Impurity-induced antiferromagnetic ordering in the spin gap system TlCuCl₃

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Magnetization measurements have been performed on the doped spin gap system $TlCu_{1-x}Mg_xCl_3$ with $x \leq 0.025$. The parent compound $TlCuCl_3$ is a three-dimensional coupled spin dimer system with the excitation gap $\Delta/k_B = 7.7$ K. The impurity-induced antiferromagnetic ordering was clearly observed. The easy axis lies in the $(0,1,0)$ plane. It was found that the transition temperature increases with increasing Mg^{2+} concentration x, while the spin-flop transition field is almost independent of x. The magnetization curve suggests that the impurity-induced antiferromagnetic ordering coexists with the spin gap for $x \leq 0.017$.

The singlet ground state with an excitation gap (spin 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 undergo magnetic ordering down to zero temperature. In the last decade, however, it has been found that very small amounts of nonmagnetic site impurities can give rise to antiferromagnetic ordering in these spin gap systems.[1–6] When nonmagnetic ions are substituted for magnetic ions, the singlet ground state is disturbed so that staggered moments are induced around the impurities. If the induced moments interact through effective exchange interactions, that are mediated by intermediate singlet spins, three-dimensional (3D) long-range order can arise. Such impurity-induced magnetic ordering is a new type of phase transition caused by the quantum effect.

Impurity-induced magnetic ordering of spin gap systems was first observed in Zn^{2+}-doped $CuGeO_3$,[1] which is a well-known inorganic spin-Peierls material,[7] and was precisely investigated in Mg^{2+}-doped $CuGeO_3$.[3] Magnetic ordering due to pinning of lattice dimerization by doped nonmagnetic impurities was also observed in $CuGe_{1-x}Si_xO_3$.[8] In $Cu_{1-x}Zn_xGeO_3$ and $CuGe_{1-x}Si_xO_3$ with low x, the coexistence of lattice dimerization and antiferromagnetic ordering has been observed in neutron-scattering experiments.[4,8] Impurity-induced antiferromagnetic ordering was also observed in Zn^{2+}-doped antiferromagnetic two-leg spin ladder $SrCu_2O_3$ (Ref. 5) and the Mg^{2+}-doped Haldane system $PbNi_2V_2O_8$.[6] The site-impurity effect on spin gap systems has been argued theoretically by many authors,[9–11] and impurity-induced antiferromagnetic ordering has been demonstrated.

As mentioned above, experimental studies of impurity-induced antiferromagnetic ordering have been performed only on quasi-1D systems to date. Therefore, for comprehensive understanding of impurity-induced antiferromagnetic ordering, it may be necessary to study the impurity effect on 3D spin gap systems. With this motivation, we studied the magnetic properties in the Mg^{2+}-doped spin gap system $TlCuCl_3$ by means of magnetization measurements.

$TlCuCl_3$ has the monoclinic structure (space group $P2_1/c$).[12] The crystal structure is composed of planar dimers of Cu_2Cl_6. The dimers are stacked on top of one another and form infinite double chains parallel to the crystallographic a axis. These double chains are located at the corners and center of the unit cell in the b-c plane, and are separated by Tl^+ ions. The magnetic ground state of $TlCuCl_3$ is the spin singlet with excitation gap $\Delta = 7.7$ K.[12–14] From the analyses of the dispersion relation obtained by neutron inelastic scattering, it was found that the origin of the spin gap of $TlCuCl_3$ is the strong antiferromagnetic interaction $J = 5.68$ meV in the chemical dimer Cu_2Cl_6, and that the neighboring dimers are coupled by the strong interdimer interactions along the double chain and in the $(1,0,-2)$ plane.[15,16] Consequently, $TlCuCl_3$ was characterized as a strongly coupled 3D spin dimer system.

Before preparing the doped $TlCu_{1-x}Mg_xCl_3$ system, we prepared single crystals of $TlCuCl_3$. The preparation of a single crystal of $TlCuCl_3$ is described in Ref. 14. Mixing $TlCuCl_3$, $TlCl$, and $MgCl_2$ in a ratio of $(1-x):x:x$, we prepared $TlCu_{1-x}Mg_xCl_3$ by the vertical Bridgman method. We obtained single crystals of 1–3 cm³ with $x = 0.008, 0.014, 0.017, 0.020, 0.022$, and 0.025. The magnesium concentration x was analyzed by emission spectrochemical analysis after the measurements. Samples used for magnetic measurements were cut to 50–150 mg. The magnetizations were measured down to 1.8 K in magnetic fields up to 7 T using a semiconducting quantum interference device magnetometer (Quantum Design MPMS XL).

First, we measured the temperature dependence of the magnetic susceptibilities $\chi = M/H$ in $TlCu_{0.975}Mg_{0.025}Cl_3$ under the magnetic field of $H = 0.1$ T perpendicular to the cleavage planes $(0,1,0)$ and $(1,0,\bar{2})$, and along the $[2,0,1]$ direction that is parallel to both $(0,1,0)$ and $(1,0,\bar{2})$ planes, respectively. These three field directions are orthogonal to one another. The results are shown in Fig. 1. With decreasing temperature, the magnetic susceptibilities display broad maxima at $T \sim 36$ K and decrease, as observed in pure $TlCuCl_3$.[12,14] However, the magnetic susceptibilities increase again below 7 K, and then exhibit sharp bend anomalies at $T_N = 3.5$ K, which is indicative of magnetic ordering, for $H \perp (1,0,\bar{2})$ and $H \| [2,0,1]$, whereas the magnetic susceptibility for $H \| b$ increases monotonically. Below T_N, the magnetic susceptibility for $H \perp (1,0,\bar{2})$ is almost independent of temperature, while that for $H \| [2,0,1]$ decreases. These results indicate that the antiferromagnetic ordering induced by Mg^{2+} doping occurs at $T_N = 3.5$ K, and that the easy axis is
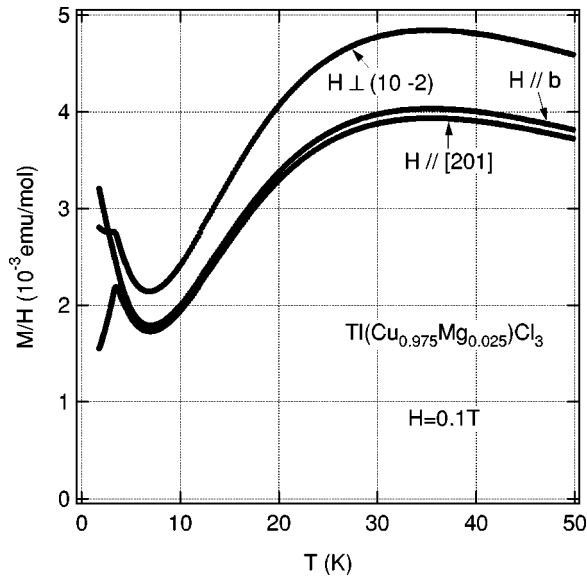
FIG. 1. Temperature dependence of the magnetic susceptibilities $\chi = M/H$ in TlCu$_{0.975}$Mg$_{0.025}$Cl$_3$ measured at $H=0.1$ T for $H\|b$, $H\perp(1,0,\bar{2})$, and $H\|[2,0,1]$.

in the (0,1,0) plane and is close to the [2,0,1] direction.

In order to determine the easy axis, we measured the magnetic susceptibility in TlCu$_{0.980}$Mg$_{0.020}$Cl$_3$, varying the field direction in the (0,1,0) plane at $T=1.8$ K. The susceptibility minimum was observed, when the magnetic field was at an angle of 38° with the a axis. This implies that the easy axis is canted by 38° from the a axis. Since the angle between the [2,0,1] direction and the a axis is 51°, the angle between the [2,0,1] direction and the easy axis is 13°.

Figure 2 shows the low-temperature magnetic susceptibilities in TlCu$_{0.978}$Mg$_{0.022}$Cl$_3$ measured at $H=0.1$ T. The magnetic field was applied along the b axis, the easy axis and the hard axis in the (0,1,0) plane, which are orthogonal to one another. With decreasing temperature, the magnetic sus-
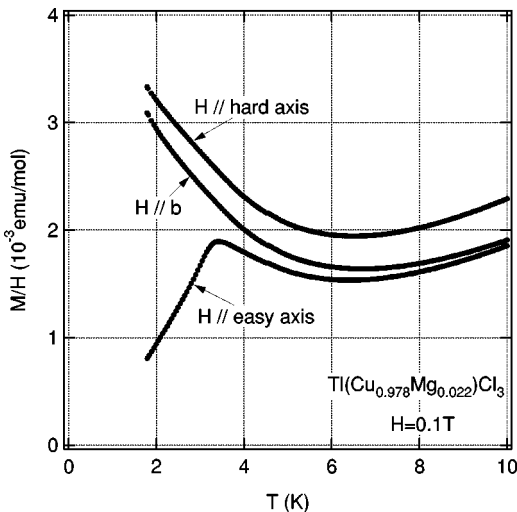

FIG. 2. Low-temperature magnetic susceptibilities in TlCu$_{0.978}$Mg$_{0.022}$Cl$_3$ measured at $H=0.1$ T for $H\|$ easy axis, $H\|$ hard axis in the (0,1,0) plane, and $H\|b$.
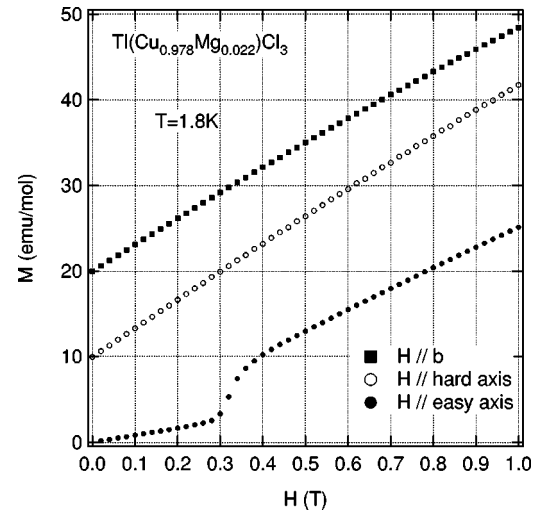
FIG. 3. Magnetization curves in TlCu$_{0.978}$Mg$_{0.022}$Cl$_3$ measured at $T=1.8$ K for $H\|$ easy axis, $H\|$ hard axis in the (0,1,0) plane and $H\|b$. The values of magnetization are shifted upward by 10 emu/mol.

ceptibility of the easy axis decreases towards zero below $T_N = 3.45$ K, while the others increase monotonically. This behavior is indicative of an antiferromagnet with collinear ordering.

Figure 3 shows the magnetization curves of TlCu$_{0.978}$Mg$_{0.022}$Cl$_3$ measured at $T=1.8$ K for $H\|$ easy axis, hard axis, and b axis. For $H\|$ easy axis, the spin-flop transition is clearly observed at $H_{sp}=0.32$ T, while no transition is observed for the other field directions. From these results, it is evident that collinear antiferromagnetic ordering along the easy axis arises below T_N. The sharp cusplike maximum of the susceptibility at T_N and the sharp spin-flop transition indicate the good homogeneity of the present sample at the macroscopic scale.

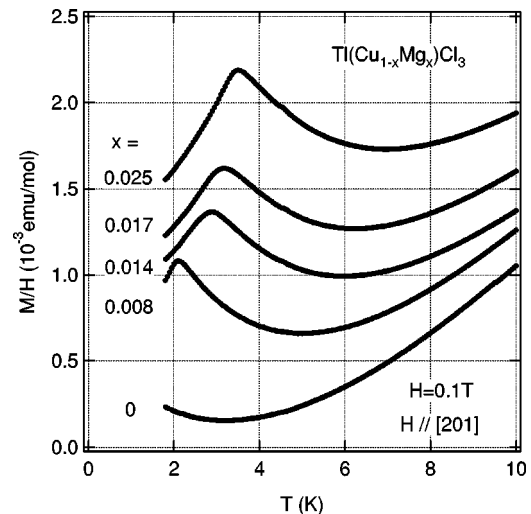Figure 4 shows the temperature dependence of the mag-

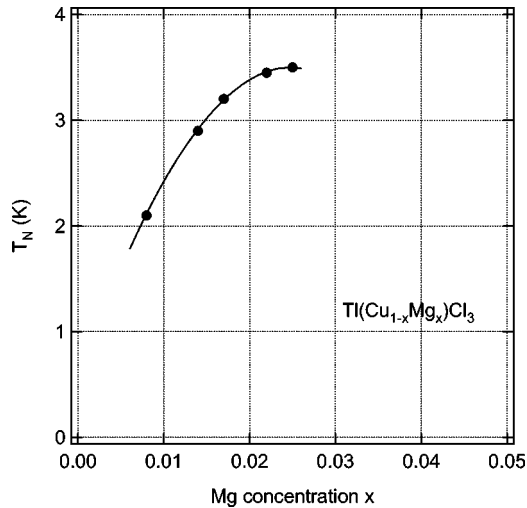FIG. 4. Low-temperature magnetic susceptibilities in TlCu$_{1-x}$Mg$_x$Cl$_3$ measured at $H=0.1$ T for $H\|[2,0,1]$ for various x.

FIG. 5. Phase-transition temperature T_N as a function of x in $TlCu_{1-x}Mg_xCl_3$. The solid line is a guide for the eyes.

FIG. 6. Magnetization curves of $TlCu_{1-x}Mg_xCl_3$ measured at $T = 1.8$ K for $H \| [2,0,1]$ for various x. The values of magnetization are shifted upward by 10 emu/mol with increasing x.

netic susceptibilities in $TlCu_{1-x}Mg_xCl_3$ with various x for $H\|[2,0,1]$. The magnetic field of 0.1 T was applied in the measurements. For $x=0$, no anomaly indicative of the magnetic ordering can be seen down to 1.8 K, although a slight increase of the magnetic susceptibility was observed due to a small amount of impurities or lattice defects. On the other hand, the cusplike anomalies indicative of antiferromagnetic ordering were clearly observed for $x \neq 0$. With increasing x, the transition temperature T_N and the magnitude of the magnetic susceptibility increase. The transition temperatures for $x \leq 0.025$ were plotted in Fig. 5 as a function of x. The transition temperature T_N shows a tendency to saturate at $T_N \approx 3.5$ K. Although the behavior of the phase transition for $x > 0.025$ is of great interest, the measurements were not performed, because it is difficult to prepare good single crystals of $TlCu_{1-x}Mg_xCl_3$ with $x > 0.025$ at present.

It is considered that the direction of the easy axis does not strongly depend on x, and is close to the $[2,0,1]$ direction, because the susceptibilities for various x display a similar cusplike anomaly for $H\|[2,0,1]$, as shown in Fig. 4. Thus, it is expected that the spin-flop transition is observed for $H\|[2,0,1]$, and the transition field is close to that for $H\|$ easy axis. Figure 6 shows the magnetization curves of $TlCu_{1-x}Mg_xCl_3$ with various x measured at $T=1.8$ K for $H\|[2,0,1]$. For $x=0$, the magnetization is almost zero up to the gap field $H_g = \Delta/g\mu_B \approx 6$ T, and then it increases rapidly. For $x \neq 0$, the magnetization increases with a finite slope, and exhibits a jump indicative of the spin-flop transition at $H \approx 0.35$ T with increasing magnetic field. It is noted that spin-flop field H_{sp} is almost independent of x, although the amount of the magnetization jump increases with increasing x.

A theoretical description of the spin-flop transition in the impurity-induced antiferromagnetic phase has not been established to date. In the conventional antiferromagnet, spin-flop field H_{sp} is proportional to the square root of the product of anisotropy energy and the exchange interactions and the magnitude of the spin moment. The small value of ≈ 0.35 T of spin-flop field H_{sp} may be indicative of the low induced
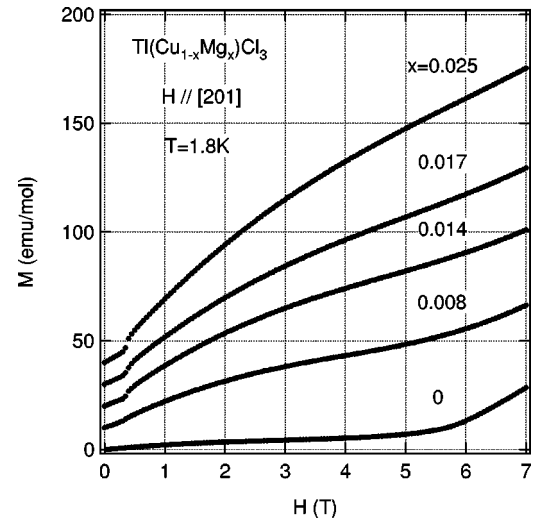
spin moments around the impurities or the low anisotropy energy. At present, however, we have no explanation for why the spin-flop field is independent of x.

For $x \leq 0.017$, the magnetization tends to increase at $H \sim 6$ T, which is almost the same as the gap field H_g of ≈ 6 T of pure $TlCuCl_3$, as shown in Fig. 6. This suggests that the excitation gap remains for $x \leq 0.017$, i.e., antiferromagnetic ordering coexists with the excitation gap. If the gap remains, field-induced magnetic ordering may occur, as observed in pure $TlCuCl_3$.[14,17,18] In $TlCuCl_3$, the magnetization has the cusplike minimum at the transition temperature.[14,17] This behavior can be described in terms of the Bose-Einstein condensation of the excited triplets (magnons).[19] In the ordered phase, transverse staggered magnetic ordering with respect to the applied magnetic field occurs.[19–21] This transverse staggered magnetic ordering, in which two spins on the same dimer are antiparallel, was confirmed by neutron elastic-scattering analysis in high magnetic fields for $H\|b$.[18] For this field direction, it was observed that spins lie in the $(0, 1, 0)$ plane at an angle of $39°$ to the a axis. This spin direction is almost the same as that of the easy axis in the impurity-induced antiferromagnetic phase for $TlCu_{0.978}Mg_{0.022}Cl_3$. Thus, the relation between the impurity-induced antiferromagnetic phase and the field-induced ordered phase is of great interest.

In order to investigate whether or not field-induced magnetic ordering occurs in Mg^{2+}-doped $TlCuCl_3$, we examined the temperature dependence of the magnetization in $TlCu_{0.992}Mg_{0.008}Cl_3$ at various magnetic fields up to 7 T for $H\|[2,0,1]$. However, no definite phase transition was detected due to the large Curie-Weiss term, although a fairly sharp inflection point indicative of the phase transition was observed for $H > 5$ T. Thus, other experiments such as specific heat and neutron-scattering measurement are required in order to determine whether field-induced magnetic ordering occurs also in Mg^{2+}-doped $TlCuCl_3$.

In conclusion, we carried out magnetization measurements in $TlCu_{1-x}Mg_xCl_3$. Impurity-induced antiferromag-

netic ordering was clearly observed for $0.008 \leq x \leq 0.025$. It was found that the easy axis of the magnetic moments lies in the $(0, 1, 0)$ plane at an angle of $38°$ to the a axis. For $x \leq 0.025$, the transition temperature increases with increasing x, while the spin-flop field is almost independent of x. The magnetization curve suggests that the energy gap remains even in the ordered phase for $x \leq 0.017$.

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