Change in magnetic ground states in nonmagnetic-impurity-doped spin-gap systems $TlCu_{1-x}Mg_xCl_3$ using muon spin relaxation

Takao Suzuki,[1,2,*] Motoki Yamada,[3] Yasuyuki Ishii,[2,†] Isao Watanabe,[2] Takayuki Goto,[4] Hidekazu Tanaka,[3] and Kenya Kubo[1]
[1]*Graduate School of Arts and Sciences, International Christian University, 3-10-2, Osawa, Mitaka, Tokyo 181-8585, Japan*
[2]*Advanced Meson Science Laboratory, RIKEN Nishina Center for Accelerator-Based Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[3]*Department of Physics, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan*
[4]*Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda ku, Tokyo 102-8554, Japan*
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Zero- and longitudinal-field muon-spin-relaxation (ZF- and LF-μSR) measurements were carried out on the impurity-doped spin gap systems $TlCu_{1-x}Mg_xCl_3$. 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 as previously reported [J. Phys. Soc. Jpn. **78**, 074705 (2009)]. Above $x = 0.006$, the existence of a static internal magnetic field is confirmed by LF-μSR, and with increasing Mg concentration of x, the internal magnetic field, and the volume fraction of a spin frozen region where the static internal magnetic field appears 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, and also suggest there exist a threshold doping ratio in the appearance of a static staggered moment in the $S = 1/2$ dimer systems weakly coupled by three-dimensional interactions.

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I. INTRODUCTION

Impurity effects and impurity-induced magnetic orderings on spin gap systems are old-yet-new problems in magnetism, and are still attracting much interest from the viewpoint of a key to the quantum nature of these systems, because magnetic behaviors induced by the impurity-doping reflect the interior character of materials, such as the spin number, the sign and the ratios of exchange interactions between each spins, and so on. So far, no little experimental and theoretical studies have been reported in various systems, spin-Peierls chain, $S = 1$ Haldane chain, $S = 1/2$ Heisenberg two-leg ladder, one-dimensional alternating $S = 1/2$ spin chain, etc.[1–9] Recently, Bobroff *et al.* proposed a new common framework to explain the generic low-temperature impurity-induced spin-freezings in low-dimensional spin gap systems using NMR, μSR, and quantum Monte Carlo simulations.[10] Unfortunately, the proposed model is not applied to the system of $S = 1/2$ dimers weakly coupled by three-dimensional interactions.

$TlCuCl_3$, which is the parent material of the subject compound in this study, is a three-dimensionally coupled Cu-3d $S = 1/2$ spin dimer system, and has the strong intradimer antiferromagnetic interaction J which is responsible for the magnetic ground states of spin singlets with an excitation gap of $\Delta_{gap}/k_B = 7.5$ K. In the spin singlet ground state, the spin dimers couple with one another through interdimer exchange interactions J', and this interdimer coupling plays an important role in the field- and the impurity-induced magnetic order.[11–15] When a magnetic field above the gap field H_g is applied, a magnetically ordered state appears, and this field-induced magnetic ordering can be described as Bose-Einstein condensation (BEC) of the excited triplets (magnons) theoretically.[16–21]

The impurity-induced magnetic order has also been reported in the Mg-doped $TlCu_{1-x}Mg_xCl_3$.[22–27] The magnetic phase transition to an ordered state is observed by magnetization and specific heat measurements in the zero-field limit, and neutron elastic scattering measurements identified that this impurity-induced ordered state is an antiferromagnetically ordered state of which the magnetic structure is the same with the case in the field-induced phase in $TlCuCl_3$. A remarkable point is that a finite spin gap still remains below the magnetic phase transition temperature T_N.[23]

The authors group has reported results of muon spin relaxation measurements in $TlCu_{1-x}Mg_xCl_3$ with $x = 0.0047$ and with $x = 0.015$.[28,29] In the case of $x = 0.015$, a fast muon spin relaxation is observed in ZF-μSR time spectra below T_N = 2.85 K, although the spontaneous muon spin precession is not observed. LF-μSR measurements revealed the existence of an internal static magnetic field of 180 gauss at 0.29 K and of 90 gauss at 2.3 K, which indicate the spin state is a spin frozen state.[29] In the case for $x = 0.0047$, however, no evidence for the existence of a static internal magnetic field is observed down to 20 mK, and LF-μSR measurements revealed that impurity-induced magnetic moments of the Cu-3d spins are slowly fluctuating at 20 mK although the specific heat measurement indicated a magnetic phase transition at $T_N = 0.70$ K. We discussed a possibility that the impurity-induced magnetic moments are fluctuating with preserving its wave vector and its relative phase, i.e., they are in *the coherently fluctuating state*.[28]

In order to clarify the change in magnetic ground states and the development of an order parameter with increasing the impurity concentration, systematic investigations are needed in the concentration region between 0.0047 and 0.15. In this study, ZF- and LF-μSR measurements in $TlCu_{1-x}Mg_xCl_3$ with $x = 0.006$ and with $x = 0.007$ are reported, and the change in ground states is discussed.

II. EXPERIMENTS

Single crystals used in this study were grown from a melt by the Bridgman method. The details of crystal growth are given elsewhere.[25] The concentration of x was determined by the inductively coupled plasma atomic emission spectrometry method. Measurements of μSR 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. A pulse width of the muon beam is approximately 70 ns full-width at half-maximum, and the upper limit of a static internal field at the muon sites detected by the spontaneous muon spin precession is about 600 gauss.[30] Single crystals were cleaved to lots of small pieces in the helium gas just before each measurement, and were mounted on a high-purity silver plate by an Apiezon N grease. Mounted samples and the silver plate were covered tightly by a high-purity silver foil (thickness 50 μm) to ensure thermal contact between the sample surface and the silver plate which is connected directly to the cold-head of ^{3}He refrigerator. In μSR measurements, spin-polarized muons are implanted into samples. The incident muon-spin direction was perpendicular to the $(1,0,\bar{2})$ plane of single crystals, and directions of crystal axis perpendicular to the incident muon-spin direction were random on the silver plate. Forward and backward counters were located on the upstream and downstream sides of the beam direction, which was parallel to the initial muon-spin direction. The asymmetry $A(t)$ was defined as follows:

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

Here, $F(t)$ and $B(t)$ were total muon events counted by the forward and backward counters at a time t. The α is a calibration factor reflecting relative counting efficiencies between the forward and backward counters, and is determined by the muon-spin-rotation in the transverse field of 20 G at temperature of 8 ∼ 10 K where no fast relaxation is observed in zero field. The initial asymmetry is defined as $A(0)$. In this study, the calibration factor α and the background subtraction were taken into account for the data analysis. All μSR time spectra are plotted using the corrected asymmetry which is normalized by $A(0)$ in each concentration of x. Measured time spectra were analyzed using the WiMDA computer program.[31]

III. RESULTS AND DISCUSSIONS

Figure 1 shows the magnetic phase transition temperature T_N as a function of Mg concentration x in $TlCu_{1-x}Mg_xCl_3$. Roughly estimated T_N for $x = 0.006$ and for $x = 0.007$ by ZF-μSR (Figs. 2 and 3) is consistent with the reported data by magnetization and by specific heat measurements.[22,25,28] The accuracy in the composition is $x = 0.006 \pm 0.0005$ and $x = 0.007 \pm 0.0006$.

Figure 2 shows ZF and LF-μSR time spectra in $TlCu_{1-x}Mg_xCl_3$ with $x = 0.006$ and with $x = 0.007$. As for ZF-μSR time spectra, drastic change in the time spectrum is observed with decreasing temperature, and a loss of the initial asymmetry is seen below T_N in the both samples. In order to confirm that the fast relaxation originates from a static internal magnetic field, the LF-μSR measurements were carried out at the lowest temperature in this study. The fast relaxation part in time spectra overlaps, and the long tail of time spectra show parallel shift with increasing the longitudinal field. This is the typical behavior in the presence of a static internal magnetic

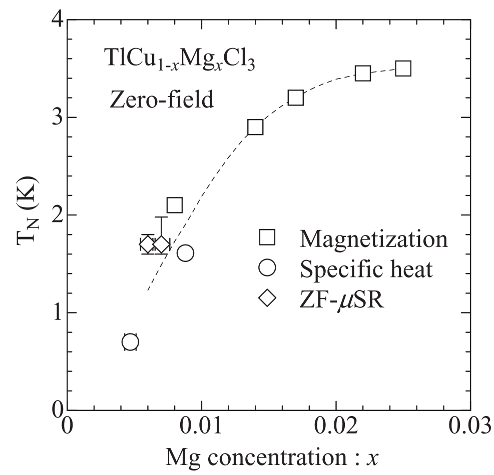

FIG. 1. Magnetic phase transition temperature T_N as a function of x in $TlCu_{1-x}Mg_xCl_3$. Open squares and open circles represent T_N deduced from magnetization (Ref. 22) and from specific heat (Refs. 25 and 28) measurements, respectively. Open diamonds denote T_N rough estimated by ZF-μSR measurements shown in Figs. 2 and 3. Large error bars for $x = 0.006$ and 0.007 are due to less number of data points in the temperature dependence. The dashed line is a guide for the eyes.

field at the muon sites.[35] Thus, the existence of a static internal magnetic field is confirmed above $x = 0.006$. In other words, the spin state is a spin frozen state below T_N. All the time spectra are analyzed using the function

$$A(t) = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} G_{KT}(\Delta, H_{LF}, t). \tag{2}$$

Here, $A_1 + A_2 = 1$. λ_1 and λ_2 are muon-spin-relaxation rates, and $G_{KT}(\Delta, H_{LF}, t)$ is the static Kubo-Toyabe function, where Δ/γ_μ is the distribution width of nuclear-dipole fields at the muon sites.[32] γ_μ is the gyromagnetic ratio of the muon spin ($2\pi \times 13.5534$ kHz/gauss), and H_{LF} is the applied external longitudinal field. In the analysis, Δ/γ_μ is constant in the whole temperature region in this study. $\Delta/\gamma_\mu = 1.06$ gauss for $x = 0.006$, and 1.09 gauss for $x = 0.007$. The analysis is the same with the case for $x = 0.015$ reported in our previous study.[29] Here, it is emphasized that no spontaneous muon spin precession is observed in $x = 0.006$ and in $x = 0.007$, and no precession indicates the spin state is not in a long range magnetically ordered state, because the deduced static internal magnetic field, which is mentioned below, is smaller than the upper resolution limit of the detection of muon spin precessions by the pulsed μSR technique. In such the case, the change to a spin frozen state from the paramagnetic state is reflected in the appearance of a fast relaxation and in a disappearance of the initial asymmetry, which are reproduced by the first exponential term of the formula (2). This result is consistent with the case for $x = 0.015$.[29]

Figure 3 shows the temperature dependence of the relaxation rate λ_2 of the slow relaxation component, and temperature dependence of the fast relaxation component amplitude A_1 in zero field. At the transition temperature T_N, the relaxation rate λ_2 has a maximum, and decreases with decreasing temperature. The amplitude A_1 begins to increase around T_N with decreasing temperature, and saturates at

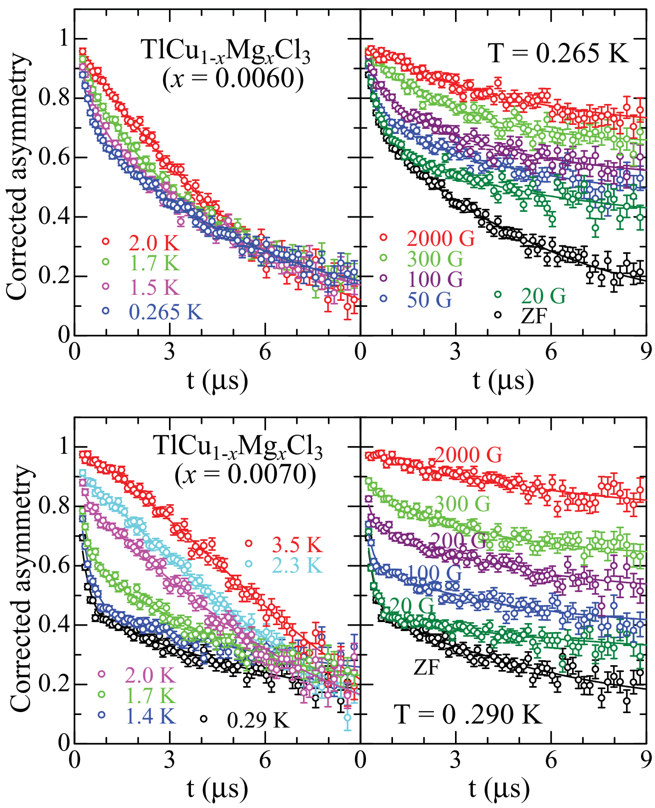

FIG. 2. (Color online) ZF and LF-μSR time spectra in $TlCu_{1-x}Mg_xCl_3$ with $x = 0.006$ and $x = 0.007$. The left side panels show spectra of ZF-μSR, and the right side panels show spectra of LF-μSR. Solid lines are fitted results using the formula (2).

lower temperatures in the both samples. Generally, implanted muon spins precess around the internal magnetic field at the muon sites, and muon spins are depolarized due to the inhomogeneous distribution of internal magnetic fields in time and in space. When there exists static internal magnetic fields, the static fields of which directions are parallel to that of the incident muon beam do not depolarize the muon spins, and if the static internal magnetic fields are randomly directed, one-third of polarized muon spins maintain their direction. In such a situation of the existence of randomly directed static fields, the asymmetry $A(t)$ remains to be $1/3$ of the initial asymmetry A_0, although $A(t)$ goes to zero in the case for dynamic fields in $t \to \infty$. Thus, the volume fraction of a spin frozen region of samples is $3/2$ of the normalized amplitude A_1 under the assumption that the static internal magnetic fields have random directions and the assumption that all the fast relaxation component originates from a static internal magnetic field. This behavior of the "1/3 recovery" caused by static internal magnetic fields is seen in ZF- and LF-μSR time spectra of Fig. 2. In zero field, below T_N, the tail of time spectrum rises up, and it crosses over time spectra in higher temperatures. In longitudinal fields at lower temperature below T_N, the long-tail of time spectra is rather flat, and shows a parallel shift with increasing H_{LF} as sited above.

Figure 4 shows longitudinal field dependence of the amplitude A_2 of the formula (2) for $x = 0.006$ and for $x = 0.007$. Implanted muon spins in materials are decoupled by longitudinal fields H_{LF} from the static internal magnetic field H_{int} at

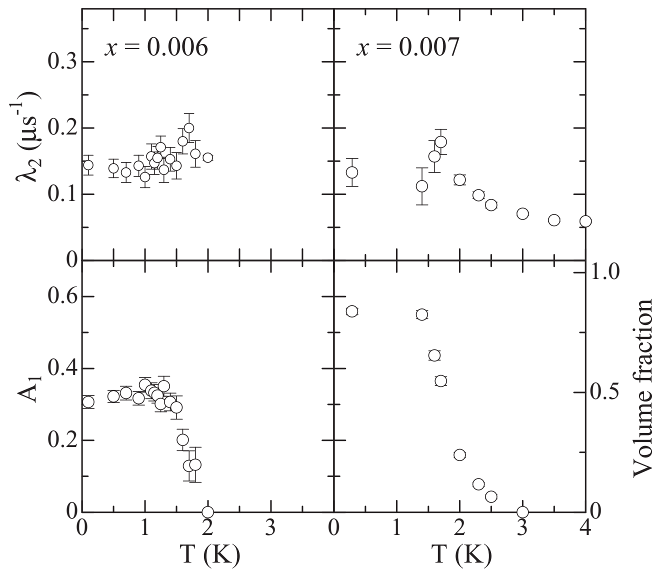

FIG. 3. Temperature dependence of the relaxation rate λ_2 of the slow relaxation component (upper panels), and temperature dependence of the fast relaxation component amplitude A_1 of the formula (2) (lower panels).

the muon sites, and it leads to a revival of the vanished initial asymmetry which is caused by the fast relaxation by static internal fields as shown in Fig. 2. This change in time spectra is represented by the increase of A_2 in the formula (2), and H_{int} at the muon sites is deduced using the formula

$$A_2(H_{LF}) - C \propto \frac{3}{4} - \frac{1}{4x^2} + \frac{(x^2-1)^2}{8x^3} \ln\left|\frac{x+1}{x-1}\right|, \quad (3)$$

where $x = H_{LF}/H_{int}$. The constant term C originates from the finite volume fraction of spin fluctuating regions. This formula is derived from the assumption that H_{int} has a unique

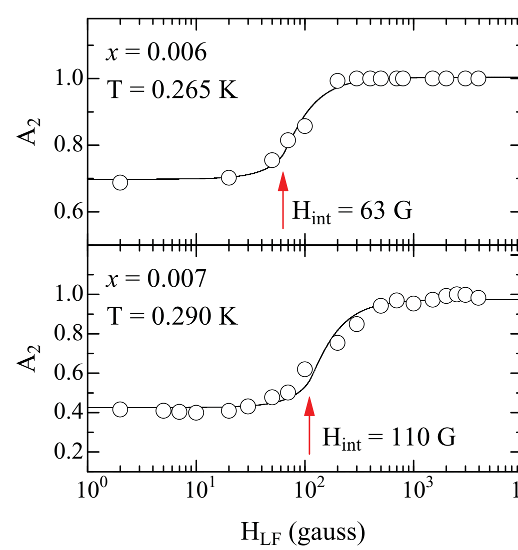

FIG. 4. (Color online) Longitudinal field dependence of the amplitude A_2 of the formula (2) for $x = 0.006$ and $x = 0.007$. Error bars are within symbols. Solid lines are fitted results using the formula (3). Arrows indicate the deduced static internal magnetic field H_{int} at the muon sites.

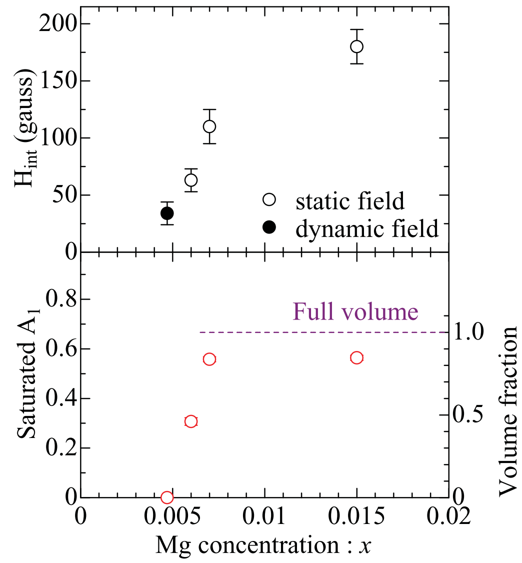

FIG. 5. (Color online) Upper panel: Mg concentration dependence of the internal magnetic field at the muon sites deduced from LF-μSR measurements. Open circles and a closed circle denote static fields and a dynamic (fluctuating) field. Lower panel: Mg concentration dependence of a saturated value of the fast relaxation component amplitude A_1 in ZF-μSR time spectra, which corresponds to the volume fraction of the spin frozen region. Error bars are within plotted circles. Data for $x = 0.0047$ and for $x = 0.15$ are from Refs. 28 and 29, respectively.

magnitude but random directions to H_{LF}.[33,34] As mentioned above, no spontaneous muon spin precession is observed, which indicates Cu-3d spins do not show a coherent order, and in addition, as shown in Fig. 4, H_{LF} dependence of A_2 is well reproduced by the formula (3). These facts mean that the assumption of randomly directed internal static fields is reasonable for the purpose of deduction of values of H_{int}.

Mg-concentration dependence of the internal magnetic field at the muon sites deduced from LF-μSR measurements is shown in the upper panel of Fig. 5. The lower panel of Fig. 5 shows Mg-concentration dependence of a saturated value of the fast relaxation component amplitude A_1 in ZF-μSR time spectra, which corresponds to the volume fraction of the spin frozen region as stated above. In both figures, the data for $x = 0.0047$ and for $x = 0.015$ are from the previous reports.[28,29] As seen in Fig. 5 clearly, with increasing the Mg concentration of x, the magnetic ground state changes as follows: In the slightly doped case of $x = 0.0047$, the impurity-induced magnetic moments are slowly fluctuating, and fluctuating H_{int} at the muon sites is 34 gauss. Above $x = 0.006$, a static H_{int} appears, and with increasing Mg concentration of x, the static H_{int} and the volume fraction of the spin frozen region increase simultaneously. Thus, the magnetic ground state changes from the spin singlet state to a spin fluctuating state, and to a spin frozen state with increasing the Mg concentration of x. It is suggested that there exists a threshold doping ratio in the appearance of a static staggered moment.

In the last, we conjecture on a reason for a fluctuating spin state and for no long range order. Generally in spin dimer systems, a substituted nonmagnetic ion for a magnetic ion is expected to release an unpaired spin, and in a finite region around it, the antiferromagnetic correlation might spread. These unpaired spins interact one another through the interdimer exchange interaction with excited states of spin dimers, and the spin system tends to the magnetic phase transition. In the case of $TlCu_{1-x}Mg_xCl_3$, a finite spin gap still remains below the magnetic phase transition temperature,[23] and it is expected that the spin system is divided into islands of a short-range ordered state (or a spin frozen state) around Mg ions and the gapped state. If interactions between a small amount of unpaired spins are further reduced by the gapped region, a spin fluctuating state might appear. Indeed, when a spin gap is collapsed by pressures, the spontaneous muon spin precessions, which indicates the appearance of a long range magnetically ordered state, are observed below T_N in the case of $x = 0.015$.[29,36]

IV. SUMMARY

Zero- and longitudinal-field muon-spin-relaxation (ZF- and LF-μSR) measurements were carried out on the nonmagnetic-impurity-doped spin gap systems $TlCu_{1-x}Mg_xCl_3$. In a slightly doped case of $x = 0.0047$, no evidence for a static internal magnetic field is observed down to 20 mK, and LF-μSR results reveal that impurity-induced magnetic moments are slowly fluctuating although the specific heat measurement result indicates the magnetic phase transition at $T = 0.70$ K. Above $x = 0.006$, the existence of a static internal magnetic field is confirmed by LF-μSR, but a spontaneous muon spin precession is not detected. These results indicate the spin system is not in a long range magnetically ordered state but in a spin frozen state. With increasing Mg concentration of x, the deduced 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 with increasing the Mg concentration of x. It is suggested that there exists a threshold doping ratio in the appearance of a static staggered moment in the $S = 1/2$ dimer systems weakly coupled by three-dimensional interactions.

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*suzuki_takao@riken.jp
†Present address: Department of Physics, Tokyo Medical University, Shinjuku-ku 6-1-1, Tokyo 160-8402, Japan.

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