High-Field ESR Measurements of $S=1/2$ Kagome Lattice Antiferromagnet $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$

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High-field electron spin resonance (ESR) measurements have been performed on vesignieite $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$, which is considered as a nearly ideal model substance of $S=1/2$ kagome antiferromagnet, in the temperature region from 1.9 to 265 K. The frequency region is from 60 to 360 GHz and the applied pulsed magnetic field is up to 16 T. Observed $g$-value and linewidth show the increase below 20 K, which suggest the development of the short range order. Moreover, a gapless spin liquid ground state is suggested from the frequency-field relation at 1.9 K.

KEYWORDS: high-field ESR, kagome lattice, frustration, vesignieite, spin dynamics

Highly frustrated magnetism has attracted much attention recently. Especially $S=1/2$ kagome lattice antiferromagnet (KAFM) is very important because it is considered to have stronger geometrical frustration than the well studied triangular lattice antiferromagnet. Therefore, the ground state of $S=1/2$ KAFM has attracted much interest, but the theoretical studies about its ground state are still controversial. The exact diagonalization studies suggest a nonmagnetic spin liquid state with a small spin gap of the order of $J/20$, where $J$ is the nearest-neighbor exchange interaction. On the other hand, the other numerical calculation studies suggest the gapless ground state. Therefore, the experimental studies using the model substance of $S=1/2$ KAFM are really required, but a few model substances are known at present.

Suggested model substances of $S=1/2$ KAFM at present are Cu$^{2+}$ minerals, herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, volborthite $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and vesignieite $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$. Herbertsmithite has a rhombohedral structure with the space group $R3m$, and is named “structurally perfect kagome compound” because of the ideal kagome geometry of Cu$^{2+}$ ions. Although the strong antiferromagnetic exchange interaction is expected in herbertsmithite from the large negative Weiss temperature $\theta=-300$ K, no long range order is observed down to 50 mK from the specific heat measurement suggesting the existence of strong frustration in the system. However, the neutron diffraction measurement suggested that about 10% of the Cu$^{2+}$ sites in the kagome plane are substituted by Zn$^{2+}$ ions, which is also supported by the NMR measurement. The divergent magnetic susceptibility toward $T=0$ observed in herbertsmithite may be related to the existence of the impurity spins caused by these substitutions. On the other hand, no such substitution of Cu$^{2+}$ sites in the kagome plane is expected in the model substance volborthite because a mutual exchange between Cu$^{2+}$ and V$^{3+}$ ions is unfavorable in terms of the ionic radius and the Madelung energy. The existence of the strong frustration is suggested because the magnetic susceptibility shows no long range order down to 60 mK, but exhibits a tiny spin glass transition at 1.1 K in spite of the large negative Weiss temperature $\theta=-115$ K. The magnetic susceptibility shows a broad maximum at 21 K and it shows a gapless behavior suggested by a large finite value at 60 mK. Very recent magnetization measurement using the high quality polycrystalline sample revealed the magnetization steps at low temperature. However, the volborthite, which has a monoclinic structure with the space group $C2/m$, has a slightly distorted kagome lattice, where the distance between two Cu atoms are 0.303 nm (Cu1-Cu2) and 0.294 nm (Cu2-Cu2) in the corner-shared isosceles Cu1-Cu2-Cu2 triangles. Recently Okamoto et al. suggested a new model substance vesignieite. Vesignieite is a natural mineral with a monoclinic structure of the space group $C2/m$. In vesignieite Cu$^{2+}$ ions form a nearly perfect kagome lattice and no antisite disorder is expected because it does not contain ions chemically similar to Cu$^{2+}$. Strong frustration is expected because no long range order is observed down to 2 K in spite of the relatively large negative Weiss temperature $\theta=-77$ K. From the fitting of the magnetic susceptibility data at high temperature to the high temperature series expansion calculation for the $S=1/2$ KAFM, the exchange coupling and the g-factor are estimated to be $J=53$ K and $g=2.16$, respectively. At low temperature the magnetic susceptibility shows a sharp increase which suggests about 7% impurity contribution. By subtracting the contribution from the impurity, the intrinsic magnetic susceptibility shows a broad maximum around 22 K suggesting the development of the short range order. In conclusion, Okamoto et al. suggest that...
vesignieite is a nearly ideal kagome lattice compared to volborthite or herbertsmithite.

On the other hand, high-field electron spin resonance (ESR) measurement provides the information about the spin dynamics of system and the precise measure of spin gap mainly at the $\Gamma$ point. Especially the high-field ESR is a powerful means to observe the signal with the linewidth beyond 1 T.\textsuperscript{15} However, previous high-field ESR results are different among model substances, which may be reflecting the characteristic features of each substance, that is the substitution of magnetic ion or the deformation of kagome lattice. $S$=3/2 KAFM SrCr$_x$Ga$_{12-x}$O$_{19}$ ($x=8$), which has the substitution of Cr$^{3+}$ ions with Ga$^{3+}$ ions in the kagome lattice, shows the g-shift and the linewidth broadening below 80 K.\textsuperscript{16} On the other hand, $S$=1/2 KAFM herbertsmithite, which has the substitution of Cu$^{2+}$ ions with Zn$^{2+}$ ions, shows almost constant g-value and linewidth down to 1.8 K,\textsuperscript{17} while volborthite, which has a deformed kagome lattice, shows a g-shift below 20 K and its frequency-field diagram at 1.8 K shows a small gap of about 40 GHz.\textsuperscript{18} In this paper, we will show our high-field ESR results on the nearly ideal $S$=1/2 KAFM vesignieite and discuss about the possible gapless spin liquid state at low temperature.

High-field ESR has been measured using pulsed magnetic fields up to 16 T and in the frequency region from 60 to 315 GHz using Gunn oscillators and multipliers. Observed temperature region is from 1.9 to 265 K. The details of our high field ESR system can be found in Refs.\textsuperscript{15, 19, 20} A polycrystalline sample of BaCu$_6$V$_2$O$_8$(OH)$_2$ (vesignieite) was prepared by the hydrothermal method. The details of the sample preparation can be found in the reference.\textsuperscript{6} The obtained sample is found to be a single phase of vesignieite by the powder X-ray diffraction analysis and the magnetic susceptibility showed the same temperature dependence as reported previously.\textsuperscript{6}

The inset of Fig. 1 shows the typical ESR spectrum observed at 265 K and 210 GHz. Very isotropic ESR absorption line is observed in spite of the fact that the magnetic ions in vesignieite are Cu$^{2+}$ ions, which typically show an anisotropic powder pattern absorption line reflecting anisotropic g-values.\textsuperscript{21} From the crystal structure, there are three different Cu$^{2+}$ sites in vesignieite as shown in Fig. 2. Each Cu$^{2+}$ site has different principal g-values reflecting each crystal field. Therefore, the angular dependence of the ESR absorption line will be different among three Cu$^{2+}$ sites in Fig. 2 if there is no exchange interaction between Cu$^{2+}$ sites. However, as there exist strong antiferromagnetic exchange interactions between Cu$^{2+}$ sites, the ESR absorption line will be averaged out by the exchange narrowing effect.\textsuperscript{22} In order to obtain the average g-value of vesignieite at 265 K, frequency dependence measurement is performed. The resonance field of the ESR absorption line is plotted in Fig. 1 and the obtained g-value is 2.14±0.01, which is consistent with the g-value of 2.16 obtained from the analysis of the magnetic susceptibility by Okamoto \textit{et al.}.\textsuperscript{6}

Fig. 3 shows the temperature dependence of ESR spectra observed at 315 GHz. As we used different cryostats and detectors above 86 K and below 86 K,\textsuperscript{19, 20} the signal to noise ratio is different. It is clear that the resonance field shifts to lower field and the broadening of absorption line occurs at low temperature. Similar results are also obtained at 160 GHz. Temperature dependences of g-values and linewidths obtained at 160 and 315 GHz are summarized in Fig. 4 and Fig. 5, respectively. Here we should point out that the linewidth in Fig. 5 is the linewidth of powder pattern lineshape and includes also the distribution of g-value because we are dealing with the polycrystalline sample. However, these results suggest that observed ESR is intrinsic and not coming from the paramagnetic impurity observed in the low temperature magnetic susceptibility because no g-shift and no broadening of linewidth at low temperature is expected.
Fig. 3. Temperature dependence of ESR spectra observed at 315 GHz. DPPH is the standard of magnetic field.

Fig. 4. Temperature dependence of g-values observed at 160 and 315 GHz.

for the paramagnetic impurity. We think that the contribution of paramagnetic impurity is buried under the broad feature of intrinsic ESR.

Fig. 4 shows that the temperature dependences of g-values are similar for all frequencies, which suggest no sign of gap opening at low temperature, and they start to increase below around 20 K. This temperature is closely related to the temperature where the intrinsic magnetic susceptibility shows a broad maximum. Therefore, the g-shifts below around 20 K can be considered as the result of the development of short range order in vesignieite. On the other hand, the temperature dependences of the linewidths seem to show the frequency dependence. For instance, the linewidth observed at 160 GHz decreases as the temperature decreases and starts to increase below around 30 K while the linewidth observed at 315 GHz is almost constant at high temperature and it starts to increase below 30 K. The overall feature resembles the temperature dependence of linewidth in the case of one dimensional antiferromagnet discussed by Ajiro et al.24 From the standard ESR theory,25 the linewidth is related to the spin correlation function, and the linewidth is expected to increase as the spin correlation length increases irrespective of the dimensionality. Therefore, the increase of linewidth below 30 K may be also related to the development of short range order in the system. However, as the linewidth in Fig. 5 is the linewidth of powder pattern lineshape, the discussion remains as a future problem.

Fig. 6 shows the frequency dependence of ESR spectra observed at 1.9 K. As the linewidth increases at low temperature as shown in Fig. 5, the observation of ESR absorption line becomes difficult below 120 GHz. Frequency-field diagram at 1.9 K is plotted in Fig. 1 and the result suggests that vesignieite is still in the paramagnetic state at 1.9 K because it can be interpreted by the linear dependence which crosses the origin. Obtained g-value is 2.24±0.01, which is still in a reasonable value range for the paramagnetic resonance of Cu$^{2+}$ ion. The result strongly suggests that the ground state at 1.9 K is in the spin liquid like state without a gap. However, we cannot exclude the possibility of a spin gap of $J/20=2.7$ K (56 GHz) suggested from the exact diagonalization study because we are not able to observe ESR below 120 GHz (5.4 K).

Recently spin liquid like ground state in the spin frustrated system is suggested experimentally in $S=1/2$ triangular lattice antiferromagnet $\kappa$-(BEDT–TTF)$_2$Cu$_2$(CN)$_3$ by NMR.26 Although the Néel order is suggested from the exact diagonalization study of $S=1/2$ Heisenberg triangular lattice system with nearest-neighbor antiferromagnetic exchange interaction,27 it is considered that the spin liquid like
state observed in $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ may be related to the Mott-insulator physics of the system.\cite{Mambrini2000}
Therefore, an investigation of spin liquid ground state in the geometrically frustrated band insulator, not a Mott-insulator, is an another issue. Moreover, the spin gap exists or not in the spin liquid ground state is expected not only in triangular lattice antiferromagnet by Anderson.\cite{Anderson1973}
Spin liquid ground state is expected not only in triangular lattice antiferromagnet but also in $S=1/2$ KAFM because the long range order is prohibited from its strong frustration. Although the existence of a spin gap in $S=1/2$ KAFM is suggested by several theoretical calculation,\cite{Waldtmann2000, Waldtmann2002} the temperature dependences of magnetic susceptibility of herbertsmithite,\cite{Collings1997} volborthite\cite{Bert2000} and vesignieite\cite{Bert2000} do not support the existence of spin gap. In case of herbertsmithite, there is a discussion that the spin gap is zero because the system is in the quantum critical point $D_{c}=0.1J$,\cite{Hiroi2007} where $D$ is the magnitude of D vector of Dzyaloshinsky-Moriya interaction determined by high frequency ESR.\cite{Hiroi2007} However, it is difficult to believe that volborthite and vesignieite are accidentally at the same quantum critical point with zero spin gap. On the other hand, dynamical properties of herbertsmithite\cite{Collings1997} and volborthite\cite{Bert2000} observed from ESR show different behaviors. In case of herbertsmithite it shows almost constant $g$-value and linewidth down to 1.8 K.\cite{Collings1997}

They may be due to the substitution of Cu$^{2+}$ ions with Zn$^{2+}$ ions in the kagome lattice but the interpretation remains as a future issue because the $g$-shift and the linewidth broadening are observed in $S=3/2$ KAFM SrCr$_x$Ga$_{12-x}$O$_{19}$ ($x=8$) which has a similar substitution of Cr$^{3+}$ ions with Ga$^{3+}$ ions in the kagome lattice.\cite{Hiroi2007}

On the other hand, volborthite is a very clean polycrystalline system\cite{Bert2000} and it is a good model substance in that sense. Its ESR shows $g$-shift below 20 K with frequency dependence.\cite{Bert2000} The frequency dependence comes from the formation of small gap of about 40 GHz at 1.8 K. Whether the formation of gap mode is related to the small deformation in the kagome lattice is still under consideration. Therefore, as vesignieite is a nearly ideal $S=1/2$ KAFM, we suggest that ESR behaviors observed in vesignieite is the intrinsic nature of $S=1/2$ KAFM.

In summary, high-field ESR measurements have been performed on nearly ideal $S=1/2$ KAFM BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesignieite). High field ESR result in the temperature region from 1.9 to 265 K suggests the development of the short range order below 20 K. Frequency-field relation at 1.9 K strongly suggested that the ground state without a gap at 1.9 K, and the possibility of spin liquid ground state is discussed.

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\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Frequency dependence of ESR spectra observed at 1.9 K.}
\end{figure}

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