Muon Spin Relaxation and Susceptibility Studies of the Pure and Diluted Spin $\frac{1}{2}$ Kagomé-Like Lattice System $(Cu_xZn_{1-x})_3V_2O_7(OH_2)$ $2H_2O$

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Muon spin relaxation and magnetic susceptibility measurements have been performed on the pure and diluted spin $\frac{1}{2}$ kagomé system $(Cu_xZn_{1-x})_3V_2O_7(OH)_2$ $2H_2O$. In the pure $x = 1$ system we found a slowing down of Cu spin fluctuations with decreasing temperature towards $T \sim 1$ K, followed by slow and nearly temperature-independent spin fluctuations persisting down to $T = 50$ mK, indicative of quantum fluctuations. No indication of static spin freezing was detected in either of the pure ($x = 1.0$) or diluted samples. The observed magnitude of fluctuating fields indicates that the slow spin fluctuations represent an intrinsic property of kagomé network rather than impurity spins.

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Geometrically frustrated interactions bring new types of cooperative phenomena to spin systems. Spins on the kagomé lattice, coupled with antiferromagnetic nearest neighbor interactions, are known as a prototype of strongly frustrated systems [1,2]. Theoretical and experimental studies of kagomé systems have been extensively performed. Materials studied as candidates of kagomé system [1,2] include $SrCr_{9p}Ga_{12-9p}O_{19}$ (SCGO) and jarosite family $AM_3(OH)_6(SO_4)_2$ (A: typically a univalent, $M = Fe^{3+}$, Cr^{3+}). Some of them (e.g., Fe jarosite) undergo a transition to long-range Néel order, while others(SCGO and Cr jarosite: both with $S = 3/2$ Cr moments) exhibit spin-glass-like behavior in susceptibility.

Quantum effects should play important roles in the magnetism of kagomé compounds, similar to the case of low dimensional spin systems. A theoretical study of $S = 1/2$ Heisenberg kagomé systems indicates that the ground state is spin singlet [3]. Ramirez *et al.* [4] reported independence of the specific heat of $S = 3/2$ kagomé system SCGO on high applied magnetic fields, and interpreted this in terms of low-energy excitations dominated by spin singlet states [4,5]. On the other hand, muon spin relaxation (μSR) results in SCGO [6] suggest that dynamic spin fluctuations persist even at $T \to 0$. Experimental studies of $S = 1/2$ kagomé systems would be useful for better understanding of quantum effects. No good candidate of $S = 1/2$ kagomé material, however, has been found until recently.

Hiroi *et al.* found that $S = 1/2$ Cu^{2+} spins in the copper volborthite $Cu_3V_2O_7(OH)_2$ $2H_2O$ (CVO) forms a spin network, which is only slightly distorted from a complete kagomé lattice [7]. Vanadium is in a nonmagnetic state, as confirmed by NMR [7]. Neither transition to long-range order nor a spin-glass-like transition was observed down to 1.8 K in magnetization, heat-capacity, and NMR measurements. An ESR study suggests the existence of short-range spin correlations below 5 K [8]. In order to characterize ground state of CVO, we have performed μSR measurements down to 50 mK.

Effects of magnetic dilution in kagomé systems are also interesting. We could possibly obtain insights both about doped and undoped systems, as demonstrated in the case of SCGO [9,10]. Thus, we attempted to substitute Cu^{2+} ions by nonmagnetic Zn^{2+} ions. $Zn_3V_2O_7(OH)_2$ $2H_2O$, with the same stoichiometry [11], has a crystal structure slightly different from that of CVO. Both the lattice parameter and atom positions are, however, quite similar between the Cu and Zn systems. We have succeeded in the synthesis of mixed compound $(Cu_xZn_{1-x})_3V_2O_7(OH)_2$ $2H_2O$. In this Letter, we report susceptibility (χ) and μSR measurements of pure and diluted CVO and discuss some exotic features of their ground states.

Measurements of μSR and χ were performed in five powder samples with nominal $x = 1.0$, 0.95, 0.90, 0.70, and 0.60. Powder samples of pure CVO ($x = 1.0$) were prepared in the method described in Ref. [7]. The diluted samples were also made in a similar method, but using $CuSO_45H_2O$, $ZnSO_4$ $5H_2O$, V_2O_5, and NaOH as starting materials. X-ray powder diffraction patterns of these samples indicated they were single phase. dc susceptibility χ at $T > 1.8$ K was measured with a SQUID magnetometer at Columbia, while μSR measurements at 50 mK $< T <$ 6 K were performed at TRIUMF. To assure cooling of samples used for μSR in a dilution refrigerator, we mixed the samples with 20 wt% of Au powder and pressed them into pellets.

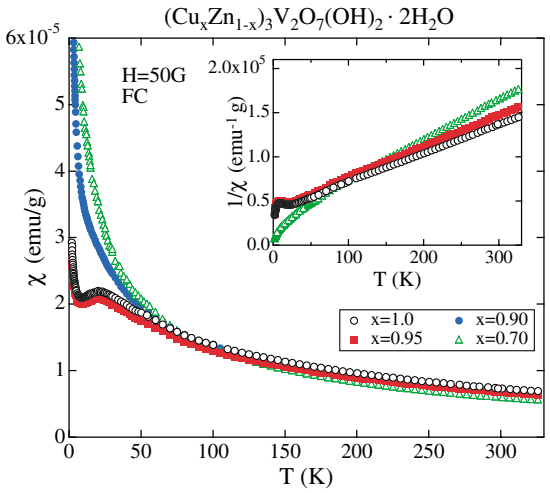

FIG. 1 (color). Magnetic susceptibility of CVO with various Cu concentrations in $H = 50$ G in the field-cooled condition. The inset shows the inverse susceptibility of $x = 1.0$, 0.95, and 0.90.

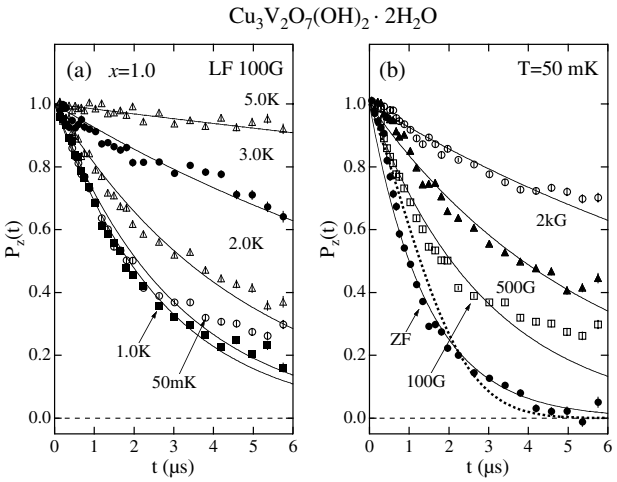

FIG. 2. (a) Temperature dependence of the time spectra of the $x = 1.0$ sample measured in $H_{LF} = 100$ G. (b) Longitudinal field dependence of the time spectra of the $x = 1.0$ sample at $T = 50$ mK. The solid lines show the results of fitting with Eq. (1). The broken line in (b) shows the spectrum at $T = 50$ mK in $H_{LF} = 100$ G multiplied to ZF spectrum at $T = 6$ K (which represents the effect of NDF).

In Fig. 1, we plot the susceptibility $\chi(T)$, as a function of temperature T, measured in a magnetic field of 50 G. Only the field-cooled results are shown, since we did not observe any hysteresis. In $x = 1.0$, $\chi(T)$ shows a broad maximum at ~20 K. Below 9 K, the susceptibility begins to increase with decreasing T. This increase indicates a Curie-like term due to impurities or lattice defects. In $x = 0.95$, the behavior is quite similar to that in $x = 1.0$. With increasing dilution, the increase of χ at low temperature becomes more pronounced, as expected for unpaired Cu moments created by Zn. The broad maximum at 20 K was no longer observed for $x \leq 0.9$. In any of these samples, we did not find any signature indicating either a transition to long-range order or spin freezing at $T > 1.8$ K. We found no anomaly in χ at the percolation threshold, $p_c = 0.65$ [12].

The inverse susceptibility for $x = 1.0$, 0.95, and 0.70 is shown in the inset of Fig. 1. In all concentrations, $1/\chi$ shows nearly linear variation with T down to ~100 K, though it slightly deviates from linearity below ~200 K. The Weiss temperature Θ estimated from $1/\chi$ above 200 K in the pure $x = 1$ compound was -117 K, consistent with Hiroi *et al.* [7], who estimated the exchange interaction $J = 84$ K from χ. The absolute value of Θ decreases with decreasing Cu concentration.

To characterize static/dynamic spin correlations with a microscopic probe, we performed μSR measurements. Figure 2(a) shows the time spectra of muon polarization, $P_z(t)$ obtained, after subtraction of a temperature-independent background/Au contribution, for $x = 1.0$ in a longitudinal field (LF) of $H_{LF} = 100$ G applied to decouple nuclear dipolar fields (NDF). The Kubo-Toyabe NDF width [13] $\Delta = 0.39/\mu$s was estimated from the spectrum at $T = 6$ K in zero field (ZF). As T decreases, the relaxation rate in Fig. 2(a) increases down to ~1 K, followed by a saturation at lower temperatures.

The time spectra at 50 mK in ZF and some selected LF are shown in Fig. 2(b). We did not observe oscillation of muon spin in ZF. The persisting relaxation in $H_{LF} > 100$ G clearly indicates that the observed relaxation at $T = 50$ mK is predominantly due to fluctuating local fields from Cu moments. In such a case, one would expect the ZF spectra to be given by a product of a low-field LF spectrum and a Kubo-Toyabe decay due to NDF [13], which is shown by the dotted line in Fig. 2(b). A reasonable agreement of this line and the ZF data further confirms the dynamic origin of the relaxation in LF.

In a further inspection of the line shape, we notice that (i) the early-time decay in $H_{LF} = 100$ and 500 G is somewhat rounder than the exponential shape (solid lines); (ii) the ZF spectrum shows slight deviation from the broken line; and (iii) the longer time decay after $t = 4\ \mu$s in LF becomes slower than exponential. These features have been found in the so-called "undecouplable Gaussian" μSR line shapes, observed in kagomé systems, SCGO [6] and Cr jarosite [14], charge-doped Haldane gap system $(Y,Ca)_2BaNiO_5$ [15], body-centered tetragonal spin system $CePt_2Sn_2$ [16], and a dimer spin-gap system $SrCu_2(BO_3)_2$ [17]. The origin of this anomalous behavior has not yet been clearly understood. In the present CVO system, however, this feature appears in a much less prominent way than in the above-mentioned systems. Therefore, to grasp dominant trends of the data, we fitted the LF time spectra at $t < 4\mu$s with a simple exponential function,

$$P_z(t) = \exp(-\lambda t), \tag{1}$$

where λ is the relaxation rate. The results of this fit are shown by the solid lines in Fig. 2.

The temperature dependence of λ is shown in Fig. 3(a). With decreasing temperature, λ starts to increase at $T \sim 4$ K and shows a saturation around $T = 1.0$ K in $x = 1.0$ and 0.95. The LF dependence of λ in $x = 1.0$ is shown in Fig. 3(b). For a Markovian correlation of local fields characterized by a Gaussian distribution $P(H_i) \propto \exp(-H_i^2/2H_\Delta^2)$ $(i = x, y, z)$ with the amplitude of H_Δ and the correlation time τ, λ follows a Lorentzian function of $H_{\rm LF}$,

$$\lambda(H_{\rm LF}) = \frac{2\gamma_\mu^2 H_\Delta^2 \tau}{1 + \gamma_\mu^2 H_{LF}^2 \tau^2}, \qquad (2)$$

where γ_μ ($\gamma_\mu = 2\pi \times 13.55 \times 10^3$ Hz/G) is the gyromagnetic ratio of muon [13]. The dotted lines in Fig. 3(b) show a fit to this function. The observed LF dependence significantly deviates from Lorentzian. This may suggest a wide distribution of H_Δ and/or τ, or nonexponential/non-Markovian type of time correlations of Cu spins.

For a Lorentzian power function of Eq. (2), $1/\tau$ can be derived from the half width at half maximum in the λ vs LF curve. Thus, assuming that the value of λ in 100 G is equal to that in zero field, we obtained the value of $H_{\rm LF}$ where λ becomes half of that in 100 G, multiplied it with γ_μ, and estimated the characteristic effective fluctuation rate $1/\tau$. We also derive the corresponding amplitude H_Δ of the instantaneous local fields from the values of λ in 100 G using Eq. (2), and show them in the inset of Fig. 3(b). As expected for ordinary spin fluctuations, H_Δ exhibits almost no temperature dependence. For $x = 1.0$ and 0.95, $H_\Delta = 35$ G gives the simple relation $\tau \sim 0.06\lambda$ for τ in [μs] and λ in [$1/\mu$s]. Thus, the correlation time τ increases with decreasing temperature and keeps a constant value of $\tau = 10$–20 ns below 1 K down to 50 mK. This suggests that dynamic Cu spin fluctuations persist below 1 K in a quantum (temperature-independent) process.

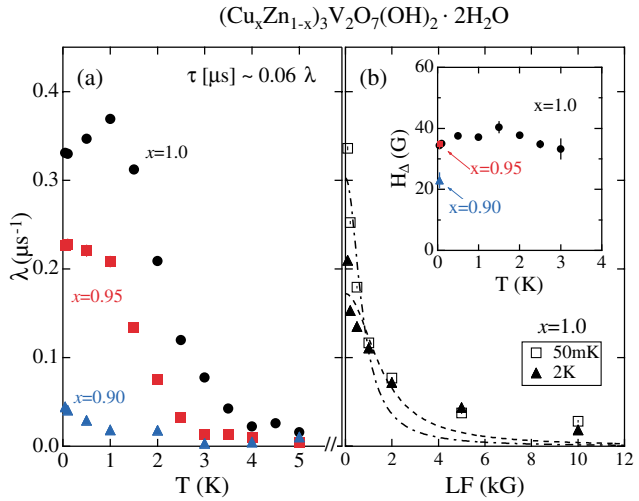

FIG. 3 (color). (a) Temperature dependence of the relaxation rate λ of the $x = 1.0$, 0.95, and 0.90 samples in $H_{\rm LF} = 100$ G. For the instantaneous local field width $H_\Delta \sim 35$ G, the correlation time becomes τ [μs] $\sim 0.06\lambda$ [$1/\mu$s]. (b) Longitudinal field dependence of λ at $T = 50$ mK and 2.0 K. The dotted curves show the results of fitting with Eq. (2). The inset in (b) shows the temperature dependence of the field amplitude H_Δ.

Figure 4(a) shows the time spectra in pure and diluted samples in $H_{\rm LF} = 100$ G at 50 mK. The relaxation rate rapidly decreases with decreasing Cu concentration. For $x = 0.70$ and 0.60, we observed almost no relaxation. We analyzed the time spectra with Eq. (1). The x dependence of λ at 50 mK is shown in Fig. 4(b). With increasing Zn doping, (decreasing x), λ rapidly decreases down to $x = 0.90$ and then gradually decreases down to 0.60. Similarly to the case of χ, the μSR results vary smoothly at the percolation threshold $p_c = 0.65$. We could not estimate H_Δ and τ for $x = 0.70$ and 0.60, since λ is almost independent of LF. In the right-hand axis of Fig. 4(b), we show the correlation time τ at $T = 50$ mK, derived by assuming $H_\Delta = 35$ G. The Cu spin correlation time τ rapidly decreases with increasing dilution (decreasing x), indicating faster spin fluctuations for less perfect spin network.

Now let us consider the ground state of pure CVO. The absence of any oscillations in the μSR time spectra down to 50 mK implies that there is no evidence for long-range order. We found slow spin fluctuations, with the correlation time of $\sim$20 ns, persisting below $T \sim 1$ K. The value of the instantaneous local field H_Δ for $x = 0.95$ was nearly equal to that of $x = 1.0$, while H_Δ decreases with further Zn doping. This suggests that the observed magnetism is not due to extrinsic states created by doped Zn^{2+} ions via breaking of nearby singlet state(s) of Cu spins, but likely reflects an intrinsic property of the entire kagomé spin network.

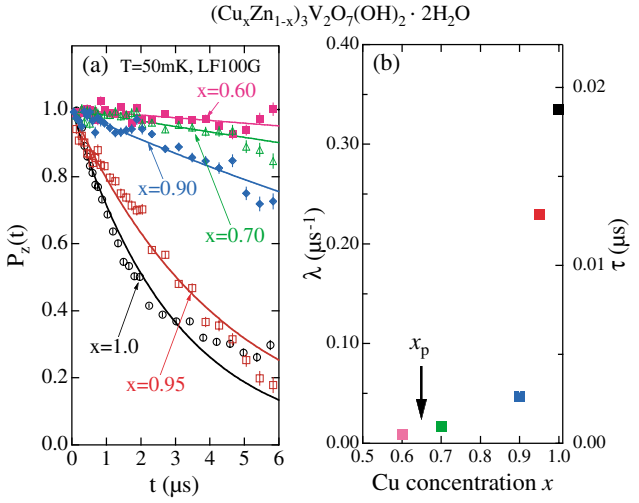

FIG. 4 (color). (a) Time spectrum in $H_{\rm LF} = 100$ G measured at 50 mK for various Cu concentrations x. (b) x dependence of the relaxation rate λ in $H_{\rm LF} = 100$ G measured at 50 mK and of the corresponding characteristic fluctuating time, τ for $H_\Delta = 35$ G.

In dilute spin glasses, the Lorentzian width of internal fields due to dipolar (or other $1/r^3$) interaction is inversely proportional to the average volume per spin [13,18]. In CVO, the width $\sim$35 G can be expected if 13% of the Cu spins have 0.5 μ_B moments pointing in random directions. If these Cu spins have antiferromagnetic correlations, one needs to assume a larger population of active Cu moments to explain the observed amplitude H_Δ. Thus, the present results indicate that a significant fraction of Cu moments remain active in the ground state, while the rest of them may form magnetically inactive singlet states.

In the present sample of nominally pure $x = 1$ CVO, the $1/T$ impurity term of χ correponds to $S = 1/2$ free impurity of well below 0.25% of Cu population. Thus the μSR results cannot be ascribed to such impurity moments. This point was further confirmed by essentially identical μSR results obtained in another sample of $x = 1$ CVO which had nearly a factor of 2 larger $1/T$ term in χ.

Some theories and numerical results suggested that the ground state of $S = 1/2$ kagomé system is a singlet state associated with a rapid decrease of χ below $T \sim 0.2J$ [5]. The broad maximum of χ observed in CVO at $T \sim 20$ K might be related to this feature. A similar broad maximum around $T \sim J/2$ was also found in NMR spin susceptibility of SCGO [19]. However, the ground states of both CVO and SCGO involve active magnetism, as indicted by: (i) the μSR relaxation in CVO (present study) and SCGO [6]; (ii) nonzero value of χ at $T \rightarrow 0$ even after the Curie-like term was subtracted; and (iii) quasistatic response in SCGO at $T \rightarrow 0$ in neutron scattering studies [20,21]. We note that we should not have seen *any* spin relaxation at $T \rightarrow 0$ in a complete singlet ground state. In both CVO and SCGO [6], the μSR relaxation rates at low temperatures are nearly independent of temperature. These results suggest a novel type of ground state in both $S = 1/2$ (CVO) and 3/2 (SCGO) kagomé networks, where slow and quantum spin fluctuations persist without static spin freezing. The existence of such a slow magnetic state in CVO provides a possible explanation for the broadening and disappearence of an ESR signal in CVO below $T \sim 4$ K [8].

A spin-glass-like behavior in χ, associated with departure of field-cooled and zero-field cooled results, was found in the kagomé systems SCGO [22] and Cr jarosite [14]. We point out that the μSR results of CVO, SCGO [6,10], and Cr jarosite [14], with persisting dynamic effects at $T \rightarrow 0$, are qualitatively different from those in ordinary spin-glass materials such as *Cu*Mn [13], where dynamic fluctuations disapper at $T \rightarrow 0$.

Finally, we discuss the effect of magnetic dilution. The present μSR results in CVO show that the correlation time becomes rapidly shorter with increasing Zn doping. Qualitatively similar dependence on magnetic dilution was found in μSR studies of SCGO [10]. These results indicate that magnetic dilution does not relieve frustration nor promote spin freezing in these systems. Zn doping may cutoff the magnetic network to smaller clusters resulting in faster spin fluctuations. The absence of an anomaly at the percolation threshold, in either CVO or SCGO, suggests that the spin fluctuations have a short-ranged/local character.

In summary, we found a signature of slowing down of spin fluctuations with decreasing temperature, followed by slow and nearly temperature-independent spin fluctuations between $T = 1.0$ and 50 mK in the $S = 1/2$ kagomé spin system CVO. These fluctuations exhibit quantum character, and persist at $T = 50$ mK without any signature of long-range or static spin order.

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[1] A. P. Ramirez, Annu. Rev. Mater. Sci. **24**, 453 (1994).
[2] P. Schiffer and A. P. Ramirez, Comments Condens. Matter Phys. **18**, 21 (1996).
[3] Ch. Waldtmann *et al.*, Eur. Phys. J. B **2**, 501 (1998).
[4] A. P. Ramirez, B. Hessen, and M. Winklemann, Phys. Rev. Lett. **84**, 2957 (2000).
[5] P. Sindzingre *et al.*, Phys. Rev. Lett., **84**, 2953 (2000).
[6] Y. J. Uemura *et al.*, Phys. Rev. Lett. **73**, 3306 (1994).
[7] Z. Hiroi *et al.*, J. Phys. Soc. Jpn. **70**, 3377 (2001).
[8] S. Okubo *et al.* Physica (Amsterdam) **294B–295B**, 75 (2001).
[9] B. Martínez *et al.*, Phys. Rev. B **46**, 10 786 (1992).
[10] A. Keren *et al.*, Phys. Rev. Lett. **84**, 3450 (2000).
[11] P. Y. Zavalij, F. Zhang, and M. Stanley, Acta Crystallogr. Sect. C **53**, 1738 (1997).
[12] J. W. Essam, in *Phase Transition and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, London, 1972), Vol. 2, p. 224.
[13] Y. J. Uemura *et al.*, Phys. Rev. B **31**, 546 (1985).
[14] A. Keren *et al.*, Phys. Rev. B **53**, 6451 (1996).
[15] K. Kojima *et al.*, Phys. Rev. Lett. **74**, 3471 (1995).
[16] G. M. Luke *et al.*, Hyperfine Interact. **104**, 199 (1997).
[17] A. Fukaya *et al.*, Physica (Amsterdam) **326B**, 446 (2003).
[18] R. E. Walstedt and L. R. Walker, Phys. Rev. B **9**, 4857 (1974).
[19] P. Mendels *et al.*, Phys. Rev. Lett. **85**, 3496 (2000).
[20] C. Broholm, G. Aeppli, G. P. Espinosa, and A. S. Cooper, Phys. Rev. Lett. **65**, 3173 (1990).
[21] Y. J. Uemura *et al.*, J. Magn. Magn. Mater. **177–181**, 701 (1998).
[22] A. P. Ramirez, G. P. Espinosa, and A. S. Cooper, Phys. Rev. Lett., **64**, 2070 (1990).