The effect of randomness on the quantum spin system Tl$_{1-x}$K$_x$CuCl$_3$ with $x = 0.44$
studied by the Zero-field Muon-Spin-Relaxation (ZF-$\mu$SR) method

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Zero-field muon-spin-relaxation (ZF-$\mu$SR) measurements were carried out down to 80 mK on
the randomness bond system Tl$_{1-x}$K$_x$CuCl$_3$ with $x = 0.44$. Time spectra are well fitted by the
stretched exponential function $\exp(-\lambda t)^{\beta}$. The muon spin relaxation rate $\lambda$ increases rapidly
with decreasing temperature, and $\beta$ tends to 0.5 at 80 mK. The divergent increase of $\lambda$ suggests
the critical slowing down of the frequency of the Cu-3d spin fluctuations toward a spin frozen
state below 80 mK, and the root-exponential-like behavior of the time spectrum indicates that
the origin of the relaxation is possibly the spatially-fixed fluctuating dilute moments.

KEYWORDS: Tl$_{1-x}$K$_x$CuCl$_3$, spin gap, magnon, Bose-Einstein condensation, randomness, Bose glass
phase, $\mu$SR

1. Introduction

The isostructural materials TlCuCl$_3$ and KCuCl$_3$ are
three-dimensionally coupled Cu-3d $S = 1/2$ spin dimer
systems, and their magnetic ground states are spin-
singlets with excitation gaps of $\Delta = 7.5$ K and 31 K,
which originate from strong intradimer antiferromagnetic interaction $J$. The spin dimers couple with one
another through interdimer exchange interactions. The excited spin triplets (magnons) in the singlet sea can
hop to neighboring dimers due to the transverse component
of the interdimer interaction, and the system
can be represented as an ensemble of bosonic partic-
les. Under strong magnetic fields higher than the
gap field $H_g = \Delta/gy_m$, a magnetically ordered state ap-
ppears, and this field-induced magnetic ordering can be
described as Bose-Einstein condensation (BEC) of the
excited triplets, because the superfluid and Mott insu-
lating phases of the system of bosonic-particles theo-
retically correspond to the field-induced ordered phase
and the gapped phase in the present spin system.

In low-dimensional spin gap systems, theoretical stud-
ies predict that the ground state can be affected by
an exchange bond-randomness and the exchange
bond-randomness effect on the quantum spin system has
been studied experimentally in many materials. In the
random bond one-dimensional Heisenberg chain system
(CH$_3$)$_2$CHNH$_2$Cu(C1$_2$Br$_{1-x})_3$, spin gap phases are ob-
served for $x < 0.44$ and $x > 0.87$, whereas a magnetically
ordered phase at zero-field is observed in the concen-
tration region of 0.44 $< x < 0.87$ by the magnetic sus-
ceptibility and specific heat measurements. The long
range ordered state was confirmed for $x = 0.85$ by a
muon-spin-rotation measurement.

In the mixed system Tl$_{1-x}$K$_x$CuCl$_3$, which is the sub-
ject of this study, the randomness of the local potential
is introduced through the difference of the value of the
dominant interdimer interaction $J$ between TlCuCl$_3$ and
KCuCl$_3$, because $J$ corresponds to the local potential of
magnons. Magnetization measurements suggest that the
ground state is negative with no gap in the mixed sys-
tem in zero field (ZF), although both the parent materi-
als are non-magnetic having finite excitation gaps. In
other words, the randomness induces a finite magnetic
density of states within the excitation gap.

The appearance of a new phase, Bose-glass phase, in
lower magnetic fields at $T = 0$ is predicted by theo-
ries. According to theoretical predictions, the Bose-
glass phase is produced between gapped and ordered
phases corresponding to Mott insulating and superfluid
phases. By the correspondence between the spin system
and the bosonic-particle system, the uniform magneti-
zation $M$ and the magnetic susceptibility $\chi = \partial M/
\partial H$ correspond to the number of the bosons $N$ and the
compressibility $\kappa$. In the BEC phase, i.e., the superfluid state
of bosons, the system is characterized by a finite stag-
gered magnetization perpendicular to the applied mag-
netic field, whereas the Bose-glass phase is distinguished
by the disappearance of the staggered magnetization
keeping the magnetic susceptibility finite. In other word,
bosons are localized due to randomness, but there is no
gap.

Shindo et al. carried out specific heat measurements in
magnetic fields, and observed field-induced phase transi-
tions which are described by the Bose-Einstein condensa-
tion of triplets of Cu-3d spins in the mixed system
Tl$_{1-x}$K$_x$CuCl$_3$. They discussed the obtained phase
diagram in connection with the appearance of the Bose-
glass phase. Bose-glass phenomena have also been stud-
ied intensively in other disordered quantum systems, vor-
tex lattices and trapped atoms.

Recently, we reported the increase of the muon-spin-
relaxation rate $\lambda$ at low temperature as well as the NMR-
$T_1$ in Tl$_{1-x}$K$_x$CuCl$_3$ with $x = 0.20$ single crystals, which
is possibly a precursor to the Bose-glass phase at
$T = 0$. These results are consistent with the theoretical
prediction that the Bose-glass phase is expected to appear for \( x > 0 \). However, it is not yet known whether or not another ground state apart from the Bose-glass phase and the gapped state appears when the randomness is enhanced with increasing the concentration of \( x \) in the system. In order to investigate microscopic magnetic properties and to obtain information about the ground state in highly random systems, we carried out the zero-field muon-spin-relaxation (ZF-\( \mu \)SR) measurements in \( \text{Tl}_{1-x}\text{K}_x\text{CuCl}_3 \) with \( x = 0.44 \) single crystals.

In ionic crystals, the positive muon \( \mu^+ \) usually stops near minus ions. For example, the muon-site in the case of high-\( T_c \) cuprates is determined to be near the \( \text{O}^{2-} \) ions.\(^{38}\) In \( \text{Tl}_{1-x}\text{K}_x\text{CuCl}_3 \), muon spins are expected to be implanted near the \( \text{Cl}^- \) ions. We expect that muon spins probe information about the Cu-\( 3d \) spins through a hyperfine interaction, because it is reported that muon spins successfully detect Cu-\( 3d \) spin fluctuations in the other quantum spin systems (\( \text{CH}_3\text{Br}_2\text{CHNH}_3\text{CuCl}_3 \) and (\( \text{CH}_3\text{Br}_2\text{CHNH}_3\text{CuCl}_3\text{Br}_{1-x} \)) which are similar compounds to \( \text{Tl}_{1-x}\text{K}_x\text{CuCl}_3 \).\(^{26,39}\)

2. Experimental

Single crystals used in this study were grown from a melt by the Bridgman method. The details of crystal growth are given elsewhere.\(^{27}\) The magnetization was measured using a superconducting quantum interference magnetometer (Quantum Design MPMS XL) in the department of physics, Tokyo Institute of Technology. Zero-field muon-spin-relaxation (ZF-\( \mu \)SR) measurements were carried out at the RIKEN-RAL Muon Facility in the U.K. using a spin-polarized pulsed positive surface-muon beam with an incident muon momentum of 27 MeV/c. 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 parameter was defined as follows:

\[
A(t) = \frac{F(t) - \alpha B(t)}{F(t) + \alpha B(t)}
\]

\( F(t) \) and \( B(t) \) were total muon events counted by the forward and backward counters at a time \( t \), respectively. The \( \alpha \) is a calibration factor reflecting relative counting efficiencies between the forward and backward counters. The initial asymmetry is defined as \( A(0) \). In this study, the calibration factor \( \alpha \) and the background subtraction were taken into account for the data analysis. The muon-spin-relaxation (\( \mu \)SR) time spectra were measured down to \( T = 80 \text{ mK} \) using a dilution refrigerator (Leiden cryogenics b. v.). The incident muon-spin direction was parallel to the b-axis of single crystals. Cleaved single crystals were attached densely by an Apiezon N grease on a five nines purity silver plate. The total size of crystals is \( 25 \times 3 \times 25 \text{ mm}^3 \).

3. Results and Discussion

Figure 1 shows the temperature dependence of the magnetic susceptibility \( \chi = M/H \) in \( \text{Tl}_{1-x}\text{K}_x\text{CuCl}_3 \) with \( x = 0.44 \) at the magnetic field of 0.1 T. The reciprocal of the susceptibility \( \chi^{-1} \) is shown in the inset of Fig. 1.

Above 60 K, \( \chi^{-1} \) has a linear temperature dependence, which means that the spins are weakly coupled in the higher temperature region. Below 60 K, however, the \( \chi^{-1} - T \) curve deviates from the Curie-Weiss law, and the susceptibility \( \chi \) begins to decrease rapidly with decreasing temperature toward a finite value after a broad peak at 30 K. The rapid decrease of the susceptibility indicates the development of the antiferromagnetic spin correlations at lower temperatures. Such temperature dependence of the susceptibility is the characteristic behavior in this system.\(^{27,31,32}\)

Figure 2 shows the temperature dependence of the magnetic susceptibility at high magnetic fields of 3, 5, and 7 T. No cusp like minimum is observed down to 1.8 K.
and up to 7 T, which suggests a shift of the field-induced magnetic phase transition point to lower temperatures and/or to higher magnetic fields region. This result is consistent with the tendency reported in Tl$_{1-x}$K$_x$CuCl$_3$ with $x<0.27$ (ref.27). A possible origin of the shift of the transition point is the enhancement of the bond-randomness introduced in the system, because the concentration of $x$ is supposed to correspond to the degree of the randomness. Another possibility is the development of a uniform spin excitation gap of the system because the excitation gap in KCuCl$_3$ is quite large compared with that in TlCuCl$_3$.

Figure 3 shows the field dependence of the magnetization ($M$-$H$ curve) at 1.8 K. A finite value of the differential $dM/dH$ at the zero-field limit indicates that the ground state is paramagnetic. As seen in Fig.3, absolute values of the magnetization $M$ and of the differential $dM/dH$ are larger compared to those reported in the samples with $x<0.27$. The increase of the magnetization with increasing $x$ means that the density of states for the spin excitations in the low-energy region is enhanced. It is suggested that the strong randomness is introduced intrinsically in the single crystals with the concentration of $x=0.44$, although it is not clear whether an excitation gap $\Delta$ develops. From these magnetization results, the spin system is not in a magnetically ordered state but in a paramagnetic state with a finite susceptibility at the zero-field limit, at least down to 1.8 K.

Figure 4 shows ZF-$\mu$SR time spectra of Tl$_{1-x}$K$_x$CuCl$_3$ with $x=0.44$ at each temperature. The shape of the time spectrum is changed drastically with decreasing temperature. The spectrum shape at 10 K is a Gaussian-like function (opens downwards). At lower temperatures, the spectrum becomes exponential-like at 3 K, and finally, a rather fast relaxation is observed at 80 mK. In order to discuss the spectrum change by one formula in the whole temperature range in this study, the $\mu$SR time spectra are analyzed using the function of the stretched exponential function $\exp(-\lambda t)^\beta$.

![Fig. 3. Magnetic field dependence of the magnetization at 1.8 K. The inset shows the magnetic field dependence of $dM/dH$.](image)

![Fig. 4. Time spectrum of the zero-field muon-spin-relaxation (ZF-$\mu$SR) of Tl$_{1-x}$K$_x$CuCl$_3$ with $x=0.44$ at each temperature. Solid lines are fitted results using the stretched exponential function $\exp(-\lambda t)^\beta$.](image)
rounding magnetic moments, we can apply these results of the nuclear-spin-relaxation analysis to the case in the \( \mu \)SR measurement.\textsuperscript{41,42} Although it is difficult to distinguish whether or not spins are fluctuating without longitudinal-field muon-spin-relaxation measurements, it can be suggested from the root-exponential-like (\( \beta = 0.65 \)) behavior observed at 80 mK in this study that the fast muon-spin-relaxation originates from the spatially-fixed dilute moments fluctuating in time, and it is suggested that spatially separated islands, which have a finite magnetic moment large enough to cause the fast muon-spin-relaxation, appear in the singlet sea at lower temperatures.

Figure 6 shows the time spectrum of the ZF-\( \mu \)SR in \( \text{Tl}_{0.20}K_x\text{CuCl}_3 \) with \( x = 0.20 \) at 0.3 K and with \( x = 0.44 \) at 80 mK. In the case of \( x = 0.20 \), the time spectrum is well fitted by a simple exponential function, and the muon-spin-relaxation rate \( \lambda \) tends to saturate at lower temperatures as shown in Fig. 5.\textsuperscript{46} The saturation of \( \lambda \) in the case of \( x = 0.20 \) is consistent with the existence of the Bose-glass phase at \( T = 0 \) by analogy with the result on the frustrated system which has quantum spin fluctuations without static local magnetic fields at muon sites down to 100 mK.\textsuperscript{44} In the case of \( x = 0.44 \), however, the shape of the time spectrum is the root-exponential-like, and the relaxation rate \( \lambda \) shows the rapid increase with decreasing temperature as mentioned above. This result observed in \( x = 0.44 \) is quite different from the case in \( x = 0.2 \), and this difference indicates the ground state changes with increasing the concentration \( x \) corresponding to the degree of the bond-randomness. The existence of a new ordered phase is expected in highly random regions. Finally, we emphasize that the result reported in this study is a new phenomenon which has not been predicted theoretically or observed previously in this system.

4. Summary

In summary, we carried out magnetization and zero-field muon-spin-relaxation (ZF-\( \mu \)SR) measurements in the bond-randomness introduced quantum spin system \( \text{Tl}_{0.20}K_x\text{CuCl}_3 \) with \( x = 0.44 \) single crystals. The muon-spin-relaxation rate \( \lambda \) increases rapidly with decreasing temperature, and the time spectrum at 80 mK shows a root-exponential like behavior. These results suggest that below 80 mK, in contrast to the predicted Bose-glass phase, there exists a critical slowing down of the frequency of the Cu-3\( d \) spin fluctuation toward a spin frozen state. The muon-spin-relaxation \( \lambda \) in this state originates from spatially-fixed fluctuating dilute moments.

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