フラストレートしたデルタ鎖化合物ユークロアイトのスピンギャップ

研究報告１４

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Spin gapped behavior of a frustrated delta chain compound euchroite

Hikomitsu Kikuchi, Yutaka Fujii[1], Daisuke Takahashi, Masaki Azuma[2,*], Yuichi Shimakawa[2], Toshifumi Taniguchi[3], Akira Matsuo[4] and Koichi Kindo[4]

Department of Applied Physics, University of Fukui, Fukui 910-8507, Japan

[1]*Research Center for Development of Far Infrared Region, University of Fukui, Fukui 910-8507, Japan*

[2]*Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan*

[3]*Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

[4]*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

Abstract

We find $Cu_2(AsO_4)(OH)\cdot 3H_2O$ (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 ^{1}H-NMR measurements are carried out using natural mineral samples of euchroite to study magnetic properties. Large spin gap of about 100 K is shown to be presented in this compound.

[*]Present address: Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, Japan.

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 $\delta E \approx 0.22J$, 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 $YCuO_{2.5}$ 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 $YCuO_{2.5}$ [5]. $[Cu(bpy)(H_2O)][Cu(bpy)(mal)\text{-}(H_2O)](ClO_4)_2$ is a ferro-antiferromagnetic 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 $Cu_2(AsO_4)(OH)\cdot 3H_2O$ (mineral name, euchroite) can be treated as the delta chain. The crystallographic structure of euchroite is orthorombic, space group $P2_12_12_1$, 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 crsytallographic c axis as schematically shown in Fig. 1 (b). Delta chains are well separated by AsO_4^{3-} 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,

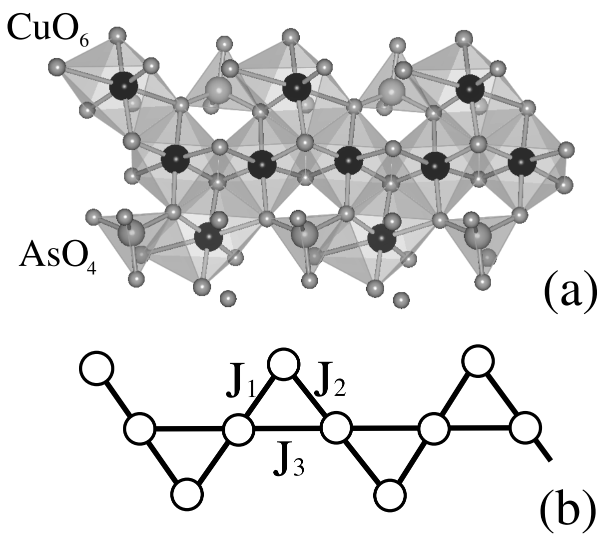

Fig. 1: (a) Structure of euchroite, (b) schematic view of the delta chain.

especially the spin gap behavior, of euchroite.

1. 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.

2. 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 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

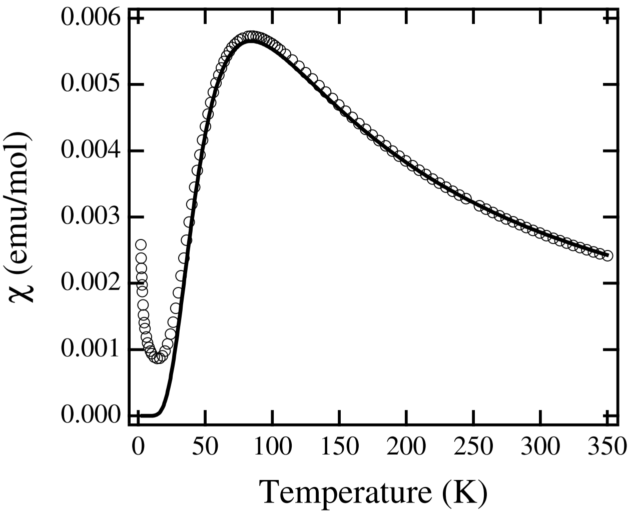

Fig. 2: Temperature dependence of magnetic susceptibility of polycrystalline euchroite. The solid line is a fitting curve of eq. (1) to the experimental data, with J/k_B=135 K and g =2.25.

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 an isolated $S = 1/2$ spin dimer system.

$$\chi_{dimer} = \frac{2Ng^2\mu_{\rm B}^2}{k_BT(3+\exp(J/k_{\rm B}T)}, \tag{1}$$

where N is Avogadro number, g is Lande's g-factor, $\mu_{\rm B}$ is Bohr magneton, $k_{\rm B}$ is Boltzmann constant and J is exchange coupling between $S = 1/2$ spins. As shown in Fig. 2, eq. (1) with $J/k_{\rm B}$ =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

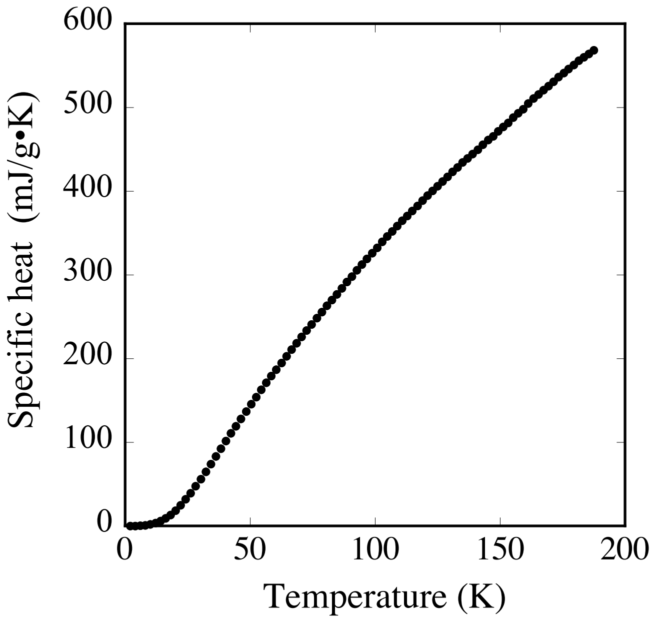

Fig. 3: Temperature dependence of specific heat of polycrystalline euchroite.

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 Δ_M of the excited state can be roughly estimated from H_c to be $\Delta_M = (g\mu_{\rm B}H_c)/k_{\rm B} = 56$ 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 $\mu_{\rm B}$, 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.

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 $T_1^{-1} \sim \exp(-\Delta/k_{\rm B}T)$ with an activation energy ≈ 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

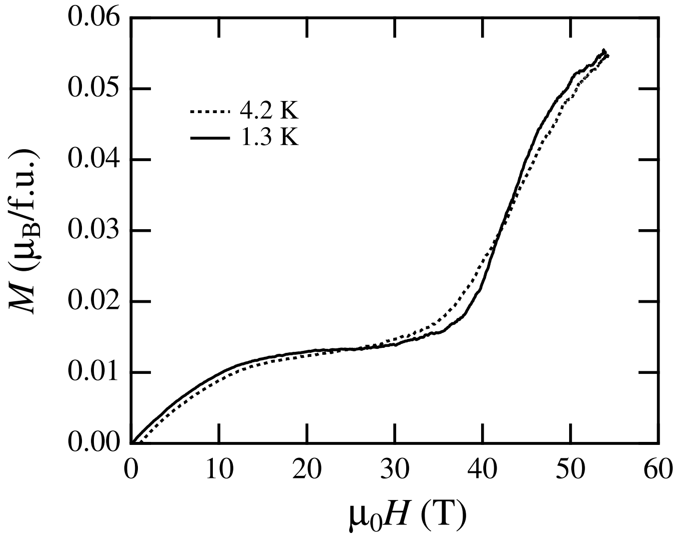

Fig. 4: High field magnetization curve of euchroite measured at 1.3 and 4.2 K up to about 55 T.

from the magnetic impurities to nuclear spin, following relation was derived as an impurity-induced part of the spin-lattice relaxation rate

$$T_1^{-1} \sim c_e \left(\frac{\tau_e}{1 + \tau_e^2 \omega_N^2} \right)^{1/4}, \tag{2}$$

where c_e is impurity concentration, τ_e is the relaxation time of the impurity electron spin, ω_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

$$T_1^{-1} = Ac_e \left(\frac{\tau_e}{1 + \tau_e^2 \omega_N^2} \right)^{1/4} + B \exp\left(-\frac{\Delta_0}{k_{\rm B}T} \right), \tag{3}$$

where Δ_0 is a modified activation energy and A and B are constants. The first term of eq. (3) is impurity-indued 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 $\Delta_0 = 95 \pm 5$ K. Notice that this value of Δ_0 differs slightly from Δ 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 $\Delta_0 = 95 \pm 5$ K obtained from NMR is larger than the gap energy Δ_M determined from the high field magnetization. Considering that Δ_M is roughly half of Δ_0, a new mid gap state can be present in this delta chain system.

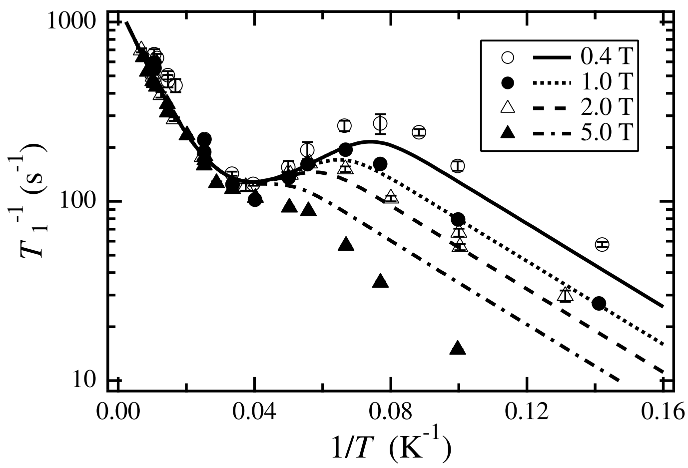

Fig. 5: Temperature dependence of spin-lattice relaxation rate T_1^{-1} of ^{1}H-NMR of euchroite measured at several magnetic fields. Fitting curves are calculated using eq. (3).

3. Conclusion

We find $Cu_2(AsO_4)(OH)\cdot 3H_2O$ (euchroite) is a model compound for the frustrated delta chain which is composed of corner-shairng 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 $\Delta_0 = 90 \pm 5$ K are shown to be presented in this compound. The presence of a new mid-gap state is suggested.

Acknowledgement

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