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Field-induced three-dimensional magnetic ordering in the spin-gap system $TlCuCl_3$

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Abstract. The temperature and field variations of the magnetization have been measured for $TlCuCl_3$ which has a singlet ground state with an excitation gap. It is found that $TlCuCl_3$ undergoes three-dimensional ordering in magnetic fields. The phase boundaries between the paramagnetic and ordered states are determined for $\boldsymbol{H} \parallel \boldsymbol{b}$ and $\boldsymbol{H} \perp (1, 0, \bar{2})$. The phase boundaries for these field directions coincide when normalized by the *g*-factor. The excitation gap at zero temperature is re-evaluated as $\Delta/k_B = 7.54(5)$ K.

1. Introduction

Recently, there has been much interest in the physics of spin ladders. Theoretical investigation [1, 2] has revealed that when the exchange interaction along the leg is antiferromagnetic, if the $S = 1/2$ Heisenberg spin ladder has an even number of legs it has a ground state that is a spin singlet with an excitation gap (spin gap), while if it has an odd number of legs, it has a gapless magnetic ground state. The gapped and gapless ground states have been experimentally observed for $SrCu_2O_3$ (two-leg ladders) [3] and $Sr_2Cu_3O_5$ (three-leg ladders) [3], respectively.

In the two-leg ladders, the interaction between the ladders suppresses the spin gap [4]. With increasing inter-ladder interaction, the gap reduces and vanishes. On the other hand, the magnetic field also suppresses the spin gap. When the applied field is higher than the critical field H_c corresponding to the gap, the coupled-ladder system becomes gapless, so 3D magnetic ordering could occur with the help of the inter-ladder interaction. Such 3D ordering was observed in the ladder system $Cu_2(C_5H_{12}N_2)_2Cl_4$ [5–7].

The field-induced 3D ordering has been observed in other spin-gap systems, such as $Ni(C_5H_{14}N_2)_2N_3(ClO_4)$ and $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ [8, 9], $Cu(NO_3)_2{\cdot}2.5H_2O$ [10, 11], and $(CH_3)_2CHNH_3CuCl_3$ [12]. They are described as an $S = 1$ Heisenberg antiferromagnetic chain, an $S = 1/2$ alternating antiferromagnetic Heisenberg chain, and an $S = 1/2$ ferromagnetic–antiferromagnetic alternating Heisenberg chain, respectively.

In this paper, we report on the field-induced 3D magnetic ordering in an inorganic ladder system, $TlCuCl_3$. Since large single crystals are obtained, using $TlCuCl_3$ is advantageous for studying physical properties. This compound is isostructural with $KCuCl_3$ which belongs to the monoclinic space group $P2_1/c$ [13, 14]. The crystal structure is composed of double chains of edge-sharing $CuCl_6$ octahedra along the *a*-axis. The double chains are located at the corners and centre of the unit cell in the *bc*-plane, and are separated by Tl^+ ions. There are three kinds of nearest-neighbour interaction, J_1, J_2, and J_3, in the double chain (see figure 1). In recent theoretical work [15] on the susceptibilities of $KCuCl_3$ [16] it was argued that the

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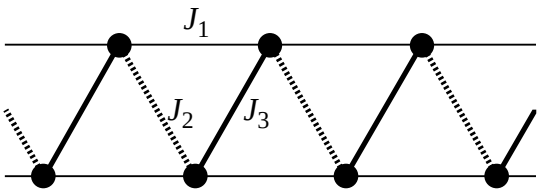


Figure 1. The structure of the nearest-neighbour interactions, J_1, J_2, and J_3, in the double chain.

interactions J_1, J_2, and J_3 are all antiferromagnetic, and that the J_2-interaction is dominant. Thus, the exchange network in the double chain is described as an $S = 1/2$ antiferromagnetic Heisenberg ladder with an additional diagonal interaction. This model has been investigated theoretically, and it has been concluded that there is a spin gap [17, 18]. At present, however, the values of J_1, J_2, and J_3 in $TlCuCl_3$ are not determined.

In reference [14], it was reported that the susceptibilities for three different field directions in $TlCuCl_3$ exhibit broad maxima at 38 K, and decrease exponentially to zero with decreasing temperature. This result indicates that the ground state is gapped. The magnitude of the spin gap was evaluated from high-field magnetization measurement as $\Delta/k_B \approx 7.5$ K [19]. Thus, the field-induced 3D ordering is expected to occur at $H \sim 6$ T due to the exchange interaction between the double chains. For $TlCuCl_3$, the inter-chain interaction cannot be neglected, because in $KCuCl_3$ the inter-chain interaction and the J_1- (or J_3-) interaction are of the same order of magnitude [20].

2. Experimental details

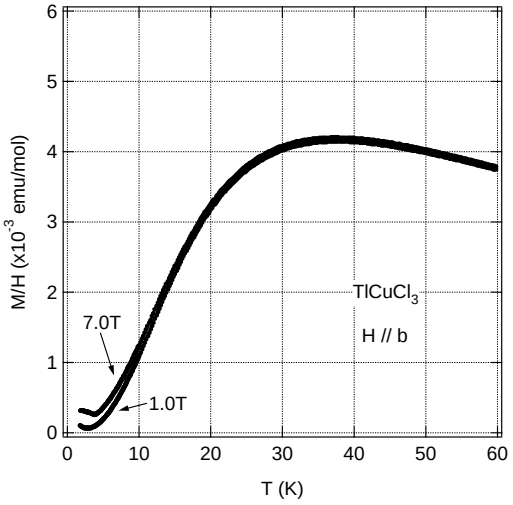
Single crystals were grown by the vertical Bridgman method from the melt of an equimolar mixture of TlCl and $CuCl_2$ sealed in an evacuated quartz tube. The temperature at the centre of the furnace was set at 550 °C. The source materials used were TlCl of 99.9% purity (Soekawa Chemical) and ultrapure $CuCl_2{\cdot}2H_2O$ (Wako Pure Chemical Industries). The TlCl and $CuCl_2{\cdot}2H_2O$ were dehydrated by heating them in vacuum at ∼150 °C and ∼100 °C, respectively, for three days. After weighing the samples, we packed first $CuCl_2$ in a quartz tube, and then TlCl. The materials were dehydrated by heating them in vacuum at ∼60 °C for three days. After collecting nice pieces of the crystals, we repeated the same procedure. Single crystals of size ∼1 cm^3 were obtained. The crystals were cleaved along the $(0, 1, 0)$ and $(1, 0, \bar{2})$ planes, which are perpendicular to each other.

The magnetizations were measured down to 1.8 K in magnetic fields up to 7 T using a SQUID magnetometer (Quantum Design MPMS XL). The magnetic fields were applied perpendicular to the cleavage planes $(0, 1, 0)$ and $(1, 0, \bar{2})$.

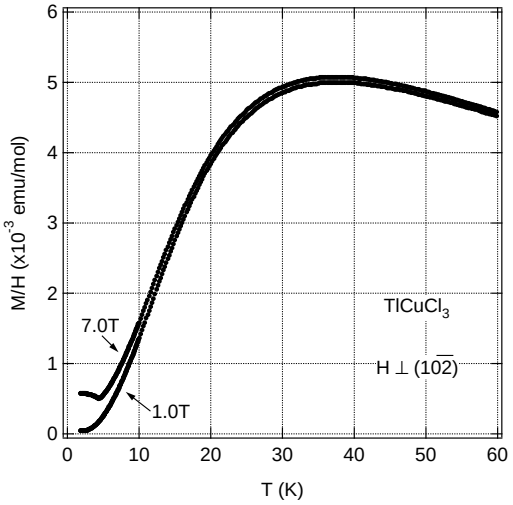
3. Results and discussion

Figure 2 shows the temperature variation of the susceptibilities (M/H) of $TlCuCl_3$ measured at 1 and 7 T for $\boldsymbol{H} \parallel \boldsymbol{b}$ and $\boldsymbol{H} \perp (1, 0, \bar{2})$. With decreasing temperature, the susceptibilities exhibit broad maxima at 38 K and decrease. The difference between the absolute values of the susceptibilities for the two different field directions is due to the anisotropy of the g-factor.

Below 10 K, the susceptibilities for $H = 1$ and 7 T behave differently. The susceptibility for $H = 1$ T decreases exponentially to almost zero with decreasing temperature. This indicates that the ground state is still gapped for $H = 1$ T. On the other hand, the susceptibility



(*a*)



(*b*)

Figure 2. The temperature dependence of the magnetic susceptibilities (M/H) of $TlCuCl_3$ measured at 1 and 7 T for (*a*) $\boldsymbol{H} \parallel \boldsymbol{b}$ and (*b*) $\boldsymbol{H} \perp (1, 0, \bar{2})$.

for $H = 7$ T shows a bend anomaly at about 4 K. Since the magnitude of the spin gap is $\Delta/k_B \approx 7.5$ K [19], the magnetic field of 7 T is strong enough to destroy the gap. Thus the ground state must be gapless for $H = 7$ T. The susceptibility in a purely 1D system shows a gradual temperature variation. For these reasons, we infer that the sharp bend of the susceptibility at about 4 K for $H = 7$ T indicates 3D magnetic ordering due to the inter-chain interaction.

Figure 3 shows the low-temperature magnetizations at various external fields for $\boldsymbol{H} \parallel \boldsymbol{b}$ and $\boldsymbol{H} \perp (1, 0, \bar{2})$. The small anomalies at 4.4 K are due to an instrumental problem and are not intrinsic to the sample. We assign the temperature at which there is an inflection point in the magnetization as the transition temperature $T_N(H)$. Thus, there is a certain amount of error in

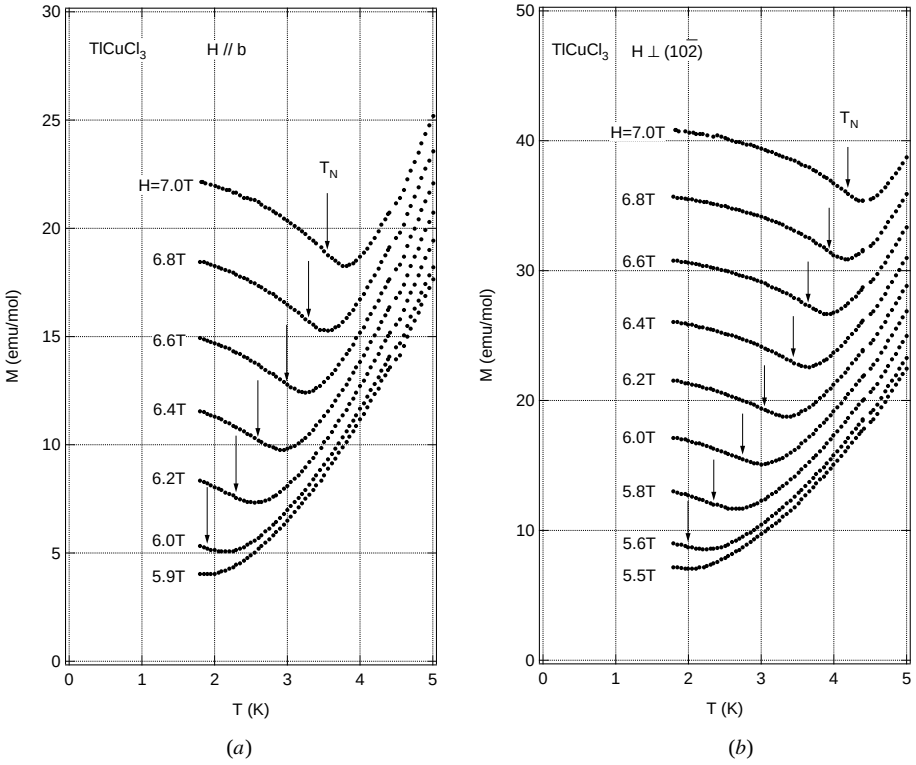


Figure 3. The low-temperature magnetizations of $TlCuCl_3$ measured at various external fields for (*a*) $\boldsymbol{H} \parallel \boldsymbol{b}$ and (*b*) $\boldsymbol{H} \perp (1, 0, \bar{2})$.

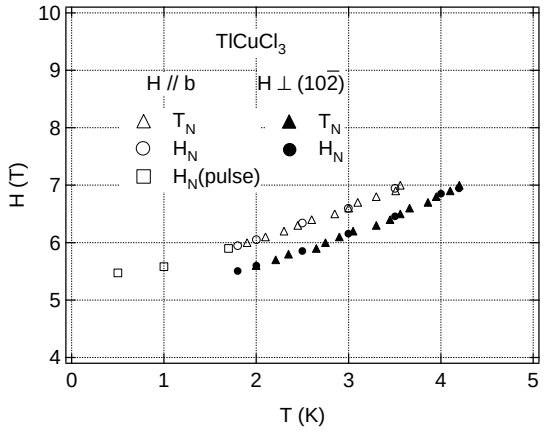


Figure 4. The phase boundaries in $TlCuCl_3$ for $\boldsymbol{H} \parallel \boldsymbol{b}$ and $\boldsymbol{H} \perp (1, 0, \bar{2})$ determined from the results on the temperature variations (△ and ▲) and field variations (○ and ●) of the magnetizations. Squares denote the transition fields determined from the magnetization measurements in pulsed magnetic fields.

determining the transition points. The arrows in figure 3 indicate the transition temperatures, which are slightly lower than the temperatures of the susceptibility minima. Upon decreasing

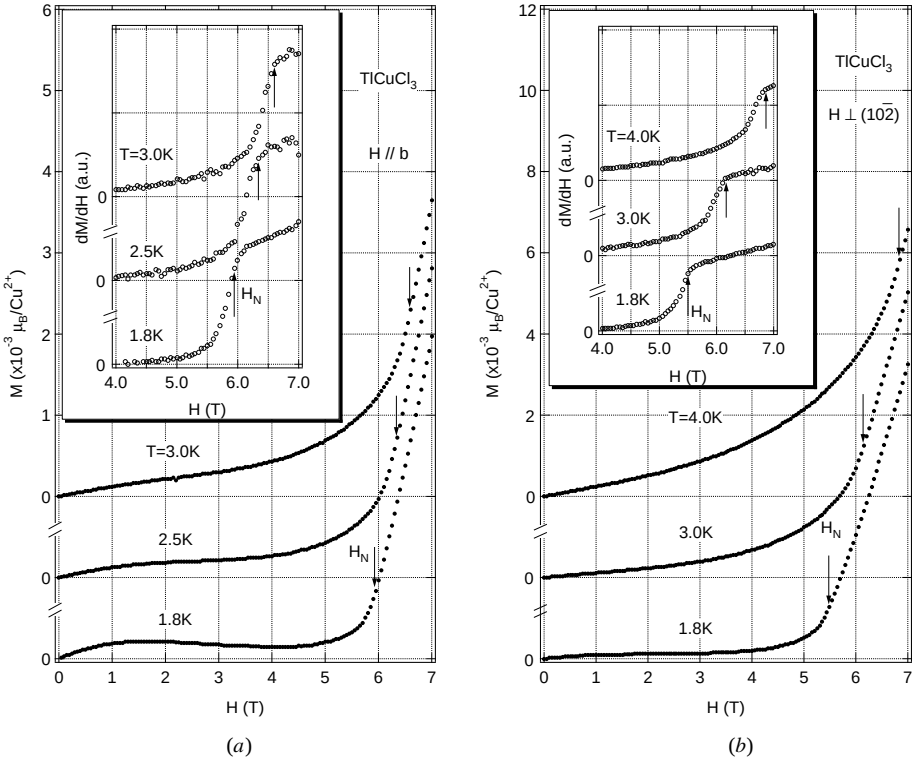


Figure 5. Magnetization curves of $TlCuCl_3$ measured at various temperatures for (*a*) $\boldsymbol{H} \parallel \boldsymbol{b}$ and (*b*) $\boldsymbol{H} \perp (1, 0, \bar{2})$. The inset shows $\mathrm{d}M/\mathrm{d}H$ versus H.

the external field from 7 T, the transition temperature decreases. The transition temperature for $\boldsymbol{H} \perp (1, 0, \bar{2})$ is higher than that for $\boldsymbol{H} \parallel \boldsymbol{b}$ at the same external field. The phase transition is not detected below 5.9 T for $\boldsymbol{H} \parallel \boldsymbol{b}$, or below 5.5 T for $\boldsymbol{H} \perp (1, 0, \bar{2})$. In figure 4, the transition temperatures $T_{\mathrm{N}}(H)$ are plotted as triangles (△ and ▲).

Figure 5 shows the magnetization and its field derivative $\mathrm{d}M/\mathrm{d}H$ measured at various temperatures. For $\boldsymbol{H} \perp (1, 0, \bar{2})$, the magnetization at 1.8 K is very small up to about 5.5 T and then increases rapidly. We see that the spin gap closes at about 5.5 T and the gapless magnetic state appears with increasing external field. For $\boldsymbol{H} \parallel \boldsymbol{b}$, a small amount of net moment is observed in low fields. After making the measurement for $\boldsymbol{H} \parallel \boldsymbol{b}$, we checked the magnetization for $\boldsymbol{H} \perp (1, 0, \bar{2})$. However, the small net moment was not observed. If the small net moment was due to the paramagnetic impurity, it would be isotropic. Thus, we consider that the small net moment observed for $\boldsymbol{H} \parallel \boldsymbol{b}$ is intrinsic to the present system.

The field derivatives of the magnetizations $\mathrm{d}M/\mathrm{d}H$ have bend anomalies at the fields indicated by arrows. We assign the fields to the transition fields $H_{\mathrm{N}}(T)$ at which the 3D ordering occurs. In figure 4, we plot the transition fields $H_{\mathrm{N}}(T)$, as circles (○and ●) together with the transition fields determined by our previous magnetization measurements using pulsed magnetic fields. Because the transition points determined from $T_{\mathrm{N}}(H)$ and $H_{\mathrm{N}}(T)$ lie almost on the same line, they are consistent with each other.

When the g-factor is anisotropic, the values of $T_{\mathrm{N}}(H)$ and $H_{\mathrm{N}}(T)$ depend on the external-field direction. We measured the g-factor by means of ESR. The g-factors obtained are $g = 2.06$

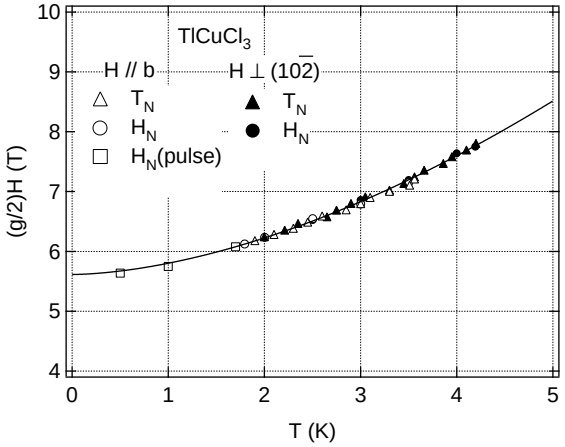


Figure 6. The phase diagram in $TlCuCl_3$ normalized by the g-factor. The solid line denotes the fitting with equation (1), with $(g/2)H_N(0) = 5.61(5)$ T and $\phi = 1.7(1)$.

for $\boldsymbol{H} \parallel \boldsymbol{b}$ and $g = 2.23$ for $\boldsymbol{H} \perp (1, 0, \bar{2})$. Figure 6 shows the magnetic phase diagram of $TlCuCl_3$ normalized by the g-factor. As seen from figure 6, the phase boundaries for $\boldsymbol{H} \parallel \boldsymbol{b}$ and $\boldsymbol{H} \perp (1, 0, \bar{2})$ coincide. This result suggests that the phase boundary is independent of the external-field direction when normalized by the g-factor. This means that the magnetic anisotropy is negligible in $TlCuCl_3$, and thus the present system can be described by an $S = 1/2$ Heisenberg model in the magnetic field.

It is considered that the phase boundary becomes parallel to the temperature axis for $T \to 0$, as predicted by the mean-field theory [21], i.e., $\mathrm{d}H_N(T)/\mathrm{d}T \to 0$ for $T \to 0$ K. In order to describe the phase boundary, we use the following formula:

$$(g/2)[H_N(T) - H_N(0)] \propto T^{\phi}. \tag{1}$$

The best fitting is obtained with $(g/2)H_N(0) = 5.61(5)$ T and $\phi = 1.7(1)$. The solid curve in figure 6 is the fitting curve. We see that the phase boundary can be described by equation (1).

The transition field H_N and the critical field H_c, at which the spin gap closes, should coincide at $T = 0$ K. Thus, the excitation gap at $T = 0$ K is re-evaluated as $\Delta/k_B = g\mu_B H_N(0)/k_B = 7.54(5)$ K. At finite temperatures, H_N and H_c are not necessarily coincident. On the basis of the present magnetization measurements, it is difficult to distinguish between them. However, their difference may be small. The spin structure in the ordered phase is unknown at present. As seen from figure 1, spin frustration exists in the present system. Thus, the spin ordering and critical behaviour may be different from those in ordinary spin systems. Besides the magnetization measurements, specific heat and neutron scattering measurements in magnetic fields are needed in order to clarify the nature of the field-induced phase transition and also to determine the transition points more definitely for $TlCuCl_3$.

4. Conclusion

We have presented the results of magnetization measurements made on the spin-gap system $TlCuCl_3$ with double chains. 3D ordering was observed in magnetic fields. The phase boundary between the paramagnetic and ordered states is determined as shown in figure 6. It was found that the phase boundary is independent of the external-field direction when normalized by the

g-factor, and is well described by equation (1). The excitation gap at zero temperature was re-evaluated as $\Delta/k_B = 7.54(5)$ K.

Acknowledgments

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