Specific heat study of the field-induced magnetic ordering in the spin-gap system TlCuCl₃

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Specific heat measurements have been performed in the coupled dimer system TlCuCl₃, which has a singlet ground state with the excitation gap $\Delta \simeq 7.5$ K. The cusplike anomaly indicative of the three-dimensional magnetic ordering was clearly observed in magnetic fields higher than the critical field H_g corresponding to the gap Δ. The phase boundary determined by the present specific heat measurements coincides with that determined by previous magnetization measurements. The phase boundary can be described by the power law $[H_c(T) - H_g] \propto T^\phi$ with $\phi = 2.1(1)$. This result supports the magnon Bose condensation picture for the field-induced magnetic ordering in TlCuCl₃ [Nikuni *et al.*, Phys. Rev. Lett. **84**, 5868 (2000)].

Recently, quantum spin systems such as $S = 1/2$ two-leg spin ladders, $S = 1/2$ ferromagnetic-antiferromagnetic alternating chains, and $S = 1$ antiferromagnetic chains have been the focus of much interest for both theorists and experimenters, because these systems have the singlet ground state with the excitation gap Δ.

One-dimensional gapless spin systems do not undergo three-dimensional (3D) magnetic ordering. However, real quasi-1D gapless spin systems can undergo 3D ordering at low temperatures due to finite 3D exchange interactions. For example, the $S = 5/2$ quasi-1D spin system $(CH_3)_4NMnCl_3$ (abbreviated TMMC) undergoes 3D magnetic ordering at $T_N = 0.835$ K at zero field.[1]

On the contrary, the above mentioned spin gap systems remain paramagnetic down to $T = 0$ K, even if there are weak 3D exchange interactions. However, when a magnetic field higher than the critical field $H_g = \Delta/g\mu_B$ is applied, the ground state becomes gapless, so the systems can undergo 3D magnetic ordering with the help of 3D exchange interactions. Such field-induced 3D ordering was observed in some quasi-1D spin gap systems, e.g., the $S = 1/2$ Heisenberg ladder system $Cu_2(C_5H_{12}N_2)_2Cl_4$,[2-5] the $S = 1$ antiferromagnetic chain systems $Ni(C_5H_{14}N_2)_2N_3(ClO_4)$[6] and $Ni(C_5H_{14}N_2)_2N_3(PF_6)$,[7] and the $S = 1/2$ exchange alternating system $(CH_3)_2CHNH_3CuCl_3$.[8]

Recently, we observed the field-induced 3D magnetic ordering in the spin-gap system TlCuCl₃ by means of magnetization measurements.[9] This compound is isomorphous with KCuCl₃ which belongs to the monoclinic space group $P2_1/c$.[10,11] TlCuCl₃ contains planar dimers of Cu_2Cl_6, in which Cu^{2+} ions have spin-1/2. These dimers are stacked on top of one another to form infinite chains parallel to the crystallographic a axis. These chains are located at the corners and center of the unit cell in the bc plane, and are separated by Tl^+ ions.

From previous magnetic measurements, the ground state of TlCuCl₃ was found to be a spin singlet with the excitation gap $\Delta \simeq 7.5$ K.[9,12-14] The origin of the gap for TlCuCl₃ is the strong antiferromagnetic exchange interaction in the chemical dimers of Cu_2Cl_6, similar to KCuCl₃.[11,15-18] The magnetic dimers are coupled three dimensionally through interdimer interactions.

TlCuCl₃ undergoes 3D magnetic ordering in magnetic fields higher than $H_g \sim 6$ T. The feature of the magnetization at low temperatures, including the phase-transition temperature T_N, and the field dependence of T_N are summarized as follows. The magnetization exhibits the cusplike minimum at T_N. The phase boundary on the temperature vs field diagram is independent of the field direction, when normalized by the g factor, and can be represented by the power law

$$(g/2)[H_N(T) - H_g] \propto T^\phi, \qquad (1)$$

with $\phi = 2.2$, where $H_N(T)$ is the transition field at temperature T.

These features for the magnetization and the phase boundary have been described in terms of the Bose-Einstein condensation (BEC) of excited triplets (magnons).[19] However, there is some ambiguity for determining T_N from the magnetization data, because the cusplike minimum of the magnetization near T_N is not sharp, but rounded.[20] In order to obtain conclusive evidence of the field-induced magnetic ordering, we performed specific heat measurements, and report the results in this paper.

Single crystals of TlCuCl₃ were grown from a melt by the Bridgman method. The details of preparation have been reported in Ref. 9. The crystal is cleaved along the (0,1,0) and $(1,0,\bar{2})$ planes, which are perpendicular to each other.

The specific heat measurements of single crystals of TlCuCl₃ were carried out at temperatures down to 0.6 K in magnetic fields up to 12 T, using a Mag Lab^{HC} microcalorimeter (Oxford Instruments) in which the relaxation method was employed. In this paper, the magnetic field was applied perpendicular to the (0,1,0) and $(1,0,\bar{2})$ planes.

Figure 1 shows the temperature dependence of the total specific heat in TlCuCl₃ measured at various magnetic fields for $H \parallel b$ and $H \perp (1,0,\bar{2})$. For $H = 0$ T, no anomaly is seen down to 0.8 K, as expected from the gapped ground state.

When the applied field is higher than the critical field $H_g \approx 5.4$ T for $H \parallel b$ and ~ 5.0 T for $H \perp (1,0,\bar{2})$ corresponding to the energy gap Δ (~ 7.5 K), a small cusplike anomaly indicative of the magnetic ordering is observed. The differ-
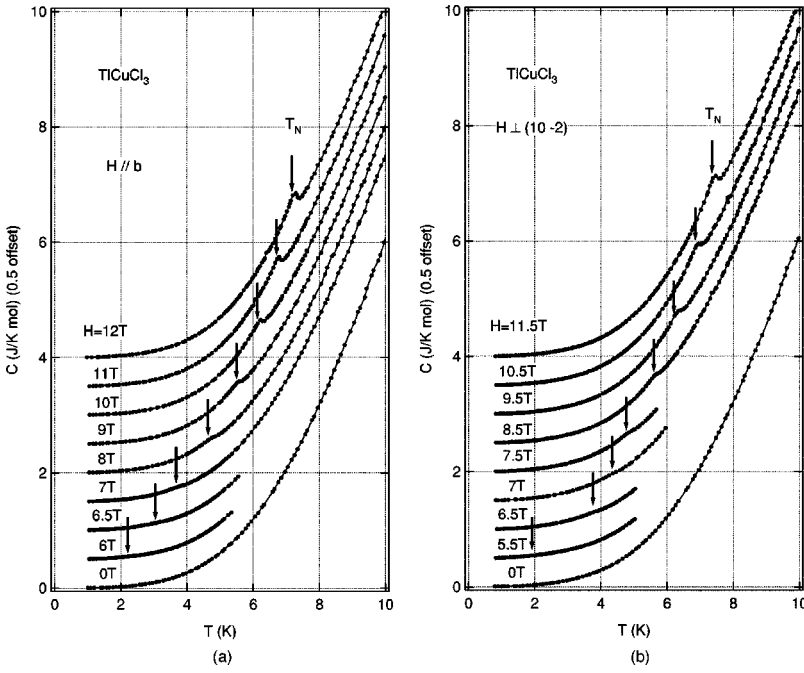
FIG. 1. The temperature dependence of the specific heat in TlCuCl$_3$ at various magnetic fields for (a) $H\|b$ and (b) $H\perp(1,0,\overline{2})$.

ence in the critical fields in the two field directions is due to the anisotropy of the g factor.[9]

The difference between the specific heats for $H=0$ T and for $H>H_g$ is slight except around the Néel temperature T_N, although large increases of the magnetic specific heat may be expected for $H>H_g$. We infer that this is because the induced magnetic moment is small for $H\sim H_g$, since the saturation field H_s is ~100 T, which is more than ten times as large as H_g.[13,21]

In Fig. 2, we plot the difference between the specific heat $C(H)$ for a magnetic field H and $C(0)$ for $H=0$ as a function of temperature. $C(H)-C(0)$ can be regarded as the specific heat relevant to the field-induced magnetic ordering.

However, it is noted that $C(H)-C(0)$ does not express the magnetic specific heat exactly, since $C(0)$ includes both the lattice part ($\propto T^3$) and the spin-gap part [$\propto \exp(-\Delta/T)$]. The λ-like anomaly due to the phase transition is clearly observed in the plot of $C(H)-C(0)$ vs T. With decreasing magnetic field, the transition temperature decreases, and the λ-like anomaly becomes smaller. This means that the spin moment relevant to the ordering is reduced when the magnetic field reaches H_g. For $H<6.5$ T, it is difficult to determine the transition temperature T_N.

In order to determine the transition point at a temperature lower than 3 K, we measured the field dependence of the specific heat at various temperatures. Examples of the mea-
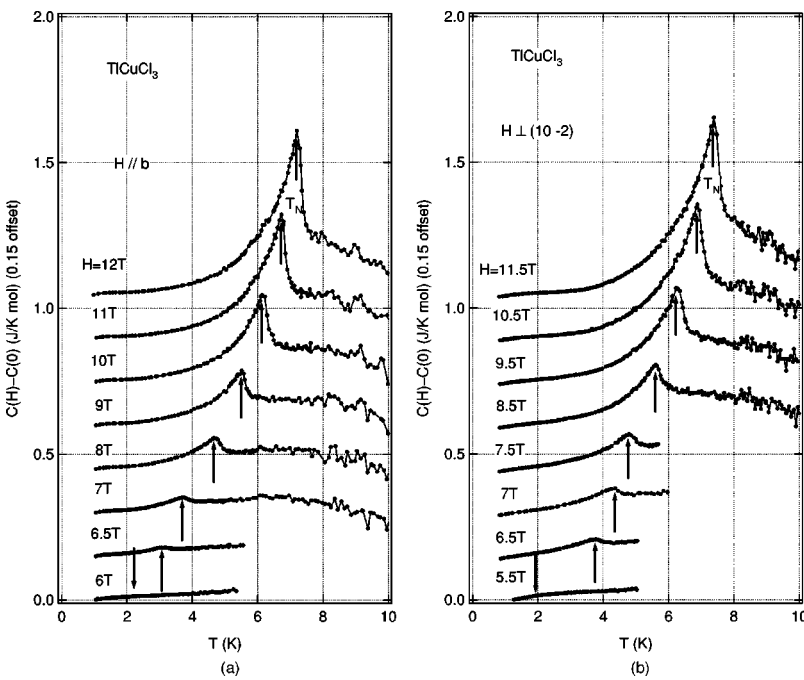

FIG. 2. The temperature dependence of the difference between the specific heat $C(H)$ at magnetic field H and $C(0)$ at zero field.
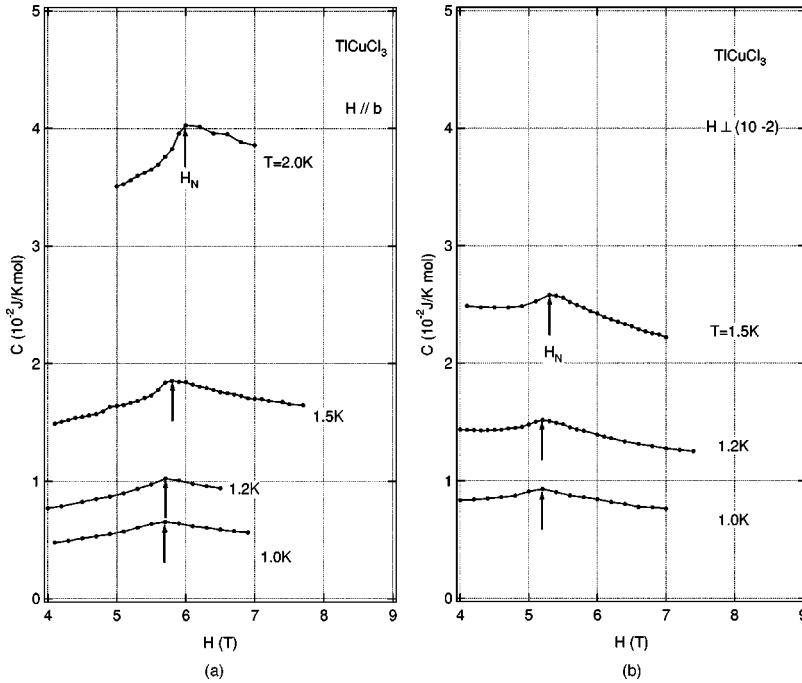
FIG. 3. The field dependence of the specific heat in TlCuCl$_3$ at various magnetic fields for (a) $H\|b$ and (b) $H\perp(1,0,\bar{2})$.

surements for $H\|b$ and $H\perp(1,0,\bar{2})$ are shown in Fig. 3. We assign the field at which the specific heat exhibits a cusplike anomaly to the transition field $H_N(T)$.

The phase transition data obtained by temperature and field scans are summarized in Fig. 4. In this figure, the transition points obtained from previous magnetization measurements are also plotted. The transition points determined from the present specific heat measurements and the magnetization measurements fall on the same line for $H\|b$ and $H\perp(1,0,\bar{2})$. This confirms that the phase transition occurs at a temperature at which the magnetization has the minimum,[20] as predicted based on the magnon BEC theory.[19] The magnetization behavior is described by the theory as follows. Since the magnon corresponds to the excited triplet, the magnetization is proportional to the number of magnons. With decreasing temperature, the number of thermally excited magnons decreases for $T>T_N$, while for $T<T_N$ the

BEC of magnons occurs, where the increase of the number of condensed magnons is larger than the decrease of the number of noncondensed magnons, so that the total number of magnons increases.

Since the phase boundary depends on the g-factor, we normalize the phase diagram using the g factor. The g factors obtained by electron spin resonance measurements are $g=2.06$ for $H\|b$ and $g=2.23$ for $H\perp(1,0,\bar{2})$. Figure 5 shows the phase diagram normalized by the g factor. The phase boundaries for $H\|b$ and $H\perp(1,0,\bar{2})$ coincide down to 0.6 K. This reconfirms that the phase boundary is independent of the external field direction when normalized by the g factor, and that the anisotropy is negligible in TlCuCl$_3$.

The phase boundary can be described by the power law of Eq. (1), as predicted based on the magnon BEC theory.[19] We fit Eq. (1) to the data for $T<4$ K, which is lower than half the gap temperature $\Delta/k_B=7.5$ K. The solid line in Fig. 5 is
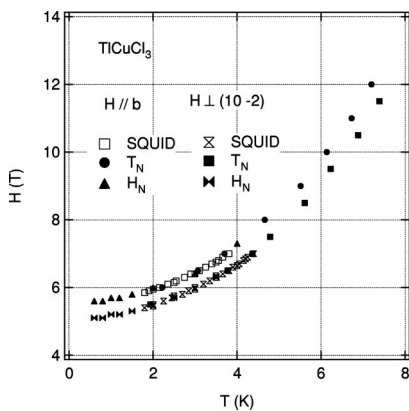

FIG. 4. The phase boundaries in TlCuCl$_3$ for $H\|b$ and $H\perp(1,0,\bar{2})$.
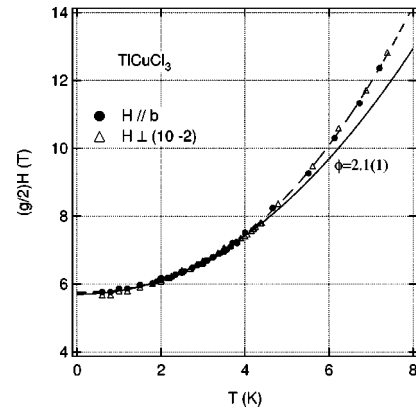

FIG. 5. The phase diagram in TlCuCl$_3$ normalized by the g factor. The solid line denotes the fit with Eq. (1) with $\phi=2.1(1)$ and $gH_g/2=5.7(1)$ T. The dashed line is a guide for the eyes.

the fit with $\phi = 2.1(1)$ where $gH_g/2 = 5.7(1)$ T. The exponent $\phi = 2.1$ obtained from the present measurements is somewhat larger than the value $\phi = 3/2$ predicted by the theory.[19] Since the theory is based on the Hartree-Fock approximation, the disagreement between the experimental and theoretical values of ϕ may be attributed to the fluctuation effect.

We have presented the results of specific heat measurements on the spin-gap system $TlCuCl_3$. The field-induced 3D magnetic ordering was clearly observed. The phase boundary between the paramagnetic phase and the 3D ordered phase was determined, as shown in Fig. 5. The present results confirm that the field-induced magnetic ordering takes place at the temperature where the magnetization has the cusplike minimum, and that the phase boundary can be described by the power law near the critical field H_g, as predicted based on the magnon BEC theory.[19] Therefore we conclude that the field-induced 3D magnetic ordering in $TlCuCl_3$ can be captured by the magnon BEC picture.

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