S=1/2 Kagome Lattice Antiferromagnet
Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O Studied by High Field ESR

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Abstract. X-band and high field electron spin resonance (ESR) measurements on S=1/2 kagome lattice antiferromagnet Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O (volborthite) have been performed. Although the kagome lattice is slightly deformed in the ab plane, no sign of magnetic order is observed down to 3.8 K, which is consistent with the magnetic susceptibility and the specific heat results, because the X-band ESR result shows no g-shift and the broadening of the linewidth down to 3.8 K. However, high field ESR results above 40 GHz show continuous g-shift below 20 K, which coincides with the broad maximum in the magnetic susceptibility. These results suggest the existence of the short range order and the field dependence in the system, and they are discussed in connection with the recent magnetization result.

1. Introduction
Kagome lattice antiferromagnet has attracted much attention because it is expected to have stronger frustration than the triangular antiferromagnet. Moreover, a S=1/2 kagome lattice antiferromagnet, in which the strong quantum fluctuation is expected, is especially interesting. The spin liquid state is expected at low temperature in a S=1/2 kagome lattice antiferromagnet, and the existence of the spin gap of the order of J/20 is under discussion theoretically [1]. On the other hand, a model substance of the S=1/2 Kagome antiferromagnet is very important for the experimental study. However, not many model substance for the S=1/2 kagome lattice antiferromagnet is known. Hiroi et al. suggested previously that Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O might be the model substance for S=1/2 kagome lattice antiferromagnet [2]. Although the kagome lattice is slightly deformed in the ab plane and the magnetic susceptibility shows a peak at 22 K, no sign of long range order is observed by the specific heat measurement. However, our previous X-band (9.5 GHz) and high field ESR measurements of Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O powder sample showed an existence of the internal field below 20 K [3]. Recently Hiroi et al. have succeeded in improving the quality of Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O powder by the annealing process, and the prominent reduction of the Curie term in the low temperature region is achieved while the overall behaviors of the magnetic susceptibility and the specific heat are the same. We have performed the X-band ESR of this new powder sample and the results will be discussed.
2. Experimental

X-band (9.5 GHz) ESR measurement has been performed in the temperature region from 3.8 to 280 K using a Bruker EMX081 at Department of Frontier Research and Technology (Venture Business Laboratory) of Kobe University. High field ESR measurements have been performed in the frequency region from 40 to 315 GHz using Gunn oscillators. Pulsed magnetic fields up to 16 T are used and the observed temperature region is from 1.8 to 265 K. The details of our high field ESR system in Kobe can be found in Refs. [4-6].

Polycrystalline volborthite samples are prepared by chemical reactions between CuO and V$_2$O$_5$ in NaOH solutions. The details can be found in the reference [2]. The production is found to be a single phase of volborthite by powder X-ray diffraction and the impurity is reduced very much by the annealing process.

3. Results and discussion

Figure 1 shows the temperature dependence of ESR observed by X-band ESR measurements. Although a small impurity resonance is seen at high temperature, the main resonance, which is very broad at 280 K, becomes sharper as the temperature decreases in Fig. 1. This tendency is similar to what we observed in the previous volborthite sample [3]. However, the main resonance remains down to 3.8 K in Fig. 1, while it became broader below 10 K and disappeared below 5 K in the previous X-band ESR measurement [3]. Therefore, the low temperature behavior of X-band ESR below 10 K is affected very much by the amount of the resultant paramagnetic impurity, which appears in the low temperature magnetic susceptibility. Moreover, the linewidth is sharper for the new annealed sample (about 0.1 T at 40 K) than that of the previous sample (about 0.18 T at 40 K [3]). Figure 2 shows the temperature dependence of ESR observed at 160 GHz.
GHz. The powder pattern ESR absorption line becomes distinct as the temperature decreases, while it was not so distinct for the previous sample [3]. This implies that the intrinsic linewidth of ESR is sharper for the new annealed sample than the previous sample. In order to check this point, the powder pattern analysis of ESR [7] observed at 315 GHz and 35 K is performed as shown in Fig. 3. The obtained g-values and linewidths are $g_{||}=2.40$, $g_\perp=2.04$, $\Delta B_{||}=0.20$ T and $\Delta B_{\perp}=0.23$ T which are rather similar to the previous values of $g_{||}=2.36$, $g_\perp=2.04$, $\Delta B_{||}=0.19$ T and $\Delta B_{\perp}=0.26$ T [3]. These results suggest that the intrinsic linewidth seems to have a field dependence, and it is sharper at low frequency for the present sample but it becomes similar to the previous sample at around 315 GHz.

The shift of the resonance peak to the higher field and then to the lower field below 20 K can be also seen in Fig. 2. The temperature dependence of g-values observed at 9.5, 80, 160 and 315 GHz is summarized in Fig. 4. The temperature dependence of the g-value observed at 160 GHz is rather identical between the new annealed sample and the previous sample [3], and such increase of the g-value at low temperature is also observed in $S=3/2$ kagome lattice antiferromagnet SrCr$_8$Ga$_4$O$_{19}$ [8, 9]. On the contrary, the temperature independent g-value is observed in
our recent ESR measurement of $S=1/2$ kagome lattice antiferromagnet ZnCu$_3$(OH)$_6$Cl$_2$ [10]. Therefore, the understanding of the spin dynamics in kagome lattice antiferromagnet requires further investigation. Moreover, the $g$-shift at low temperature is larger for the lower frequency in Fig. 4, except for the X-band. This results suggest the opening of a gap in the frequency-field relation. Therefore, the frequency dependence measurements of ESR are performed at 1.8 K. The result is shown in Fig. 5, and it clearly shows the existence of a gap of about 40 GHz, which is, to our surprise, very similar to our previous result [3]. Moreover, the change of the ESR mode is observed around 2 T, which is also similar to our previous result [3]. This result may have a connection with the anomaly around 4 T observed in the recent magnetization measurement by Hiroi et al. [11]. As there is no sign of the magnetic order down to 1.8 K [11], the observed gap cannot be the antiferromagnetic gap. Two possibilities can be considered. One is the short range order suggested by the magnetic susceptibility, and the other is the spin glass like behavior induced by the magnetic impurities because such a frequency-field relation can be observed in a spin glass system [12]. Further detailed study is required to clarify this point, together with the detailed frequency dependence measurement between the X-band and 40 GHz is required because it is difficult to understand the X-band ESR result at low temperature (Fig. 1) and the existence of the gap suggested by the high frequency ESR result (Fig. 5) simultaneously.

4. Conclusion

X-band and high field ESR measurements on $S=1/2$ kagome lattice antiferromagnet Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O (volborthite) have been performed. No sign of magnetic order is observed down to 3.8 K because the X-band ESR result shows no $g$-shift and the broadening of the linewidth down to 3.8 K. However, high field ESR results above 40 GHz show continuous $g$-shift below 20 K, and the existence of the spin gap of about 40 GHz is suggested from the frequency dependence measurements at 1.8 K. Further detailed study is required to understand the difference between the X-band and high frequency results.

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