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Thermodynamic properties of quadrupolar states in the frustrated pyrochlore magnet $Tb_2Ti_2O_7$

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Abstract. The low-temperature thermodynamic properties of the frustrated pyrochlore $Tb_{2+x}Ti_{2-x}O_{7+y}$ have been studied using the single crystal of $x = 0.005$ sitting in a long range ordered phase in the x–T phase diagram. We observed that the specific heat exhibits a minimum around 2 K and slightly increases on cooling, similar to a Schottky-like anomaly for canonical spin ices. A clear specific-heat peak observed at $T_c = 0.53$ K is ascribable to the phase transition to a quadrupolar state, which contributes to a relatively large change in entropy, $S \simeq 2.7$ J $K^{-1}mol^{-1}$. However, it is still smaller than $R\ln 2$ for the ground state doublet of the Tb ions. The entropy release persists to higher temperatures, suggesting strong fluctuations associated with spin ice correlations above T_c. We discuss the field dependence of the entropy change for $H||[111]$ and $H||[001]$.

1. Introduction

Geometrically frustrated magnets have attracted much attention because of the realization of new type of electronic and magnetic phenomena with unconventional order parameters [1, 2]. In particular, the pyrochlore-lattice magnet $Tb_{2+x}Ti_{2-x}O_{7+y}$, a putative candidate of quantum spin liquid (QSL) [3, 4], shows unique properties including an unknown long range order (LRO) in the vicinity ($x_c = -0.0025 \leq x < 0.04$) of the QSL state [5, 6]. Indeed a clear specific-heat peak was observed at $T_c \simeq 0.5$ K for the sample with $x = 0.005$, while no LRO associated with the large magnetic and/or structural phase transitions was confirmed [5]. Although the only small Bragg peak with the order of 0.1 μ_B/Tb appears below T_c, it is too small to explain the corresponding entropy change in the specific heat. It is thus apparently different from the magnetic dipole order inferred by earlier theories [7, 8]. This mysterious, or hidden, order is an important subject for the study of the actual nature of the ground state of $Tb_2Ti_2O_7$ [9–18].

Recently, we have investigated the hidden order of $Tb_{2+x}Ti_{2-x}O_{7+y}$ using a single crystalline sample with $x = 0.005$ ($T_c = 0.53$ K) by means of neutron scattering, specific heat, magnetization measurements [19, 20]. From the semi-quantitative analysis based on the theoretical model proposed by Onoda and Tanaka [21, 22], we have demonstrated that the ordered state originates from electric quadrupole moments inherent in the non-Kramers ion of Tb^{3+}. It is remarkable that the estimated parameter set is located very close to the phase boundary between the quadrupolar and U(1) QSL states. This result naturally explains the previous experimental result that the minute change in x induces a phase transition between the QSL and LRO states [5, 6]. These results also showed remarkable behaviors and possibilities for magnetic field, such as a two dimensional (2D) quadrupole order for $H||[111]$, where the system behaves as decoupled 2D kagomé layers of quadrupole moments separated by triangular layers of polarized magnetic moments, which is reminiscent of the so-called kagomé ice (KI) state of spin ice (SI) materials [23–29].

Therefore, it is intriguing to examine thermodynamic properties of the quadrupolar state in $\mathrm{Tb}_{2+x}\mathrm{Ti}_{2-x}\mathrm{O}_{7+y}$ under magnetic field. For this purpose, we studied specific heat (C_P) and the entropy (S) change of a sample showing the LRO. Here we focus on experiments in the [111] and [001] field directions and show the $T-$ and $H-$dependence of S and $\Delta S[= S(0.55\mathrm{K}, H) - S(0.15\mathrm{K}, H)]$. We found that the plateau-like behavior of ΔS appears in fields around 0.5 T only for $H||[111]$, while the change is soon suppressed for $H||[001]$. This plateau state is attributed to the change in states or the formation of the quadrupole order on the kagomé layers perpendicular to the magnetic field.

2. Experimental

Single crystals of $\mathrm{Tb}_{2+x}\mathrm{Ti}_{2-x}\mathrm{O}_{7+y}$ were grown by a floating zone method [6]. We used the crystal with $x = 0.005$. Specific heat C_P was measured by a quasi-adiabatic heat-pulse or thermal relaxation method. In a temperature range below 2 K, we used a dilution, ^{3}He, and an adiabatic demagnetization refrigerators, while above 2 K we used a Quantum Design PPMS system. The in-field data presented here were obtained using a vector magnet system where an accuracy of the field direction to the sample is below 1°. In order to reduce the demagnetization effect, we used a plate-like crystal along the $\langle 110\rangle$ plane which includes the [111], [110], and [001] axes. The sample is approximately $0.7 \times 0.9 \times 0.1$ mm^3 which is 0.35 mg in weight. Since the demagnetization factor for the [111] and [001] directions is small enough ($N \simeq 0.09$), demagnetization corrections were not performed in the present study.

3. Results and Discussion

Temperature dependence of C_P at zero field is shown in Fig. 1. The specific heat C_P exhibits a minimum around 2 K and slightly increases on cooling toward $T_\mathrm{c} = 0.53$ K, implying a Schottky-type anomaly characterized by SI correlations [30]. A clear peak at T_c results in the phase transition to the quadrupolar state [20]. These behaviors are compatible with the experimental results of the polycrystalline sample of $x = 0.005$ [5].

In order to analyze the low-T behavior of the specific heat of the ground state doublet (C_GND) and its entropy change, it is important to estimate other contributions and subtract those from the measured C_P data. The specific heat of insulating $\mathrm{Tb}_{2+x}\mathrm{Ti}_{2-x}\mathrm{O}_{7+y}$ is represented as $C_P = C_\mathrm{GND} + C_\mathrm{CEF} + C_\mathrm{L} + C_\mathrm{N}$. Here C_CEF is a contribution attributed to higher-energy crystal electric field (CEF) states. This contribution was calculated by taking the CEF scheme obtained by Ref. [31] and assuming the Schottky specific heat. It is slightly visible at temperatures above 2 K and becomes negligible below 1 K. C_L is the lattice specific heat estimated in the same way as described in Ref. [7]. As reference, this is negligibly small at low temperatures (viz. below 3 K) [7, 32]. C_N is the nuclear specific heat showing the Schottky anomaly. It is finite in a LRO state with the finite magnetic-dipole or electric-quadrupole hyperfine field from $4f$ moment [33, 34] or in external magnetic field [35], because of the nuclear level splitting of the nuclear spin $I = 3/2$ of ^{159}Tb with the natural abundance 100%, which mostly contributes to C_N. For this estimation, we fitted the low-T part in the range between 0.1 and 0.4 K using the relation of $C_P \simeq C_\mathrm{GND} + C_\mathrm{N} = AT^n + B/T^2$, where C_GND is assumed to be the power law temperature dependence with respect to low-T excitations for the phase transition, and C_N is tentatively used as the term proportional to $1/T^2$: A and B are the coefficients of these T dependences. One of the fitting results is shown in Fig. 1. The low-T behavior down to 0.15 K can be fitted by this simple relation. However, it is not applicable for the data below

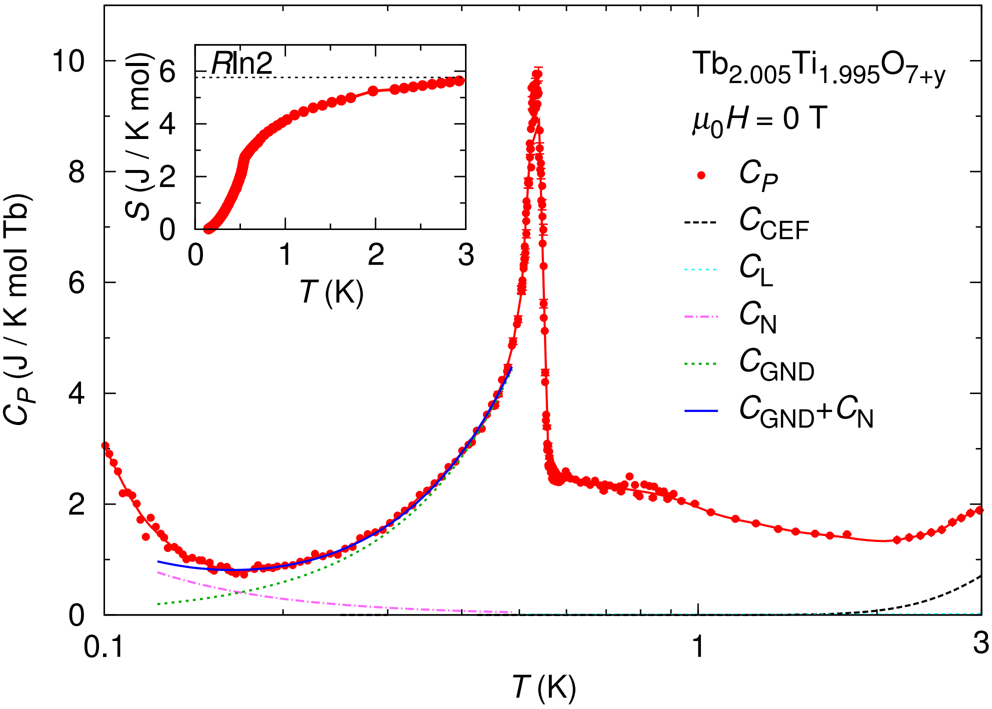

Figure 1. Temperature dependence of the specific heat C_P of single-crystalline $\mathrm{Tb}_{2+x}\mathrm{Ti}_{2-x}\mathrm{O}_{7+y}$ with $x = 0.005$ at zero field. The red filled circles represent the measured C_P data from 3 to 0.1 K. C_{CEF}, C_{L}, C_{N}, and C_{GND} represent the calculated or fitted results of the contribution from excited CEF to the specific heat, the lattice specific heat, the nuclear specific heat, and the specific heat of the low-T excitations of the phase transition, respectively. Inset shows the temperature dependence of the entropy evaluated from the integration of $(C_P - C_{\mathrm{CEF}} - C_{\mathrm{L}} - C_{\mathrm{N}})/T$ from 0.15 K.

0.15 K. Although we extended to fit the data using higher order terms of C_{N} obtained by both considerations of magnetic dipole hyperfine coupling and electric nuclei-quadrupole coupling [36], the fitting was not improved. This may reflect low energy fluctuations or other anomalous contributions such as photon-like excitations and the proximity of quantum criticality [5, 37]. It is also considered that a coupling between low energy fluctuations of $4f$ moments and nuclear spins (and also quadrupole moments) of the Tb nuclei may give rise to the anomalous enhancement of C_P. Indeed, the energy scale of 0.1 K corresponds to 10 μeV and then the inelastic neutron spectrum previously observed around $E = 0$ [5] could be ascribable to the possible existence of such low energy excitations, although higher resolution experiments are needed to clarify this point. Otherwise, the anomalous enhancement of C_P might be related to the lowering of the thermal conductivity of the sample on cooling, which may cause temperature gradient inside the sample and overestimation of the C_P value, although the small and thin crystal was used for the experiments. Note that such a large enhancement of C_P has been also observed in a QSL of the metallic pyrochlore $\mathrm{Pr}_2\mathrm{Ir}_2\mathrm{O}_7$ [38]. More precise and careful measurements are required for further understanding. The fitting yields $A = 24(2)$, $n = 2.4(1)$, and $B = 0.014(2)$. Since the coefficient B is written to be $B = R(1.25\alpha'^2 + P^2)$ using the magnetic hyperfine constant α', quadrupole coupling constant P, and gas constant R [36], it is roughly estimated that $\alpha' \sim 0.037$ K when $P = 0$ or $P \sim 0.041$ K when $\alpha' = 0$ (or then α' and P are expected within half values of those). These values are the same order of the values for systems including Tb

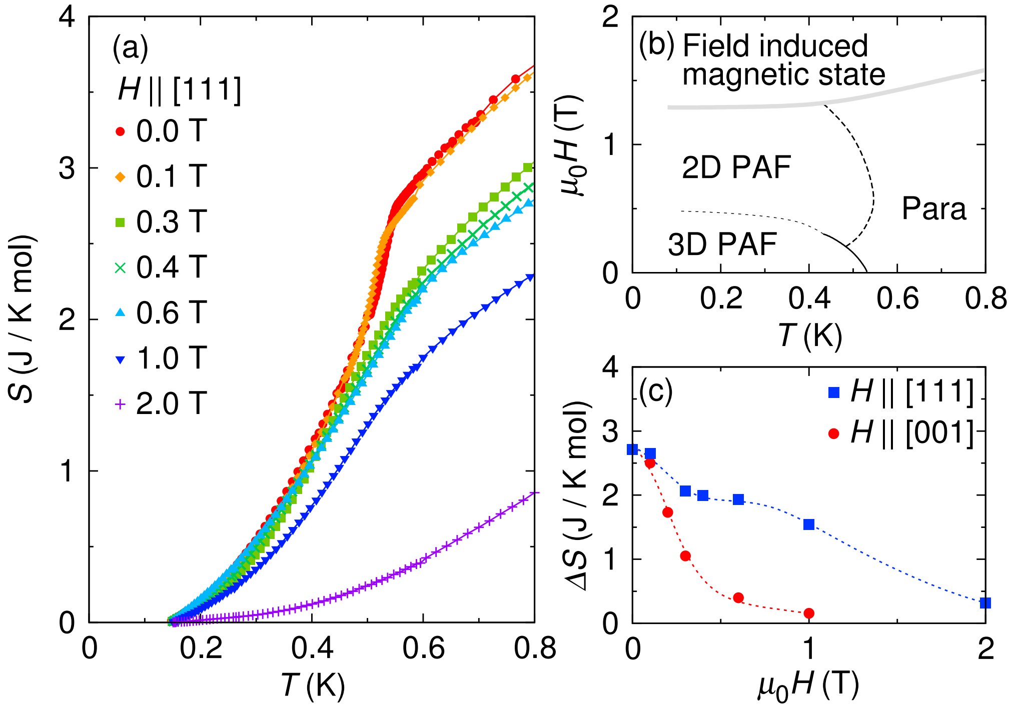

Figure 2. (a)Temperature dependence of the entropy for several magnetic fields for $H||[111]$. (b)H–T phase diagram for $H||[111]$ [20]. The black solid line up to 0.4 T indicates the phase boundary between the 3D quadrupolar state of the planar antiferropseudospin (PAF), 3D PAF, and the paramagnetic paraquadrupole state. The black dashed line is the phase boundary between the 2D quadrupolar state, 2D PAF, and the paramagnetic paraquadrupole state. The black dotted line represents the line of the crossover or phase transition between the 3D and 2D PAF states. The gray solid line is the putative phase boundary between the 2D PAF state and the field-induced magnetic state, which is estimated from a kink of the magnetization. (c)Field dependence of the entropy change $\mathit{\Delta} S[= S(0.55\mathrm{K}, H) - S(0.15\mathrm{K}, H)]$ for $H||[111]$ and $H||[001]$. The lines are guides to the eyes.

nuclei and the theoretical expectation for the case of the Tb metal [39, 40]. We thus considered that the estimation of C_N is approximately reasonable and intended to focus on the data above 0.15 K at present for the evaluation of the entropy, which was calculated from the integration of $\mathit{\Delta} C/T = (C_P - C_{\mathrm{CEF}} - C_{\mathrm{L}} - C_{\mathrm{N}})/T$. The corresponding entropy change in temperature is shown in the inset of Fig. 1.

It is remarkable that the entropy in zero field at T_{c} is 2.7 J $\mathrm{K}^{-1}\mathrm{mol}^{-1}$. This value is about 50% of $R\ln 2$ expected for a non-Kramers doublet of the Tb ions. Even when we consider the low-T contribution below 0.15 K, it doesn't reach $R\ln 2$. Instead, the entropy release persists to higher temperatures and is saturated around 3 K, as seen in the inset of Fig. 1. This behavior is similar to that of previous experiments for a sample showing LRO [41]. These results imply that strong fluctuations still persist to temperatures higher than T_{c}. It is also suggested that a QSL-like state or the proximity of it could realize at temperatures between near T_{c} and ~ 1 K, where C_P slightly increases like a Schottky anomaly signified by SI correlations and the value is also large enough (~ 2 J K^{-1}mol-Tb^{-1}): these imply finite excitation density of states or large magnetic fluctuations of quantum or thermally-excited monopoles, although S does not exhibit the plateau of the residual entropy, which is masked or must be released by the sharp peak of

C_P at T_c.

Figure 2(a) shows the temperature dependence of the field variation of the entropy, $S(T, H)$, for $H||[111]$. For these estimations, we used the same method described above, assuming that C_CEF and C_L in fields are also negligibly small at low temperatures below 1 K. Interestingly, it is found that $S(T, H)$ exhibits quantitatively the same behavior in fields around 0.5 T, while it decreases (or increases) with increasing (or decreasing) magnetic fields in a temperature range up to 0.8 K. These behaviors reflect the properties of the H–T phase diagram for $H||[111]$ [Fig. 2(b)], where the 3D quadrupolar state is considered to be replaced by the 2D quadrupolar state, and then by the magnetic state at low temperatures. In fact, as plotted in Fig. 2(c), the field dependence of the entropy change around zero-field T_c, ΔS, exhibits a plateau-like behavior around 0.5 T for $H||[111]$. This decreases rapidly for $H||[001]$ reflecting the relatively small field that induces the magnetic state above 0.3 T [42]. It is considered that at the intermediate field ($\sim$ 0.5 T) for $H||[111]$, the phase transition occurs only due to the change of the state in each kagomé-lattice layer, which could only contribute to the change in entropy. Therefore, this situation may lead to almost the same temperature dependence of $S(T, H)$ around 0.5 T and the plateau state of ΔS.

Now we find that the difference of ΔS between at 0 and around 0.5 T for $H||[111]$ is about 0.7 J K^{-1}mol^{-1}. Then, a question is what does this value mean? An interesting scenario is that, if the states in 0 and about 0.5 T around 1 K are similar to the classical SI and KI states and the residual entropies of these states are released by the phase transition and then zero as expected from the quantum model [43], the difference of ΔS between at 0 and around 0.5 T may possibly correspond to the difference between the SI residual entropy (1.68 J K^{-1}mol^{-1}) [44] and the KI residual entropy (0.67 J K^{-1}mol^{-1}) [45, 46]; i.e., $\sim$ 1 J K^{-1}mol^{-1}. In fact, the value of 0.7 J K^{-1}mol^{-1} is close to this value. It is considered that this entropy will be released at temperatures higher than 0.8 K. For this context, further detailed experiments at higher temperatures under magnetic field are interesting future subjects.

4. Conclusion

In conclusion, we reported thermodynamic properties of the quadrupole-order sample of $\mathrm{Tb}_{2+x}\mathrm{Ti}_{2-x}\mathrm{O}_{7+y}$ with $x = 0.005$. We observed that the specific heat shows a minimum around 2 K and slightly increases on cooling, which is similar to a Schottky-type anomaly for canonical spin ices. A clear peak at $T_\mathrm{c} = 0.53$ K results in the phase transition to the quadrupolar state. The entropy change at T_c is 2.7 J K^{-1}mol^{-1}, which is smaller than $R \ln 2$ and suggests the strong fluctuations that remains at higher temperatures than T_c. The field dependence of the entropy change around 0.5 K and in 0.5 T for $H||[111]$ exhibits a plateau. This characteristic feature probably reflects the formation of the two-dimensional quadrupolar state by the [111] magnetic field.

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