Heterogeneous spin state in the field-induced phase of volborthite as seen via $^{51}$V nuclear magnetic resonance

M. Yoshida, M. Takigawa, H. Yoshida, Y. Okamoto, and Z. Hiroi

$^1$Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
$^2$Superconducting Materials Center, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

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We report results of $^{51}$V NMR in the field-induced phase of volborthite Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O, a spin-1/2 antiferromagnet on a distorted kagome lattice. In magnetic fields above 4.5 T, two types of V sites with different spin-echo decay rates are observed. The hyperfine field at the fast decaying sites has a distribution, while it is more homogeneous at the slowly decaying sites. Our results indicate a heterogeneous state consisting of two spatially alternating Cu spin systems, one of which exhibits anomalous spin fluctuations contrasting with the other showing a conventional static order.

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Possibility of exotic quantum states in two-dimensional (2D) spin systems with frustrated interactions have attracted strong attention. In particular, the ground state of the spin-1/2 Heisenberg model with a nearest-neighbor antiferromagnetic (AF) interaction on a kagome lattice, a 2D network of corner-sharing equilateral triangles, is believed to develop no long-range magnetic order. Theories have proposed various ground states such as spin liquids with no broken symmetry with or without an excitation gap or symmetry breaking valence-bond-crystal states. Candidate materials known to date, however, depart from the ideal kagome model in some aspects, such as disorder, structural distortion, anisotropy, or longer range interactions. Effects of the Dzyaloshinsky-Moriya (DM) interaction, spatially anisotropic exchange interactions, and longer range Heisenberg interactions have been theoretically investigated.

Volborthite Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O is a layered compound, in which distorted kagome layers are formed by isosceles triangles of Cu ions carrying a spin 1/2. Consequently, there are two Cu sites, Cu1 and Cu2, and two kinds of exchange interactions, $J$ and $J''$, as shown in Fig. 1. The Cu2 sites form linear chains, which are connected through the Cu1 sites. The magnetic susceptibility $\chi$ obeys the Curie-Weiss law $\chi = C/(T + \theta_W)$ above 200 K with $\theta_W = 115$ K, exhibits a broad maximum at 20 K, and approaches a finite value at the lowest temperatures. An unusual magnetic transition has been observed near 1 K which is much lower than $\theta_W$, consistent with strong frustration in a kagome lattice. However, a recent density functional calculation proposed a ferromagnetic $J$ and a sizable AF interaction $J''$ between second neighbors along the chain as shown in Fig. 1. In this model, frustration arises from the competition between $J$ and $J''$ along the chain rather than the geometry of a kagome lattice. The appropriate spin model for volborthite has not been settled yet. Recently, anomalous sequential magnetization steps were reported in a high quality polycrystalline sample at 4.3, 25.5, and 46 T. Kaneko et al. showed a classical Heisenberg model on a spatially distorted kagome lattice exhibits a magnetization step by the Monte Carlo method. A magnetic transition in volborthite at $T^* \sim 1$ K was detected by $^{51}$V-NMR and muon spin relaxation experiments. Our previous NMR measurements revealed a sharp peak in the nuclear spin-lattice relaxation rate $1/T_1$ and onset of broadening of the NMR spectrum due to development of spontaneous moments for the magnetic field below 4.5 T. A kink was also observed in the heat capacity. Most recently, development of short range spin correlation was detected by neutron inelastic scattering. However, the low $T$ phase, which we call phase I, shows various anomalies incompatible with a conventional magnetic order. The NMR line shape is not rectangular but fits to a Lorentzian (Fig. 2b), suggesting spatial modulation of static moments. The behavior $1/T_1 \propto T$ provides evidence for dense low-energy excitations. The spin-echo decay rate $1/T_2$ is anomalously large, pointing to unusually slow spin fluctuations.

Above 4.5 T, at which the first magnetization step oc-

FIG. 1: (color online) Schematic structure of volborthite projected onto the a-b plane. The H and O sites are not shown. The V sites are located below and above the Cu kagome layers. The upper and lower V sites are related by inversion with respect to the Cu sites, hence all V sites are equivalent. See the text for the definition of various symbols.
curs, another magnetic phase appears with the different NMR line shape and dynamics. The spin state in this phase, which we call phase II, has not been well characterized yet. In this paper, we report results of $^{51}$V NMR in phase II, which revealed coexistence of two types of V sites with different $1/T_2$ and line shapes. Our results indicate that phase II exhibits a unique heterogeneous spin state, where two distinct types of Cu spins, one with non-uniform magnitude and large temporal fluctuations and the other with a more conventional static order, form a periodic structure.

$^{51}$V NMR measurements have been performed on a high-quality powder sample synthesized as described in Ref. 12. The NMR spectra were obtained by summing the Fourier transform of the spin-echo signal at equally spaced frequencies in a fixed $B$. The pulse sequence $\pi/2 - \tau - \pi/2$ was used with the pulse width of 1-3 $\mu$s and the pulse separation $\tau$ in the range of 10-150 $\mu$s. We determined $1/T_2$ by fitting the spin-echo intensity $I(\tau)$ as a function of $\tau$ to an exponential decay $I(\tau) = A_0 \exp(-2\tau/T_2)$. Likewise, $1/T_1$ was obtained by fitting the nuclear recovery curve $I(t)$, which is the spin-echo intensity as a function of the time $t$ between the saturating comb pulses and the first $\pi/2$ pulse, to the exponential function $I(t) = I_{eq} - I_0 \exp(-t/T_1)$. When this function did not fit the data due to inhomogeneous distribution of $1/T_1$, we used the stretched exponential function $I(t) = I_{eq} - I_0 \exp(-(t/T_1)\beta)$ to determine the representative value of $1/T_1$.

Figure 2(a) shows the $\tau$ dependence of the NMR spectra at 6.0 T and 0.3 K (phase II). The spectrum for $\tau = 10 \mu$s is identical to one of the spectra shown in Fig. 4(a) of Ref. 13 except that it was plotted against the shift in resonance field rather than the frequency in Ref. 13. In addition to the overall decay of the intensity with $\tau$, the line shape also changes with $\tau$. The broad peak near the center of the spectrum observed for $\tau = 10$ and 25 $\mu$s disappears for $\tau \geq 40 \mu$s. Instead the two peaks indicated by the arrows become more pronounced with increasing $\tau$. Such $\tau$ dependence indicates that the spectrum consists of two or more components characterized by different values of $1/T_2$. On the other hand, the line shape at 1 T (phase I) does not depend on $\tau$ as shown in Fig. 2(b).

We confirmed the two-component behavior in phase II by direct measurements of $1/T_2$. Figure 3 shows the spin-echo decay curves at 0.3 K measured at the center of the spectrum obtained in the field of 1, 6, and 12 T. The data at 1 T can be fit to the single exponential function, providing unique $1/T_2$. On the other hand, the data at 6 and 12 T show a convex curve, which can be well fit to the two-component exponential function

$$I(\tau) = A_f \exp(-2\tau/T_{2f}) + A_s \exp(-2\tau/T_{2s})$$

as shown by the solid lines. The fast and slowly decaying components at 6 T are shown separately by the dashed lines. The decay rate of the fast component, $1/T_{2f}$, is nearly equal to $1/T_2$ at 1 T.

![FIG. 2: (color online) NMR spectra for various values of $\tau$ at 0.3 K in the magnetic field of (a) 6 T and (b) 1.01 T. The spectra in (c) and (d) show decomposition of the NMR spectra at 0.3 K into the fast decaying (solid circles) and slowly decaying (open circles) components for the magnetic field of 6 T and 12 T.](image)

We define the two V sites showing the fast and slow decay rates as the $V_f$ and $V_s$ sites, respectively. The coefficients $A_f$ and $A_s$ in eq. (1) are proportional to the number of these sites within the frequency window covered by the exciting rf-pulse. Therefore, the decomposition of a NMR spectrum into the fast and slow components can be accomplished by measuring the spin-echo decay curve at many frequency points covering the entire spectrum and plotting $A_f$ and $A_s$ against frequency. The decomposed spectra thus obtained at 6 and 12 T are shown in Fig. 2(c) and (d). The pulse width was set to 3 $\mu$s covering about $\pm 0.1$ MHz. The two-component fit of the spin-echo decay curve was successful at all frequencies. The integrated intensities of the “fast” and “slow” spectra correspond to the total number of the $V_f$ and $V_s$ sites. For the spectra shown in Fig. 2(c) and (d), the integrated intensities of the two components are nearly equal within the experimental error, indicating equal abundance of the $V_f$ and $V_s$ sites.

The inset of Fig. 3 shows the $B$ dependence of $1/T_2$ at 0.3 K measured at the center of the spectrum. In phase I, the spin-echo decay curve can be always fit to the single exponential function. Such a clean behavior is brought by the improvement of sample quality since two-component behavior was observed even near 2 T in earlier studies. The decrease of $1/T_2$ with increasing $B$ indicates suppression of slow spin fluctuations by magnetic fields. On the other hand, $1/T_1$ is insensitive to $B$ in phase I. In phase II, the decay curve can be well fit to the two-component function (1). Both $1/T_{2f}$ and $1/T_{2s}$ slightly decreases with increasing $B$. Near the transition at 4.5 T, the two-component fit does not work well probably due to coexistence of the two phases.
curve for $\tau/T$ not depend on $\tau$ be reproduced by the exponential function and $1/T$. The exponential function for $(\text{triangles})$ together with the previous data at $1 \text{T}$ and solid triangles represent $1/T$ depend on $\tau$ on temperatures. The inset shows the $B$ dependence of $1/T_2$ at $0.3 \text{K}$. The open squares indicate $1/T_2$ in phase I. The solid and open circles represent $1/T_{2f}$ and $1/T_{2a}$ in phase II.

Figure 3: (color online) Spin-echo decay curves at $0.3 \text{K}$ in the magnetic field of $1, 6$, and $12 \text{T}$. The fast and slowly decaying components for the $6 \text{T}$ data are shown by the dashed lines. The fast and slowly decaying components of 1/T2 at $0.3 \text{K}$. The open squares indicate 1/T2 in phase I. The solid and open circles represent 1/T2 and 1/T2s in phase II.

Figure 4(a) shows the $T$ dependence of 1/T2 at $6 \text{T}$ together with the previous data at 1 T. The spin-echo decay at 1 T follows the single exponential function at all temperatures (crosses). At 6 T, the decay curve can be fit by the single exponential function for $1.5 \leq T \leq 2 \text{K}$. When 1/T2 becomes small for $T > 2.0 \text{K}$, the Gaussian contribution to the spin-echo decay due to the nuclear spin-spin coupling has to be taken into account. Then the decay curve can be fit to the “exponential + Gaussian” function $I(\tau) = A_0 \exp\{-2\tau/T_2 - 2(\tau/T_{2G})^2\}$. The Gaussian decay rate is almost temperature independent ($1/T_{2G} = 2 \times 10^3 \text{s}^{-1}$). The decay curve exhibits the two-component exponential behavior below 1.5 K, which is the boundary between the uniform paramagnetic phase and phase II. We then determined 1/T2f (solid circles) and 1/T2s (open circles) by using eq. (1). Although 1/T2f and 1/T2s are different in magnitude, they show similar $T$ dependences and decrease slightly with decreasing $T$. This $T$-dependence is nearly identical to the behavior at 1 T (Fig. 4a). Below 1.1 K, the ratio $A_f/A_f$ is almost $T$-independent, indicating that the numbers of the $V_f$ and $V_s$ sites stays nearly equal. The two-component fit does not work well near 1.5 K probably due to coexistence of the paramagnetic phase and phase II.

Figure 4(b) shows the $T$ dependence of 1/T1 at 6 T (triangles) together with the previous data at 1 T (asterisks). The recovery curve at 1 T follows the exponential function for $T \geq 1 \text{K}$, while the stretched exponential function is required to fit the data at lower temperatures. Although the recovery curves do not depend on $\tau$ at 1 T (phase I), they do in phase II. The open and solid triangles represent 1/T1 at 6 T for $\tau = 10$ and $80 \mu$s, respectively. Above 1.5 K, the recovery curve can be reproduced by the exponential function and 1/T1 does not depend on $\tau$. Below 1.5 K (phase II) the recovery curve for $\tau = 10 \mu$s was fit to the stretched exponential function. We then obtained 1/T1 $\propto T^{1.5}$ behavior but $\beta$ depends on $T$ and reaches an extremely small value of 0.25 at 0.14 K. This can be now accounted for by coexistence of the $V_f$ and $V_s$ sites for short $\tau$. The recovery curve for $\tau = 80 \mu$s can be fit to the stretched exponential function with constant $\beta \approx 0.6$, which is also the case at 1 T. Since the signal from the $V_f$ sites has decayed at long $\tau$ and is nearly absent at $\tau = 80 \mu$s, 1/T1 thus obtained should correspond to the $V_s$ sites. The solid line in Fig. 4(b) shows a 1/T1 $\propto T$ behavior, which fits the data for both 6 T and 1 T. This indicates that the $V_s$ sites in phase II are affected by anomalously dense low-energy excitations that have been identified in phase I in Ref. 13. The smaller values of 1/T1 at 6 T indicates that the $V_s$ sites couple to these excitations more weakly than the $V$ sites in phase I.

How can we understand the spin state in phase II? The $V_f$ and $V_s$ sites show significantly different relaxation rates and line shapes. The spectra at the $V_f$ sites show a round shape (Fig. 2cd), indicating a distribution in the magnitude of the hyperfine field, which can be generated, for instance, by a spin-density-wave order or spatially disordered static moments. Therefore, the large 1/T2f at the $V_f$ sites should be ascribed to unusually slow fluctuations of the Cu spins with non-uniform moments. On the other hand, the $V_s$ sites show a rectangular spectral shape, which is compatible with conventional AF order. The relatively small 1/T2f and 1/T1 show that the effects of the unusual spin fluctuations are weak at the $V_s$ sites.

How are the two $V$ sites distributed spatially? Two cases can be considered. In one case, a magnetic superstructure is formed in phase II yielding two inequivalent $V$ sites. Alternatively, macroscopic phase separation may occur and each phase contains only one of the two $V$ sites.
Our NMR results definitely support the first case. The numbers of the \(V_f\) and \(V_v\) sites are nearly equal in the entire region of phase II, which covers a wide range of \(B\) and \(T\). This is quite natural if a microscopic superstructure is formed but very unlikely for the phase separation scenario, since the relative stability of the two phases should change with \(B\) and \(T\). In addition, the two \(V\) sites show similar \(T\) dependences of \(1/T_2\) in spite of the difference in magnitude (Fig. 4a). This indicates a common source of the fluctuating hyperfine field for the two \(V\) sites. The different magnitudes should then be attributed to the difference in the hyperfine coupling between the fluctuating spins and the nuclei. Since the range of hyperfine interaction is short with an atomic scale, this is not possible for the case of phase separation.

Although we cannot determine the superstructure from the NMR data on a powder sample alone, let us discuss most likely possibilities. Since the numbers of the two \(V\) sites are equal, we expect a doubled unit cell due to formation of a superstructure. For the ideal kagome lattice, the three directions \(k_1\), \(k_2\), and \(k_1 + k_2\) (Fig. 1) are all equivalent. However, since the structure of volborthite is uniform along \(k_2\) and inequivalent \(Cu\)1 and \(Cu\)2 sites alternate along \(k_1\), we consider the wave vector of the superstructure is likely to be along \(k_1\). The two \(V\) sites then alternate along \(k_1\). The \(V\) sites \(V_f\) and \(V_v\) in Fig. 1 correspond to the \(V_f\) and \(V_v\) sites. Likewise, each of the \(Cu\)1 and \(Cu\)2 sites is divided into two inequivalent sites \(Cu\_1p\), \(Cu\_1s\), \(Cu\_2s\), and \(Cu\_2\lambda\), as shown in Fig. 1.

Since a \(V\) site is located approximately above or below the center of the \(Cu\) hexagon of the kagome lattice, the dominant source of the hyperfine field at \(V\) nuclei should be confined within the six \(Cu\) spins on a hexagon. Because of the distorted structure of volborthite, there are three distinct hyperfine coupling tensors \(A_{\alpha}\), \(A_{\beta}\), and \(A_{\gamma}\) as shown in Fig. 1. The coupling tensors to the other three spins \(A_{\alpha}'\), \(A_{\beta}'\), and \(A_{\gamma}'\) are generated by the mirror reflection perpendicular to the \(b\) axis at the \(V\) site. The hyperfine fields at \(V_{\alpha}\) and \(V_{\beta}\) are written as \(B_{\alpha} = (A_{\alpha}s_{\alpha} + A_{\alpha}'s_{\alpha}') + (A_{\alpha}s_{\beta} + A_{\alpha}'s_{\beta}') + (A_{\alpha}s_{\gamma} + A_{\alpha}'s_{\gamma}')\) and \(B_{\beta} = (A_{\beta}s_{\alpha} + A_{\beta}'s_{\alpha}') + (A_{\beta}s_{\beta} + A_{\beta}'s_{\beta}') + (A_{\beta}s_{\gamma} + A_{\beta}'s_{\gamma}')\), respectively, where \(s_{\alpha}\) and \(s_{\alpha}'\) denote two neighboring spins on the same type of sites. (\(\epsilon\) stands for \(Cu\_1p\), \(Cu\_1s\), \(Cu\_2s\), or \(Cu\_2\lambda\)).

Both \(1/T_1\) and \(1/T_2\) are determined by the time-correlation function of the hyperfine field. If all the hyperfine coupling tensors \(A_{\alpha}\), \(A_{\beta}\), and \(A_{\gamma}\) are largely isotropic and have similar magnitudes, the different \(1/T_2\) for the two \(V\) sites must be ascribed to the difference in the time-correlation functions of \(s_{\rho}\) and \(s_{\kappa}\). A plausible situation is illustrated in Fig. 1. The \(Cu\_\beta\) sites develop a conventional long range magnetic order. Hence, the spin fluctuations of these sites have a small amplitude with a conventional time scale typically described by spin waves. On the other hand, the \(Cu\_p\) sites show modulated spin structure. The absence of fully developed static moments would allow unusually slow fluctuations responsible for the large \(1/T_2\) at the \(V_f\) sites. By studying the anisotropic kagome model in the limit \(J > J'\), Schnyder et al. proposed a spiral order with large (small) ordered moments on the \(Cu\_1\) (\(Cu\_2\)) sites.

Although the different magnitudes of the ordered moments for the two \(Cu\) sites is a feature in common to our results, our observation of two distinct \(V\) sites requires an enlarged magnetic unit cell. The spin structure of the \(Cu\_\alpha\) sites could be a spiral order with a small wave vector as proposed theoretically.

Alternatively, the low symmetry of the volborthite structure may result in large difference in the hyperfine coupling. In particular, \(A_{\alpha}\) and \(A_{\gamma}\) involve significantly different O-Cu hybridization paths. If one of them, say \(A_{\alpha}\), is the dominant coupling, the different \(1/T_2\) for the two \(V\) sites must be ascribed to the different dynamics of \(s_{\alpha}\) and \(s_{\kappa}\) spins.

In conclusion, our NMR results show coexistence of the two types of \(V\) sites with different relaxation behavior and spectral shapes in the field-induced phase II of volborthite. Our results indicate that the high field phase of volborthite exhibits a unique heterogeneous magnetic state, where a non-uniform order with anomalous fluctuations alternates with a more conventional static order.

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