Dzyaloshinsky-Moriya Interaction Estimated by AFMR of Kagome Like Substance Cu$_2$O(SO$_4$) Observed at 1.8K

Naoki Takahashi$^1$, Susumu Okubo$^2$, Hitoshi Ohta$^2$, Takahiro Sakurai$^3$, Masashi Fujisawa$^4$, Hikomitu Kikuchi$^4$

$^1$Graduate School of Science, Kobe University, Kobe, Japan
$^2$Molecular Photoscience Research Center, Kobe University, Kobe, Japan
$^3$Center for Supports to Research and Education Activities, Kobe University, Kobe, Japan
$^4$Department of Applied Physics, University of Fukui, Fukui, Japan

E-mail: hohta@kobe-u.ac.jp

Abstract. Dolerophanite Cu$_2$O(SO$_4$) is one of model substances for $S = 1/2$ kagome like antiferromagnet. Although many X-ray diffraction studies have been performed on natural mineral Cu$_2$O(SO$_4$), little is known about its magnetic property. Therefore, the multi-frequency electron spin resonance (ESR) measurements of dolerophanite powder sample have been performed using pulsed magnetic fields up to 16 T in the frequency range from 50 GHz to 315 GHz in the temperature range from 1.8 K to 86 K. Antiferromagnetic resonance (AFMR) has been observed below $T_N = 20$ K, which is consistent with the previous magnetic susceptibility result by Asano et al. Moreover, the frequency-field relation at 1.8 K suggests typical easy-plane type AFMR with Dzyaloshinsky-Moriya (DM) interaction, which is also consistent with the weak ferromagnetism below $T_N$ suggested by Asano et al. As the estimation of DM interaction is very important to discuss the quantum phase transition in kagome antiferromagnet as suggested by Cépas et al. [2008, Phys. Rev. B 78 140405(R)], we have estimated the D term of DM interaction as 6.98 ± 0.01 K from our AFMR results.

1. Introduction
Low dimensional highly frustrated spin systems, such as $S = 1/2$ diamond chain antiferromagnet azurite [1,2] and $S = 1/2$ kagome lattice antiferromagnets [3-5], have attracted much interest recently. Especially $S = 1/2$ kagome lattice antiferromagnet is considered to be very important because it has stronger geometrical frustration than the well studied triangular lattice antiferromagnet. Recently herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$ [3], vorborthite Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O [4] and vesigniete BaCu$_3$V$_2$O$_8$(OH)$_2$ [5] are suggested as model substances of $S = 1/2$ kagome lattice antiferromagnet, and high-field electron spin resonance (ESR) measurements provided much information about these model substances [6-9]. Here we have studied dolerophanite Cu$_2$O(SO$_4$), which is a new model substances of $S = 1/2$ kagome like antiferromagnet, by high-field ESR.

The crystal structure of Cu$_2$O(SO$_4$) is reported as $a = 9.370$, $b = 6.319$, $c = 7.639$, $\beta = 122.34$ Å, with a space group $C2/m$ (12) [10]. The crystal structure of Cu$_2$O(SO$_4$) is shown in Fig. 1 and Fig. 2 where only Cu$^{2+}$ ions are shown for simplicity. Fig. 1 shows the structure in
the $a$-$b$ plane and it looks like a kagome lattice. However, if you look from the tilted direction as shown in Fig. 2, it consists of tetrahedrons. As kagome like layer in the $a$-$b$ plane, which consists of tetrahedrons, is well separated from other layers, dolerophanite can be considered as a quasi two dimensional system.

Only report on the magnetic property of dolerophanite is by Asano et al. [11]. The magnetic susceptibility follows the Curie-Weiss law and shows a weak ferromagnetic behavior below around $T_N = 20$ K, which is also supported by the specific heat measurement. As the obtained Weiss temperature $\theta$ is about nine times larger than $T_N$, strong geometrical spin frustration is suggested in dolerophanite [11].

2. Experimental

High-field multi-frequency ESR measurement have been performed using pulsed magnetic fields up to 16 T in the frequency range from 50 GHz to 315 GHz in the temperature range from 1.8 K to 86 K. The details of our high-field ESR system can be found in references [12-14].

$\text{Cu}_2\text{O(SO}_4\text{)}$ is synthesized by placing finely-powdered $\text{Cu(SO}_4\text{)}$·5$\text{H}_2\text{O}$ in an open porcelain crucible in a muffle furnace for one hour at a temperature about 660 °C as reported previously [15]. By this manner, orange brown powder substances of $\text{Cu}_2\text{O(SO}_4\text{)}$ is synthesized. The obtained sample is found to be a single phase of $\text{Cu}_2\text{O(SO}_4\text{)}$ by X-ray diffraction analysis and the magnetic susceptibility showed the same temperature dependence as reported previously [11].

3. Results and discussion

Temperature dependence of ESR spectra observed at 160 GHz is shown in Fig. 3 (a) where DPPH is the field marker with $g = 2.0032$. Absorption line B close to DPPH shows no change at $T_N = 20$ K and its intensity increases monotonically as the temperature decreases. The integrated intensity of absorption line B follows the Curie law suggesting the paramagnetic behavior even below $T_N$. Moreover, as shown in Fig. 4, which shows the frequency field relation of absorption, the line B at 1.8 K crosses linearly the origin, suggesting the paramagnetic behavior. Therefore, we think that the absorption line B is coming from the impurity or the lattice defect in the sample. On the other hand, the absorption line A appears below $T_N$ and shifts to lower field as the temperature decreases. These are typical behavior of antiferromagnetic
Before going into the analysis of AFMR, we will discuss the Dzyaloshinsky-Moriya (DM) interaction, $H = D S_1 \times S_2$, in Cu$_2$O(SO$_4$) in terms of the crystal symmetry. From the crystal structure (Fig. 1 and Fig. 2), the inversion symmetry exists between Cu dimers along the $c$-direction. Therefore, no DM interaction is expected for these Cu dimers. On the other hand, Cu dimers in the $a$-$b$ plane, which form sides of hexagon in Fig. 1, have mirror planes perpendicular to the midpoint of the side of hexagon. In this case, the D-vector exists in the mirror plane from the Moriya’s rules of DM interaction [16]. Therefore, the DM interaction exists from the symmetry consideration and it will be the origin of the weak ferromagnetism observed in the magnetic susceptibility of Cu$_2$O(SO$_4$).

Next we will discuss about the analysis of AFMR. Curved frequency-field relation of absorption line A in Fig. 4 is the typical easy-plane type AFMR with the DM interaction observed in case of MnCO$_3$ which shows the weak ferromagnetism [17]. Easy-plane type AFMR with DM interaction can be described by
\[
(\omega/\gamma)^2 = H_m(H_m + H_{\text{DM}}) + 2H_EH_A
\]
where $\omega$, $\gamma$, $H_m$, $H_{\text{DM}}$, $H_E$, $H_A$ are angular frequency, gyro-magnetic ratio, modified field, DM field, exchange field and anisotropy field, respectively [17]. Here we assumed $g = 2$ for the modified field because intrinsic ESR was not observed at high temperature. We obtained $H_{\text{DM}} = 5.23 \pm 0.13$ T, and $2H_EH_A = 0.72 \pm 0.07$ T$^2$ in order to interpret the frequency-field relation of absorption line A as shown by the solid line in Fig. 4. From the obtained value of $H_{\text{DM}}$, D term is calculated as $6.98 \pm 0.01$ K by using the formula
\[
D = (\mu_B/S) \cdot H_{\text{DM}}.
\]
Cépas et al. discussed the importance of DM interaction in kagome lattice [18]. The small anisotropic interactions, such as DM interaction, break the full rotation symmetry of the Heisenberg model, reduce the quantum fluctuations, and tend to induce magnetic phases at low
temperature. They show that the quantum critical point is \( D_c = 0.1 \) \( J \) (\( J \): exchange interaction) using exact diagonalizations and finite-size scaling, where the system is in a moment-free phase for \( D < D_c \), and the system develops antiferromagnetic long-range order for \( D > D_c \). As we observed AFMR and weak ferromagnetism below about 20 K in Cu\(_2\)O(SO\(_4\)), we can say that the obtained \( D = 6.98 \pm 0.01 \) K is in the region of \( D > D_c \), which limits the exchange interaction \( J < 69.8 \) K. Although Cu\(_2\)O(SO\(_4\)) is not really a kagome lattice, the estimation of exchange interaction by the neutron measurement remains as a future issue.

4. Conclusion

AFMR measurements of Cu\(_2\)O(SO\(_4\)) have been performed below \( T_N = 20 \) K using pulsed magnetic field up to 16 T in the frequency range from 50 to 315 GHz. Obtained AFMR result shows clearly the existence of DM interaction, and our analysis suggests the D term of DM interaction is \( D = 6.98 \pm 0.01 \) K. Obtained result is discussed in connection with the calculated result by Cépas et al., which suggests the quantum phase transition at \( D_c = 0.1 \) \( J \) in the kagome antiferromagnet.

4.1. Acknowledgments

This work was partly supported by a Grant-in-Aid for Scientific Research (C) No. 22540348 from the Japan Society for the Promotion of Science (JSPS) and a Grant-in-Aid for Scientific Research on Priority Area (No. 19052005 ”Novel States of Matter Induced by Frustration”) from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). One of authors (NT) would like to acknowledge the financial support from Molecular Photoscience Research Center, Kobe University.

References

[1] Kikuchi H, Fujii Y, Chiba M, Mitsudo S, Idehara T, Tonegawa T, Okamoto K, Sakai T, Kuwai T and Ohta H 2005 Phys. Rev. Lett. 94 227201
[2] Ohta H, Okubo S, Kamikawa T, Kunimoto T, Inagaki Y, Kikuchi H, Saito T, Azuma M and Takano M 2003 J. Phys. Soc. Jpn. 72 2464
[3] Shores M P, Nytko E A, Bartlett B M and Nocera D G 2005 J. Am. Chem. Soc. 127 13462
[4] Hiroi Z, Hanawa M, Kobayashi N, Nohara M, Takagi H, Kato Y and Takigawa M 2001 J. Phys. Soc. Jpn. 70 3377
[5] Okamoto Y, Yoshida H and Hiroi Z 2009 J. Phys. Soc. Jpn. 78 033701
[6] Zorko A, Nellutla S, Tol J van, Brunel L C, Bert F, Duc F, Trombe J -C, Vries M A de, Harrison A and Mendels P 2008 Phys. Rev. Lett. 101 026405
[7] Okubo S, Tomoo M, Ohta H and Kikuchi H 2009 J. Phys.: Conf. Ser. 145 012011
[8] Okubo S, Ohta H, Hazuki K, Sakurai T, Kobayashi N and Hiroi Z 2001 Physica B 294–295 75; Ohta H, Zhang W, Okubo S, Tomoo M, Fujisawa M, Yoshida H, Okamoto Y and Hiroi Z 2009 J. Phys. : Conf. Ser. 145 012010.
[9] Zhang W, Ohta H, Okubo S, Fujisawa M, Sakurai T, Okamoto Y, Yoshida H and Hiroi Z 2010 J. Phys. Soc. Jpn. 79 023708
[10] Effenberger H 1985 Monatshefte für Chemie 116 927-931
[11] Asano T, Ichimura S, Nishimura T, Wada H 2007 presented at Spring Meeting of Phys. Soc. Jpn.
[12] Motokawa M, Ohta H and Makita N 1991 Int. J. Infrared MMW 12 149
[13] Kimura S, Ohta H, Motokawa M, Mitsudo S, Jang W-J, Hasegawa M and Takei H 1996 Int. J. Infrared MMW 17 833
[14] Ohta H, Okubo S, Kawakami K, Fukuoka D, Inagaki Y, Kunimoto T and Hiroi Z 2003 J. Phys. Soc. Jpn. 72 Supplement B 26
[15] Mrose M E 1961 The American Mineralogist 46 146-154
[16] Moriya T 1960 Phys. Rev. 120 91-98
[17] Date M 1960 J. Phys. Soc. Jpn. 15 2251-2254
[18] Cépas O, Fong C M, Leung P W, Lhuillier C 2008 Phys. Rev. B 78 140405 (R)