Determination of Exchange Parameters for CaV$_4$O$_9$

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Abstract

Magnetic susceptibility measured for CaV$_4$O$_9$ is analyzed by a method with high temperature expansion. The analysis is consistent with the $g$-value which is close to 2 and is observed by an ESR experiment. Four exchange parameters in a two-dimensional Heisenberg model are determined to represent CaV$_4$O$_9$. All the exchange parameters are about 500 K and strongly frustrated. The observed spin gap originates from the frustration.

keywords: CaV$_4$O$_9$, spin gap, magnetic susceptibility, high temperature expansion, two-dimensional antiferromagnet, frustration

1 Introduction

Spin gaps in low dimensional materials have been investigated by a number of researchers. While origins and effects of spin gaps are fundamentally and generally interesting, those for two-dimensional materials are especially important in possible relevance to the high temperature superconductivity. Recently Taniguchi et al. $[1]$ found a spin gap in CaV$_4$O$_9$ by magnetic susceptibility and NMR measurements. CaV$_4$O$_9$ is a layered insulator and has spin
Figure 1: Lattice structure for vanadium spins in a layer of CaV$_4$O$_9$. The Heisenberg model examined in text includes 4 dependent exchange parameters $J_e$ (bold solid line), $J_e'$ (solid line), $J_c$ (bold dashed line) and $J_c'$ (dashed line).

degrees of freedom at vanadium ions. [2] This is the first clear observation of a spin gap in a two-dimensional spin system.

Theoretical efforts have been done to describe CaV$_4$O$_9$ as a two-dimensional Heisenberg model and to explain the origin of the spin gap. [3, 4, 5, 6, 7, 8, 9, 10, 11, 12] Almost models considered are included, as special cases, in a Heisenberg model with 4 kinds of exchange parameters; $J_e$ for edge-sharing plaquette links, $J_e'$ for edge-sharing dimer links, $J_c$ for corner-sharing plaquette links and $J_c'$ for corner-sharing dimer links as shown in Fig. 1. In these studies authors assumed values or constraints for the parameters and constructed their theories. Among them, Troyer [6] performed a quantum Monte Carlo simulation and argued that the system does not form a spin gap in the unfrustrated homogenous case of $J_e = J_e' \neq 0$ and $J_c = J_c' = 0$. The spin gap is possibly formed by inhomogeneity: i. e. the difference between $J_e$ and $J_e'$. It is also possible that the spin gap originates from frustration due to nonzero $J_c$ and $J_c'$.

In a previous paper, [5] we roughly estimated $J_e$ and $J_c$ on the condition of $J_e' = J_e$ and $J_c' = J_c$. We fitted a high-temperature expansion to the order of $1/T^3$ for the susceptibility to experimental data. The result was $J_e \simeq 610$ K and $J_c \simeq 150$ K with keeping the opposite possibility. [5] Calculation
of numerical diagonalization shows that the frustration among interactions with $J_e$ and $J_c$ enhances the spin gap in comparison with the case of $J_c = 0$. This enhancement agrees with the result of a perturbation calculation.

Most recent experiments give more detailed information on this material: (i) Neutron scattering measurement \cite{16} suggests $J_c > J_e$. (ii) ESR measurement \cite{17} precisely determined the $g$-value as $g = 1.96$, which is rather close to 2. The Curie constant is then $C = 0.003713$ emu/g. As for our previous paper, experiment (i) rather supports the opposite possibility for the values of the exchange parameters; i. e. $J_c \simeq 610$ K and $J_e \simeq 150$ K. On the other hand, we have used $g = 2$ of a free spin for $g$-value without explicit notice there. This $g$-value is close to the truth. Gelfand et al. estimated the exchange parameters as $J_e \simeq J_e' \simeq 190$ K and $J_c \simeq J_c' \simeq J_e / 2$ by various expansions. In the estimation, they determined the $g$-value as $g = 1.77$. The difference between this value and the experimental value seems to be hardly explained.

In view of the above, we expect that the previous estimation for $J_c$ and $J_e$ is roughly realistic, if we exchange the values of them. However, the estimation still includes unsatisfactory points. First we examined a Heisenberg model including only two independent exchange parameters, $J_e$ and $J_c$. It is at least necessary to independently treat parameters for plaquette and dimer links in order to determine the origin of the spin gap. Second we have a room to improve the fitting method. We obtained an expansion of the susceptibility of the Heisenberg model up to a finite order and fitted it directly to the experimental data. This method is rather usual for high temperature fitting. However the estimation is rough unless fairly high order expansion is carried out, and it is hard to calculate high order terms of expansion for a system with many independent exchange parameters.

In this paper, we determine the exchange parameters of the Heisenberg model to describe CaV$_4$O$_9$ in a novel fitting method. Following this method, we first construct an experimental formula for the magnetic susceptibility in power series of $1/T$. This procedure is explained in detail in section 2. On the other hand, we obtain a high temperature expansion of the susceptibility for a Heisenberg model with 4 independent exchange parameters; the expansion coefficients are functions of the exchange parameters. We determine the parameters by fitting the expansion coefficients to the coefficients of the experimental formula. The fitting is carried out in section 3. The result
shows that the origin of the spin gap for this material is the frustration rather than the inhomogeneity. Discussion is devoted in section 4.

2 Experimental formula for susceptibility at high temperatures

The experimentally obtained magnetic susceptibility, $\chi^{\text{EXP}}(T)$, is a set of data for $T \lesssim 700$ K. We construct an experimental formula for the data in a power series of $1/T$. The formula will be used to compare the experiment to a theory at high temperatures. To make expansion coefficients dimensionless we use $x = T_0/T$ as the expansion parameter, where $T_0$ is an arbitrary constant with the dimension of temperature. We hereafter employ $T_0 = 700$ K without spoiling generality. The formula is then written as

$$\chi(T) = \lim_{n \to \infty} \chi^{(n)}(T),$$

$$\chi^{(n)}(T) = \frac{C}{T}[1 + \sum_{m=1}^{n} A_m x^m]$$

with Curie constant $C$ determined by the ESR measurement. Here the expansion coefficients $A_m$’s are fitting parameters. \[18\]

To determine $A_m$’s we introduce a novel fitting method as will be explained below. We first define the quantity

$$\phi_m(x) = A_m + \sum_{l=1}^{\infty} A_{m+l} x^l$$

for each $m$. It is important that the quantity reduces to coefficient $A_m$ in the high temperature limit:

$$\phi_m(0) = A_m.$$  \[3\]

$\phi_m(x)$ is also defined by the recursion equation:

$$\phi_0(x) = \frac{T}{C} \chi(T),$$

$$\phi_m(x) = (\phi_{m-1}(x) - A_{m-1}) \frac{1}{x}$$
for \( m = 0, 1, 2, \cdots \) with \( A_0 = 1 \). The experimental data corresponding to \( \phi_m(x) \) is similarly defined in the recursive transformation:

\[
\begin{align*}
\phi_0^{\text{EXP}}(x) &= \frac{T}{C} \chi^{\text{EXP}}(T), \\
\phi_m^{\text{EXP}}(x) &= \left( \phi_{m-1}^{\text{EXP}}(x) - A_{m-1} \right) \frac{1}{x}.
\end{align*}
\] (5)

Here \( \phi_m \) fits \( \phi_m^{\text{EXP}} \) because \( \chi \) is constructed to fit \( \chi^{\text{EXP}} \). It is noticed that \( \phi_m \) is only formally introduced since the starting function \( \chi \) is now unknown and is the object which we will obtain finally. On the other hand we have the data \( \chi^{\text{EXP}} \) and so \( \phi_m^{\text{EXP}} \) is actually obtained as is mentioned below.

Now we determine \( \{A_m\} \) together with \( \{\phi_m^{\text{EXP}}(x)\} \) one by one. For \( m = 0 \), we have \( \phi_0^{\text{EXP}}(x) \) by multiplying \( T/C \) to \( \chi^{\text{EXP}}(T) \) and have \( A_0 = 1 \) by the definition. Next we obtain \( \phi_1^{\text{EXP}}(x) \) by the transformation

\[
\phi_1^{\text{EXP}}(x) = \left( \phi_0^{\text{EXP}}(x) - \phi_0^{\text{EXP}}(0) \right) \frac{1}{x}
\]

with \( m = 1 \). To obtain \( A_1 \) we use a simple fitting function

\[
f_1(x) = a_1 + b_1 \exp(-c_1 x)
\]

and determine the parameters \( a_1, b_1, c_1 \) to make \( f_1(x) \) fit \( \phi_1^{\text{EXP}}(x) \) by the least square method. Using these parameters, \( A_1 \) is given by \( A_1 = f_1(0) = a_1 + b_1 \) corresponding to \( A_1 = \phi_1(0) \) in eq. (3) with \( m = 1 \). By repeating this process, we obtain \( \phi_m(x) \) and \( A_m \) for arbitrary \( m \): When \( \phi_{m-1}(x) \) and \( A_{m-1} \) have been known, \( \phi_m^{\text{EXP}}(x) \) is given by eq. (5). Then we make function

\[
f_m(x) = a_m + b_m \exp(-c_m x)
\] (6)

fit \( \phi_m^{\text{EXP}}(x) \) and determine parameters \( a_m, b_m, c_m \). \( A_m \) is obtained by

\[
A_m = f_m(0) = a_m + b_m
\]

corresponding to eq. (3). Thus we can determine any coefficient \( A_m \) inductively.

In Fig. 2, we show \( \phi_m^{\text{EXP}}(x) \) along with \( f_m(x) \) for \( m = 1 \) to 4. Here we have used a weight function \( \exp(-1000/T) \) for fitting by the least square method. Optimal values for \( a_m, b_m, c_m \) and \( A_m \) are shown in Table 1. In principle we can obtain coefficient \( A_m \) for any \( m \). However, experimental data \( \phi_m^{\text{EXP}}(x) \) becomes dispersive as \( m \) increases, so that \( A_m \) with very large \( m \) cannot be obtained. When we change the weight function, the values of \( A_m \)'s change with a strong correlation: \( |A_m| \)'s have a tendency to increase or decrease simultaneously. The error depending on the choice of the weight function seems to be roughly several percents.

We have obtained values for \( A_m \)'s within some accuracy. They are independent of \( n \) if \( n \) is sufficiently large. It is now instructive to substitute the
Figure 2: Transformed experimental data $\phi^{EXP}_m(x)$ and fitting function $f_m(x)$ for $m = 1$ to 4.

| $m$ | $a_m$     | $b_m$     | $c_m$     | $A_m$     |
|-----|-----------|-----------|-----------|-----------|
| 1   | -0.20907  | -0.76379  | 1.2496    | -0.97286  |
| 2   | 0.15067   | 0.77787   | 0.68028   | 0.92854   |
| 3   | -0.10418  | -0.42303  | 0.41366   | -0.52721  |
| 4   | 0.04797   | 0.12828   | 0.29549   | 0.17624   |
| 5   | -0.01365  | -0.02554  | 0.26649   | -0.03918  |
| 6   | 0.00249   | 0.00484   | 0.26474   | 0.00733   |
| 7   | -0.00024  | -0.00104  | 0.15695   | -0.00127  |
| 8   | 0.00002   | 0.00014   | 0.08627   | 0.00016   |
Figure 3: $\chi^{(n)}$'s as functions of $T$. They are given by eq. (1) with $A_m$'s in Table 1. Data of the experimental susceptibility $\chi^{EXP}$ are also shown by open circles.

values for $A_m$'s into $\chi^{(n)}$ in eq. (1) with small $n$ as well as large $n$. Results for several values of $n$ are shown in Fig. 3. $\chi^{(n)}$ approaches to $\chi^{EXP}$ as $n$ increases, confirming the validity of this method.

3 High temperature expansion for a Heisenberg model and determination of exchange parameters

We assume that spins at vanadium sites in a layer of CaV$_4$O$_9$ are described by a two-dimensional Heisenberg model which is represented in Fig. 1. The Hamiltonian is written as

$$H = \sum_{<i,j>} J_{ij} S_i \cdot S_j,$$  \hspace{1cm} (7)

where $S_i$ is the spin at site $i$. The exchange parameter $J_{ij}$ is $J_e$, $J'_e$, $J_c$ or $J'_c$ if it corresponds to a link indicated in Fig. 1 and is zero otherwise.

By the high temperature expansion, magnetic susceptibility of a Heisen-
The Berg model is generally written in the following form:

$$\chi^{HTE}(T) = \frac{C}{T}[1 + \sum_{m=1}^{\infty} F_m x^m]$$  \hspace{1cm} (8)

with $x = T_0/T$ and the experimentally determined Curie constant $C$. We have used $T_0 = 700$ K as in the previous section. The coefficients $F_m$’s are functions of the exchange parameters and are calculated by the standard diagramatic method. [19]

In the present model of eq.(7), the coefficients $F_m$’s are functions of $J_e$, $J_e'$, $J_c$ and $J_c'$. We obtained them for $m = 1, 2$ and 3 as

$$F_1 T_0 = -\frac{1}{4}(2J_e + J_e' + 2J_c + J_c'),$$

$$F_2 T_0^2 = \frac{1}{4^2}[(4J_e - J_e')J_e' + 2(2J_e + J_e')(2J_c + J_c') + (4J_c - J_c')J_c'],$$

$$F_3 T_0^3 = \frac{1}{3 \cdot 4^3}[(8J_e^3 - 12J_e^2 J_e' + 6J_e J_e'^2 + J_e^3) + 3J_e'(6J_e^2 - 12J_e J_e' + J_e'^2)] - 6J_e(4J_e^2 + 7J_e J_e' - J_e'^2) - 3(4J_c^2 + 12J_c J_c' - J_c'^2)(2J_e + J_e') + (8J_c^3 - 12J_c^2 J_c' + 6J_c J_c'^2 + J_c'^3)].$$  \hspace{1cm} (9)

If the Hamiltonian (7) completely describes the material, we have $\chi^{HTE}(T) = \chi(T)$ or $F_m = A_m$ for all $m$, where $A_m$’s are in Table 1. However the Hamiltonian may only approximately describe the real material. We can estimate optimal values for the exchange parameters by minimizing the $k$th deviation

$$D_k = \sqrt{\frac{1}{k} \sum_{m=1}^{k} (F_m - A_m)^2}. \hspace{1cm} (10)$$

In the present case, the exchange parameters are $J_e$, $J_e'$, $J_c$ and $J_c'$. We numerically minimized $D_3$ with $F_m$’s in eq.(9) and obtained the optimal values as

$$J_e \simeq 480 \text{ K}, \quad J_e' \simeq 530 \text{ K},$$

$$J_c \simeq 580 \text{ K}, \quad J_c' \simeq 540 \text{ K}. \hspace{1cm} (11)$$

This estimation is the main result of this paper. The result shows that inhomogeneity is weak and frustration is strong in this material. Thus the observed spin gap originates from frustration. These values yield deviation $D_3 \simeq 0.11$ and possible reasons of the deviation are discussed in the next section.
4 Discussion

We introduced a novel method to estimate exchange parameters. This method is fairly general and so applicable to various systems when we compare a Hamiltonian to experiment data. In the first step of this method, we constructed an experimental formula for magnetic susceptibility in the power series of $T_0/T$. To examine the accuracy of this method, we applied it to a known case: a Heisenberg model on a simple square lattice. The formula of high temperature expansion for this model is already calculated. [19]. Using this formula instead of experimental data, we obtained coefficients $A_m$’s in the way of section 2. We confirmed that the coefficients approximate reproduce the original formula.

We applied the method to CaV$_4$O$_9$ to describe it by a two-dimensional Heisenberg model (7). The optimal values for exchange parameters are shown in eq. (11). The result shows that the strong frustration opens a spin gap in this material. The optimal values yield a deviation of $D_3 \simeq 0.11$. We cannot decide now whether or not this deviation is only an error within this method itself. We point out other possible origins of the deviation. It is possible that the deviation comes from unexpected components, e. g. VO$_2$, CaV$_2$O$_5$, CaV$_3$O$_7$, included in samples of CaV$_4$O$_9$. The deviation also possibly means that the material includes some degree of freedom which cannot be described by a Heisenberg model (7); it might come from itinerant effect or effect of degeneracy of atomic orbitals. Anyway what we have done is to approximately represent CaV$_4$O$_9$ by the Heisenberg model (7).

The values of exchange parameters are plausible if similar materials have similar values. In CaV$_2$O$_5$ we estimated $J \sim 600$ K by fitting the formula for the one-dimensional Heisenberg model to experiment. This value is similar to a typical exchange parameter $\sim 500$ K for CaV$_4$O$_9$. In CaV$_3$O$_7$, $J_c \approx J_e$ is argued [20] by using a theoretical result. [21] These results are actually similar to our result for CaV$_4$O$_9$.

Using the values of the exchange parameters, we calculated the spin gap of the Hamiltonian (7) by the numerical diagonalization. The extrapolated spin gap $\Delta$ is given as $\Delta \sim 170$ K. Considering the 10 % deviation of the coefficients and errors for extrapolation, this result seems to be consistent with the observed value of $\Delta \sim 110$ K.
Acknowledgements

We thank Masatoshi Sato, Satoshi Taniguchi, Hiroshi Harashina and Katsuaki Kodama for useful discussion and presentation of detailed experimental data before publication. We also thank K. Kubo for useful discussion on high temperature expansion of Heisenberg models. One of us (K. T.) carried out this work partially in Department of Physics of Nagoya University as a Guest Associate Professor. This work is partially supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. The computation in this work was carried out partially by using facilities of the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

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The first and the second order terms in high-temperature expansion formula of the susceptibility are symmetric with respect to the exchange between $J_e$ and $J_c$. Hence the opposite possibility of $J_e = 150$ K and $J_c = 610$ K remains.

One might expect that $A_m$'s are determined by fitting $\chi^{(n)}$ with finite $n$ to $\chi^{EXP}$ directly by the least square method. However it fails even if the $n$ is fairly large. Fitting $\chi^{(n)}$ to $\chi^{EXP}$ gives $A_m$'s which are strongly depend on $n$ and does not seem to converge. It is due to the lack of data in the high temperature regime ($0 < x < \sim 1$) in $\chi^{EXP}$. The shape of polynomial $\chi^{(n)}$ in this regime sometimes oscillates unrealistically. We have introduced another fitting method to overcome this difficulty.