Gradual evolution in spin dynamics of TlCu\textsubscript{1-x}Mg\textsubscript{x}Cl\textsubscript{3} probed by muon-spin-relaxation (\(\mu\)SR) technique

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Abstract. Longitudinal-field muon-spin-relaxation (LF-\(\mu\)SR) measurements in TlCu\textsubscript{1-x}Mg\textsubscript{x}Cl\textsubscript{3} were carried out to investigate the spin dynamics in the non-magnetic impurity doped spin gap system. As reported before, in the case of \(x\) = 0.006, LF-\(\mu\)SR time spectra are well fitted by the two components function, which means the phase separation to a spin frozen region and to a spin fluctuating region. In this report, we focus on the spin fluctuating region, and discuss the gradual change in its magnetic properties with increasing the Mg-doping.

1. Introduction

TlCuCl\textsubscript{3} is well known as a three-dimensionally coupled Cu-3\textit{d} \(S = 1/2\) spin dimer system, and its magnetic ground state is spin-singlet with excitation gap of \(\Delta_{\text{gap}} = 7.5\) K, which originates from strong intradimer antiferromagnetic interaction [1, 2].

In the nonmagnetic impurity doped TlCu\textsubscript{1-x}Mg\textsubscript{x}Cl\textsubscript{3} system, it is reported that the magnetic phase transition to an ordered state is observed by magnetization and specific heat measurements, and that neutron elastic scattering measurements identified the impurity-induced ordered state is the antiferromagnetically ordered state of which the magnetic structure is the same with the case of the field-induced phase in TlCuCl\textsubscript{3} [3, 4]. The inelastic neutron scattering measurement revealed that a finite spin gap still remains below the transition temperature in TlCu\textsubscript{1-x}Mg\textsubscript{x}Cl\textsubscript{3} [5].

We have reported gradual changes of spin states probed by zero- and longitudinal-field muon-spin-relaxation (ZF, LF-\(\mu\)SR) measurements as follows [6, 7, 8]. In a slightly doped case of \(x = 0.0047\), no evidence for a static internal magnetic field was observed down to 20 mK although the specific heat indicated the magnetic phase transition at \(T = 0.70\) K. Above \(x = \)
0.006, the existence of a static internal magnetic field is confirmed, and with increasing Mg-concentration of $x$, the internal magnetic field and the volume fraction of a spin frozen region increase simultaneously. These results suggest that the magnetic ground state changes from the spin singlet state to a spin fluctuating state, and to a spin frozen state by the impurity doping. In our previous reports, mainly, the evolution of the static spin state region was discussed. Thus, in this report, we focus on the spin fluctuating region, and discuss the gradual change in its magnetic properties.

2. Experimental

Single crystals used in this study were grown from a melt by the Bridgman method, and the concentration of $x$ was determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES) method. Muon-spin-relaxation (μSR) measurements were carried out at the RIKEN-RAL Muon Facility in the U.K. using a spin-polarized double-pulsed positive surface-muon beam with an incident muon momentum of 27 MeV/c [9], and at the Swiss Muon Source (SμS), Paul Scherrer Institut (PSI), Villigen, Switzerland. In μSR measurements, spin-polarized muons are implanted into samples. The asymmetry was defined as follows:

$$A(t) = \frac{F(t) - \alpha B(t)}{F(t) + \alpha B(t)}$$  \hspace{1cm} (1)

Here, $F(t)$ and $B(t)$ were total muon events counted by the forward and backward counters at time $t$ respectively. The $\alpha$ is a calibration factor reflecting relative counting efficiencies between the forward and backward counters. All time spectra in this study were analyzed using the data analysis program named WiMDA [10].

3. Results and Discussions

Figure 1 is summarized data of LF-μSR time spectra of TlCu$_{1-x}$Mg$_x$Cl$_3$ at lowest temperatures in this study. Data of Fig.1 (a) are quoted from ref.[6], and data of Fig.1 (b) and (c) are from ref.[8]. In Fig. 1 , all the time spectra are plotted as the corrected asymmetry in the same horizontal scale for comparison between spectra quoted from different studies. As for Fig.1 (d), time spectra at $T = 0.290$ K are not shown in ref.[7], namely, it is the first report. The time spectra for $x = 0.0047$ are well fitted using the function of $A(t) = e^{-\Delta KT/H_LF} G_{KT}(\Delta, H_{LF}, t)$. $\lambda$ is the muon-spin-relaxation rate, and $G_{KT}(\Delta, H_{LF}, t)$ is the static Kubo-Toyabe function, where $\Delta/\gamma_{\mu}$ is the distribution width of nuclear-dipole fields at the muon sites [11]. $\gamma_{\mu}$ is the gyromagnetic ratio of the muon spin ($2\pi \times 13.5534$ kHz/auuss), and $H_{LF}$ is the applied external longitudinal-field. As discussed in ref.[6], this behavior means that no evidence for the existence of a static internal magnetic field is observed down to 20 mK, and that impurity-induced magnetic moments of the Cu-3$d$ spins are slowly fluctuating at 20 mK.

In the case of $x \geq 0.006$, a fast relaxation in the earlier time range below 1 $\mu$s of ZF time spectra is observed, and LF dependence is not able to be reproduced using the one component function of $A(t) = e^{-\Delta KT/H_{LF}}$. Thus, in the previous study, LF time spectra are analyzed by a two component function of $A(t) = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} G_{KT}(\Delta, H_{LF}, t)$. Here, $A_1 + A_2 = 1$. The first term and the second term represent a fast and slow relaxation components, respectively. As discussed in ref.[7] and ref.[8], the fast relaxation corresponds to the disappearance of the initial asymmetry $A(0)$, which reveals the existence of the static internal magnetic field at the muon sites. The two components function means that the system is in a phase separated state to a spin frozen state and to a spin fluctuating (paramagnetic) state. In this study, we focus on the spin fluctuating region, and discuss the LF dependence of the muon spin relaxation rate $\lambda_2$ of the the spin fluctuating region at low temperatures below 0.3 K.
Figure 1. Time spectra of the LF-μSR in TlCu$_{1-x}$Mg$_x$Cl$_3$. Solid lines are fitted results. The detailed analysis is explained in ref.[6, 7, 8].

Figure 2 shows LF dependence of the muon spin relaxation rate $\lambda_2$ of the spin fluctuating region in TlCu$_{1-x}$Mg$_x$Cl$_3$. Zero-field data are plotted at $H_{LF} = 0.1$ gauss. $A_2$ corresponds to a volume fraction of the spin fluctuating region.

Figure 2. LF dependence of the muon spin relaxation rate $\lambda_2$ of the spin fluctuating region in TlCu$_{1-x}$Mg$_x$Cl$_3$. A value of $A_2$ corresponds to the volume fraction of the spin fluctuating region. In the case of $x = 0.006$, with increasing $H_{LF}$, $\lambda_2$ begins to increase around 20 gauss, and has a peak around 300 gauss. Such behavior in the LF dependence is quite strange, and can not be explained in usual paramagnetic spin states.

This kind of behavior is observed in the pure (no-impurity) spin singlet state of KCuCl$_3$ [12]. Higemoto et al. discussed the possibility of the muon disturbance effect, i.e., implanted muons break spin singlet pairs, and generate free spins near muons. These free spins might cause a strange LF dependence of the muon spin relaxation rate. If so, it is consistent with the measurement results that spin state is in the phase separation to the spin fluctuating region which is in truth the spin singlet state, and to the spin frozen region which causes the disappearance of the initial asymmetry. Here, we emphasize the non-impurity TlCuCl$_3$ is in the spin singlet state at low temperatures. This discussion has not been guaranteed by any theoretical study, but in this stage, this idea is weighty candidate. Similar discussion is reported in the organic triangular-lattice quantum spin magnet $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ [13].

In the case of $x = 0.007$ and 0.015, however, the LF dependence of $\lambda_2$ shows a linear decrease with increasing the $H_{LF}$. This means that muon spins feel widely spread distribution of the local magnetic fields $H_{loc}$ and of the frequency of fluctuation $f$ at the muon sites, because when the distribution of the magnitude of $H_{loc}$ and of spin fluctuation frequencies is homogeneous in time
and in space, the LF dependence of $\lambda_2$ should have a cut-off structure described by the Redfield formula of $\lambda(H_{\text{LF}}) = 2\gamma_\mu^2 H_{\text{loc}}^2 \tau^2 / (1 + \gamma_\mu^2 H_{\text{LF}}^2 \tau^2)$, where $\tau = 1/f$ is the correlation time of muon spins [14, 15, 16]. In other words, the distribution is "white". Thus, the small amount of the spin fluctuating state ($A_2 \sim 0.15$) is in the paramagnetic state for the case of $x = 0.007$ and 0.015.

In the last, we summarize the change of magnetic ground states with Mg-doping to the spin singlet dimer system. In the slightly doped region of $x = 0.0047$, impurity-induced magnetic moments of the Cu-$3d$ spins are slowly fluctuating at 20 mK. In the case of $x = 0.006$, a half of the system is in a spin frozen state, and the other region is in possibly the spin singlet state. Above $x = 0.007$, a static internal magnetic field region extends, and the remained region is in a paramagnetic state.

4. Summary
We carried out zero- and longitudinal-field muon-spin-rotation measurements in the nonmagnetic impurity doped spin singlet system TlCu$_{1-x}$Mg$_x$Cl$_3$. Especially in the case of $x = 0.006$, the system goes in the phase separation to a spin frozen region and to possibly a spin singlet region.

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