Low-temperature phases of the pyrochlore compound $Tb_2Ti_2O_7$

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Low-temperature magnetic states of the pyrochlore compound $Tb_2Ti_2O_7$ with a geometrical frustration have been determined by measuring the specific heat, the susceptibility, and the residual magnetization of single-crystal samples. The moments of the lowest doublet of the Tb^{3+} ions set into a short-range ordering below about 2 K and show a maximum of the specific heat at $T_{sr} \approx 0.7$ K. At $T_c = 0.37$ K, we observed a sharp peak of the specific heat which suggests that the second-order transition occurs. The static and the ac susceptibilities show another transition into a spin-glass or cluster-glass state below $T_g = 0.2$ K. In the temperature range between 1.5 and 0.2 K, a residual magnetization was observed. The time dependencies of the residual magnetization and the dissipation of the ac susceptibility suggest existence of metastable states with a distribution of the relaxation times.

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The low-temperature states of pyrochlore compounds $RE_2Ti_2O_7$ with magnetic rare-earth cations RE^{3+} have attracted much interest because their spins on the corner-sharing tetrahedra have strong geometrical frustration. They are frustrated not only for the nearest-neighbor antiferromagnetic interaction, but also for the ferromagnetic interaction under a uniaxial crystal anisotropy. The latter is the case for titanates with RE=Ho (Refs. 1–3) and Dy,[4,5] of which ground state is the ''spin-ice'' state.[4] In the case of the antiferromagnetic interaction, the long-range magnetic order has been observed for RE=Gd (Ref. 6) and Er.[7] $Tm_2Ti_2O_7$ has shown that each Tm^{3+} ion has a nonmagnetic singlet ground state.[8]

For $Tb_2Ti_2O_7$, low-temperature magnetic states are induced by several interactions which have the same order of magnitude. The negative Curie-Weiss temperature indicates that the nearest-neighbor interaction between Tb^{3+} moments is antiferromagnetic.[9] The dipolar interaction is estimated to be of the order of 1 K.[10] The direction dependence of the magnetic susceptibility has indicated that the anisotropy of $Tb_2Ti_2O_7$ is much smaller than that of the spin-ice system $Ho_2Ti_2O_7$.[11] Since the competition among the interactions is qualitatively different from Ho and Dy titanates, other frustrated magnetic states have been reported for $Tb_2Ti_2O_7$. From a muon spin-relaxation (μSR) measurement, Gardner *et al.* have shown that the Tb^{3+} moments remain in a collective paramagnet or spin-liquid state down to 70 mK.[9] On the other hand, our recent neutron-scattering experiment has shown that a relaxation of the moments becomes slow in the time scale of hours below about 1.5 K.[11] In the magnetization measurement, a spin-glass-like behavior of the moments has been observed below about 0.1 K.[12] In addition, recently it was reported that the antiferromagnetic ordered state coexists with the spin-liquid state below 2 K under high pressures above 1.5 GPa.[13]

In order to determine the low-temperature magnetic state of $Tb_2Ti_2O_7$, we have carried out thermodynamic experiments, concentrating on the low-temperature region below 2 K. We have measured the specific heat, the ac susceptibility, and the magnetization. In contrast to the earlier results of others, our results show that several magnetic transitions exist below about 2 K.

All measurements were made using single-crystal samples of $Tb_2Ti_2O_7$ cut from one crystal with a volume of ~ 1 cm^3. The crystal was prepared by the floating-zone method as reported in our previous paper on neutron-scattering studies.[11] Details of the crystal growth can be found in Ref. 14. The specific heat was measured by means of the adiabatic heat-pulse method. The ac susceptibility was measured at frequencies between 95 and 315 Hz and an amplitude less than 0.5 μT, by a mutual-inductance bridge circuit using a dc–Superconducting quantum interference device (dc-SQUID) magnetometer as a null detector. Absolute values of the susceptibilities were calibrated by fitting to the previous data[11] between 2 and 7 K. The static susceptibility and the magnetization were also measured simultaneously by the same dc-SQUID magnetometer.

The specific heat C was measured down to 0.15 K. The T dependence of C is shown by solid circles in Fig. 1. Three peaks are observed at 0.4, 0.7, and 5 K. An upturn of C below 0.2 K is attributed to a nuclear specific heat C_n. It is known that contributions of the hyperfine energy splitting to the specific heat become dominant below 0.4 K for Tb-based

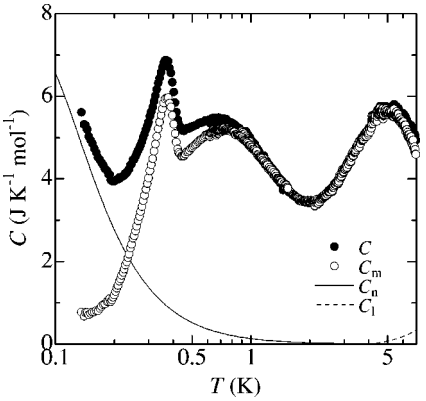

FIG. 1. Temperature dependence of the specific heat of $Tb_2Ti_2O_7$ in zero field. Solid circles show the total specific heat. The nuclear specific heat C_n and the lattice specific heat C_l are plotted by solid and dashed lines, respectively. The magnetic specific heat C_m which is obtained by subtracting C_n and C_l from the total specific heat C is shown by open circles.

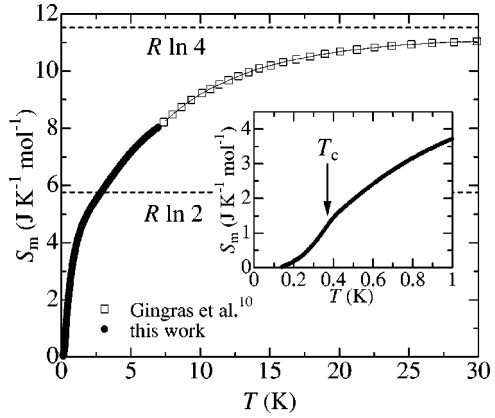

FIG. 2. Magnetic entropy for Tb^{3+} cations estimated by integrating C_m/T from 0.15 K. Present data are shown by solid circles. The data for temperatures higher than 7 K are plotted by open squares, using the data reported in Ref. 10 (see text). Values of $R\ln 2$ and $R\ln 4$ are also indicated by dashed lines. The inset shows the low-temperature region, in relation to the C peak at $T_c = 0.37$ K. The arrow indicates T_c.

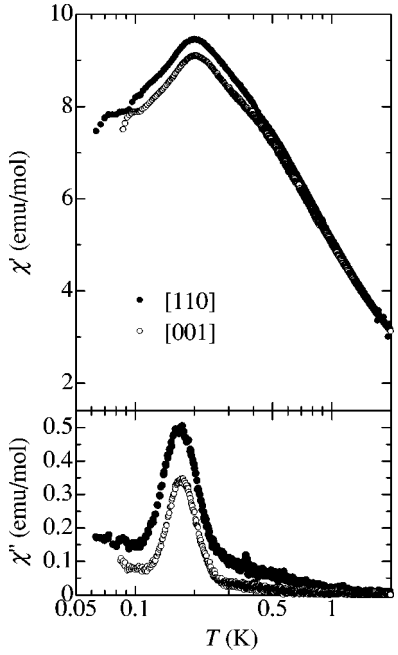

FIG. 3. The ac magnetic susceptibilities $\chi = \chi' - i\chi''$ of the single crystal of $Tb_2Ti_2O_7$, for the ac field of 175 Hz applied along two directions.

compounds.[15] Assuming that the C_n has the form of the Schottky specific heat $C_n = 2R(2\Delta/k_BT)^2\exp(2\Delta/k_BT)[1 + \exp(2\Delta/k_BT)]^{-2}$, where Δ is an energy gap, we subtracted the contribution of nuclear magnetism. The solid line in Fig. 1 corresponds to the estimated C_n, assuming that $\Delta = 0.09$ K which is the same order of hyperfine interaction ~ 0.3 K obtained previously.[15] The lattice specific heat C_l was estimated in the same manner as described in Ref. 10 and is shown by a dashed line in the figure. Open circles indicate the magnetic specific heat C_m that is obtained by subtracting C_n and C_l from the total specific heat C.

Two peaks of the C_m-T curve found at 5 and 0.7 K are likely to correspond to those observed at 6 and 1.5 K in the previous reports,[10] respectively. Crystal-field calculations have shown that the lowest crystal-field levels consist of a doublet and an excited doublet,[10] which has also been observed in neutron-scattering experiments.[9,16,17,11] According to the doublet-doublet scheme, the C peak at 5 K is due to an excitation to the upper doublet, and the peak at $T_{sr} \approx 0.7$ K is attributed to the lowest doublet. Recent neutron-scattering experiments[11,16] have shown that the excitation to the upper doublet has, at 0.4 K, the energy dispersion of about 10 K with the center energy of ~ 15 K. Thus the energy gap between the ground state and the bottom of the dispersion can be estimated to be ~ 10 K. The temperature of the C peak (~ 5 K) exhibits quantitative agreement with the value expected from the gap energy.

The sharp peak at $T_c = 0.37$ K has not been reported previously. Although there is no remark about it in the paper, the C data in Fig. 4 of Ref. 18 seem to have a small anomaly at 0.4 K. The shape of the sharp peak at T_c indicates the second-order phase transition.

The magnetic entropy S_m of Tb^{3+} moments was obtained as shown in Fig. 2, by integrating C_m/T from 0.15 K, where C_m is given in Fig. 1. The inset in Fig. 2 shows that S_m at $T_c = 0.37$ K is 21% of the entropy $R\ln 2$ of the lowest doublet. The S_m becomes $R\ln 2$ at 2.85 K. Thus, the entropy $R\ln 2$ for the lowest doublet comes from the peaks at $T_{sr} \approx 0.7$ K and $T_c = 0.37$ K. The entropy of 7 K obtained here is larger by 0.42 J/(K mol) than that estimated previously.[10] Open squares indicate the previous estimation offset so as to join with the present results at 7 K. The entropy at 30 K is likely to almost recover the doublet-doublet entropy $R\ln 4$. Therefore, there is no evidence for the frozen entropy at zero temperature, in contrast to the spin-ice systems which have macroscopic entropies at zero temperature.

As shown by the specific heat (Fig. 1) and the entropy (Fig. 2), magnetic orderings of the Tb-titanate take place within the lowest doublet of the Tb^{3+} spins below around 2 K. Growth of the short-range order below 2 K is shown by the maximum at $T_{sr} \approx 0.7$ K. The sharp peak at $T_c = 0.37$ K indicates the second-order transition below which some kind of long-range order appears.

As noted in the introduction, recently it has been reported that the static susceptibility below about 0.1 K shows the difference between a zero-field cooling (ZFC) and a field cooling (FC) similar to the spin-glass state.[12] We made detailed measurements of the ac susceptibility and the residual magnetization for the sample which we used in the C measurements. We measured the ac susceptibility $\chi = \chi' - i\chi''$ down to 0.08 K, by applying the ac field with the frequency of 175 Hz along the directions of [001] and [110]. The T dependence of the real part χ' is shown in the upper panel in Fig. 3, where the demagnetizing-field correction has not been made. The true magnitude of χ can be calculated by using the demagnetizing factor N. The values of $1/4\pi N$ were roughly estimated to be 24 and 12 emu/mol along [110] and [001], respectively, with large uncertainties of about 50%. Since the difference of the magnitude for χ is small compared with the influence of the demagnetization, an anisot-

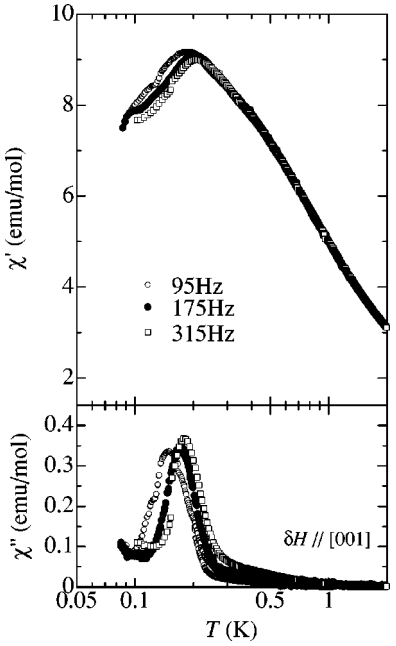

FIG. 4. Temperature dependences of the ac magnetic susceptibilities $\chi=\chi'-i\chi''$ of $Tb_2Ti_2O_7$ for various frequencies of the ac field applied along the [001] direction of a single crystal.

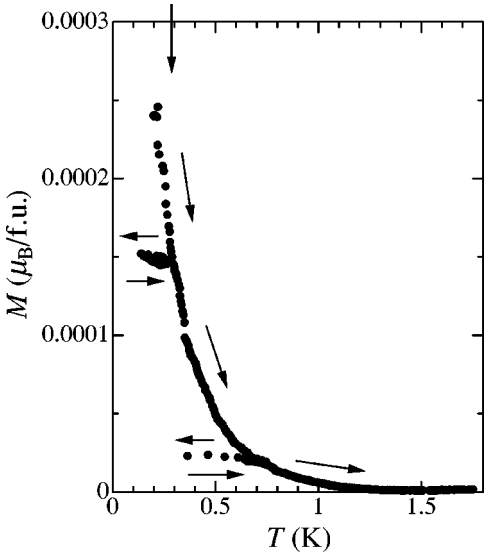

FIG. 5. Residual magnetization of $Tb_2Ti_2O_7$ in zero field, after cooling down to a temperature below 0.1 K in a magnetic field of 2 mT along the [110] direction. Arrows indicate the time order of the T variation.

ropy of the true susceptibility was not indicated in Fig. 3. The T dependences of χ' for both field directions show a cusp at $T_g=0.2$ K, without any clear anomaly of the specific heat (Fig. 1). The χ'-T curve changes the slope around 0.4 K, which seems to correspond to the transition with the sharp peak of C at $T_c=0.37$ K. The χ'' shown in the bottom panel of Fig. 3 has a peak at 0.17 K which is slightly lower than T_g. These behaviors are similar to the spin-glass transitions. Another possibility of the weak ferromagnetic transition should be examined, because the peak magnitude of χ', about 9 emu/mol ($\sim$0.11 emu/cm^3), is the same order as the saturation value $1/4\pi N$. To clarify the transition at $T_g=0.2$ K, we measured the frequency dependence of the ac susceptibility in the region between 95 and 315 Hz, as shown in Fig. 4. The peak temperatures of both χ' and χ'' shift towards higher temperature with increasing frequency. This frequency dependence is a typical behavior of the spin-glass or cluster-glass transition. We also observed the difference of the static susceptibilities between FC and ZFC below 0.2 K, similar to that reported previously.[12] They suggest that the phase below $T_g=0.2$ K is a kind of the spin-glass or cluster-glass state. The observed χ agrees with the earlier measurement[12] except that the transition temperature of $T_g=0.2$ K is a little higher than the previous result about 0.1 K, and that the maximum magnitude is about twice. These differences seem to be due to the field dependence, the frequency dependence, or the sample dependence in the measurement. The ground state of the spin glass for $Tb_2Ti_2O_7$ is different from the long-range ordered states of the other antiferromagnetic pyrochlores of the RE-titanates [RE=Gd (Ref. 6) and Er (Ref. 7)].

χ'' in Figs. 3 and 4 have additional long tails up to about 1.5 K, besides a peak at 0.17 K due to the spin-glass behavior. This suggests that the moment arrangements responsible for the large susceptibility are metastable with the relaxation rate of the order of 10 msec which corresponds to the employed frequencies. To see properties of the metastable states in longer time scale, we also measured the residual magnetization M_{res} in zero field, after cooling the sample down to a temperature below 0.1 K in a magnetic field of 2 mT along the [110] direction. Figure 5 shows M_{res} on the way to warming up. Arrows in the figure show the T history in the measurements. Below 0.2 K, M_{res} was too large to be measured by our setup of the SQUID magnetometer. This is attributed to the residual magnetization retained in the state with spin-glass behavior below $T_g=0.2$ K. As T increased from the lowest temperature below 0.1 K, M_{res} decreased steeply, and small M_{res} was left when T reached 0.2 K. As T increased further, M_{res} decreased slowly. At about 0.3 K, we attempted to decrease the temperature. In that case, the magnitude of M_{res} at 0.3 K was preserved. When we again increased the temperature, M_{res} was almost constant until 0.3 K, and then began to decrease again. Similar behavior was also observed around 0.7 K, when we again attempted a temporary cooling and warming. Then, M_{res} became almost zero at 1.5 K. These behaviors indicate that there are metastable states with a small residual magnetization dependent on temperatures. These states have a relaxation time sufficiently longer than the time scale of our measurements ($\sim$10 min). In addition, intensities of the magnetic Bragg reflections have been studied at several temperatures by our neutron-scattering experiments.[11,16] At temperatures below 1.5 K, a time evolution of the magnetic peak was observed in a time scale of several hours. Thus it is concluded that below 1.5 K, $Tb_2Ti_2O_7$ has metastable states with a wide distribution of the relaxation times from milliseconds to hours.

In conclusion, we observed magnetic short-range ordering and two transitions for $Tb_2Ti_2O_7$ by measurements of the

specific heat, the static and the ac susceptibilities, and the residual magnetization. With decreasing temperature, the magnetic spin ordering grows below about 2 K for the lowest doublet of the Tb^{3+} moments. The spin ordering shows a maximum of the heat capacity at $T_{sr} \approx 0.7$ K. At $T_c = 0.37$ K, a second-order transition was indicated by the sharp peak of the specific heat. At $T_g = 0.2$ K, another transition into a spin-glass or cluster-glass state was indicated by the susceptibility. In the ac susceptibility measurement, dissipation was observed between 1.5 K and T_g in addition to the peak by the glass transition. In the same temperature range below about 1.5 K, we observed the residual magnetization. The dissipation and the residual magnetization suggest existence of metastable states with a wide distribution of the relaxation time.

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