Magnetic Susceptibility for CaV_4O_9

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We examine experimental magnetic susceptibility \( \chi_{\text{mag}}(T) \) for CaV_4O_9 by fitting with fitting function \( \alpha \chi_{\text{mag}}(T) + c \). The function \( \chi_{\text{mag}}(T) \) is a power series of \( 1/T \) and the lowest order term is fixed as \( C/T \), where \( C \) is the Curie constant as determined by the experimental \( g \)-value \( (g=1.96) \). Fitting parameters are \( \alpha \), \( c \) and expansion coefficients except for the first one in \( \chi_{\text{mag}}(T) \). We determine \( \alpha \) and \( c \) as \( \alpha \approx 0.73 \) and \( c \approx 0 \) for an experimental sample. We interpret \( \alpha \) as the volume fraction of CaV_4O_9 in the sample and \( \chi_{\text{mag}}(T) \) as the susceptibility for the pure CaV_4O_9. The result of \( \alpha \neq 1 \) means that the sample includes nonmagnetic components. This interpretation consists with the result of a perturbation theory and a neutron scattering experiment.

KEYWORDS: CaV_4O_9, magnetic susceptibility, volume fraction, high temperature expansion, spin gap, two-dimensional Heisenberg model

§1. Introduction

A few years ago, Taniguchi et al. measured the magnetic susceptibility of layered material CaV_4O_9 and found a spin gap of 107 K by analyzing its temperature dependence. Since then CaV_4O_9 has been investigated as an interesting example of two-dimensional spin systems with spin gap. There is much theoretical effort to understand the spin gap by starting from Heisenberg models. However it was not successful to consistently explain various experiments. In particular it was very difficult to find the values of exchange parameters to reproduce the experimental magnetic susceptibility and the \( g \)-value measured by ESR.

From the lattice structure, the system is expected to be described by the two-dimensional Heisenberg model:

\[
H = \sum_{<ij>} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,
\]

where \( \mathbf{S}_i \) is the spin at vanadium site \( i \). The exchange parameter \( J_{ij} \) is nonzero if the pair < \( i, j \) > corresponds to a link indicated in Fig. 1: i.e. \( J_{ij} \) is \( J_e \) for an edge-sharing plaquette link, \( J_{e}' \) for an edge-sharing dimer link, \( J_c \) for a corner-sharing plaquette link and \( J_c' \) for an corner-sharing dimer link. Almost models which have been considered are included in this model as special cases.

We summarize important experimental results as follows:

(a) Temperature dependence of magnetic susceptibility shows that the material has a spin excitation gap and its value is about 110 K.\[2^\text{[13]}\]

(b) ESR measurement precisely determined the \( g \)-value as \( g = 1.96 \), which is rather close to 2.\[3^\text{[13]}\] The Curie constant is then \( C = 0.003713 \text{ emu/g.} \)

(c) Neutron scattering experiment is performed to give a dispersion relation for spin excitations.\[3^\text{[13]}\] The result shows a spin gap at momentum \((0,0)\) and its value consists approximately with the values of other experiments. Also the analysis of the scattering intensity directly suggests \( J_e > J_c \).

Theoretically the consistency between the suscepti-

\[\text{Fig. 1. Lattice structure for vanadium spins in a layer of CaV}_4\text{O}_9. \text{ The Heisenberg model examined in text includes 4 dependent exchange parameters } J_e \text{ (bold solid line), } J_{e}' \text{ (solid line), } J_c \text{ (bold dashed line) and } J_c' \text{ (dashed line).}\]


bility and the \( g \)-value is the issue. Before experiments (b) and (c) appeared, Gelfand et al. estimated the exchange parameters as \( J_c \simeq J'_c \simeq 190 \text{ K} \) by assuming \( J_c \simeq J'_c \simeq J_c/2 \) by using various expansions. In the estimation, they determined the \( g \)-value as \( g = 1.77 \), which is different from \( g = 1.96 \) in experiment (b). The values for the exchange parameters produce the minimum at momentum \((\pi, \pi)\) in the dispersion relation against \((0, 0)\) in experiment (c). In a previous article, we estimated exchange parameters as \( J_c(\equiv J'_c) \simeq 610 \text{ K} \) and \( J_c(\equiv J'_c) \simeq 150 \text{ K} \) with the assumption of \( g = 2 \). The estimation comes from the determination of the lowest-order coefficient in the high temperature expansion of the susceptibility. To confirm and refine this result we calculated the high-temperature expansion to the third order and carried out the fitting to the experimental susceptibility data with keeping the measured \( g \)-value \((g = 1.96)\). However there is no solution satisfying the obtained set of equations to determine the exchange parameters. Katoh and Imada examined various possibilities by taking account of plural atomic levels. However their theory includes discrepancy in the compatible explanation of the susceptibility and the \( g \)-value in experiments. These theories shed light on some aspects of the susceptibility of this material, although no one succeeded to give a consistent explanation of all the experimental results.

In this paper, we overcome this difficulty by taking account of the possibility that the experimental sample is a mixture of \( \text{CaV}_4\text{O}_9 \) and other nonmagnetic materials. We only assume that the susceptibility can be generally expanded in a power series of \( 1/T \). From the coefficient of \( 1/T \) in the expansion formula, we estimate the volume fraction \( \alpha \) of the \( \text{CaV}_4\text{O}_9 \) component in the sample. We further show that the value of \( \alpha \) is consistent with that obtained by exchange parameters determined by a neutron scattering experiment and the third order perturbation calculation.

### §2. Determination of volume fraction

To solve the discrepancy we consider that the susceptibility for the sample is smaller than the true value by a constant factor. This is possible if the sample is a mixture and includes nonmagnetic components. The constant factor is then the volume fraction of the magnetic component. We have two sets of data for susceptibility by Taniguchi et al. and by Isobe and Ueda. They are shown in Fig. 2. Since the latter set is definite for the temperature region under 300 K, we compared the two sets below 300 K. As a result, we found that the latter is precisely 1.17 times larger than the former over all temperatures below 300 K. Hence we infer that the experimental susceptibility includes a sample dependent factor corresponding to the amount of nonmagnetic components.

In general, the susceptibility is expanded in a power series of \( 1/T \) and the high temperature behavior is described by the expansion formula. This is true for even the present case where the sample may be a mixture. We make a fitting to the experimental data \( \chi_{\text{tot}}(T) \) by a polynomial of sufficiently large order to determine the expansion coefficients. To make the expansion coefficients dimensionless we take the expansion parameter as \( x = T_0/T \) with arbitrary constant \( T_0 \) of the dimension of temperature. We choose it as \( T_0 = 100 \text{ K} \) without spoiling the generality. The polynomial for fitting function is accordingly written as

\[
f(x) = \frac{C}{T_0} \sum_{m=0}^{L} a_m x^m. \tag{2}
\]

Here the expansion coefficients \( a_m \)'s are fitting parameters. The order \( L \) of the polynomial is chosen to be sufficiently large so that \( a_m \)'s do not change largely when \( L \) changes by a few integers.

We carried out the fitting for each \( L \) less than 19 and obtained the values of expansion coefficients. Results for \( L = 12 \) to 19 are shown in Table I. Averages over \( L \) for 12 to 19 are also shown in the last row. Viewing this table we see that the values for \( a_0 \) and \( a_1 \) have only small fluctuation and are relatively reliable. In contrast the values for \( a_2 \) seem to largely fluctuate and include an amount of fitting error. The fitted curve is shown in Fig. 3 together with \( \chi_{\text{tot}}(T) \).

![](image)

**Fig. 2.** Experimental susceptibilities of Taniguchi et al. and of Isobe and Ueda. The result of 1.17 times the former is also shown.

| \( L \) | \( a_0 \)  | \( a_1 \)  | \( a_2 \)  | \( a_3 \)  | \( a_4 \)  |
|-------|---------|---------|---------|---------|---------|
| 12    | 0.00117 | 0.72014 | -1.2709 | 1.4170  | -1.0914 |
| 13    | 0.00188 | 0.71909 | -1.2276 | 1.3167  | -0.9596 |
| 14    | 0.00039 | 0.73013 | -1.3176 | 1.5224  | -1.2233 |
| 15    | 0.00092 | 0.72310 | -1.2830 | 1.4379  | -1.1060 |
| 16    | -0.00106 | 0.74988 | -1.4173 | 1.7711  | -1.5742 |
| 17    | -0.00048 | 0.74183 | -1.3752 | 1.6604  | -1.4074 |
| 18    | 0.00001 | 0.73513 | -1.3409 | 1.5733  | -1.2814 |
| 19    | 0.00043 | 0.72941 | -1.3123 | 1.5028  | -1.1832 |
| Av    | 0.00041 | 0.73007 | -1.3181 | 1.5252  | -1.2283 |
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The polynomial \( \chi^{\text{tot}}(T) \) is rewritten as
\[
f(x) = \frac{C}{T_0}[a_0 + a_1 x(1 + a_2' x + a_3' x^2 + \cdots)]
\]
with \( a_i' = a_i/a_1 \) for \( i \geq 2 \). Correspondingly we analyze the experimental susceptibility \( \chi^{\text{tot}}(T) \) in the following form:
\[
\chi^{\text{tot}}(T) = \gamma \frac{C}{T_0} + \alpha \chi^{\text{mag}}(T),
\]
where \( \gamma = a_0 \) and \( \alpha = a_1 \). Then \( \chi^{\text{mag}}(T) \) is approximately represented as
\[
\chi^{\text{mag}}(T) \simeq \frac{C}{T}(1 + A_1 x + A_1 x^2 + \cdots)
\]
with \( A_i = a_i'/i+1 \). Hence we estimate the values of \( \gamma \) and \( \alpha \) as
\[
\gamma \simeq 0.00, \quad \alpha \simeq 0.73.
\]

For an ideal localized spin system, no constant term appears in the magnetic susceptibility. The constant term of \( \gamma \) in eq. (3) comes from other than the electronic spins if it exists. Candidates for the contribution are the Van Vleck term and the diamagnetic term. However these terms have been already subtracted in the present data of eq. (2). The present result, \( \gamma = 0 \), confirms that the original subtraction is precise. We note that the present method uses only the general property that the susceptibility is expanded in power series of \( 1/T \). In contrast the method for the original subtraction explicitly uses the facts that the system is a spin system and is two-dimensional.

If the sample consists only of CaV\textsubscript{4}O\textsubscript{9}, the observed susceptibility must be \( \chi^{\text{mag}}(T) \) instead of \( \chi^{\text{tot}}(T) \). This is because the Curie constant \( C \) is fixed as \( C = 0.003713 \) emu/g due to experiment (c) and the constant \( \alpha \) must be unity. The result of \( \alpha < 1 \) means that the sample includes nonmagnetic materials, which do not have spin degree of freedom. Precisely the sample is a mixture consisting of 73 \(^\circ\) magnetic and 27 \(^\circ\) nonmagnetic materials. Thus \( \alpha \) is the volume fraction of the magnetic part in the whole sample. We infer that the nonmagnetic part is due to incomplete chemical reactions and hence CaO and VO\textsubscript{2} are candidates. We believe that this is the reason why the effective \( g \)-value in some past theories are much smaller than the observed value by the ESR measurement.

§3. Consistency with the Perturbation Theory

As mentioned in experiment (c), Kodama et al. obtained the dispersion relation of a spin excitation for CaV\textsubscript{4}O\textsubscript{9} by neutron scattering. They also theoretically calculated a dispersion formula by a perturbation of the second order for the Hamiltonian (1). By fitting the formula to the experimental dispersion, they determined the exchange parameters. The resultant values approximately reproduced the experimental dispersion relation. Recently, Fukumoto and Oguchi recalculated and corrected the second order perturbation formula of the dispersion relation. They further extended the perturbation formula up to the third order. In the third order perturbation, their result is given as \( J_c = 162 \text{ K}, J_c = 20 \text{ K} \) and \( J'_c = J_c = 79 \text{ K} \). Using the third-order values for the exchange parameters, we numerically diagonalized the Hamiltonian (1) and obtained energy levels. The diagonalization was done for lattices with \( N = 8 \) and 16 (\( N \): the number of lattice sites) under the periodic boundary condition. We then calculated the magnetic susceptibility \( \chi^{\text{num}}(T) \) by the energy levels. The results are shown in Fig. 4. The curve for 8 sites is close to that for 16 sites. We extrapolate the results to the infinite system size by assuming the system size dependence 1/\( N \). We plotted the values of 0.7 times the extrapolated data in Fig. 4. The resultant curve is close to the experimental susceptibility and shows that the volume fraction is given as \( \alpha' \sim 0.7 \). This result consists with the interpretation obtained from the analysis of the magnetic susceptibility.

The difference between \( \alpha \) and \( \alpha' \) is not serious since some errors may be included in the processes determining them. There is a possible error for \( \alpha' \) in the fitting of a polynomial (2) to the experimental data \( \chi^{\text{tot}}(T) \). Further there is a possible error in \( \alpha' \) accompanied with the truncation of the perturbation series to the third order.

§4. Summary

We examined the experimentally obtained magnetic susceptibility \( \chi^{\text{tot}}(T) \) for CaV\textsubscript{4}O\textsubscript{9}. By using the fact that the susceptibility is generally expanded in the power series of \( 1/T \), we showed that the sample includes nonmagnetic components. We estimated the volume fraction of CaV\textsubscript{4}O\textsubscript{9} as \( \alpha \sim 0.73 \). The existence of nonmagnetic components enable us to consistently understand all the experimental results: the magnetic susceptibility, the \( g \)-value by ESR and the dispersion relation by neutron scattering.
Fig. 4. Susceptibility obtained by the numerical diagonalization of the Hamiltonian \( H \). Dash-dotted (dashed) line is for \( N = 8 \) (\( N = 16 \)) lattice. The solid line is for 0.7 times the large \( N \) limit of these numerical results. Experimental data are also shown. The values of the exchange parameters in the Hamiltonian are what Fukumoto and Oguchi\[{10}\] determined.

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[23] To estimate the accuracy of the fitting method in \( \S 4 \), we applied the same fitting to the data of the numerical diagonalization \( (N = 16) \) instead of the real experimental data. We found that approximately 2% error is involved in the estimated coefficient for the first order term, corresponding to the volume fraction.
Fig. 1. K. Takano & K. Sano
$\chi [x 10^{-6} \text{emu/g}]$

$T[K]$

$N=16$  
$N=8$

Exp.