$^{63,65}$Cu-NMR study on Mg-doped quantum spin system

$\text{TlCu}_{1-x}\text{Mg}_x\text{Cl}_3$

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Abstract. NMR measurements were carried out on the impurity doped quantum spin system $\text{TlCu}_{1-x}\text{Mg}_x\text{Cl}_3$ with nominal concentration $x = 0.03$ and 0.01, in which the magnetic phase transition is expected at 3.6 K and 2.2 K, respectively. For the sample $x = 0.03$, the peaks of NMR spectra split clearly below $T = 3.8$ K. However, for the sample $x = 0.01$, no peak splitting was observed down to $T = 1.52$ K. This result supports the idea of coherent spin fluctuation in the impurity-induced ordered state as suggested by Suzuki et al. [2009 J. Phys. Soc. Jpn. 78 074705.].

1. Introduction

The singlet ground state with an excitation gap has been found in many quantum spin systems such as the Haldane chain, spin-Peierls system, spin ladder, exchange alternating chain, and coupled spin dimer system. These spin gap systems do not have a magnetic ordering down to zero temperature, and possess gapped ground state that arises from the dimerization of spins localized in magnetic ions. Therefore, when a small number of nonmagnetic ions are substituted for magnetic ions, singlet spin dimers are partially broken, so that unpaired spins are produced near the nonmagnetic ions. Unpaired spins can interact through effective exchange interactions that are mediated by singlet dimers [1-5].
and hence may show a three-dimensional Néel ordering. Such impurity-induced magnetic ordering is observed in many spin gap systems [6-8].

Recently, impurity-introduced TlCu$_{1-x}$Mg$_x$Cl$_3$ single crystals have been grown, and new intriguing phenomena have been reported. Oosawa et al. and Fujisawa et al. reported, by magnetization and neutron scattering experiments, a coexistence of the spin gap and the impurity-induced magnetic order [9-11]. When the magnetic field reaches the critical field $H_C$, the gap is collapsed and magnons are induced. The system can undergo field-induced magnetic ordering when the concentration of these field-induced magnons reaches the critical value in still higher field. It is not clear whether field- and impurity-induced ordered states have the same spin state. Furthermore, even in the ordered state, no muon spin rotation was observed at temperatures well below the Néel temperature $T_N$ for the sample with an extremely small impurity concentration $x = 0.0047$ [12]. The purpose of our research is to investigate microscopically the difference of spin states between field- and impurity-induced magnetic orders by NMR.

2. Experimental

The single crystals of TlCu$_{1-x}$Mg$_x$Cl$_3$ used in this study were grown from a melt by the Bridgman method. The details of crystal growth are given in ref. 13. The TlCu$_{1-x}$Mg$_x$Cl$_3$ crystal is easily cleaved parallel to the planes (0, 1, 0) and (1, 0, 2). The single crystals were cleaved in a glove box filled with dry nitrogen gas to reduce the amount of hydrate phase on the sample surfaces. We measured the temperature dependence of $^{63,65}$Cu-NMR spectra for single crystals of TlCu$_{1-x}$Mg$_x$Cl$_3$ with nominal concentration $x = 0.03$ and 0.01 in the temperature region down to 1.52 K. We also measured the specific heat with $x = 0.03$ by the apparatus of PPMS, Quantum Design, Inc.

3. Results and Discussion

Fig. 1(a) shows the temperature dependence of NMR spectra corresponding to the satellite transition ($I_z = 3/2 \leftrightarrow 1/2$) for the sample with nominal concentration $x = 0.03$. The applied field is much smaller than the critical field, approximately $H_c = 6$ T at $T = 2$ K [13], where the spin gap is collapsed. At high-temperature region above $T > 4$ K, where the system is paramagnetic, sharp six peaks were observed. These two pairs of satellite peaks, #1, #3 and #4, #6, are considered to arise, because the local magnetic environment of the Cu sites nearest-neighbouring or second nearest-neighbouring to the Mg atoms is slightly modified due to the substitution. As lowering temperature, every peak showed a gradual broadening, and below $T < 3.8$ K, these peaks split drastically as indicated on, for example, peak #5 by arrows in Fig. 1(a). Fig. 2 shows the results of specific heat measurements on the present sample. A small peak was observed at $T \cong 3.5$ K and 3.6 K for $H = 0$ T and 5 T, respectively. Therefore, under the field of NMR measurements, $T_N$ was expected to be near 3.6 K which was consistent with the above mentioned temperature $T = 3.8$ K of the beginning of the peak #5 splitting. We plotted the temperature dependence of the split width of peak #5 in Fig. 3. In the impurity-induced
magnetic order, the split width continuously increased without a jump below $T_N$, indicating that it is of the second-order phase transition, while in the field-induced magnetic order [14], the split width shows a finite jump, indicating the involvement of spin-lattice coupling. The hyperfine field in the impurity-induced magnetic order is estimated from the splitting width to be $\Delta \nu/2\gamma \approx 0.07$ T, at the lowest temperature. From a comparison of split widths in field- and impurity-induced magnetic orders [14], the hyperfine field in the impurity-induced magnetic order is a twentieth of that in the field-induced magnetic order. This is consistent with the neutron experiment, which reports that the impurity-induced magnetic moment is much smaller than the full moment of Cu$^{2+}$ [10].

**Figure 1.** The temperature dependence of NMR spectra. (a) For the sample with $x = 0.03$. (b) For the sample with $x = 0.01$.

**Figure 2.** The specific heat measurements for the sample with $x = 0.03$. The Néel temperature is shown by arrows.

**Figure 3.** The temperature dependence of the split width of peak #5 under a field 4.6 T. The curve shown is a guide to eyes.
Fig. 1(b) shows the temperature dependence of NMR spectra for the sample $x = 0.01$. Similar to the case of $x = 0.03$, sharp eight peaks were observed at high-temperature region and showed a gradual broadening as lowering temperature. However, peak splitting was not observed down to $T = 1.52$ K, which is lower than the reported $T_N \approx 2.2$ K [12]. Here we insist on that the observed gradual broadening of the peaks starts at around $T = 6$ K, which is much higher than $T_N$, and hence irrelevant of the magnetic order. This means that the impurity-induced magnetic order is invisible through a probe of NMR for the sample $x = 0.01$, indicating that the ordered moments field in this system might fluctuate dynamically and coherently as suggested in ref. 12. If the fluctuation is faster than the hyperfine field, a splitting should be invisible due to the motional narrowing, although their spatial coherence allows well the Bragg scattering of neutron experiments [10], which have an extremely short time scale.

4. Conclusion
We have presented the results of $^{63,65}$Cu-NMR measurements on Mg-doped quantum spin system TICu$_{1-x}$Mg$_x$Cl$_3$ with nominal concentration $x = 0.03$ and 0.01. For the sample $x = 0.03$, the peaks of NMR spectra split clearly below $T_N \approx 3.8$ K, demonstrating the existence of the impurity-induced magnetic order. However, for the sample $x = 0.01$, no peak splitting was observed suggesting that the static field in this system coherently fluctuates even in the ordered state [12].

5. Acknowledgement
This work was partly supported by a Grant-in-Aid for Scientific Research on Innovative Areas “New Frontier of Materials Science Opened by Molecular Degrees of Freedom” (No. 20110003) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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