µSR study on the ground state of bond-disordered spin gap system \((\text{CH}_3)_2\text{CHNH}_3\text{Cu(Cl}_{1-x}\text{Br}_x)_3\) \((x=0.95, 0.88)\)

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Abstract. Solid solution of the two spin gap systems \((\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3\) and \((\text{CH}_3)_2\text{CHNH}_3\text{CuBr}_3\) was reported from results of macroscopic measurements to be gapless when fraction of Cl content \(x\) is in between 0.44 and 0.87, and otherwise remains gapped. We have investigated by µSR the ground state of Cl-rich gapped region \(x=0.95\) and 0.88 to find that they are microscopically phase separated into two components, magnetic tiny islands and singlet sea surrounding them. With decreasing temperature, the characteristic frequency of spin fluctuation in islands showed a significant slow down. However, the slow down ceased around 1 K, below which the spin fluctuation spectrum did not change down to 15 mK. These results indicate that unlike the Br-rich system \(x<0.44\) where appearance of an exotic ground state has been argued, the Cl-rich system \(x>0.87\) persists to be paramagnetic without showing a long-range order. This difference is considered to be originated in the robustness of Haldane gap against disorder.

1. Introduction
The effect of disorder to the ground state of quantum spin systems is not one-way. While a small number of doped holes in high-\(T_C\) cuprates destroy the antiferromagnetic order in parent compounds [1], non magnetic impurities in spin Peierls system induce a long range magnetic order[2]. Furthermore, Fisher et al. predicted an existence of exotic ground state Bose-glass [3] in a disordered Boson system. Their model can be applied to spin dimer systems if one accepts a mapping between singlet site and triplet site to vacuum and Boson particle [4]. On the other hand, Hida discussed the robustness of Haldane gap against bond disorder and concluded that spin gap remains in the presence of bond disorder.[5] Nakamura showed by numerical calculation that with increasing bond disorder, the gap persists until a critical concentration of disorder, where the gap collapse abruptly and the system enters a magnetically ordered phase.[6] Thus, the effect of disorder to the ground state of quantum spin systems is not evident and is expected to show an effect unexpected from a classical point of view.

In this paper, we investigate the effect of bond disorder in a solid solution of the two spin gap systems \((\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3\) (IPA-CuCl₃) and \((\text{CH}_3)_2\text{CHNH}_3\text{CuBr}_3\) (IPA-CuBr₃). The former system is a two legged spin ladder with a ferromagnetic rung, and can be considered as composite Haldane
chain, where the two spins on the rung couple to build up an $S=1$ spin$^8$. The latter is, to the best of our knowledge, considered to be AF-AF bond alternating chain$^7,17$. The energy gap of spin excitation is reported to be 14 and 80 K for Cl and Br system, respectively$^7,8$. So far, it has been reported from macroscopic experiments that there exist the two quantum critical points (QCPs) $x_C=0.44$ and 0.87 in the solid solution system IPACu(Cl$_{1-x}$Br$_x$)$_3$, and that the system recovers magnetism and shows a long range magnetic order with $T_N=11-17K$ only when $x$ resides between the two $x_C$’s$^7$. The microscopic evidence of the antiferromagnetic order has been reported by NMR and $\mu$SR experiments$^9,10,11$. The system with $x$ outside this intermediate region, that is, when $x<0.44$ or $x>0.87$, was believed previously to be non-magnetic and possess a finite gap in spin excitation spectrum. Recently, however, we have shown by $\mu$SR and NMR that the spin fluctuation does exist in $x=0.35$ $^{12,13}$ and 0.40 $^{17}$, and that its spectrum shows a critical slow down toward absolute zero indicating an existence of possible phase transition to Bose-glass phase. In Cl-rich phase $x>0.84$, which is described as a composite Haldane chain$^8$, though there is a suggestion that the system is not simply in gapped state$^{16}$, the point whether or not the spin state is different from Br-rich phase is still veiled. Here we are reporting results of the muon spin relaxation investigation on the Cl-rich phase in the dilution temperature range to show that the ground state of the Cl-rich and Br-rich phase is different.

2. Experimental

Single crystals of IPA-Cu(Cl$_{1-x}$Br$_x$)$_3$ with $x=0.95$ and 0.88 were prepared by evaporation method$^7$, and their $x$ values were determined by Inductively Coupled Plasma (ICP) analysis. Typical shape of crystal is $2\times4\times10$ mm$^3$ of rectangular solid. $\mu$SR experiments were performed at PSI in Switzerland and Riken-RAL in UK. Muon spin relaxation was measured with approximately ten crystals set on the silver cold plate by Apiezon N grease with $b^*$-axis aligned parallel with the muon spin polarization under both zero field (ZF) and longitudinal field (LF) down to the dilution temperature region.

3. Results and Discussion

Figure 1 shows typical time evolution of the muon asymmetry, namely, the decay of the muon spin polarization after injected to the sample$^{14}$. Either two samples did not show any rotational signal down to the dilution temperature region, indicating that there is no long range magnetic order. This observation is consistent with the reports on the macroscopic quantities$^7$. Observed decay curves were expressed by the function consisting of two components $A_1G_{KT}(\Delta, \tau)e^{-\lambda_1\tau}+A_2e^{-\lambda_2\tau}$, where $G_{KT}$ is Kubo-Toyabe function representing the quasi-static random field with distribution $\Delta$ contributed from
the slow fluctuation of nuclear spins, and two exponential functions with relaxation rates \( \lambda_1 \) and \( \lambda_2 \) represent the contribution from dynamically fluctuating field produced by electron spins. The value of \( \Delta=0.3 \mu s^{-1} \) was temperature independent. Note that \( G_{KT} \) is omitted in the second term, because \( \lambda_2 \) is much larger than \( \lambda_1 \) so that the contribution of \( G_{KT} \) is masked in the second term. The amplitude of the two components \( A_1 \) and \( A_2 \) showed a slight temperature dependence; with decreasing temperature, \( A_2 = 33\% \) at 3K increases to 62\% at 2K and stayed constant down to 15 mK. As shown in Fig. 1, the fitting between the utilized function expressed by solid curves and the observed data are fairly well. We also tried to fit the data with a single component including only either \( A_1 \) or \( A_2 \), as shown by dashed curves in Fig. 1 to find that it is not appropriate. Detailed method of the parameter determination is described in ref. 12.

The Fourier spectrum of the electron spin fluctuation is obtained from the so-called decoupling experiment in the longitudinal field \( H_{LF} \), because \( \lambda(H_{LF}) \) selectively probes the Fourier component with frequency \( \omega=\gamma H_{LF} \), where \( \gamma=13.5534 \) kHz/Oe is the muon gyromagnetic ratio, in the spin fluctuation spectrum[12]. Figure 2 shows the spectrum of the two components \( \lambda_1 \) and \( \lambda_2 \) of the sample \( x=0.88 \) measured at 15 mK. Note that spectra of the two components are quite different both in frequency \( \omega=\gamma H_{LF} \) and amplitude. The spectrum of \( \lambda_2 \) is well described by Redfield formula

\[
\frac{2(\gamma\delta H_{loc})^3 \tau_c}{1+(\gamma H_{LF}\tau_c)^2},
\]

indicating that those electron spins contributing to \( \lambda_2 \) component fluctuate randomly with a unique characteristic time constant \( \tau_c \) and produce a hyperfine field with an amplitude \( \delta H_{loc} \) at muon site. From the curve fitting shown in Fig. 2, we obtained parameters for \( \lambda_2 \) as \( \tau_c=0.6 \mu s \) and \( \delta H_{loc}=63 \) Oe. As for the component of \( \lambda_1 \), one can see that both the frequency and amplitude are much smaller than that of \( \lambda_2 \), though the determination of parameters cannot be done due to the lack of the low field data.

Figure 3 show the temperature dependence of \( \lambda_2 \) under \( H_{LF}=100 \) Oe, for the two samples \( x=0.88 \) and 0.95. The data above 0.3 K of the latter is taken from ref. 9. With decreasing temperature \( \lambda_2 \) increases until 1 K, below which it stays constant at around 0.5 \( \mu s^{-1} \), which is nearly the same for \( x=0.95 \) and 0.88, indicating that there is no quantum critical behaviour toward QCP of \( x_c=0.87 \). This result is consistent with the fact that this QCP is of first order[7]. Next, we plot three dimensionally the temperature dependence of \( \lambda_2 \) under various \( H_{LF} \)'s in Fig. 4, where one can see how the spin fluctuation spectrum changes with temperature. With decreasing temperature, while the higher frequency component above 300 Oe rapidly decreases, the lower frequency component below 100 Oe increases and stays constant at a rather high value around 0.7 \( \mu s^{-1} \) below 1 K down to 15 mK.
The fact that the two components of $\lambda_1$ and $\lambda_2$ have the different characteristic time constants indicates the microscopic phase separation in this system. The component of $\lambda_1$, from its smallness in amplitude, is considered to correspond to the non-magnetic phase, and $\lambda_2$ to the magnetic phase. The characteristic length scale of the phase separation should be microscopic, because otherwise the magnetic phase should show a long-range order with $T_N=11-17$ K. Thus, the system can be modelled as the magnetic islands with the net volume fraction $A_2$ sprinkled in the singlet sea. The temperature dependence of the volume fraction of $A_2$ component is explained by this model. As the magnetic correlation in island spins develops at low temperatures, those spins in the boundary region must come under the influence of the correlation and hence be correlating themselves. This leads the slight increase in the fraction of $A_2$ component at low temperatures.

The mean size of the magnetic islands is estimated as follows. The upper limit is determined from the condition that the thermodynamical phase transition is absent, and the lower from the condition that all the spins in each islands antiferromagnetically correlate well so that the Curie term in the uniform susceptibility is suppressed as observed [7]. This conclusion on the phase separation is identical to that reported in Br-rich phase (x<0.44) [12,13]. However, the temperature dependence of the spin fluctuation is completely different in the two systems. In Br-rich systems of $x=0.35$[12] and 0.40[17], with decreasing temperature, the spin fluctuation in magnetic islands slows down toward absolute zero indicating an existence of the phase transition with critical temperature of absolute zero. On the other hand, in Cl-rich systems, the spin fluctuation ceases slowing down at 1 K, below which spins fluctuate with temperature independent time constant down to dilution temperature region. This may keep the system from the long range order and make it looks like gapped when viewed from macroscopic experiments. The absence of further slowing down below 1 K may be rooted in the weakness of the inter-islands spin interaction in Cl-rich phase compared with Br-rich phase.

Finally, our conclusions of the island model support Hida’s theoretical consideration on the robustness of Haldane systems against disorder [5], and is consistent with our previous NMR reports on the phase separation in the Cl-rich system[16].

Acknowledgement
The authors are grateful to Christopher Baines for his assistance and technique in muon experiments with a dilution refrigerator.

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