI: 10.1088/0953-8984/16/11/008)

Abstract

Motivated by recent inelastic neutron scattering experiments we examine the magnetic properties of LiV_2O_4. We consider a model which describes the half-filled localized A_{1g} spins interacting via frustrated antiferromagnetic Heisenberg exchange and coupled by local Hund's interactions with the 1/8-filled itinerant E_g band and study it within an exact diagonalization scheme. In the present study we limited the analysis to the case of the cluster of two isolated tetrahedrons. We found that both the ground state structure and low-lying excitations depend strongly on the value of Hund's coupling, which favours the triplet states. With increasing temperature the triplet states become more and more populated, which results in the formation of non-zero residual magnetic moment. We present the temperature dependence of the calculated magnetic moment and of the spin–spin correlation functions at different values of Hund's coupling and compare them with the experimental results.

1. Introduction

In recent years, there has been a great deal of interest in the study of the origin of the heavy fermion (HF) behaviour observed in the paramagnetic transition-metal oxide LiV_2O_4. This compound has a spinel structure and its pyrochlore lattice consists of corner-shared tetrahedrons of $V^{3.5+}$ ions located in a slightly distorted oxygen octahedron. It is the first metal showing heavy fermion behaviour without any f orbitals [1]. The electronic specific heat coefficient $\gamma = C_e/T = 0.42\ \mathrm{J\ mol^{-1}\ K^{-2}}$ at $T = 1.0$ K is the highest value measured for 3d transition-metal oxides.

In addition to having quasi-particles with an unusually heavy effective mass, LiV_2O_4 has some peculiar magnetic properties. The magnetic susceptibility and inelastic neutron

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scattering measurements indicate a spin-liquid behaviour over a large range of intermediate temperatures [2, 3]. The absence of magnetic order indicates that geometrical frustration, due to the pyrochlore structure, is relevant in this system[6]. On the other hand, recent neutron scattering experiments [4] reveal that, in addition to antiferromagnetic correlations, ferromagnetic-like correlations on V sites appear over some temperature range. These observations are inconsistent with the 'classical' spin-liquid picture and demonstrate that the itinerant contribution of strongly correlated electrons, which could lead to the effective ferromagnetic exchange interaction between localized spins, is also important.

There were some suggestions [9] to explain HF behaviour in LiV_2O_4 using an analogy with 4f systems where these effects are attributed to the hybridization of localized 4f levels and itinerant spd bands. This analogy has been based on the fact that, according to band structure calculations [8, 5], the trigonal distortion splits t_{2g} orbitals into singlet A_{1g} and doublet E_g states, and the centre of the A_{1g} band lies lower than that of the E_g band. Therefore, one can make a plausible assumption and treat the A_{1g} level as being occupied by a localized electron, while also considering the E_g doublet as a quarter-filled conducting band [5].

In this paper we study the magnetic properties of LiV_2O_4 within the exact diagonalization analysis of a small cluster. The model that we consider includes both a purely Heisenberg-like contribution from the super-exchange interaction among localized spins and an effective ferromagnetic double-exchange contribution driven by the itinerant electronic excitations.

In order to capture some charge fluctuation of the system, we solve the model exactly for the cluster consisting of two disconnected tetrahedrons with either 5 and 7 electrons, or only with 6 electrons, projecting out higher energy states with 4 and 8 electrons.

2. The model

To consider some charge fluctuations, we study a cluster of two isolated tetrahedrons, i.e. we do not take into account either the super-exchange interaction between localized spins of different tetrahedrons or the hopping of electrons between them. For this cluster, we can write the total Hamiltonian as $H = H_1 + H_2$, where $H_{1(2)}$ is defined on a single tetrahedron:

$$H_a = \sum_{ij,\alpha\beta\sigma} t_{ij}^{\alpha\beta} [c_{i\sigma\alpha}^{a\dagger} c_{j\sigma\beta}^{a} + \text{h.c.}] - J_{\text{H}} \sum_i \mathbf{S}_i^a \sigma_i^a + J \sum_{i \neq j} \mathbf{S}_i^a \mathbf{S}_j^a. \tag{1}$$

Here $a = 1, 2$ is the tetrahedron's index, $\mathbf{S}_i^a$ are $\frac{1}{2}$-spins representing the localized A_{1g} electrons and $c_{i\sigma\alpha}^{a\dagger}$ ($c_{j\sigma\beta}^{a}$) is the creation (annihilation) operator of an itinerant electron with spin $\sigma = \uparrow, \downarrow$ and orbital $\alpha = 1, 2$, corresponding to the E_g-doublet.

The first term in the Hamiltonian equation (1) describes the electron hopping between the nearest-neighbour V ions, $t_{ij}^{\alpha\beta}$ being the transfer amplitude. The second term concerns the Hund coupling J_{H} between the localized spins $\mathbf{S}_i$ and the local spin density σ_i of the itinerant E_g electrons. Finally, the last term describes the nearest-neighbour antiferromagnetic super-exchange interaction J between localized spins. Here we consider infinite on-site Coulomb repulsion between itinerant electrons and project out states with double occupancy.

Considering only direct overlap between 3d wavefunctions [$(\text{dd}\sigma) = -0.281$ eV, $(\text{dd}\pi) = 0.0076$ eV] [6], transfer matrix elements $t_{ij}^{\alpha\beta}$ can be easily calculated using table 1 of the paper by Slater and Koster [7].

In further analysis, we consider the value of the Heisenberg exchange coupling $J = 10$ meV which is in agreement with the estimates given in the literature [10, 12]. Hund's

[6] The theoretical study of the role of the geometrical frustration in LiV_2O_4 has been performed by many authors (see, for example, [10–12]).

coupling J_H is known to be little screened in solids and can be simply related to its atomic value. The estimates reported in the literature suggest that $J_H = 0.68$–1.0 eV [13, 14, 5, 16]. We use in our study the value $J_H = 0.8$ eV obtained by LDA + U *ab initio* calculations [5]. However, we also consider the variation of J_H over a wider range.

2.1. Hilbert space sectors

To define the Hilbert space, we choose a basis in which each state $|n\rangle$ is a product:

$$|n\rangle = |N_2, \mathcal{S}_2, \alpha_2\rangle_2 \otimes |N_1, \mathcal{S}_1, \alpha_1\rangle_1, \tag{2}$$

where the state $|\cdots\rangle_a$ characterizes the tetrahedron $a = 1, 2$. The index N_a is the number of electrons (localized plus itinerant) for the tetrahedron a, with an average charge of 6 electrons per tetrahedron $N_1 + N_2 = 12$. For a given tetrahedron, the spin state $\mathcal{S}_a \equiv \sum_{i=1}^{4} \mathbf{S}_i^a$ characterizes the total spin of the four localized electrons. These four spins can be coupled either to singlet, triplet or quintet states. If Hund coupling is neglected, considering only the antiferromagnetic super-exchange interaction, the ground state consists of a two-fold-degenerate singlet with energy -3 J, followed by nine-fold-degenerate triplet states and five quintet states with energy 3 J. The quantum number α_a describes all the remaining degrees of freedom: in our case, the spin state, the orbital and site occupancy of the itinerant electrons on the tetrahedron considered.

In order to calculate both the ground state and the finite-temperature properties of the cluster of two isolated tetrahedrons, first we performed a numerical exact diagonalization of the Hamiltonian H_1 characterizing one tetrahedron. Because of large degeneracy, the Hilbert space of one tetrahedron consists of 256, 1536 and 4096 states for 5, 6 and 7 electrons, respectively. However, since the Hamiltonian is invariant under rotation of the total spin, it is also diagonal by blocks in the basis of the eigenstates of the total spin (itinerant plus localized).

2.2. Probabilities

For a given temperature $T \equiv 1/\beta$, the average value of an operator Ξ (e.g. the nearest neighbours' spin–spin correlation) is defined by the usual relation

$$\langle \Xi \rangle = \frac{1}{\mathcal{Z}} \sum_n \langle n| \exp(-\beta H) \Xi |n\rangle. \tag{3}$$

Choosing a basis diagonalizing either the operator Ξ or the Hamiltonian, this relation can be rewritten as

$$\langle \Xi \rangle = \sum_n p(n, T) \langle n| \Xi |n\rangle. \tag{4}$$

Here, the density matrix $p(n, T) \equiv \frac{1}{\mathcal{Z}} \langle n| \exp(-\beta H)|n\rangle$ is the probability for the state $|n\rangle$ to be occupied at temperature T. Using the definition (2) of the state $|n\rangle$ of the cluster of two isolated tetrahedrons, the probability $P(N, \mathcal{S})$ that the tetrahedron 1 occupies a state with N electrons and a local spin state $\mathcal{S}$ is

$$\begin{aligned} P(N, \mathcal{S}) &= \frac{1}{\mathcal{Z}} \sum_{\alpha_1, \alpha_2, \mathcal{S}_2} \langle N, \mathcal{S}, \alpha_1 | \langle 12 - N, \mathcal{S}_2, \alpha_2 | \exp(-\beta H) | 12 - N, \mathcal{S}_2, \alpha_2 \rangle | N, \mathcal{S}, \alpha_1 \rangle \\ &= \frac{\mathcal{Z}_{12-N}}{\mathcal{Z}} \sum_{\alpha_1} \langle N, \mathcal{S}, \alpha_1 | \exp(-\beta H_1) | N, \mathcal{S}, \alpha_1 \rangle, \end{aligned} \tag{5}$$

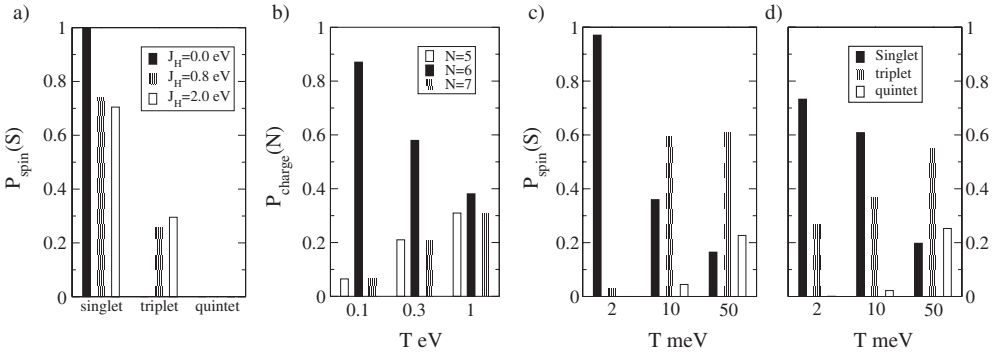

Figure 1. (a) Ground state spin probabilities at different values of Hund's coupling J_{H}. (b) Charge probabilities at temperatures $T = 0.1$, 0.3 and 1.0 eV for $J_{\mathrm{H}} = 0.8$ eV. (c) and (d) Spin probabilities at temperatures $T = 2$, 10 and 50 meV for $J_{\mathrm{H}} = 0.0$ and 0.8 eV, respectively.

where the partition function for *one* isolated tetrahedron with $N = 5, 6$ or 7 electrons is defined as $\mathcal{Z}_N \equiv \sum_{\mathcal{S},\alpha} \langle N, \mathcal{S}, \alpha | \exp(-\beta H_1) | N, \mathcal{S}, \alpha \rangle$. The partition function of the two-tetrahedron system can be cast as

$$\mathcal{Z} = \mathcal{Z}_5 \mathcal{Z}_7 + \mathcal{Z}_6 \mathcal{Z}_6 + \mathcal{Z}_7 \mathcal{Z}_5. \tag{6}$$

For further analysis, it is convenient also to define the probability that the tetrahedron 1 occupies a state with a total local spin $\mathcal{S}$:

$$P_{\mathrm{spin}}(\mathcal{S}) = \sum_{N} P(N, \mathcal{S}), \tag{7}$$

and the probability to occupy a state with N electrons:

$$P_{\mathrm{charge}}(N) = \sum_{\mathcal{S}} P(N, \mathcal{S}). \tag{8}$$

3. Results and discussion

3.1. Low energy states

First, let us discuss the weight of the different spin subsectors in the ground state. Figure 1(a) illustrates the spin probabilities $P(N = 6, \mathcal{S})$ for $T = 0$ and different values of Hund's coupling. At $J_{\mathrm{H}} = 0.0$ eV (decoupled spins and conducting electrons), the ground state is a two-fold-degenerate singlet. As soon as Hund's coupling is switched on, the spin degeneracy of the ground state is lifted and some triplet components occur. The weight of the triplet states is more than 20% for a realistic coupling $J_{\mathrm{H}} = 0.8$ eV, but the singlet components remain important even for much larger coupling $J_{\mathrm{H}} = 2.0$ eV. For the three values of coupling that we considered, the quintet contributions to the ground state are negligible. In figure 1(a) we present only the probabilities of states corresponding to the tetrahedron with $N = 6$ electrons because the states with 5 and 7 electrons are higher in energy and, therefore, all the probabilities $P(5, \mathcal{S})$ and $P(7, \mathcal{S})$ are equal to zero. At low temperatures, as in the ground state, mainly the states with $N = 6$ electrons are occupied. The charge sectors with $N = 5$ and 7 contribute only at rather high temperatures. In figure 1(b) the temperature evolutions of $P_{\mathrm{charge}}(N)$ are presented for $J_{\mathrm{H}} = 0.8$ eV. However, we should note that only static charge fluctuations are taken into account here, and considering interacting tetrahedrons would certainly increase the contribution of charge fluctuations at low temperatures.

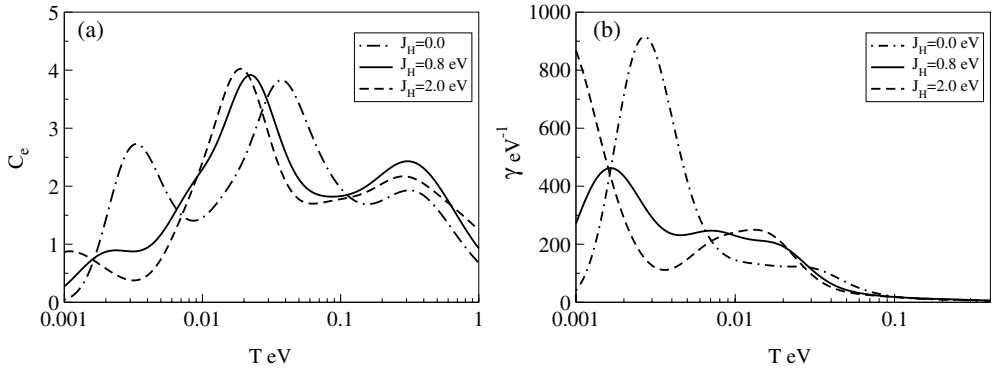

Figure 2. The temperature dependence of (a) the specific heat C_e and (b) the coefficient $\gamma = C_e/T$. On both (a) and (b), the temperature axis is logarithmic.

The evolution of the spin probabilities $P_{spin}(\mathcal{S})$ with increasing temperature is presented in figures 1(c) and (d) for $J_H = 0.0$ and 0.8 eV, respectively. The weights of the triplet states become substantial at $T \simeq 10$ meV and the spin probabilities are mainly proportional to the spin degeneracies at $T \simeq 50$ meV.

To conclude the description of the low energy excitations, let us discuss the thermodynamical properties such as the electronic specific heat C_e and the coefficient $\gamma = C_e/T$. In figures 2(a) and (b) we present the temperature dependence of C_e and γ, respectively. For all values of Hund's coupling, the specific heat has three peaks at finite temperatures. Two low-energy peaks correspond to spin excitations. For a non-zero Hund's coupling, the energies of the magnetic states are decreased and the corresponding peak occurs at a lower temperature. The third and highest temperature peak characterizes the charge sector excitations and it is independent of the Hund coupling.

3.2. Local moment and magnetic correlation functions

We discuss now the temperature dependence of the spin correlation functions at different values of Hund's coupling. We denote as $\mathbf{S}_i^{tot} = \mathbf{S}_i + \sigma_i$ the total spin at a given V ion. In figure 3(a), we plot the nearest-neighbour spin correlation function $\langle S_{1z}^{tot} S_{2z}^{tot} \rangle$. At low temperatures the correlations are antiferromagnetic for the three values of J_H considered. When the temperature is increased the correlations change from antiferro- to ferro-type at a temperature $T \sim 30$ meV for $J_H = 0.8$ and 2.0 eV, whereas it is always antiferromagnetic for $J_H = 0.0$ eV. To emphasize the role of the itinerant electrons, we plot on the inset of figure 3(a) the nearest-neighbour correlation functions $\langle S_{1z} S_{2z} \rangle$ of the localized spins only, which remain antiferromagnetic at any temperature and J_H.

This observation is in qualitative agreement with the inelastic neutron scattering measurements of Murani *et al* [4] where the correlations are antiferromagnetic (with a wavevector around $Q = 0.6$ Å^{-1}) below $T \approx 2$ K and develop ferromagnetic-like correlations (corresponding to a peak at $Q = 0$) with increasing temperature. A possible interpretation of these data could be the following: at low temperatures the ferromagnetic exchange, induced by the itinerant electrons due to the double-exchange mechanism [15], is weaker than the direct antiferromagnetic exchange and the resulting correlations are antiferromagnetic. With increasing temperature, carriers become more mobile and, as a consequence, the effective ferromagnetic exchange grows. In figure 3(b) we present the local effective moment per

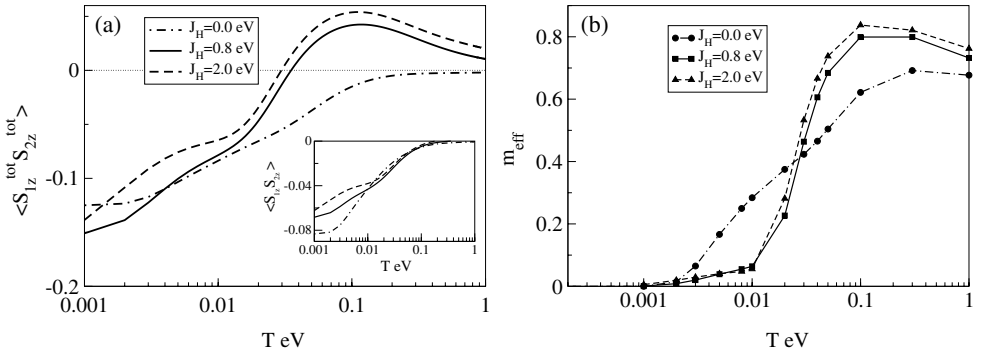

Figure 3. (a) Temperature dependence of the total spin nearest-neighbour correlation functions. The inset shows, for comparison, the correlations of only the localized spins. (b) Temperature dependence of the local magnetic moment. On both (a) and (b), the temperature axis is logarithmic.

site, which is defined as: $m_{\rm eff}(m_{\rm eff}+1) \equiv \langle(\sum_i \mathbf{S}_i^{\rm tot})^2\rangle/4$. At $J_{\rm H} = 0.0$ eV, when the localized spins are completely decoupled from the itinerant electrons, the magnetic moment is determined only by the localized spins. At zero temperature, the ground state is a singlet and the magnetic moment is zero. With increasing temperature low lying triplet states become thermally populated and this causes the formation of the local moment. At high temperature the obtained value of 0.67 corresponds to a paramagnetic moment of 1.5 electrons on average for a V ion.

At $J_{\rm H} = 0.8$ and 2.0 eV, the ground state has some triplet components but the weight of the singlet is still important. As a consequence, the effective moment is small at low temperature.

Finally, we calculated the static magnetic susceptibility, defined as $\chi(T) = \langle(S_{\rm tot}^z)^2\rangle/T$. At high temperature, for all values of Hund's coupling the inverse susceptibilities show linear behaviour, corresponding to a Curie–Weiss law. The Curie–Weiss temperatures extrapolated from high temperatures ($T \simeq$ 500–1000 K) are $\theta = -551$, -475 and -360 K for $J_{\rm H} = 0$, 0.8 and 2.0 eV, respectively. A detailed analysis of the magnetic susceptibility measurements [1] gives $\theta_{\rm CW} \approx -37$ K when the fit is performed over the range $T \simeq$ 100–300 K, but it gives $\theta \simeq -600$ K if fitted over the range $T \simeq$ 500–1000 K. This latter value is of the same order as the one we have calculated and we guess that the corresponding range of temperatures is such that the correlations between tetrahedrons are negligible. According to our calculations, this temperature does mainly characterize the spin correlations but in the charge sectors $N = 5$ and 7. The value $\theta_{\rm CW} \approx -37$ K, fitted at lower temperatures, would be more characteristic of spin correlations in the $N = 6$ charge sector.

4. Conclusion

We have performed an exact diagonalization of the small cluster, consisting of two disconnected tetrahedrons. The size of the cluster, constraint on the number of electrons and no exchange between two tetrahedrons gives us the possibility to make some qualitative descriptions of the system, its spectrum and magnetic behaviour.

We find that the ground state is a two-fold-degenerate singlet when the contribution from the itinerant electrons is not considered. The degeneracy is lifted and some important triplet components appear when the itinerant electrons are coupled to the localized spins by Hund's exchange interaction with a realistic value. Consistent with experimental observations [4],

the temperature dependence of the spin correlation function shows a crossover from antiferromagnetic to ferromagnetic behaviour when the temperature is increased. The increasing population of the magnetic states with temperature results in the formation of a non-zero residual magnetic moment which is also observed in experiment.

Acknowledgments

We thank A P Murani, J R Iglesias and G Jackeli for valuable discussions.

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