Spin Gap of Two-Dimensional Antiferromagnet Representing CaV$_4$O$_9$

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We examined a two-dimensional Heisenberg model with two kinds of exchange energies, $J_e$ and $J_c$. This model describes localized spins at vanadium ions in a layer of CaV$_4$O$_9$, for which a spin gap is found by a recent experiment. Comparing the high temperature expansion of the magnetic susceptibility to experimental data, we determined the exchange energies as $J_e \approx 610$ K and $J_c \approx 150$ K. By the numerical diagonalization we estimated the spin gap as $\Delta \sim 0.2J_e \approx 120$ K, which consists with the experimental value 107 K. Frustration by finite $J_c$ enhances the spin gap.

**KEYWORDS:** CaV$_4$O$_9$, spin gap, two-dimensional antiferromagnet, frustration, high temperature expansion, numerical diagonalization
Low-dimensional antiferromagnets with spin gap attract much interest due to the possible relevance to the high-$T_c$ superconductivity. For one dimension, many systems with spin gap have been examined theoretically. For example, the ladder model opens a spin gap up to about $0.5J$.\cite{1,2,3} The Majumdar-Ghosh model, a typical frustrated system, has a spin gap of about $0.24J$.\cite{4,5,6,7,8} A series of Heisenberg models with linearly decreasing exchange interactions also have finite spin gaps in the range between $0.25J$ and $0.75J$.\cite{9,10} In the above, $J$ is a typical exchange energy included in each model. Experimentally, finite spin gaps are found in $(VO)_2P_2O_7$\cite{11} and SrCu$_2$O$_3$.\cite{12,13} These materials are represented well as ladder spin systems arranged in parallel and coupled weakly.

For two dimensions, Taniguchi et al.\cite{14} recently found a finite spin gap for a layered material CaV$_4$O$_9$. They estimated the spin gap as $\Delta \approx 107$ K by measuring the magnetic susceptibility of $d$-electron spins at vanadium ions (V-spins) and the spin-lattice relaxation rate of $^{51}$V nuclear moment. As long as we know, this is the first experiment showing clearly the spin gap for (quasi-) two-dimensional spin systems. The lattice structure of CaV$_4$O$_9$ shows that there are two kinds of important exchange interactions between edge sharing V-spins and between corner sharing V-spins in a layer. We denote the corresponding exchange energies as $J_e$ and $J_c$, respectively. Katoh and Imada\cite{15} examined the spin gap by assuming $J_c = 0$. They estimated
as $\Delta \simeq 0.11J_e$ by the Quantum Monte Carlo simulation and explained the ground state character by a perturbation calculation, although they did not estimate effects of $J_c$. Ueda et. al. [16] carried out a similar perturbation calculation for finite $J_c$. However, since these perturbation calculations are not justified for realistic parameter values, their results have not been definite yet.

In this letter, we construct a reasonable spin model with realistic values for $J_e$ and $J_c$ and explain the measured spin gap for V-spins in CaV$_4$O$_9$. The exchange energies are determined by carrying out the high temperature expansion (HTE) of the magnetic susceptibility for the model and by comparing them to experimental data. We examine the spin gap by numerically diagonalizing the Hamiltonian for finite systems. After the extrapolation to an infinite system is taken, the estimated spin gap is shown to be fairly close to the experimentally obtained spin gap.

To construct the Hamiltonian, we survey the structure of a layer in CaV$_4$O$_9$. [14, 17] A layer consists of VO$_5$ pyramid-shaped clusters with apical oxygen atoms above and below a basal plane. Each pyramid contains a vanadium ion V$^{4+}$ roughly in its center. An electron in the $d\epsilon_{xy}$ orbital of a V$^{4+}$ ion forms a localized spin (V-spin). [18] Superexchange interactions may occur between V-spins in edge sharing pyramids and between V-spins in corner sharing pyramids by hybridization of $d\epsilon_{xy}$ orbitals with $p_x$ or $p_y$.
orbitals of adjacent oxygens. These superexchange interactions contribute to \( J_e \) and \( J_c \) respectively. There may be also a direct exchange interaction between V-spins in edge sharing pyramids due to the overlap of the \( d_{\epsilon xy} \) orbitals, which contributes to \( J_e \). Since it is difficult to calculate the values of \( J_e \) and \( J_c \) by starting from the first principle, we determine them by comparing experimental data of the magnetic susceptibility to the HTE calculation, as will be shown. Thus we describe magnetic properties of \( \text{CaV}_4\text{O}_9 \) by a two-dimensional antiferromagnetic Heisenberg model with two kinds of exchange energies \( J_e \) and \( J_c \).

The Hamiltonian for \( \text{CaV}_4\text{O}_9 \) is written as

\[
H = H_0 + H_A + H_B, \tag{1}
\]

\[
H_0 = J_e \sum_{\langle i, \alpha \rangle} \mathbf{S}_i \cdot \mathbf{S}_\alpha, \quad H_A = J_c \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad H_B = J_c \sum_{\langle \alpha, \beta \rangle} \mathbf{S}_\alpha \cdot \mathbf{S}_\beta, \tag{2}
\]

where \( \mathbf{S}_i \) (\( \mathbf{S}_\alpha \)) is the V-spin at site \( i \) (\( \alpha \)) belonging to the \( A \) (\( B \)) sublattice. The lattice structure in a layer is shown in Fig. 1(a). A small circle (square) represents V-spins above (below) the basal plane. We have called the set of sites denoted by small circles (squares) the \( A \) (\( B \)) sublattice. The exchange interactions for \( \langle i, \alpha \rangle \) is denoted by bold solid line in Fig. 1 (a); the corresponding exchange energy is \( J_c \). The exchange interactions for \( \langle i, j \rangle \) (\( \langle \alpha, \beta \rangle \)) are denoted by thin (dashed) solid lines; the exchange energy is \( J_e \). We note that the sub-Hamiltonian \( H_A \) (\( H_B \)) consists only of spins belonging to the \( A \) (\( B \)) sublattice, while \( H_0 \) consists of spins belonging to both. In the case
of $J_c = 0$, the Hamiltonian reduces simply to $H_0$. The lattice for $H_0$ given by thin solid lines in Fig. 1(a) is topologically the same as the lattice of Fig. 2. In the case of $J_c = 0$, spins on the A sublattice are described only by the sub-Hamiltonian $H_A$ and do not interact with spins on the B sublattice, which are described only by $H_B$. Hence we can consider $H_A$ and $H_B$ separately. The sublattice for $H_A$ ($H_B$) represented by thin solid (dashed) lines in Fig. 1(a) is topologically the same as the lattice shown in Fig. 2. Thus all sub-Hamiltonians $H_0$, $H_A$ and $H_B$ are equivalently represented by the unfrustrated lattice of Fig. 2. The ratio $\gamma = J_c/J_e$ changes the strength of frustration; the system is unfrustrated both in the limits of $\gamma = 0$ and $\gamma = \infty$.

To determine the exchange energies, $J_e$ and $J_c$, we carry out the HTE for magnetic susceptibility and compare the result to experimental data. The experimental susceptibility $\chi_E$ is shown in Fig. 3 as a function of $1/T$. The HTE is known to precisely reproduce a high-temperature part of a thermodynamic quantity of quantum spin systems. We derived the HTE formula for the magnetic susceptibility $\chi_H$ of the Hamiltonian (1). It is written as

$$\chi_H = C \left[ \frac{1}{T} - \frac{3(1 + \gamma)J_e}{4T^2} + \frac{3(1 + 6\gamma + \gamma^2)J_c^2}{16T^3} \right] + O\left(\left(\frac{1}{T}\right)^4\right),$$

(3)

where $C = n(g\mu_B)^2/4k$ with $n$ being the number of vanadium ions per gram in $\text{CaV}_4\text{O}_9$, $g$ the $g$-value, $\mu_B$ the Bohr magneton and $k$ the Boltzmann constant. To precisely compare the HTE susceptibility (3) to the experimental
data, we introduce the quantity, $\tilde{\chi}_H = (\chi_H - \frac{C}{T})T^2$. Then eq. (3) gives a linear function of $1/T$ for $\tilde{\chi}_H$ as $\tilde{\chi}_H = c_0 + c_1/T$ with $c_0 = -\frac{3}{4}(1 + \gamma)J_e$ and $c_1 = \frac{3}{16}(1 + 6\gamma + \gamma^2)J_e^2$. We plotted the corresponding experimental quantities $\tilde{\chi}_E = (\chi_E - \frac{C}{T})T^2$ as a function of $1/T$ in the inset of Fig. 3. The coefficients, $c_0$ and $c_1$, are determined so that $\tilde{\chi}_H$ represents the tangential line of $\tilde{\chi}_E$, as shown in the inset; i.e. $c_0 = -2.21$ emu/gK$^2$ and $c_1 = 693$ emu/gK. From the coefficients, we obtain $J_e \simeq 610$ K, $J_c \simeq 150$ K and then $\gamma \simeq 0.25$. Using these values we plotted the $\chi_H$ in Fig. 3 by the dashed line. The exchange energy of $J_e \simeq 610$ K seems to be fairly large in vanadium oxides and becomes a half of cuprates. The value of $J_c$ is smaller than $J_e$ but is not negligible, so that the real system is frustrated. We should carefully consider the contribution of $J_c$ when we examine the magnetic properties of CaV$_4$O$_9$.

To obtain the spin gap, we numerically diagonalize the Hamiltonian (1) by Lanczos’ method for finite systems with the periodic and/or the antiperiodic boundary conditions. In the case of $\gamma = 0$ we can use the systems with $N= 12, 16, 18$ and $24$, which are shown in Fig. 2. However in the case of finite $\gamma$, systems with $N = 16$ and $24$ among them only fit to the boundary conditions; these finite systems are shown in Fig. 1(b). This is because the lattice of $\gamma = 0$ (Fig. 2) is more symmetric than that of $\gamma \neq 0$ (Fig. 1(a)). We calculate the excitation energies $\Delta$ from the singlet ground states
to the lowest triplet states both for $\gamma = 0$ and $\gamma = 0.25$ and compare them. For the extrapolation, we assume the system-size dependence of $\Delta \sim 1/N$. The results are shown in Fig. 4. Data for $\gamma = 0$ fit a straight line well and confirms the system-size dependence. Hence the spin gap for $\gamma = 0$ is estimated as $\Delta \simeq 0.13J_e$ in the thermodynamic limit. This agrees with the result obtained by the Quantum Monte Carlo calculation.\[13\] We expect this system-size dependence is correct even for small but finite $\gamma$ and apply it to the realistic case of $\gamma = 0.25$. Then the spin gap for $\gamma = 0.25$ is estimated as $\Delta \sim 0.2J_e$ in the thermodynamic limit, as shown in Fig. 4. This result shows that frustration remarkably enhances the spin gap. Using the exchange energy $J_e \simeq 610$ K, the spin gap is evaluated as $\Delta \sim 120$ K. This result is fairly close to the experimentally obtained spin gap 107 K.

We finally discuss the origin of the spin gap. First we consider the case of $J_c = 0$ represented by the lattice of Fig. 2. The Hamiltonian $H_0$ consists of two different types of interaction bonds. An interaction bond is one of four bonds forming a plaquette and another connects two plaquettes. We call them a plaquette bond and a dimer bond, respectively. Accordingly $H_0$ is written as $H_0 = H_{0p} + H_{0d}$, where $H_{0p}$ ($H_{0d}$) consists only of plaquette (dimer) bonds. We calculated the expectation values of $H_{0p}$ and $H_{0d}$ in the ground state by the numerical diagonalization. In the thermodynamic limit these values are $\langle H_{0p} \rangle \simeq -0.20J_eN$ and $\langle H_{0d} \rangle \simeq -0.07J_eN$, when the numerical
results are extrapolated as a function of $1/N$. Hence the portions of the energy gains in plaquette parts and in dimer parts are $\langle H_{0p} \rangle / \langle H_0 \rangle \simeq 0.74$ and $\langle H_{0d} \rangle / \langle H_0 \rangle \simeq 0.26$, respectively. This result agrees with the picture in which singlet clusters are formed in plaquette parts. \[15, 16\] Next we consider the general case of $J_c \neq 0$ in terms of the spin-spin correlation function $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$. This quantity is evaluated by the numerical diagonalization and the extrapolation, again. At a plaquette bond we obtained $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \simeq -0.60$ for $\gamma = 0.25$ against $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \simeq -0.54$ for $\gamma = 0$. At a dimer bond we obtained $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \simeq -0.24$ for $\gamma = 0.25$ against $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \simeq -0.39$ for $\gamma = 0$. This result shows that parts gaining the correlation energy move from dimer bonds to plaquette bonds as $\gamma$ increases. This tendency corresponds to the enhancement of the spin gap with frustration.

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References

[1] E. Dagotto, J. Riera and D. Scalapino: Phys. Rev. B45 (1992) 5744.

[2] S. Gopalan, T. M. Rice and M. Sigrist: Phys. Rev. B49 (1994) 8901.

[3] M. Troyer, H. Tsunetsugu and D. Würtz: Phys. Rev. B50 (1994) 13515.

[4] C. K. Majumdar and D. K. Ghosh: J. Math. Phys. 10 (1969) 1399;

[5] C. K. Majumdar: J. Phys. C3 (1970) 911.

[6] B. S. Shastry and B. Sutherland: Phys. Rev. Lett. 47 (1981) 964.

[7] T. Tonegawa and I. Harada: J. Phys. Soc. Jpn. 56 (1987) 2153.

[8] K. Sano and K. Takano: J. Phys. Soc. Jpn. 62 (1993) 3809.

[9] K. Takano: J. Phys. A: Math. Gen. 27 (1994) L269;

[10] K. Takano: J. Phys. Soc. Jpn. 63 (1994) 4565.

[11] T. Barnes, J. Riera: Phys. Rev. B50 (1994) 6817.

[12] M. Takano, Z. Hiroi, M. Azuma and Y. Takeda: Jpn. J. Appl. Phys. 7 (1992) 3.

[13] K. Ishida, Y. Kitaoka, K. Asayama, M. Azuma, Z. Hiroi and M. Takano: J. Phys. Soc. Jpn. 63 (1994) 3222.
[14] S. Taniguchi, T. Nishikawa, Y. Yasui, Y. Kobayashi, M. Sato, T. Nishioka, M. Kontani and K. Sano: J. Phys. Soc. Jpn. 64 (1995) 2758.

[15] N. Katoh and M. Imada: preprint.

[16] K. Ueda, H. Kontani, M. Sigrist and P. A. Lee: preprint.

[17] P. J. Bouloux and J. Galy: Acta Crystallogr. 29 (1973) 1335.

[18] We did not take account of $d\varepsilon_{xz}$ and $d\varepsilon_{yz}$ orbitals, since any anomaly indicating the Jahn-Teller effect is not observed in the magnetic susceptibility for $5 \, K \lesssim T \lesssim 700 \, K$.

[19] For example, G. S. Rushbrooke, G. A. Baker, Jr. and P. J. Wood: Phase Transition and Critical Phenomena, eds. C. Domb and M. S. Green (Academic Press, London and New York, 1974) Vol. 3, Chap. 5, p245.

[20] The HTE calculation for this system does not exclude the opposite possibility of $J_c \simeq 610 \, K$ and $J_e \simeq 150 \, K$ because of the symmetry between $J_e$ and $J_c$ in eq. (3). To correctly select one of two possibilities, we carried out a similar calculation for another material $\text{CaV}_2\text{O}_5$ which gives an asymmetric HTE equation. The comparison of the HTE and an experiment (S. Taniguchi and M. Sato: private communication) for the susceptibility suggests that $J_e$ is larger than $J_c$ in $\text{CaV}_2\text{O}_5$. In this let-
ter, we have assumed that the result is valid even for CaV$_4$O$_9$, although it should be directly confirmed by experiments.
Figure Captions

Fig. 1. (a) The lattice structure for V-spins in a layer of CaV$_4$O$_9$. Small circles (squares) represent V-spins belonging to the $A$ ($B$) sublattice and are in pyramids above (below) the basal plane. The exchange energy for a bold solid line is $J_e$. Those for a thin solid line and a thin dashed line are $J_e$. (b) Parts of the lattice used in the numerical diagonalization.

Fig. 2. The lattice representing a sub-Hamiltonian $H_0$, which becomes the total Hamiltonian when $J_e = 0$. This lattice also represents each of $H_A$ and $H_B$, which are separated from each other when $J_e = 0$. Parts of the lattice used in the numerical diagonalization are also shown by the thin solid line.

Fig. 3. Magnetic susceptibilities of the experiment[14] and the HTE calculation. The HTE curve is determined so that $\tilde{\chi}_H$ becomes a tangential line of $\tilde{\chi}_E$ as shown in the inset.

Fig. 4. System size dependence of the spin gap $\Delta$ for $\gamma = 0$ (circles) and 0.25 (squares). The extrapolations are done with the solid and the dashed lines determined by the method of least squares with data of $N \geq 16$. 