Magnetic properties of the antiferromagnetic spin-$\frac{1}{2}$ tetramer compound CuInVO$_5$

Masashi Hase$^1$, Masashige Matsumoto$^2$, Akira Matsuo$^3$ and Koichi Kindo$^3$

$^1$Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305-0047, Japan
$^2$Department of Physics, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka-shi, Shizuoka 422-8529, Japan
$^3$The Institute for Solid State Physics (ISSP), The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan

E-mail: HASE.Masashi@nims.go.jp

Abstract. We measured the temperature dependence of the magnetic susceptibility and specific heat and the magnetic-field dependence of the magnetization of CuInVO$_5$. An antiferromagnetically ordered state appears below $T_N = 2.7$ K. We observed a $\frac{1}{2}$ quantum magnetization plateau above 30 T at 1.3 K. The probable spin model for CuInVO$_5$ is an interacting spin-$\frac{1}{2}$ tetramer model. We evaluated the values of the intratetramer interactions as $J_1 = 240 \pm 20$ K (antiferromagnetic) and $J_2 = -142 \pm 10$ K (ferromagnetic) and the value of the effective intertetramer interaction as $J_{eff} = 30 \pm 4$ K. The ground state of the isolated spin tetramer with the $J_1$ and $J_2$ values is spin singlet. The shrinkage of ordered magnetic moments by quantum fluctuation can be expected. Longitudinal-mode magnetic excitations may be observable in CuInVO$_5$.

1. Introduction

Two types of magnetic excitations exist in a magnetically ordered state. They are gapless transverse-mode (Nambu-Goldstone mode) [1] and gapped longitudinal-mode (amplitude Higgs mode) [2, 3, 4] excitations corresponding to fluctuations in directions perpendicular and parallel to ordered moments, respectively. The transverse-mode (T-mode) excitations are well known as spin wave excitations. Investigations of the longitudinal-mode (L-mode) are now in progress. The L-mode excitations were observed in a pressure-induced or magnetic-field-induced magnetically ordered state of interacting antiferromagnetic (AF) spin-$\frac{1}{2}$ dimer compounds TiCuCl$_3$ [5, 6, 7, 8, 9] and KCuCl$_3$ [10].

According to results of theoretical investigations, the L-mode excitations may be observed in an antiferromagnetically ordered state appearing on cooling at atmospheric pressure and zero magnetic field in interacting AF spin-cluster compounds [11]. A shrinkage of ordered magnetic moments by quantum fluctuations leads to a large intensity of the L-mode excitations. If the ground state (GS) of the corresponding isolated spin cluster is a spin-singlet state, the shrinkage of ordered moments can be expected in an ordered state generated by the introduction of intercluster interactions.
We focus on spin-1/2 tetramers. The Hamiltonian of the spin tetramer is expressed as
\[ \mathcal{H} = J_1 S_2 \cdot S_3 + J_2 (S_1 \cdot S_2 + S_3 \cdot S_4). \] (1)

When \( J_1 > 0 \) and \( J_2 \) has negative or small positive values, the GS is the spin-singlet state and \( \Delta/J_1 \) can be sufficiently small [12]. Here \( \Delta \) is the energy difference (spin gap) between the singlet GS and first-excited triplet states. An ordered state is possible by the introduction of weak intercluster interactions. An antiferromagnetically ordered state appears in spin-1/2 tetramer compounds \( \text{Cu}_2\text{CdB}_2\text{O}_6 \) [13, 14, 15] and \( \text{SeCuO}_3 \) [16].

Recently, we found an antiferromagnetically ordered state below \( T_N = 2.7 \) K in the spin-1/2 tetramer compound \( \text{CuInVO}_5 \). We report results of magnetization and specific heat.

![Figure 1.](image)

**Figure 1.** (a) Schematic drawing of positions of \( \text{Cu}^{2+} \) ions having spin-1/2 and \( \text{O}^{2-} \) ions connected to \( \text{Cu}^{2+} \) ions in \( \text{CuInVO}_5 \) [17]. Red and blue bars represent the shortest and second-shortest Cu-Cu distances, respectively. We define \( J_1 \) and \( J_2 \) as the exchange interaction parameters for the Cu1-Cu1 and Cu1-Cu2 pairs, respectively. The \( J_1 \) and \( J_2 \) interactions form a spin-1/2 tetramer. (b) Interacting spin tetramer model used to calculate magnetization using a mean-field theory based on the tetramer unit (tetramer mean-field theory).

**2. Experimental and Calculation Methods**

Crystalline \( \text{CuInVO}_5 \) powder was synthesized by a solid-state reaction. Starting materials are \( \text{CuO}, \text{In}_2\text{O}_3, \) and \( \text{V}_2\text{O}_5 \) powder. Their purity is 99.99 %. A stoichiometric mixture of powder was sintered at 1,023 K in air for 100 h with intermediate grindings. We measured an x-ray powder diffraction pattern at room temperature using an x-ray diffractometer (RINT-TTR III; Rigaku). We confirmed that our sample was a nearly single phase of \( \text{CuInVO}_5 \). The space group is \( P2_1/c \) (No. 14). The lattice constants are \( a = 8.776(1), b = 6.158(1), c = 15.268(1) \) Å, and \( \beta = 106.48(1)^\circ \). These are almost the same as the values reported in the literature [17].

We measured the specific heat using a physical property measurement system (Quantum Design). We measured the magnetization in magnetic fields of up to 5 T using a superconducting quantum interference device magnetometer magnetic property measurement system (Quantum Design). High-field magnetization measurements were conducted using an induction method with a multilayer pulsed field magnet installed at the Institute for Solid State Physics (ISSP), the University of Tokyo.

We obtained the eigenenergies and eigenstates of isolated spin-1/2 tetramers using an exact diagonalization method [12]. We calculated the temperature \( T \) dependence of the magnetic susceptibility and the specific heat and the magnetic-field \( H \) dependence of the magnetization \( M(H) \) using the eigenenergies. We calculated \( M(H) \) for the model shown in Fig. 1(b) using a mean-field theory based on the tetramer unit (tetramer mean-field theory). Finite magnetic moments were initially assumed on the Cu sites in the tetramer. The mean-field Hamiltonian was then expressed by a \( 16 \times 16 \) matrix form under consideration of the external magnetic...
field and the molecular field from the nearest-neighbor sites. The eigenstates of the mean-field Hamiltonian were used to calculate the expectation value of the ordered moments on the Cu sites. We continued this procedure until the values of the magnetic moments converged. We finally obtained a self-consistently determined solution for $M(H)$.

3. Results and discussion
The red circles in Figs. 2 and 3 show the $T$ dependence of the specific heat $C(T)$ of CuInVO$_5$ in zero magnetic field and the magnetic susceptibility $\chi(T)$ of CuInVO$_5$ in a magnetic field of $H = 0.01$ T, respectively. We can observe a peak in $C(T)$ at 2.7 K and a clear decrease in $\chi(T)$ below this temperature, indicating the occurrence of an AF long-range order. A broad maximum can be seen around 8 K in $C(T)$ and around 11 K in $\chi(T)$, indicating a low-dimensional AF spin system. As $T$ is increased, $\chi(T)$ decreases rapidly up to $T = 40$ K then decreases slowly at higher temperatures. We estimated the Weiss temperature to be 42 K from $\chi(T)$ above 200 K. Other phase transitions were not observed in $C(T)$ and $\chi(T)$ below 300 K.

![Figure 2](image2.png)

**Figure 2.** Temperature $T$ dependence of the specific heat $C(T)$ of CuInVO$_5$ (circles) in zero magnetic field. A green line indicates $C(T)$ calculated for an isolated spin-$\frac{1}{2}$ tetramer. The $J_1$ and $J_2$ values are listed in Table 1.

![Figure 3](image3.png)

**Figure 3.** Temperature $T$ dependence of the magnetic susceptibility $\chi(T)$ of CuInVO$_5$ (circles) in a magnetic field of $H = 0.01$ T below 20 K (a) and 300 K (b). Green lines indicate $\chi(T)$ calculated for an isolated spin-$\frac{1}{2}$ tetramer. The $J_1$ and $J_2$ values are listed in Table 1.

The thick red line in Fig. 4 shows the $H$ dependence of the magnetization $M(H)$ of CuInVO$_5$ measured at 1.3 K. We can observe a $\frac{1}{2}$ quantum magnetization plateau above 30 T. The $g$ value was evaluated to be $2.09 \pm 0.02$ from the magnetization of the plateau.

We compare $\chi(T)$, $C(T)$, and $M(H)$ of CuInVO$_5$ with those calculated for isolated spin tetramers. The green line in Fig. 3 indicates $\chi(T)$ calculated for an isolated spin tetramer with
Figure 4. Magnetic-field dependence of the magnetization of CuInVO$_5$ (thick red line) at 1.3 K. Blue and green lines indicate the magnetization calculated for the interacting spin-$\frac{1}{2}$ tetramer model in Fig. 1(b) and for an isolated spin-$\frac{1}{2}$ tetramer. The labels w/$J_{\text{eff}}$ and w/o$J_{\text{eff}}$ mean the calculated $M(H)$ containing $J_{\text{eff}}$ and non-containing $J_{\text{eff}}$, respectively. The values of the exchange interactions are listed in Table 1.

Table 1. Values of exchange interaction parameters and $g$ value.

| $J_1$ (K) | $J_2$ (K) | $J_{\text{eff}}$ (K) | $g$          |
|-----------|-----------|----------------------|--------------|
| 240 ± 20  | −142 ± 10 | 30 ± 4               | 2.09 ± 0.02  |

$J_1 = 240$ and $J_2 = −142$ K. The $J_1$ and $J_2$ values are listed in Table 1. The agreement between the experimental and calculated $\chi(T)$ is nearly perfect above 30 K, whereas a discrepancy is seen below 30 K. The green line in Fig. 2 indicates $C(T)$ calculated for the same isolated spin tetramer. The positions of the broad maximum in the experimental and calculated $C(T)$ are close to each other. However, the specific heat around the broad maximum is larger in the calculated result. The green line in Fig. 4 indicates $M(H)$ calculated for the same isolated spin tetramer. The isolated spin tetramer model fails to reproduce the experimental $M(H)$ at 1.3 K. We could not find a set of exchange parameters that reproduced the experimental $M(H)$ at 1.3 K and $C(T)$ at low T on the basis of an isolated tetramer.

We assumed intertetramer interactions between Cu2 spins as shown in Fig. 1(b) because the magnetization of Cu2 spins was expected to be large. The most dominant interaction is the $J_1$ interaction. The spin state of Cu1 spins is similar to the singlet state in AF dimers [18, 19, 20]. Therefore, the magnetization of Cu1 spins is small at low T. The two Cu2 spins in a tetramer are weakly and antiferromagnetically coupled to each other through a Cu1-Cu1 dimer in the same tetramer. Thus, the magnetization of Cu2 spins is large. Mean-field theories become less valid for calculation of susceptibility when the temperature approaches $T_N$ owing to strong fluctuations. At low T, on the contrary, the ordered moment becomes substantial and the fluctuations are suppressed. Mean-field theories are reliable for $M(H)$. The blue line in Fig. 4 indicates $M(H)$ calculated for the interacting spin tetramer with $J_1 = 240$, $J_2 = −142$, and $J_{\text{eff}} = 30$ K using the tetramer mean-field theory. The experimental and calculated magnetizations are in agreement with each other. Intertetramer interactions have a greater effect on the magnetization at lower T. Therefore, the discrepancy between the experimental results and those calculated for the isolated spin tetramer appears at low T. We evaluated $T_N = 8.7$ K for the same model using the tetramer mean-field theory. The $T_N$ value is larger than the experimental $T_N$ (2.7 K). The difference is mainly caused by fluctuations that mean-field theories cannot treat properly. We will determine the magnetic structure. We will consider which intertetramer interactions are effective to stabilize the magnetic structure. We will calculate the magnetic susceptibility of a
more realistic model using quantum Monte Carlo techniques.

We roughly estimated the errors of the $J_1$, $J_2$, $J_{\text{eff}}$, and $g$ values and listed them in Table 1. A discrepancy between the experimental and calculated $\chi(T)$ appears around 80 K when $J_1$ deviates from 240 K. The experimental and calculated $\chi(T)$ are not in agreement with each other when $J_1 = 220$ or 260 K. A discrepancy between the experimental and calculated $\chi(T)$ appears around 11 K when $J_2$ deviates from -142 K. The peak heights of the experimental and calculated $\chi(T)$ are not in agreement with each other when $J_2 = -132$ or -152 K. The magnetic field at which the $\frac{1}{2}$ magnetization plateau appears increases with increasing $J_{\text{eff}}$. We roughly estimated the error of $J_{\text{eff}}$ to be $\pm 4$ K. The error of the magnetization of the plateau is less than 1 %. We estimated the error of $g$ to be 0.02.

We consider that the probable spin model for CuInVO$_5$ is an interacting spin-$\frac{1}{2}$ tetramer model. This cuprate may be useful for studying the L mode under the atmospheric pressure. We can investigate the L mode by measuring a longitudinal or scalar susceptibility. It is difficult to observe the L mode in a longitudinal susceptibility that INS probes [21], because the longitudinal susceptibility exhibits an infrared singularity, which can obscure an amplitude peak at a finite energy. The L mode can be well-defined in terms of a scalar susceptibility, because the scalar susceptibility can display a sharp amplitude peak [21]. In magnetic systems, Raman spectra can measure the scalar susceptibility. One-magnon Raman scattering indicating L-mode magnetic excitations was actually observed in the pressure-induced ordered state of KCuCl$_3$ [10, 9] and in the magnetic-field-induced ordered state of TiCuCl$_3$ [5]. We intend to form single crystals of CuInVO$_5$ and perform Raman scattering experiments on them.

4. Conclusion

We measured the temperature dependence of the magnetic susceptibility and specific heat and the magnetic-field dependence of the magnetization of CuInVO$_5$. An antiferromagnetically ordered state appears below $T_K = 2.7$ K. We observed a $\frac{1}{2}$ quantum magnetization plateau above 30 T at 1.3 K. An isolated antiferromagnetic spin-$\frac{1}{2}$ tetramer model with $J_1 = 240$ and $J_2 = -142$ K can account for the magnetic susceptibility above 30 K. The magnetization curves can be explained using the interacting spin tetramer model with the effective intertetramer interaction $J_{\text{eff}} = 30$ K. The probable spin model for CuInVO$_5$ is an interacting spin-$\frac{1}{2}$ tetramer model. Longitudinal-mode magnetic excitations may be observable in CuInVO$_5$.

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