New category of the frustrated quantum magnets composed of spin-1/2 triple-chains

Masashi Fujisawa¹, Hikomitsu KikuchiA, Yutaka FujiiB, Seitaro MitsudoB, Akira MatsuoC, Koichi KindoC

Headquarters for the Advancement of High Priority Research, University of Fukui, Fukui 910-8507, Japan
ADepartment of Applied Physics, University of Fukui, Fukui 910-8507, Japan
BResearch Center for Development of Far-Infrared Region, University of Fukui, Fukui 910-8507, Japan
CInstitute for Solid State Physics, Univ. of Tokyo, Kashiwa, Chiba 277-8581, Japan
E-mail: fujisawa.m.ad@m.titech.ac.jp

Abstract. Cu₃(OH)₄MO₄, which is a natural mineral szenicsite, has been studied by the magnetic susceptibility, the specific heat, and the high field magnetization measurement. This compound consists of S =1/2 triple-chain of the edge-sharing octahedra CuO₆. On the basis of the crystal structure in szenicsite, spin frustration can strongly affect the ground state. The magnetic susceptibility has a broad maximum around 80 K, which is characteristic of the quasi-one-dimensional antiferromagnet. There are no sign of magnetic phase transitions from 300 K down to 2 K in our measurements. The magnetization curve measurement up to 48 T at 1.3 K indicates that neither magnetic order nor spin gap is present. Assuming the triple-chains as the isolated uniform chains, we estimated the dominant exchange interaction J/k_B = −66 K.

1. Introduction
Spin frustration is one of big issues in the solid state physics. Recently much attention has been paid to peculiar magnetic properties of a new category of frustrated quantum magnets, spin-1/2 triple-chains. Antlerite (Cu₃(OH)₄SO₄) [1, 2, 3, 4] and szenicsite (Cu₃(OH)₄MoO₄)[5] are candidates for spin-1/2 triple-chains. Figure 1(a) and (b) show the exchange interactions of triple-chains which represent antlerite and szenicsite, respectively. Because triple-chains include competing interactions, spin frustration can strongly affect their ground state.

In antlerite, the magnetic susceptibility above 40 K follows the Curie-Weiss law with the Weiss temperature θ = 1.69 K. The magnetic susceptibility has broad maximum at 6.5 K, which is characteristic of quasi-one-dimensional antiferromagnet. Antlerite has a magnetic phase transition at T_N = 5 K observed by magnetic susceptibility and specific heat measurement[1, 2]. The anomalous spin state, which is called “idle-spin”, is realized at low temperature in antlerite [1, 3].

Natural mineral szenicsite is also a model substance of an S = 1/2 triple-chain system. The crystal structure of szenicsite belongs to orthorhombic, space group Pnma with a= 8.5201(8) Å, b = 12.545(1) Å, and c = 6.0794(6) Å. Figure 2(a) shows the crystal structure of szenicsite.
The Cu\textsuperscript{2+} triple-chains are separated from each chains by MoO\textsubscript{4} tetrahedra. Edge-sharing CuO\textsubscript{6} octahedra form one-dimensional chain of Cu\textsuperscript{2+} ions, and these three chains form $S = 1/2$ triple-chains along c-axis. From the crystal structure of szenicsite, we can expect than the hole orbitals $d(x^2 - y^2)$ lie in a shaded square, and are linked together along the chain, as shown in Fig. 2 (b).

No magnetic properties of szenicsite have yet been reported. As shown in Figs. 1 (a) and (b), the symmetry of exchange interactions in szenicsite is different from that of antlerite. Therefore novel magnetic properties are expected. In order to investigate the magnetic properties of szenicsite, we have performed the magnetic susceptibility, the high field magnetization and the specific heat measurements.

![Exchange interactions for (a) antlerite, (b) szenicsite, (c) a uniform chain and alternating chains, and (d) three uniform chains.](image)

**Figure 1.** Exchange interactions for (a) antlerite, (b) szenicsite, (c) a uniform chain and alternating chains, and (d) three uniform chains.

**2. Experiment**

The natural mineral of szenicsite, which was purchased at a stone shop, was used for the measurements because it is difficult to synthesize this compound. The magnetic susceptibility were measured down to 1.9 K at $H = 0.1$ T using a SQUID magnetometer (Quantum Design MPMS XL). The high-field magnetization measurement was performed using an induction method with a multilayer pulse magnet at the Ultra-High Magnetic Field Laboratory, Institute for Solid State Physics, the University of Tokyo. The specific heat measurement was carried out down to 1.9 K using a Quantum Design PPMS by the relaxation method.

**3. Results and Discussion**

Figure 3 shows the temperature dependence of magnetic susceptibility of szenicsite measured at $H = 0.1$ T. Above 200 K, the susceptibility can be fitted to the Curie-Weiss law $\chi(T) = C/(T - \theta)$, where $C$ is Curie constant and $\theta$ is Weiss temperature. The Curie-Weiss fit leads to Weiss temperature $\theta = -70 \pm 5$ K. Therefore the main exchange interactions are antiferromagnetic in szenicsite.

The magnetic susceptibility has a broad maximum around $T_{\text{max}} = 80$ K, which indicates that szenicsite can be classified as quasi-one-dimensional antiferromagnets. The rapid increase of the magnetic susceptibility below 30 K results from a paramagnetic impurity contribution.
Figure 2. (a) Crystal Structure viewed along the c-axis in szenicsite. The triple-chains are located at the corner and the center of the chemical unit cell in the a − b plane. (b) A triple-chain structure of Cu$^{2+}$ in szenicsite. The hole orbitals \(d(x^2 - y^2)\) of Cu$^{2+}$ ions lie in shaded square.

Figure 3. Temperature dependence of magnetic susceptibility in szenicsite measured at \(H = 0.1 \text{ T}\). Open circles, solid, dashed, and dashed-and-dotted lines denote the experimental data, the calculation of uniform chain model \((J/k_B = -66 \text{ K})\), the calculation of paramagnetic impurity, and the calculation of uniform chain and paramagnetic impurity, respectively.

Figure 4. Magnetization curve in szenicsite measured at \(T = 1.3 \text{ K}\). Solid line, dashed line, dotted line, and dashed-and-dotted line denote the experimental data, the calculation of paramagnetic impurity, the calculation of linear term, and the calculation of paramagnetic impurity and linear term, respectively.

because the magnetic susceptibility below 20 K is described by \(\chi_{\text{imp}} \propto 1/T\). Magnetic phase transition is not observed from \(T = 300 \text{ K}\) to 2.0 K. The absence of magnetic order and the broad maximum of magnetic susceptibility can prove the low dimensionality of szenicsite.

Figure 4 shows the high-field magnetization process measured at 1.3 K in magnetic field
of up to 48 T. The magnetization smoothly increased as the field was increased. Below 7 T, the magnetization due to paramagnetic impurities, which is described by Brillouin function, is dominant. The intrinsic magnetization, which is given by subtraction of the impurity contribution from the raw data, has linear dependence on the magnetic field. From these results, the experimental magnetization can be reproduced by,

\[ M(H) \propto \frac{N_{\text{imp}} g \mu_B}{2} \tanh \left( \frac{g \mu_B H}{2 k_B T} \right) + aH, \tag{1} \]

where \( a \) and \( N_{\text{imp}} \) are constant and the number of paramagnetic impurity, respectively. The experimental data agree well the calculation as shown in Fig. 4. Even if this system has spin gap, the magnitude of the gap is negligible.

Figure 5 shows the total specific heat in szenicsite. There are no anomalies in the measured range. Magnetic phase transition is not observed above 2.0 K. This result is consistent with that of magnetic susceptibility. On the other hand, the specific heat of antlerite has the \( \lambda \) like anomaly, which indicates magnetic phase transition\[2\].

Even though the crystal structure of szenicsite is similar to that of antlerite, the magnetic properties of szenicsite are considerably different compared to those of antlerite. From the experimental results, the exchange interactions between the triple-chains via MoO\(_4\) octahedra is negligible and the absolute value of the dominant exchange interactions in szenicsite are expected to be large compared to that in antlerite.

It is difficult to analyze the magnetic properties of szenicsite without simplification because the triple-chains of szenicsite has the five different exchange interactions. We tried to reproduce the temperature dependence of magnetic susceptibility by employing a simple and reasonable model. In order to analyze the magnetic susceptibility, we let us take assumptions on the basis of crystal structure.

Table 1 shows the distance between Cu-Cu and the angle between Cu-O-Cu in the exchange interactions \( J_i \) (\( i = 1, 2, 3, 4, 5 \)) in szenicsite. The Cu-O-Cu angles in szenicsite are from 99.4° to 104.9°. Hase et al. reported that the exchange interaction between the coppers is antiferromagnetic if the Cu-O-Cu angles are larger than 97° in the exchange pass of Cu-O-Cu[6]. Therefore the exchange interactions \( J_i \) (\( i = 1, 2, 3, 4, 5 \)) of szenicsite are supposed to be antiferromagnetic.

![Figure 5. Total specific heat in szenicsite measured at zero field.](image)
Table 1. Cu-Cu distance and Cu-O-Cu angle for $J_i$.

| $J_i$ | Cu-Cu distance (˚A) | Cu-O-Cu angle (°) |
|-------|----------------------|-------------------|
| $J_1$ | 3.034                | 103.6             |
| $J_2$ | 3.046                | 104.9             |
| $J_3$ | 3.211                | 103.8             |
| $J_4$ | 3.213                | 104.2             |
| $J_5$ | 3.040                | 99.4              |

The magnitude of the exchange interaction $J_3$ can be close to that of $J_4$ because the Cu-O-Cu angle and the Cu-Cu distance in $J_3$ are close to those in $J_4$. And we suppose the magnitude of $J_3$ and $J_4$ is smaller than $J_1, J_2,$ and $J_5$ because the distances of Cu-Cu in $J_3$ or $J_4$ are larger than those of $J_1, J_2,$ and $J_5$.

In addition, geometrical spin frustration can affect the magnetic properties of szenicite because the network of the exchange interactions in the triple-chains are composed of triangle units and each of the exchange interactions is antiferromagnetic. Therefore the effect of $J_3$ and $J_4$ can be canceled out. If we ignore the effect of zig-zag rung exchange interactions $J_3$ and $J_4$, we can regard the network of the exchange interactions in szenicite (as shown in Fig. 1 (b)) as a simple network composed of both a uniform chain and two alternating chains (as shown in Fig. 1 (c)).

Furthermore the magnitude of $J_1$ can be close to $J_2$ because the Cu-O-Cu angle and the Cu-Cu distance in $J_1$ are close to those in $J_2$. Generally a ground state of alternating spin chain is singlet. However if the alternation parameter $\alpha = J'/J$ is close to 1, the temperature dependence of the magnetic susceptibility is similar to that of the uniform chain except for very low temperatures ($T << J/k_B$)[7]. Because the distances between Cu-Cu of $J_1, J_2$ and $J_5$ are close to each other, we would assume $J_1 = J_2 = J_5 = J$ as shown in Fig. 1(d).

The magnetic susceptibility of $S = 1/2$ antiferromagnetic uniform chain is calculated[8, 9]. Figure 3 shows the reproduction of temperature dependence of magnetic susceptibility by using uniform chain term and impurity term. By comparing the calculation and the experimental data, we estimated the exchange interaction $J/k_B = -66$ K. The discrepancy between experimental data and calculation below 70 K is attributed to oversimplification of our model.

4. Conclusion
We have performed the magnetic susceptibility, the specific heat, and the high field magnetization measurements on the $S = 1/2$ triple-chain antiferromagnet szenicite (Cu$_3$(OH)$_4$MO$_4$). The magnetic susceptibility exhibits broad maximum around 80 K, which is characteristic of the one-dimensional antiferromagnet. Specific heat data from $T = 2.0$ K to 300 K indicate no magnetic phase transition. High field magnetization process up to 48 T at 1.3 K has revealed that szenicite has neither magnetic phase transition and nor spin gap. Even though the framework of exchange interactions in szenicite is similar to that of antlerite, the magnetic properties of szenicite are fairly different from those of antlerite. The magnetic properties of szenicite can be described by the $S = 1/2$ triple-chain model with the exchange interactions along the leg ($J_1, J_2$ in outer alternating chains and $J_3$ in center uniform chain) and the zig-zag diagonal exchange interactions ($J_3$ and $J_4$). We reproduced the temperature dependence of magnetic susceptibility by using the simple model, in which the exchange interactions $J_i$ were satisfied with the following relations from the crystal structural point of view: $J_1 = J_2 = J_5 = J \neq 0$ and $J_3 = J_4 = 0$. We estimated the dominant exchange interaction $J/k_B = -66$ K.
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