Spin gapped behavior of a frustrated delta chain compound euchroite

Hikomitsu Kikuchi, Yutaka Fujii¹, Daisuke Takahashi, Masaki Azuma², 5, Yuichi Shimakawa², Toshifumi Taniguchi³, Akira Matsuo⁴, Koichi Kindo⁴
Department of Applied Physics, University of Fukui, Fukui, Japan
¹Research Center for Development of FIR, University of Fukui, Fukui, Japan.
²Institute for Chemical Research, Kyoto University, Kyoto, Japan.
³Graduate School of Science, Osaka University, Toyonaka, Japan.
⁴Institute for Solid State Physics, University of Tokyo, Kashiwa, Japan.
E-mail: kikuchi@apphy.u-fukui.ac.jp

Abstract. We find Cu²⁺(AsO₄)(OH)·3H₂O (euchroite) is a model compound for the frustrated delta chain which is composed of corner-sharing triangles. Magnetic susceptibility, specific heat, high field magnetization and ¹H-NMR measurements are carried out using natural mineral samples of euchroite to study magnetic properties. Large spin gap of about 100 K are shown to be presented in this compound.

1. Introduction
Quantum one-dimensional (1D) Heisenberg antiferromagnet (HAF) has attracted much interest because of its large quantum fluctuations. New phenomena such as quantum phase transition are expected to occur if a geometrical frustration effect is introduced into the quantum 1D HAF. Delta chain spin model is one of the frustrated 1D quantum spin systems, in which corner-sharing triangles run along 1D chain direction. Theoretical studies revealed that the delta chain system composed of regular triangle has a spin gap δE ≈ 0.22J, where J is an exchange coupling constant[1]. Specific heat is expected to have characteristic double peaks, and the peak at lower temperature is discussed in terms of kink-antikink soliton like excitations. Theoretical works on more general delta chain, which is composed of scalene triangles, were developed. Nakamura and his cowoker studied the delta chain with bond dimerization where one of the oblique bond is dimerized [2]. They show that the double peak structure of the specific heat is taken over by single peak structure as increasing a degree of dimerization. A case where one of the exchange coupling is ferromagnetic is studied by Hida [3] and the ground state phase diagram is revealed to be divided into Haldane, ferromagnetic and ferrimagnetic phases. A few compounds which approximate the delta chain spin model have been found and their magnetic properties were investigated. The first example of the delta chain is YCuO₂₅ in which large spin gap of about 650 K was found by NMR relaxation rate measurement [4]. However, some additional exchange interactions besides original delta chain interactions were found to need to explain experimental data of YCuO₂₅ [5]. [Cu(bpy)(H₂O)][Cu(bpy)(mal)·(H₂O)][ClO₄]₂ is a ferro-antiferromagnetic

⁵ Present address : Materials and Structures Laboratory, Tokyo Institute of Technology, Tokyo, Japan.
delta chain whose ground state is ferrimagnetic without the spin gap [6]. These compounds thus are insufficient to be a representative compound for the delta chain. New material for the quantum delta chain is needed to investigate the properties of this spin model.

Recently, we found that Cu$^{2+}$ ($S = 1/2$) ions in Cu$_2$(AsO$_4$)(OH)-3H$_2$O (mineral name, euchroite) can be treated as the delta chain. The crystallographic structure of euchroite is orthorhombic, space group P2$_1$2$_1$2$_1$, $a = 10.07$ Å, $b = 10.52$ Å, $c = 6.11$ Å[7]. Its structure is shown in Fig. 1 (a). Magnetic Cu$^{2+}$ ions are surrounded by six oxygen ions and exchange coupling between Cu$^{2+}$ takes place through two oxygen ions. Cu$^{2+}$ ions in euchroite form delta chain running parallel to crysytallographic c axis as schematically shown in Fig. 1 (b). Delta chains are well separated by AsO$_4^-$ ion groups. Bond lengths between Cu$^{2+}$ in a unit triangle are different from each other (3.01, 3.06 and 3.17 Å), but their difference is within the range of several percent and not so large. Because no magnetic properties of euchroite have been reported so far, we carried out magnetic susceptibility, specific heat, high field magnetization and $^1$H-NMR measurements using a natural mineral polycrystalline samples to study the magnetic properties, especially the spin gap behavior, of euchroite.

![Figure 1.](image)

**Figure 1.** (a) Structure of euchroite, (b) schematic view of the delta chain.

2. Experiments

Polycrystalline natural mineral samples of euchroite were purchased at a mineral shop. Sample quality was checked using powder X-ray diffraction. Impurity peaks were not observed. Magnetic susceptibility was measured using SQUID magnetometer (Quantum Design) from 2 to 350 K with an applied field of 100 Oe. Specific heat was measured using PPMS (Quantum Design) by relaxation method from 2 to 200 K. The high field magnetization curve was measured up to about 55 T using a pulsed magnet at Ultra High Magnetic Field Laboratory, Institute for Solid State Physics, University of Tokyo. $^1$H-NMR spectra and spin-lattice relaxation rate $T_{1}^{-1}$ were measured using a conventional pulsed NMR apparatus down to 1.4 K.

3. Results and Discussion

Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ measured at applied field of 100 Oe. $\chi(T)$ shows round peak at around 85 K, characteristic of low dimensional
Figure 2. Temperature dependence of magnetic susceptibility of polycrystalline euchroite. The solid line is a fitting curve of eq. (1) to the experimental data, with $J/k_B=135$ K and $g=2.25$.

Figure 3. Temperature dependence of specific heat of polycrystalline euchroite.

antiferromagnet, and decreases toward zero at low temperature, indicating the presence of a spin gap. Fitting to Curie-Weiss law ($\chi = C/(T - \Theta)$) in higher temperature range ($>150$ K) gives $\Theta \approx -50$ K and $C = 0.51$ emu K/mol. The negative Weiss temperature indicates dominant exchange coupling of euchroite is antiferromagnetic. Curie-like upturn observed in the lowest temperatures originates in very small amount ($\sim 0.5\%$) of magnetic impurities.

There is no theoretical calculation of magnetic susceptibility for the general delta chain whose
exchange couplings are different from each other. At first, we try to explain experimental data with a theoretical curve [4] for the delta chain whose all exchange couplings have same value but result was not good. This failure is expected because exchange constants of euchroite $J_1, J_2$ and $J_3$ must have different values each other. Next, we tentatively tried a simple equation (1) for a isolated $S = 1/2$ spin dimer system.

\[
\chi_{\text{dimer}} = \frac{2Ng^2\mu_B^2}{k_B(T+\exp(J/k_BT))},
\]  

(1)

where $N$ is Avogadro number, $g$ is Lande's g-factor, $\mu_B$ is Bohr magneton, $k_B$ is Boltzmann constant and $J$ is exchange coupling between $S = 1/2$ spins. As shown in Fig. 2, eq. (1) with $J/k_B = 135$ K and $g = 2.25$ reproduce fairly well the observed data. This result suggests that the ground state of euchroite is in a dimer phase [2]. Theoretical calculation of $\chi(T)$ of the general delta chain is desired to determine exchange constants quantitatively.

Figure 3 shows temperature dependence of the specific heat $C(T)$ of euchroite. The lattice contribution is included in these data because nonmagnetic isostructural compound is not known. No sign of the magnetic long range ordering is observed. A broad peak is observed at around 80 K. Reminding that $\chi(T)$ data also show maximum at this temperature, it is natural to think that the broad peak in $C(T)$ originates in the magnetism.

Figure 4 shows the high field magnetization ($M$ vs $H$) curve of euchroite obtained at 1.3 and 4.2 K. Lower field magnetization is due to the magnetic impurities and their concentration is consistent with that obtained from $\chi(T)$ data. An abrupt increase of the magnetization is observed above about 40 T. This behavior clearly indicates the presence of finite spin gap. As increasing magnetic field, the first excited magnetic energy crosses the nonmagnetic ground state at certain critical field $H_c$ and the magnetization appears. It is rather difficult experimentally to point out the accurate $H_c$. If we define $H_c$ as the field where the magnetization starts to increase, $H_c$ is approximately determined to be 40 T. The energy level $\Delta_M$ of the excited state can be roughly estimated from $H_c$ to be $\Delta_M = (g\mu_BH_c)/k_B = 56$ K. The magnetization tends to saturate at 50 T, suggesting that a magnetization plateau begins at about 50 T. Since full
saturation magnetization $M_{sat}$ per formula weight of euchroite is about $2 \mu_B$, the magnetization of this plateau will be about $1/40$ of $M_{sat}$. To investigate detail of the new plateau, we need higher magnetic field, which is beyond our accessible field.

$$T_1^{-1}(S^{-1})$$

$1/T$ (K$^{-1}$)

![Figure 5](image)

Figure 5. Temperature dependence of spin-lattice relaxation rate $T_1^{-1}$ of $^1$H-NMR of euchroite measured at several magnetic fields. Fitting curves are calculated using eq. (3).

In order to investigate microscopic properties of euchroite, we measured $^1$H-NMR. Figure 5 shows the temperature dependence of $T_1^{-1}$ of euchroite. As decreasing temperature $T_1^{-1}$ decreases exponentially as expected for the spin gapped system. $T_1^{-1}$ above about 10 K is well fitted with the Arrhenius-type equation $T_1^{-1} \sim \exp(-\Delta/k_B T)$ with an activation energy $\approx 70$ K. As further decreasing temperature, unexpected behavior is observed that $T_1^{-1}$ shows anomalous peak which shift toward lower temperatures as resonance frequency decreases. Similar behavior was reported for the $S=1$ 1D antiferromagnet with the Haldane gap and was successfully explained by applying a general theory for the nuclear magnetic relaxation in nonmagnetic solid including paramagnetic impurities [8]. Taking into accounts of an effect of spin diffusion from the magnetic impurities to nuclear spin, following relation was derived as an impurity-induced part of the spin-lattice relaxation rate

$$T_1^{-1} \sim c_e \left( \frac{\tau_e}{1 + \tau^2_e \omega^2 N} \right)^{1/4},$$

where $c_e$ is impurity concentration, $\tau_e$ is the relaxation time of the impurity electron spin, $\omega_N$ is NMR angular frequency [8, 9].

If this relation is applicable to our system, temperature dependence of $T_1^{-1}$ in whole temperature region should be given as

$$T_1^{-1} = A c_e \left( \frac{\tau_e}{1 + \tau^2_e \omega^2 N} \right)^{1/4} + B \exp(-\Delta_0/k_B T),$$

where $\Delta_0$ is a modified activation energy and $A$ and $B$ are constants. The first term of eq. (3) is impurity-induced relaxation and the second term is contribution from the bulk sample. Fitting curves with eq.(3) to the observed data measured at different applied magnetic field (i.e., at different frequency) are shown in Fig. 5. Calculated curves agree well to the experimental data. Best fit is obtained with $\Delta_0 = 95\pm5$ K. Notice that this value of $\Delta_0$ differs slightly from $\Delta$.
which was obtained without considering the effect of the impurity related relaxation. Influence of the impurity must be taken into accounts to estimate the precise value of the spin gap. The spin gap $\Delta_0 = 95\pm5$ K obtained from NMR is larger than the gap energy $\Delta_M$ determined from the high field magnetization. Considering that $\Delta_M$ is roughly half of $\Delta_0$, a new mid gap state can be present in this delta chain system.

4. Conclusion

We find Cu$_2$(AsO$_4$)(OH)·3H$_2$O (euchroite) is a model compound for the frustrated delta chain which is composed of corner-shairing triangles. Magnetic susceptibility, specific heat, high field magnetization and $^1$H-NMR measurements are carried out using natural mineral samples of euchroite to study magnetic properties. Large spin gap of about $\Delta_0 = 90\pm5$ K are shown to be presented in this compound. The presence of a new mid-gap state is suggested.

5. Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area (Grant No. 19052005) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] Kubo K 1993 Phys. Rev. B 48 10552
[2] Nakamura T and Kubo K 1996 Phys. Rev. B 53 6393
[3] Hida K 2008 J. Phys. Soc. Jpn. 77 044707
[4] Sen D, Shastry B S, Walstedt R E and Cava R 1996 Phys. Rev. B 53 6401
[5] Le Bacq O, Pasturel A, Lacroix C and Nunez-Regueiro M D 2005 Phys. Rev. B 71 014423
[6] Inagaki Y, Narumi Y, Kindo K, Kikuchi H, Kamikawa T, Kunimoto T, Okubo S, Ohta H, Saito T, Azuma M, Takano M, Nojiri H, Kaburagi M and Tonegawa T 2002 J. Phys. Soc. Jpn. 74 2831
[7] Finney J J 1966 Acta Cryst. 21 437
[8] Goto T, Satoh S, Matsumura Y and Hagiwara M 1997 Phys. Rev. B 55 2709
[9] Abragam A 1961 The Principles of Nuclear Magnetism (Oxford: Clarendon Press ) Chap. IX.